**Task 3.0 - Advanced Power Systems
Subtask 3.18 - Ash Behavior in Power Systems**

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TASK 3.0 – ADVANCED POWER SYSTEMS

SUBTASK 3.18 – ASH BEHAVIOR IN POWER SYSTEMS

1.0 INTRODUCTION

Advanced power systems such as integrated gasifier combined cycle systems and fluidized bed systems are at the forefront of power industry research because of the need for increased efficiency and the reduction of greenhouse gases. Ash behavior in power systems can have a significant impact on the design and performance of these systems. The Energy & Environmental Research Center (EERC) has developed a focused research initiative aimed at filling gaps in the understanding of fundamental mechanisms of ash behavior, which has relevance to commercial application and marketable products associated with advanced power systems. This program develops methods and means to better understand and mitigate adverse coal ash behavior in advanced power systems and can act to relieve the U.S. reliance on diminishing recoverable oil resources and other greenhouse-producing fossil fuels.

2.0 OBJECTIVES

The overall goal of this initiative is to develop fundamental knowledge of ash behavior in power systems for the purpose of increasing power production efficiency, reducing operation and maintenance costs, and reducing greenhouse gas emissions into the atmosphere. The specific objectives of this initiative focus primarily on ash behavior as related to advanced power systems and include the following:

- Determine the current status of the fundamental ash interactions and deposition formation mechanisms as already reported through previous or ongoing projects at the EERC or in the literature.
- Determine sintering mechanisms for temperatures and particle compositions that are less known and remain for the most part undetermined.
- Identify the relationship between the temperature of critical viscosity (T_{cv}) as measured in a viscometer and the crystallization occurring in the melt.
- Perform a literature search on the use of heated-stage microscopy (HSM) for examining in situ ash-sintering phenomena and then validate the use of HSM in the determination of viscosity in spherical ash particles.
- Ascertain the formation and stability of specific mineral or amorphous phases in deposits typical of power systems, including sulfide ash deposits in gasifiers.
- Evaluate corrosion for alloys being used in supercritical combustion systems.

3.0 APPROACH

Subtask 3.18 is structured as three tasks. Task 1 pertains to summarizing the critical issues in ash behavior, especially for advanced power systems. Task 2 focuses on fundamental ash sintering and viscosity-ash composition relationships that are critical for developing a better mechanistic understanding of ash deposit formation and for predicting ash behavior. Task 3 is aimed primarily at determining the role of the ash chemistry and phase relationships for specific ash interactions in advanced power systems. The role of sulfides in the formation of ash deposits in gasification systems and the factors that influence alloy corrosion in supercritical boilers will be specifically analyzed.

The primary questions that are being addressed in this subtask and the scientific approach to finding potential answers to the questions and achieving the objectives of the project are outlined below by task.

3.1 Task 1 – Critical Issues in Ash Behavior

3.1.1 Task 1 Objectives

Over the past 25 years, the EERC has studied various aspects of ash behavior in combustion and gasification power systems. The results of the different projects that have been undertaken to understand ash behavior in advanced power systems need to be synthesized into a cohesive report that can be used as a synopsis of the current status of the EERC knowledgebase. This information, coupled with a review of literature on ash behavior in advanced power systems from sources outside the EERC, provides excellent focus and direction to this project. Key questions addressed in this task are as follows:

- What are the critical issues and the current status in understanding ash behavior for advanced power systems?
- Does the EERC already have mechanistic information on ash behavior for advanced power systems or for reducing conditions in general that can be used to enhance the structured initiative?
- What are some key studies in the literature that relate to advanced power system deposits?

3.1.2 Task 1 Results

The EERC has generated a wealth of data through several research projects in the last several years that need to be summarized and reported concisely and distributed to key personnel. The summary report and a selective survey of key literature relating to ash behavior for advanced power systems will provide a sound basis for determining the status of current knowledge and understanding in ash behavior for advanced systems. Projects at the EERC developing critical information pertaining to ash deposition mechanisms in gasification or reducing environments

are given in Table 1. Some of the project information that is proprietary will not be distributed; however, the fundamental mechanistic principles for ash formation and behavior established through these projects are available for review and summary.

TABLE 1

Projects to Be Summarized	
Project Name	Description
Coal Ash Behavior in Reducing Environments (CABRE)	Study of laboratory and full-scale entrained-flow gasifier-type deposits, deposit mechanisms, and novel analytical methods
DOE Cooperative Agreement – Alkali Capture in Advanced Power Systems	Alkali formation and capture in advanced power systems
DOE Cooperative Agreement – The EERC Transport Reactor Demonstration Unit	Demonstration of a pilot-scale pressurized fluidized-bed gasifier
DOE Cooperative Agreement – The Fuel Quality Advisor	Development of ash deposition and coal-handling predictive models within a user-friendly computer platform
DOE Cooperative Agreement – Fuel Utilization Properties	Fundamental properties of entrained ash deposit formation in combustion and in reducing environments
Hot-Gas Filter Ash Characterization Project	Characteristics of ash material in hot-gas filters and formation mechanisms for filter-blinding deposits.
Fireside Performance Indices Project	Predictive indices formulated for coal-fired boilers that assess ash deposition potential and stack gas opacity
Fluidized-Bed Combustion Agglomeration	Determination of key mechanisms for bed agglomeration in fluidized-bed combustion (FBC) systems
Project Calcium	Mechanistic algorithms and predictive software for predicting ash deposition from high-calcium coals
Project Sodium	Low-rank coal fouling deposit formation, especially for western fuels, and the role of sodium in the formation of ash deposits

A "three-ring binder" approach to organizing and summarizing the research data has been formulated. This will allow easy expansion and updating, with summaries of the current knowledge of key ash transformation issues along with references to applicable EERC project information and seminal literature articles. Combustion and gasification processes are seen as being sufficiently different to warrant separate treatment, although some redundancy will occur. The entry for each key issue will consist of a summary page(s) giving the level of research priority, a synopsis of current knowledge, a statement of unanswered research questions, and a link to an associated reference page. The reference page(s) will contain abstracts of relevant EERC findings by project, abstracts of key literature information, and references to the projects and literature.

A preliminary template covering several key issues is presented in Appendix A. It is apparent from the past and current analysis of work performed on ash behavior that there is a wealth of information on the mechanism of ash formation and deposition for conventional coal-fired power systems. However, for advanced power systems, fundamental mechanistic information pertaining to ash behavior is sporadic and much of the research in this area has been proprietary and excluded from public literature venues.

3.2 Task 2 – Sintering Mechanisms

3.2.1 Task 2 Objectives

Despite the importance of ash physical properties, specifically viscosity, in the temperature range where boiler fouling and wall slagging occur, there is an almost complete lack of experimental measurements in this range. The viscosity range of interest where fouling occurs for conventional and advanced power systems is 10^5 to 10^8 poise. The non-Newtonian behavior and the presence of both solid and liquid phases make interpretation and modeling of the ash behavior particularly difficult. Existing models based on lower viscosities at higher temperatures are used, although not known to be strictly applicable. Further, the relationship of ash properties to real-world fouling and slagging behavior is known in only a qualitative way, seriously hampering understanding of ash behavior in real-world combustion and gasification systems. One objective in Task 2 is to achieve the ability to better predict fouling and slagging behavior under oxidizing conditions from coal and ash mineral composition, which will significantly enhance the ability of the EERC to assist commercial clients with urgent problems related to ash deposition. It is hoped that the database of information currently available and added to in this work will result in a better predictive model, eventually also applied to reducing environments typical of advanced power systems.

Some of the key questions answered in this task relating to ash deposit sintering mechanisms and viscosity include the following:

- Can the distribution of solids and liquids in a slag be predicted using thermodynamic calculations?

- Does the amount of crystalline phase present regulate the viscosity, or does the resultant residual glassy material describe the viscosity?

3.2.2 Task 2 Results – Viscosity and Crystallization Relationships

Measurements of fundamental ash properties of ash slag were performed using heated-stage x-ray diffractometry on ash slag that had previously been characterized for viscosity–temperature–composition relationships. The ash slag was heated to a molten state and then cooled through the temperature of critical viscosity and the crystallization path determined. This information was compared to phase diagrams of the principle chemical constituents to determine if the crystallization path followed in the slag is that found in pure compounds. This information is also being used to enhance viscosity models that have been developed at the EERC.

Heated-stage x-ray diffraction was performed on six coal slags including a Powder River Basin subbituminous coal from the Rochelle mine, a Rochelle coal with fluxing additives, two North Dakota Center mine lignites supposedly having different slagging performances in a conventional cyclone boiler, and two Illinois No. 6 coals, one containing a calcium-fluxing agent additive. A heated-stage x-ray diffraction (XRD) capability is being added to a new Phillips X' Pert x-ray diffractometer at the EERC; however, the system was not available for testing during this period. Samples were taken to Oak Ridge National Laboratory and analyzed. Data are still being assembled from the heated-stage XRD work at Oak Ridge, but preliminary results show that only the Rochelle coal slags show clear crystalline paths of mineral components. The final report for this project will contain all results and conclusions for this crystallization work.

Empirical models of the composition–temperature–viscosity relationship in coal ash slag exist in the literature. Many of them are applicable to only limited ranges of temperature and composition. Coal ash slags can have an extremely wide variation in composition and encounter a large temperature distribution in the combustor. In an attempt to build a model encompassing a broader temperature and composition range, a back propagation-of-errors (BP) neural network was trained and implemented. The data set used to train and validate the network was culled from the glass, metallurgical, and coal literature. The model was tested on slags of various compositions. To assess the model's effectiveness, the results were compared to two of the more recent viscosity models in the coal ash and slag literature.

Figures 1 and 2 illustrate the performance of the BP neural network built to predict viscosity. The predicted viscosity of the BP neural network is compared to measured viscosity as well as to that generated by a recently developed viscosity model. Table 2 shows the composition of the two coal ash slags used in the validation of the neural network model.

Figure 1. BP- and Kalmanovitch-predicted viscosity compared to the measured viscosity for Coffeen slag.

Figure 2. BP- and Senior-predicted viscosity compared to measured viscosity for MTI 254 slag.

TABLE 2

Composition of the Coal Ash Slags Used in the Validation of the Neural Network Model

Element, wt%	Coffeen	MTI 254
Na	0.77	4.2
Mg	1.18	3.7
Al	16.06	15.3
Si	52.12	50.9
K	1.58	1.8
Ca	13.19	14.2
Ti	0.65	0.7
Fe	14.27	8.0
Ba	0.00	0.0

3.2.3 Task 2 Results – Sintering Studies Using HSM**3.2.3.1 Apparatus**

Experimental sintering measurements were performed using a Leitz heated-stage microscope. The apparatus comprised a Leitz Metallux II optical microscope with a water-cooled heating stage rated to 1750°C, a tantalum (Ta) heating strip, a black-and-white video camera for recording the data, a computer for logging temperatures, and a computer-video mixer to overlay computer data on the video. A 0.4-mm (0.016-in.) Type S thermocouple attached to the heating strip with high-temperature ceramic cement provided temperature monitoring and control.

As was previously reported, preliminary calibration and sintering tests indicated the need for more precise control of the heated stage. Consequently, a temperature controller was incorporated into the HSM electrical heating system to maintain a near-constant ($\pm 5^\circ\text{C}$) strip temperature.

3.2.3.2 Sintering Material Selection and Preparation

Two materials were used for HSM sintering experiments, a commercial glass of certified composition and a slag produced from the combustion of an Illinois No. 6 bituminous coal. Properties of the model glass, such as viscosity and surface tension, were available in the literature. The bituminous coal has been previously characterized by the EERC.

Preparation of the coal slag for HSM consisted of a three-step process of 1) homogenizing via crushing and reheating, 2) sizing, and 3) spheridizing by passing through a drop-tube furnace (DTF) at 1300°C and a residence time of 1.2 seconds. The DTF products were examined by scanning electron microscopy (SEM) to verify that good sphericity had been obtained. The soda-lime glass was obtained in the form of spheres.

The glass and coal slag spheres were sized using a sonic sieve to two different size ranges: 20–38 µm and 38–50 µm. The sintering temperatures of the two materials were identified using the HSM. Two particles of similar size were viewed during heating to observe when sintering began and when melting of the spheres occurred. Three temperatures were then chosen (nominally 20–30 degrees less than the onset of sintering temperature). The sintering tests were done on pairs of particles for each size range at the three temperatures.

3.2.3.3 HSM Operating Procedure

Particles were transported to the heating strip within the HSM on the tip of a needle. The needle was tapped lightly on the surface of the heating strip, depositing many particles on the strip. Several areas were then viewed through the microscope to identify a pair (or pairs) of particles of the same size and in the proper juxtaposition. The computer, video equipment, and heated stage were then prepared for a run. The temperature was ramped at approximately 150°C/min and held at temperature until sintering was well progressed. The HSM heated stage was purged with a slow flow (10 cc/min) of Argon. The temperature logging and video imaging were initiated when the run temperature was attained. The videotape recorder provided a continuous record of the sintering behavior of the particles under observation, with the video mixer superimposing time and temperature data on the video image. Upon completion of a sintering test, the videotape was reviewed and particle radius and neck growth measurements obtained on the selected pairs of sintered particles.

Standard glass beads, 30 µm in size, were imaged and recorded prior to sintering tests to provide a size calibration reference. Measurements were taken either from the video monitor or from frame-grabbed images. Calibration of the HSM strip temperature was done using standards of known melting points: lead wire (327°C), sodium sulfate (884°C), and copper wire (1083°C). A plot of recorded vs. actual temperature was generated, with a statistical best fit determined. Recorded (thermocouple) temperatures were corrected using the calibration data. Calibrations were checked with sodium sulfate when the heating strip or thermocouple was changed.

3.2.3.4 Sample Analysis

Bulk chemical analysis via x-ray fluorescence (XRF) was performed on the glass spheres and the coal slag spheres. Select samples of the coal slag spheres were viewed by SEM microprobe to determine particle chemistry and homogeneity. Similarly, select sintered slag particles (although not those observed and measured during HSM sintering) were viewed by SEM microprobe to determine neck and particle chemistry.

3.2.3.5 Results of Sample Analysis

Table 3 shows the XRF-determined bulk chemistry of the soda-lime glass spheres and slag spheres that were subjected to sintering via HSM. The slag was formed in the Central Illinois Public Service Coffeen Plant cyclone-fired boiler, which burns Illinois No. 6 bituminous coal. Limestone is blended with the coal prior to combustion to reduce the slag viscosity.

TABLE 3

Chemistry of Glass Spheres and Illinois No. 6 Slag		
Oxide	Glass	Slag
Na ₂ O	14.75	1.00
MgO	2.78	0.89
Al ₂ O ₃	0.00	17.27
SiO ₂	71.21	50.73
P ₂ O ₅	0.15	0.56
SO ₃	0.32	1.07
K ₂ O	0.00	2.12
CaO	0.23	7.79
TiO ₂	9.83	1.36
Fe ₂ O ₃	0.67	17.20

Figures 3 and 4 show SEM photomicrographs of slag spheres and sintered slag particles, respectively. Chemical analyses were obtained for several areas on the particles and on the neck growth areas; average values are reported. The chemistry of slag spheres selected for microprobe analysis (Table 4) showed a rather wide variation in composition. Further, it was noted that the spheres appeared to be enriched in iron at the surface, apparently due to segregation of material as the molten slag spheres cooled. The segregation of iron was somewhat unexpected. The chemistry of sintered slag spheres (Table 5) showed the particles to be quite homogeneous, with no significant change in chemistry. The neck growth areas also show analysis consistent with the particle analysis. The points shown in Figure 4 correspond to the points in Table 5.

3.2.3.6 HSM Growth Rate Measurements

Particle radius and neck growth measurements were obtained by reviewing the videotaped sintering runs. The Illinois No. 6 slag spheres were more difficult to observe under HSM due to their dark color; therefore neck growth measurements were more difficult to obtain. The particle radius and neck growth measurements were used to calculate the degree of sintering x/r , where x is the radius of the sintering neck and r is the arithmetic average radius of the sintering particles.

— 10μ

Figure 3. SEM photomicrograph of slag spheres.

Figure 5 shows x/r plotted against time (sec) for the soda-lime spheres at three temperatures: 674°, 684°, and 690°C. Similarly, Figure 6 shows x/r vs. time for the Illinois No. 6 slag spheres at 783°, 810°, and 930°C. The replicate plots at each temperature represent different pairs of sintered particles and give an indication of the repeatability of the data.

From the plots, it appears that the sintering should be done for a longer time to more definitively show the curvature of the plots. The test with the soda-lime glass at 690°C apparently was not continued long enough to observe the curvature seen at the other two temperatures. The downward curvature with the Illinois No. 6 slag at 810°C may be due to each of these particle pairs having a third particle attached to it, with one particle pair growing at the expense of the neck of the other particle pair.

3.2.3.7 Viscosity Calculation with HSM Measurements

The particle radius and neck growth measurement data were used to calculate dynamic viscosity using four analytical models: Frenkel (1) Frenkel-Eshelby (2), Hopper (2, 3) and Modified Frenkel (4). Frenkel's model, shown in Eq. 1, describes the rate of coalescence occurring by Newtonian viscous flow under the action of surface tension for two identical spheres.

$$x/r = [1.5 (\gamma t)/(\eta r)]^{1/2} \quad [1]$$

where η = viscosity (Pa·sec)
 x = radius (m) of neck between two spherical particles
 t = time (sec)
 r = particle radius (m) at time t
 γ = surface tension (N/m)

Figure 4. SEM photomicrograph of sintered slag spheres.

TABLE 4

Analysis of Illinois No. 6 Slag Spheres

Particle	Size, μm	Element, wt%									
		Na	Si	Ca	Mg	Al	P	S	K	Ti	Fe
1	25.0	1.71	47.06	9.72	1.23	18.03	0.13	0.19	3.22	1.05	17.66
2	32.5	1.31	48.30	9.74	0.88	19.34	0.09	0.05	2.21	1.14	16.95
3	12.5	0.37	28.66	10.03	0.99	11.85	1.30	2.49	4.95	3.32	36.04
4	10.0	1.78	49.16	8.98	1.85	20.91	0.37	0.00	3.36	1.38	12.22
5	27.5	0.54	40.74	12.28	0.67	15.45	0.20	0.00	3.06	2.45	24.61
6	25.0	0.90	30.46	15.50	0.47	10.41	0.00	0.07	3.40	1.89	36.91
8	30.0	1.00	47.89	12.20	1.08	17.88	0.25	0.23	2.92	0.91	15.65
9	26.7	1.07	43.18	10.43	0.90	16.58	0.66	0.77	3.54	0.75	22.13
10	26.7	1.61	40.06	8.97	0.95	16.25	0.12	0.00	3.34	1.29	27.42
11	23.3	1.52	46.56	9.06	1.05	18.75	0.07	0.32	3.16	1.20	18.32
12	13.3	1.27	40.54	7.02	0.67	15.11	1.06	7.31	2.13	2.04	22.87
13	10.0	1.30	45.90	8.79	1.33	17.92	0.00	0.00	3.20	1.12	20.43
15	15.2	1.98	49.54	9.25	1.13	19.06	0.92	0.00	3.23	1.25	13.63
16	15.2	0.74	34.54	9.43	0.14	11.17	0.99	1.74	3.34	1.88	36.02
17	30.3	1.25	45.77	9.65	0.71	18.38	0.62	0.24	3.24	1.67	18.46
18	30.3	2.25	46.74	10.86	0.97	17.90	0.27	0.00	3.04	0.79	17.18
19	9.1	1.69	50.45	9.78	1.44	18.71	0.73	0.00	3.10	1.43	12.67
20	3.0	1.59	44.22	10.16	1.15	17.07	0.28	0.58	2.98	0.98	20.98
Average		1.33	43.32	10.10	0.98	16.71	0.45	0.78	3.19	1.47	21.67
Standard Deviation		0.50	6.42	1.81	0.38	2.93	0.41	1.77	0.57	0.65	7.83

TABLE 5

Analysis of HSM-Sintered Illinois No. 6 Slag Spheres

Point	Element, wt%									
	Na	Si	Ca	Mg	Al	P	S	K	Ti	Fe
1	2.27	31.76	12.46	0.81	12.61	0.53	0.50	1.18	2.29	35.35
2										
3	2.73	33.68	9.48	1.05	12.92	0.69	0.05	2.43	1.16	35.74
4	2.51	38.28	9.40	1.24	13.78	0.00	0.10	2.89	1.27	29.57
5	2.50	42.04	9.24	1.60	14.95	0.00	0.00	0.00	1.34	27.71
6	2.89	36.28	14.14	0.00	16.60	0.00	0.00	0.00	1.95	27.23
7	3.62	40.75	6.17	1.86	17.36	0.36	0.00	0.92	0.97	27.38
8	1.72	36.10	7.99	1.06	15.96	0.09	0.18	2.83	1.25	32.64

Frenkel's model was corrected by Eshelby to satisfy the continuity equation for an incompressible fluid. The corrected model, referred to as the Frenkel-Eshelby model (Eq. 2), and the Frenkel model are both limited to Newtonian flow and only in the early stages of sintering when the particle diameters remain relatively constant, i.e., $x/r < 0.3$.

$$x/r = [(\gamma t)/(\eta r)]^{1/2} \quad [2]$$

Hopper's model for sintering is based on the exact analytical solution of the Navier-Stokes equation for two-dimensional viscous flow driven by capillary forces acting on the free surface. Hopper's analysis was applied to two long cylinders having an inverse ellipse as their cross section (2, 3). The Modified Frenkel model, as developed by Pokluda, Bellehumeur, and Vlachopoulos, is based on an approach similar to that used by Frenkel and Eshelby in their model derivations (4). However, in contrast to the Frenkel and Frenkel-Eshelby models, the Modified Frenkel model is applicable to all stages of spherical particle sintering. Further, the Modified Frenkel model considers the change in particle radius as sintering progresses.

Solutions of the Hopper and Modified Frenkel models, although not trivial, were not required for this test program. Values of dimensionless time $[(\gamma t)/(\eta r_f)]$ and the corresponding degree of sintering (x/r_f) have been computed by Hopper (3) and are presented in Table B-1, Appendix A. Similarly, values of $[(\gamma t)/(\eta r_o)]$ and x/r have been computed by Pokluda, Bellehumeur, and Vlachopoulos (4) and are presented in Table B-2, Appendix B. The variable r_f is the final particle radius for the Hopper model, and r_o is the initial particle radius for the Modified Frenkel model.

Figure 5. Plot of x/r versus time for soda-lime spheres.

Figure 6. Plot of x/r versus time for Illinois No. 6 slag spheres.

For this study, a best-fit curve was generated from the tabulated values (dimensionless time, τ , and degree of sintering, X) for both the Hopper and Modified Frenkel models. The general equations for the best-fit curves for the Hopper and Modified Frenkel models are shown in Eqs. 3 and 4, respectively.

$$\tau = [(a + cX + eX^2)/(1 + bX + dX^2 + fX^3)] \quad [3]$$

$$\tau = [(a + cX^2 + eX^4)/(1 + bX^2 + dX^4 + fX^6)] \quad [4]$$

The independent variable X is (x/r_f) for the Hopper model and (x/r) for the Modified Frenkel model. Similarly, the dependent variable τ is $[(\gamma t)/(\eta r_f)]$ for the Hopper model and $[(\gamma t)/(\eta r_o)]$ for the Modified Frenkel model. For the Hopper model, r_f is $r_o(2)^{1/2}$. Coefficients a , b , c , d , e , and f for both models are presented in Table 6.

TABLE 6

Coefficients for Hopper and Modified Frenkel Equations						
Model	Coefficient					
	a	b	c	d	e	f
Hopper	-0.0136	-1.3067	0.82496	-0.1083	-0.7982	0.4169
Modified Frenkel	-0.0129	-0.5603	1.32777	-1.5526	-1.3050	1.1140

Dynamic viscosity values were calculated from each of the four models for each x/r (and corresponding t) value. The Frenkel and Frenkel-Eshelby models, Eqs. 1 and 2, respectively, were rearranged to solve for the unknown variable, η . In applying the Hopper and Modified Frenkel models, Eqs. 3 and 4 were each used to compute dimensionless time values (τ) for each corresponding x/r value. The dynamic viscosity was then calculated from Eq. 5, where r is r_f from the Hopper model or r_o from the Modified Frenkel model. The surface tension (γ) value for the soda-lime glass, 0.304 N/m, was obtained from the literature (5). As an approximation, the same value was used as the surface tension for the Illinois No. 6 slag.

$$\eta = (\gamma t)/(\tau r) \quad [5]$$

The dynamic viscosity values computed from the four models are presented in Table 7 for the soda-lime glass and Illinois No. 6 slag spheres. The value presented for each pair of sintered particles is an arithmetic average of the dynamic viscosities calculated at each measured x/r

(and t). Owing to the small number of observations for each pair of sintered particles, no data points were excluded from the averaging. Viscosities were also estimated for the soda-lime glass and Illinois No. 6 slag using the VISCALC (6) thermodynamic equilibrium program; an Urbain equation, with parameters taken from the literature (6), was used to estimate viscosity for the soda-lime glass. Viscosity values predicted with VISCALC and the Urbain equation are also shown in Table 7.

The $\log_{10}(\eta/T)$ vs. $1/T$ is plotted for the soda lime glass and Illinois No. 6 slag in Figures 7 and 8, respectively. The viscosity (η) is in poise and temperature (T) is K.

3.2.3.8 Discussion

Preliminary tests indicate that HSM may be a very useful tool to obtain sintering measurements of coal ash or boiler deposits under controlled conditions to allow predictions of low-temperature viscosities. Selection of an appropriate sintering model, however, may be contingent on corroboration with other low-temperature viscosity data, e.g., values generated from stress-strain measurements. Although the sintering tests were not allowed to progress for a

TABLE 7

Model Calculations of Soda-Lime Glass and Illinois No. 6 Slag Viscosities									
Viscosity (poise) $\times 10^{-8}$ Model									
Material	Temp., °C	Pair	Particle Size, μm	Frenkel	Frenkel-Eshelby	Modified Frenkel	Hopper	VISCALC	Urbain
Glass	674	1	42,46	19.6	13.1	11.9	6.24	0.0080	6.31
		2	52,47	9.42	6.29	5.22	3.72		
	684	1	42,52	6.44	4.29	3.76	2.31	0.0062	3.63
		2	42,39	7.57	5.05	4.42	2.70		
		3	41,40	6.51	4.34	3.72	2.43		
Slag	690	1	22,19	9.47	6.31	5.95	2.38	0.0048	2.63
	783	1	22,24	5.17	3.28	2.65	2.13	0.047	
		2	18,16	7.39	4.92	3.85	3.04		
		3	16,16	6.13	4.08	2.85	2.69		
		4	24,22	7.27	4.85	4.01	2.74		
		5	22,26	6.71	4.48	3.65	2.54		
	810	1	17,13	5.38	3.59	2.25	2.38	0.013	
		2	17,20	6.29	4.19	3.20	2.64		
	930	1	40, 39	3.14	2.09	1.56	1.35	0.0022	
		2	36, 44	3.42	2.28	1.68	1.47

Figure 7. Plot of $\log_{10} (\eta/T)$ versus $1/T$ for the soda-lime glass.

Figure 8. Plot of $\log_{10} (\eta/T)$ versus $1/T$ for the Illinois No. 6 slag.

sufficient time, it is presumed that truly homogenous particles would closely follow the rate of sintering predicted by the Modified Frenkel model if particle mass and density were maintained and phase separation or reaction did not occur.

The limited data indicate that all four analytical sintering models predicted viscosities within the range of interest for low-temperature fouling (10^5 to 10^8 poise). Further, at any given sintering temperature, all four models predicted viscosities within one order of magnitude. The reproducibility of viscosity predictions at any given temperature was quite good for the Illinois No. 6 slag. The model predictions also correctly exhibited a decrease in viscosity with an increase in sintering temperature.

Viscosities predicted by the Frenkel-Eshelby and Modified Frenkel models differ by less than 20% for the soda-lime glass. Most of the viscosities were calculated at x/r values below 0.6. At values of x/r above 0.6, where most viscosities were calculated for the Illinois No. 6 slag, the Frenkel-Eshelby and Modified Frenkel model predictions show much greater divergence. Because the Modified Frenkel model becomes asymptotic with the Frenkel-Eshelby model as x/r approaches 0, predictions with these two models are similar at low x/r .

Predictions of viscosities for the soda-lime glass using the Urbain equation were of the same order of magnitude as predictions generated by the sintering models. However, no one sintering model tended to closely parallel the Urbain predictions throughout the range of sintering temperatures. The VISCALC thermodynamic equilibrium program predicted viscosities of two to three orders of magnitude lower than values predicted by the sintering models or the Urbain equation.

3.2.3.9 Conclusions

- At any given sintering temperature, all four models will predict viscosities within one order of magnitude.
- It is not possible, without further corroborating viscosity measurements, to select a model that most closely predicts the sintering behavior of coal slag or ashes.

3.3 Task 3 – Ash Deposit Chemistry and Phase Relationships

3.3.1 Task 3 Objectives

Although it is well established that sulfides readily break down in combustion environments, usually into oxides of iron (7), the mechanisms of sulfide formation in gasification are not well understood. Work by Benson and Sondreal (8) revealed that initial sulfidation of coal ash or bed material may have led to Ca-Mg-rich aluminosilicate deposits that formed in a pressurized circulating fluidized-bed gasifier. Volatile sulfide species can exist in the temperatures noted for the gasifier studied by Benson and Sondreal (8) and also in other gasification environments. Low-melting-point sulfides of Ca, Fe, or possibly even Na are stable at temperatures of less than 900°C in these environments, but the specific interaction that causes

the sulfides to lead to other silicate and oxide components becoming the "glue" material in a deposit is not understood.

For alloy corrosion studies in this task, there are several questions relating to the specific impacts of gas and ash composition, alloy type, and temperature on the magnitude and rate of corrosion of alloys that are being used in the construction of high-temperature components of advanced supercritical boilers. Ultrasupercritical (USC) boilers employing higher temperatures and pressures than conventional coal-fired boilers require improved materials to achieve high performance and long life. These energy systems will be required to fire low-grade solid fuels and meet higher energy conversion efficiencies. The steam cycle used in a typical conventional power system is limited to a maximum pressure of 175 bar and a metal temperature of 550°C, with efficiencies around 35%. To boost the efficiency significantly, up to 50%, working pressures and temperatures of 325° bar/625°C are required, exposing the metal system components to a much more corrosive environment.

Japanese researchers are already utilizing USC parameters in two liquefied natural gas (LNG)-fired units at Kawagoe, which have been operating extremely well since being commissioned in 1989 and 1990. Danish workers are also in the process of building two USC units (CONVOY), along with three contractors working on low-emission boiler systems (LEBS) for the U.S. Department of Energy. This illustrates how utilities are being pushed toward lower emissions and higher efficiencies.

A few key components to consider in a USC system are the thick-walled sections of the boiler, steam tubes, and the superheaters. The main properties required of an alloy for these systems are resistance to ash corrosion and creep rupture strength. Of these two properties, little information on the corrosion resistance of these alloys is currently available. Knowledge of the expected integrity of various alloys over time is crucial to the success of supercritical boilers.

Several questions need to be answered in this task relating to ash deposits in advanced power systems, including the following:

- How does the formation of sulfide species in a gasification system impact the formation of deposits?
- What are some of the mechanisms of fine particulate agglomeration and deposition in gasifiers?
- How does ash composition, flue gas composition, and the composition of various alloys impact corrosion severity and rates of corrosion for alloy materials of the type used in high-efficiency supercritical boilers?

3.3.2 Task 3 Results – Deposit Ash Chemistry and Phase Relationships

This program obtained deposit samples from the transport reactor demonstration unit (TRDU), which is a 200–300-lb/hr pressurized circulating fluid-bed gasifier similar to the

gasifier being tested at the Wilsonville facility. The TRDU has an operating gas temperature of up to 980°C (1800°F), a gas flow rate of 325 scfm, and an operating pressure of 120–150 psig. The TRDU system can be divided into three sections: the coal feed section, the TRDU, and the product recovery section. The TRDU proper, as shown in Figure 9, consists of a riser reactor with an expanded mixing zone at the bottom, a disengager, and a primary cyclone and standpipe. The standpipe is connected to the mixing section of the riser by a J-leg transfer line. All of the components in the system are refractory-lined and designed mechanically for 150 psig and an internal temperature of 1090°C (2000°F).

The premixed coal and limestone feed to the transport reactor can be admitted through three nozzles, which are at varying elevations. Two of these nozzles are located near the top of the mixing zone (gasification), and the remaining one is near the bottom of the mixing zone (combustion). During operation of the TRDU, feed is admitted through only one nozzle at a time. The coal feed is measured by an rpm-controlled metering auger. Oxidant is fed to the reactor through two pairs of nozzles at varying elevations within the mixing zone. For the combustion mode of operation, additional nozzles are provided in the riser for feeding secondary air. Hot solids from the standpipe are circulated into the mixing zone, where they come into contact with the nitrogen and the steam being injected into the J-leg. This feature enables spent char to contact steam prior to the fresh coal feed. This staged gasification process is expected to enhance the process efficiency. Gasification or combustion and desulfurization reactions are carried out in the riser as coal, sorbent, and oxidant (with steam for gasification) flow up the tube. The solids circulation into the mixing zone is controlled by the solids level in the standpipe.

Figure 9. Schematic of the TRDU.

The riser, disengager, standpipe, and cyclones are equipped with several internal and skin thermocouples. Nitrogen-purged pressure taps are also provided to record differential pressure across the riser, disengager, and the cyclones. The data acquisition and control system scans the data points every 1/2 second, but saves the process data only every 30 seconds. The bulk of entrained solids leaving the riser is separated from the gas stream in the disengager and circulated back to the riser via the standpipe. A solids stream is withdrawn from the standpipe via an auger to maintain the system's solids inventory. Gas exiting the disengager enters a primary cyclone that has been modified to provide variable particulate collection performance. Solids from the primary cyclone are collected in a lock hopper. Gas exiting this cyclone enters a jacketed-pipe heat exchanger before entering the hot-gas filter vessel. The cleaned gases leaving the HGC filter vessel enter a quench system before being depressurized and vented to a flare.

The quench system uses a sieve tower and two direct-contact water scrubbers to act as heat sinks and remove impurities. All water and organic vapors are condensed in the first scrubber, with the second scrubber capturing entrained material and serving as a backup. The condensed liquid is separated from the gas stream in a cyclone that also serves as a reservoir. Liquid is pumped either to a shell-and-tube heat exchanger for reinjection into the scrubber or down to the product receiver barrels.

3.3.2.1 TRDU Fuel Analysis

The fuels that have been tested in the TRDU to date have consisted of a Powder River Basin (PRB) subbituminous coal from the Wyodak seam at the Belle Ayr mine in Gillette, Wyoming, and a Illinois No. 6 bituminous coal from Seam 6 of the Baldwin mine in Illinois. Table 8 shows the proximate, ultimate, and XRF analysis of the two coals. Both coals were mixed with Plum Run dolomite from the Greenfield formation before testing in the TRDU. The dolomite was mixed with the respective coals to provide a Ca:S ratio of approximately 2 on a sorbent-only basis (~ 5 wt% for the PRB coal and 17 wt% for the Illinois No. 6 coal). Table 9 summarizes the major minerals identified by computer-controlled scanning electron microscopy (CCSEM) analysis of the PRB coal as a function of mineral particle diameter. This analysis shows that the mineral sizes are small (70.5 wt% < 10 μm). In addition, the difference between the ash concentration as identified as minerals and the total ash content of the coal suggests that approximately 25 weight percent of the ash is organically associated (mostly calcium).

3.3.2.2 TRDU Operation

A test campaign was conducted February 19–28, 1997. During these weeks, approximately 204 hours of coal feed and 198 hours of gasification (over 190 hours of continuous operation) were achieved, with the system gases and fly ash passing through the filter vessel during the whole test campaign except during off-line cleaning experiments performed during the later stages of the test campaign. The TRDU gasification system performed well and the desired 200 hours were achieved.

TABLE 8

As-Received, Belle Ayr Coal, Illinois
No. 6 Coal, and Plum Run Dolomite Analyses

	Belle Ayr Subbituminous Coal	Illinois No. 6 Bituminous Coal	Plum Run Dolomite, - 35 mesh
Proximate Analysis, as received, wt%			
Moisture	16.7	8.5	NA ²
Volatile Matter	37.9	36.0	
Fixed Carbon	40.6	44.8	
Ash	4.9	10.7	
Ultimate Analysis, as received, wt%			
Carbon	57.5	63.4	NA
Hydrogen	6.18	5.55	
Nitrogen	0.70	1.01	
Sulfur	0.36	3.24	
Oxygen	30.40	16.1	
Ash	4.87	10.7	
Ash Composition, % as oxides			
Calcium, CaO	26.6	3.2	66.6
Magnesium, MgO	7.0	1.6	27.5
Sodium, Na ₂ O	1.3	1.1	0.3
Silica, SiO ₂	27.8	53.9	2.7
Aluminum, Al ₂ O ₃	13.1	21.2	1.0
Ferric, Fe ₂ O ₃	5.5	13.6	1.3
Titanium, TiO ₂	1.3	0.9	0.0
Phosphorus, P ₂ O ₅	1.0	0.2	0.0
Potassium, K ₂ O	0.3	1.9	0.3
Sulfur, SO ₃	16.0	2.5	0.4
HHV, ² as received, Btu/lb	9746	11289	NA
Loss on Ignition, as-run	NA	NA	43.1

¹ Not applicable.

² Higher heating value.

TABLE 9

Summary of CCSEM Results for Belle Ayr
(Wyodak) Subbituminous Coal, wt% on a mineral basis

Particle-Size Distribution, μm :	1.0-3.2	3.2-10.0	10.0-31.6	31.6-100.0	100-316	>316	Total
Quartz	5.2	9.1	6.3	2.4	0.2	0.0	23.2
Rutile	0.1	0.3	0.1	0.0	0.0	0.0	0.5
Calcite	0.2	0.1	0.0	0.0	0.0	0.0	0.3
Kaolinite	3.0	14.0	4.8	4.2	1.7	1.8	29.5
Montmorillonite	2.0	8.9	1.3	0.0	0.4	0.0	12.7
K Al-Silicate	0.1	0.2	0.0	0.0	0.2	0.0	0.5
Ca Al-Silicate	0.4	0.1	0.0	0.0	0.0	0.0	0.5
Aluminosilicate	0.8	2.4	1.0	0.2	0.0	0.0	4.4
Mixed Al-Silicate	0.1	0.1	0.1	0.0	0.0	0.0	0.3
Pyrite	0.2	0.4	1.5	0.0	0.0	0.0	2.1
Gypsum	0.0	0.1	0.0	0.0	0.0	0.0	0.1
Barite	0.2	0.8	0.0	0.0	0.0	0.0	1.0
Ca Al-P	5.0	3.5	1.6	0.0	0.0	0.0	10.1
Gypsum-Barite	0.1	0.1	0.0	0.0	0.0	0.0	0.2
Gyp.-Al-Silicate	0.1	0.0	0.0	0.0	0.0	0.0	0.1
Si-Rich	0.5	4.4	0.3	0.2	0.0	0.0	5.4
Ca-Rich	0.2	0.1	0.0	0.0	0.0	0.0	0.3
Unknown	3.0	4.9	0.8	0.2	0.0	0.0	8.8
Total	21.1	49.4	17.8	7.3	2.5	1.8	100. 0

The TRDU was operated at a higher average temperature of 875°C since no deposition problems were seen in the riser and disengager as reported in previous tests. The last day, the gasifier temperature was decreased to 825°C to see if standpipe carbon levels could be increased. Table 10 summarizes the operational performance for the TRDU during the 200-hour test period. Coal feed rates ranged from 266 up to 390 lb/hr, and the gasifier pressure averaged 120 psig. The dry product gas produced ranged from 3.9% to 6.4% CO, 6.3% to 9.6% H₂, 7.6% to 11.0% CO₂, 0.2% to 1.5% CH₄, with the balance being N₂ and other trace constituents. The moisture in the fuel gas averaged 15%. The H₂S concentration started at approximately 500 ppm and increased to approximately 1200 ppm when recycling of dipleg material was terminated. Calculated

TABLE 10

TRDU Actual Operating Conditions	
Parameter	Test P051
Conditions	Gasification
Coal	Wyodak
Moisture Content, %	23.3
Pressure, bar	9.3
Steam:Coal Ratio	0.30
Air:Coal Ratio	2.5
Ca:S Ratio, mole	4.7
Coal Feed Rate, lb/hr	< 390
Mixing Zone, °C , avg. (min.) (max.)	878 (742) (930)
Riser, °C , avg. (min.) (max.)	856 (766) (991)
Standpipe, °C , avg. (min.) (max.)	760 (624) (751)
Conversion, % (excluding dipleg)	92 (98)
Carbon in Bed, %, in Standpipe (dipleg)	6 to 15 (15 to 35)
Riser Velocity, ft/s	24 to 30 (32 to 38)
Standpipe Velocity, ft/s	0.15 to 0.27
Circulation Rate, lb/hr	2600 to 4400
Duration, hr	204
Time	15:45-18:45
Date	2-20 to 2-28, 1997

recirculation rates started at approximately 4500 lb/hr and slowly decreased to approximately 2500 lb/hr until the standpipe fluffing nitrogen was turned up at the end of the test where it increased back to 4200 lb/hr. Relative bed density dropped from 98% for a 100% silica sand bed to approximately 62% with the high-carbon and coal ash bed.

Figures 10 and 11 show the particle-size distributions of the bed material and primary cyclone ash as they varied with time. The bed particle size slowly increased over the duration of the test from 170 to 200 μm . Primary cyclone ash was becoming progressively finer during the test while the dipleg material was being recycled. After recycling of the dipleg material was stopped, the particle size initially increased and then started to return to the smaller size distribution until the significant increase in solids recirculation rate increased the particle size at the end of the test.

Figure 10. Particle-size distribution of bed material as a function of time.

Figure 11. Particle-size distribution of primary cyclone ash as a function of time.

Figures 12 and 13 show the bulk ash chemistry of the bed material and the primary cyclone ash as functions of time. Based on silica and calcium balances, it appears that approximately 60 wt% of the bed material was converted over to coal ash in 3 days, while the primary cyclone was essentially all coal ash after 1 day of operation. Primary cyclone ash was recycled continuously to the mixing zone during the first 4 days, while bed material, termed L-Ash, was removed from the standpipe during the first 3 days. At this point, it was becoming apparent that further feeding of dipleg material was only resulting in this material blowing over the primary cyclone and would not add to the standpipe bed height. One batch of start-up silica sand was added on the fifth day, resulting in a small increase in silica in the standpipe sample for that day; however, this silica returned to the steady-state baseline concentration over the next day. Little additional solids inventory was added or removed from the system over the remaining days of the test campaign.

During the last 30 hours of this test, a gas purge of nitrogen to the transition from the horizontal riser to the vertical inlet of the disengager cyclone was shut off. It appears that the presence of this purge is enough to keep the deposits that formed in this area from occurring, since approximately 12 hours after the purge was shut down, some process upsets occurred, which would be indicative of some type of deposit forming in this area. These deposits were formed at a relatively low temperature of 825° to 875°C in an area where the gas and solid flow make a 90° turn using a flooded tee. The deposits were white in color on the inside edge where they were exposed to air during shutdown, while the outside edge was black in color as a result of the carbon contained in the deposit that was not exposed to air during the shutdown.

Table 11 shows the bulk chemical composition of various steady-state solid samples obtained from the TRDU during the time period that these deposits formed. The standpipe sample is the material large enough to be removed by the disengager cyclone, while the dipleg leg material is the finer material removed by primary cyclone, and the filter sample is the finest-size material, which is removed by the hot-gas filter on the system. The material flowing past the deposition point in the TRDU riser is the sum of all three samples.

Figures 14 and 15 are photographs showing some of the points that were analyzed. Table 12 shows the elemental analysis of the interstitial "glue" used to hold the deposit together. A comparison of the glue chemistry with that of the bulk samples from the TRDU indicate that the glue is enriched in the smallest ash particles, particularly the high concentration of organically associated calcium, which should form very fine aerosols. There did not appear to be any appreciable sulfur in either the white oxidized layer or the black carbonaceous layer of the deposit, perhaps suggesting that the formation of a sticky calcium sulfide is not a major mechanism for the deposit formation. The presence of very small mineral particles, especially high concentrations of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and the fact that the organically associated calcium will form vapor or very fine aerosols can lead to the formation of lower-melting-point aluminosilicates such as calcium aluminosilicates and montmorillonite ($[(0.5 \text{ Ca, Na})0.7(\text{Al, Mg, Fe})_4(\text{Si, Al})_8\text{O}_{20}(\text{OH})_4]$). Previous tests using this same coal showed significant increases in calcium aluminosilicates and montmorillonite in the hot-gas filter ash (i.e., the smallest particle sizes), suggesting the formation of these compounds under the operating conditions of the TRDU. The data suggest that the "glue" might be a calcium-aluminosilicate that was possibly the result of vapor-phase calcium from the organically

Figure 12. Bulk ash chemistry of the bed material as a function of time.

Figure 13. Bulk ash chemistry of the primary cyclone ash as a function of time.

TABLE 11

XRF Chemical Composition of TRDU Samples from Test P051, 02/27/97

	Coal Ash	Standpipe	Dipleg	Filter
Si	19.7	37	21.6	16.6
Al	10.5	4.8	5.5	9.5
Fe	4.2	4.0	5.1	10.1
Ti	1.0	0.6	0.8	1.6
P	0.5	0.1	0.2	0.6
Ca	41.4	38.5	47.4	48.3
Mg	13.3	13.1	17.7	10.9
Na	1.4	0.8	0.6	0.3
K	0.5	0.2	0.1	0.2
S	7.7	0.9	0.9	1.9
Total	100.0	100.0	99.9	100

Figure 14. SEM photomicrograph of TRDU deposit showing Points 1-3.

Figure 15. SEM photomicrograph of TRDU deposit showing Point 6.

TABLE 12

SEM Microprobe Analysis of TRDU Riser Deposit Glue from Test P051

SEM Point Number: Description:	Point 1 with Dolomite	Point 3 with Dolomite	Point 5 with Silica Sand	Point 6 with Si-Dolomite
Normalized Elemental wt%				
Na	1.9	0.0	0.0	0.0
Mg	2.8	1.3	2.3	0.0
Al	5.7	22.5	7.4	2.2
Si	20.3	10.7	11.8	18.0
P	0.8	0.7	0.4	0.5
S	0.6	0.0	0.3	0.0
K	0.6	0.4	0.0	0.7
Ca	59.3	51.6	59.2	71.7
Ti	1.3	1.1	1.9	0.5
Fe	4.4	11.6	11.9	3.3
Ba	2.3	0.0	4.9	3.1
Total	100.0	99.9	100.1	100.0

associated calcium in the coal reacting directly with the fine coal/ash to form a low-melting-point eutectic coating on the bed material and dolomite particles.

Two other gasification tests were performed using the Wyodak subbituminous coal, with a short test approximately 6 hours long. At the end of this test, some deposits were found in the mixing section and burner throat. In addition, a dark-colored semispherical agglomerate was recovered from the bed material after Test P055 using the Illinois No. 6 coal. The burner throat deposit was white and appeared to be fused sand particles. This deposit is a result of high-temperature combustion in this area during the preheating transition from natural gas to coal combustion and is not an artifact of steady-state operation.

Figure 16 is a photograph of a deposit from the mixing zone of the TRDU showing some of the points analyzed by SEM morphology. Table 13 shows the elemental chemical composition of these points. It was found that chemical composition toward the inside edge of these deposits was substantially higher in iron than the outer edge (which probably started forming during use of the low-iron Wyodak coal) and previous deposits obtained from the TRDU. Figures 17 and 18 show some photographs of the agglomerate obtained from the postrun TRDU bed material. Table 14 shows the elemental chemical composition of various points in the agglomerate. The glue or fill material appears to be a high Fe-Ca silicate, while the white spots are iron spinel-type crystals, which possibly precipitated from the amorphous glue. The length of time on the Illinois No. 6 coal was too short to determine the long-term impacts of these deposits on operation. The data suggest that when a higher-iron coal is gasified, iron could have a significant impact on forming deposits and agglomerates in gasifiers under the indicated operating conditions.

Figure 16. SEM photomicrograph of a deposit from the mixing zone of the TRDU.

TABLE 13

SEM Microprobe Analysis of TRDU Mixing Zone Deposits from Test P055

SEM Point Number	520-1	520-2	520-3
Description	Fill	Fill	Fill
Normalized Elemental Wt%			
Na	0.0	0.0	0.4
Mg	12.4	23.9	15.6
Al	14.7	4.3	6.4
Si	8.3	9.7	10.0
P	0.2	0.0	0.3
S	0.7	2.1	4.7
K	0.0	0.0	0.3
Ca	51.2	41.5	45.0
Ti	2.4	1.4	1.4
Fe	8.7	17.0	14.9
Ba	1.6	0.0	0.9
Total	100.2	99.9	99.9

Figure 17. Photograph of agglomerate from the postrun TRDU bed material showing Points 1 and 2.

Figure 18. Photograph of agglomerate from the postrun TRDU bed material showing Points 5 and 6.

TABLE 14

SEM Microprobe Analysis of TRDU Agglomerate from Test P055

SEM Point Number:	519-1	519-2	519-4	519-5	519-6	519-7	519-8
Description:	Crystal	Fill	Crystal	Fill	Fill	Crystal	Crystal
Normalized Elemental wt%							
Na	2.6	0.4	2.1	3.1	2.3	2.1	2.3
Mg	2.6	3.4	2.0	1.0	1.1	3.2	0.9
Al	2.0	7.3	4.7	12.3	11.0	2.8	2.9
Si	2.4	46.0	13.4	58.1	62.9	9.2	8.6
P	0.0	0.4	0.0	0.3	0.0	0.0	0.1
S	0.1	0.0	0.0	0.2	0.0	0.3	0.1
K	0.0	0.4	0.1	0.9	0.6	0.3	0.1
Ca	0.9	19.6	0.3	9.9	9.9	1.3	1.3
Ti	0.2	0.7	0.2	0.2	0.0	0.0	0.3
Fe	88.7	21.9	77.3	14.1	11.8	80.8	83.5
Ba	0.5	0.0	0.0	0.0	0.5	0.0	0.1
Total	100.0	100.1	100.1	100.1	100.1	100.0	100.2

3.3.2.3 Effect of Gas Purge on Deposit Formation

For most of this test, this purge averaged about 510 scfh (ranging from 460 to 730 scfh) of nitrogen, which was injected through a concentric nozzle located across from the crossover section. The nitrogen is injected through a 0.375-in.-OD by 0.305-in.-ID tube at 120 psig and 260°C, resulting in a gas velocity of approximately 57.5 ft/sec. This purge gas is injected into the riser gas stream (approximately 18,000 to 20,000 scfh) at system operating temperatures of 825° to 875°C in a 3.5-in.-diameter pipe and acts a sootblower. It is felt that the presence of this purge does eliminate the deposition, but the reason has not yet been defined. Two possible mechanisms for the reduced deposition might be either 1) this relatively cool gas is able to quench the particles before they impact, or 2) this relatively small amount of purge gas might be enough to help turn or deflect the bed particles before they actually impact the particles in the flooded tee. The improvement is probably a function of both effects, but the relative significance of each effect is not yet understood. DOE FETC at Morgantown, West Virginia, is currently using Fluent™ to look at various gas velocity and gas temperature distributions to determine if the importance/negligible impact of these two effects could be modeled.

3.3.3 Task 3 Results – Alloy Corrosion

The objective of the alloy corrosion portion of this task is to evaluate and compare the corrosion resistance of superheater and reheater tube materials in the presence of high-alkali ash from low-rank coal. Many studies have been completed in which alloys were subjected to the temperatures and pressures seen in modern and future combustion systems, but very few included the high-alkali ash required to simulate conditions of a coal-fired boiler.

The four alloys to be tested in the high-temperature alloy corrosion objective have been selected. The alloys to be evaluated are TP347HFG, HR3C, 253MA, and NF709. There will also be a reference material included in the test matrix to allow comparison of the newer alloys to one now commonly used. The alloys selected are highly alloyed steels with improved high-temperature corrosion resistance and creep strength. These alloys are expected to allow steam temperatures of up to 630°C. For each of these steels, there is limited knowledge of their long-term high-temperature corrosion behavior in coal-fired systems. Evaluating these materials in a simulated coal-fired boiler environment will permit the desired hot corrosion information to be acquired. The alloys to be tested were selected by reviewing articles published on USC systems, talking with ELSAM engineers, and also reviewing specific studies of alloys. Table 15 contains candidate materials for superheater tubes at 325 bar/620°–630°C. Many of these were considered for use in the ELSAM system in western Denmark.

All four samples have been received and prepared for testing by sizing and weighing them. The corrosion-testing tube furnace and accessories have been set up. The ceramic tube reaction chamber was modified to be pressure-sensitive for only slightly above atmospheric pressure in order to isolate reaction or combustion gases from furnace elements. A digital camera and macro lens assembly will allow corrosion photographs to be taken and placed into reports more efficiently and will allow photographs to be stored on disk for future use. A 35-mm microscope adapter to allow photographs to be taken at higher magnitudes will also be added to the system in the near future.

TABLE 15

Material, wt%	Candidate Tube Materials						
	Cr	Ni	Mo	W	Nb	Ti	Other
TP347HFG	18	10	—	—	1.0	—	—
St3Cu	18	9	—	—	0.4	—	Cu, N
NF709	20	25	1.5	—	0.25	0.05	N
253MA	21	11					C, Si, Mn, P, S, N, Ce
SUPER 304	18	9	—	—	0.45	—	Cu, N
800 HT	21	32.5	—	—	—	0.38	Si, Cu, Al, Al+Ti
HR3C	25	20	—	—	0.4	—	N
HR6W	23	43	1	6	0.2	0.1	—
HCM9M	9						
HCM 12	12	—	0–3.0	0–3.0	0–0.4	—	V, N

The next step will be to begin exposing the samples to the temperature and gas atmosphere found in actual systems for specific periods of time. Multiple samples of each alloy will be coated with ash and corrosion rates determined as a function of time, ash type and thickness, and gas composition. A commonly used alloy and a sample of each alloy without ash will serve as references. Scanning electron microscopy will be used to examine the physical and chemical detail of the corrosion, with the goal of determining the mechanism of corrosion under these conditions.

4.0 FUTURE WORK

Future work for this project includes the following:

- Complete analyses will be conducted of other deposits as they become available. Thermochemical equilibrium modeling will be performed to determine if the formation of these lower-melting-point eutectics can be predicted.
- The current status of ash behavior research report will be completed, and a publication will be submitted from the report.
- Additional coal slags will be analyzed for crystallization pathways of mineral species using the new EERC heated-stage XRD.
- Corrosion tests will be completed for at least four different alloys.

5.0 REFERENCES

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APPENDIX A

PRELIMINARY SUMMARY OF KEY ISSUES IN ASH BEHAVIOR

PRELIMINARY SUMMARY OF KEY ISSUES IN ASH BEHAVIOR

ISSUE: PREDICTION OF COAL GRINDABILITY

EERC Expertise (0-5): 4

Research Priority (0-5): 2

Summary: Prediction of grindability of coal and coal blends is a useful, although not a high-priority focus area. Blending of coals generally results in the concentration of the harder material in larger-size fractions and the softer material in the finer-size fractions, affecting the distribution of ash and volatile matter. Moisture has a profound effect on the grindability and handling properties of western subbituminous coals and is not well modeled. Other factors, in particular the effect of moisture on mill temperature and throughput, often are of more significance in fuel switching than grindability.

Unanswered Research Questions:

- Quantitative relationship of moisture to grindability of western coals
- Effect of hard/soft coal blends on ash distribution in coal fractions
- Inclusion of mill capacity as a function of moisture into performance indices

Applicable EERC Research and Reports:

Zygarlicke, C.J.; Galbreath, K.C.; McCollor, D.P.; Toman, D.L. "Development of Fireside Performance Indices," final topical report for DOE Contract No. DE-FC21-93MC30098; Nov. 1995.

Sulfur and moisture content were related to the Hardgrove grindability index (HGI) of 11 western subbituminous coals. Selected mineral abundances and the degree of mineral-maceral association, represented by the ratio of included to excluded minerals, for six of the test coals (Antelope, Big Sky, Black Thunder, Caballo Rojo, Rochelle, and Spring Creek [MNPL]) were also examined as possible predictors of grindability. A correlation analysis was performed to identify the coal properties that most significantly relate to the HGI; correlation coefficients with absolute values of ≥ 0.7 were considered significant. The coal moisture contents showed some degree of correlation to the HGI, even though the range in moisture content represented by most of the coals was limited. For example, the moisture contents for seven of the coals (Antelope, Big Sky, Black Thunder, Caballo Rojo, Dietz, Rochelle, and Spring Creek) ranged from only 21% to 25%, yet the HGI values ranged from 39 to 53, indicating that other factors are involved in the HGI variation. Grindability correlates best to the total sulfur and ash contents of the coals. The correlation of ash with HGI improves greatly (coefficient increases to 0.866) when the Wyodak coal is excluded from the linear regression analysis. The maceral and mineral abundances and included-excluded mineral ratio are insignificantly correlated to coal

grindability. An equation for predicting the HGI of subbituminous coals was derived from a multiple regression analysis of the ash and total sulfur variables; the predicted values compared favorably to the analytically determined HGI values. The regression equation was incorporated into the PCQUEST computer program to calculate a grindability index. Application of the index should be restricted to comparing the grindabilities of subbituminous coals that have moisture contents similar to those used in this study, i.e., 21 to 33 wt% on an as-received basis.

Gunderson, J.R.; Moe, T.A.; Selle, S.J.; Harding, N.S. "Technology Assessment for Blending Western and Eastern Coals for SO₂ Compliance," EPRI Final Report TR-105748; May 1996.

An assessment of mill performance primarily related to mill capacity and temperature limitations. Grindability was not called out as an issue.

Gunderson, J.R.; Moe, T.A.; Abbott, M.; Douglas, B.; Selle, S.J. "Pilot Plant Assessment of Blend Properties," final report; Oct. 1996.

A series of tests was performed to determine the effects of blending eastern bituminous coals with western subbituminous coals on utility boiler operation. Mill performance tests were performed by CONSOL, Inc., at its facility in Library, Pennsylvania. Mill performance tests indicated that at design pulverizer conditions (relative to pulverization of bituminous coal), the decreased thermal input of the subbituminous coals resulted in derates on the mill of up to 55% of the maximum thermal input of the bituminous coals. One Pittsburgh seam bituminous coal, one Illinois No. 6 seam bituminous coal, and two Powder River Basin (PRB) subbituminous coals were tested. By raising the mill outlet temperature between 5° and 25°F, thermal throughput for the subbituminous coals could be increased by 10% to 20%. Increasing the air:fuel ratio also tended to increase thermal throughput, but at the expense of a coarser product. At the maximum thermal throughput for the subbituminous coals and at the highest air:fuel ratio, product fineness (less than 200 mesh) decreased by up to 15 percentage points. Interestingly, the lowest-heat-content subbituminous coal exhibited the lowest thermal derate of the two PRB coals tested, but required much higher mill energy input.

Allan, S.E.; Anderson, C.M.; Erickson, T.E.; Jensen, R.R.; McCollor, D.P.; Zygarlicke, C.J. "Fuel Quality Advisor," final report for the period Jan. 1, 1995, through Sept. 30, 1996, for DOE Contract No. DE-FC21-93MC30097; Nov. 1996.

The Fuel Quality Advisor coal handleability model rates the dust handling for coal by making a correlation between type of coal, particle-size distribution, and moisture content. Early attempts were made to use maceral content to help group the various lignite, subbituminous, and bituminous coals; however, maceral data were inconclusive and varied dramatically within each region. The as-received moisture content relative to the coal's original bed moisture content was the main factor in determining the overall coal handleability indices. A slacking index was also developed based upon information compiled by the Bureau of Mines for various ranks of coal.

Zygarlicke, C.J.; McCollor, D.P. "Validation of Fireside Performance Indices Fouling Assessment of Coal and Soil-Waste Blends," final report for Duke Power Company; March 1996.

The PCQUEST computer model-predicted grindability is compared to the Hardgrove grindability index for western subbituminous coals. The predicted HGI of five eastern bituminous coals and the expected grindability based on experience were compared. Also included was a calculated HGI from a formula developed by Gomez and Hazen based on 735 coal samples. The PCQUEST grindability index significantly underestimates the HGI, while the formula of Gomez and Hazen significantly overestimates it. It is to be noted that with the exception of one coal, the Gomez and Hazen formula produces values that bear a linear relation to the expected Hardgrove values. Both predictive methods perform very poorly compared to the expected values. Significant further improvement was seen to be needed in the PCQUEST grindability algorithms to allow them to accommodate bituminous coals.

Key Literature Information:

Vecci, S.J.; Moore, G.F. "Determine Coal Grindability," *Power* **1978**, *March*, 74.

The article is a discussion of industry approaches to obtaining reliable Hardgrove grindability indices for western coals. One method is to obtain grindability indices at a range of moisture levels from as-received to the American Society for Testing and Materials (ASTM) air-dried levels. A second standard continuous grindability index has also been developed.

Gomez, M.; Hazen, K. "Prediction of Coal Grindability from Exploration Data," USBM Report of Investigations R1; 7421, 1970.

A general prediction model for the Hardgrove grindability index was constructed for 735 coal samples using the proximate analysis, heating value, and sulfur content. The coals used to develop the general index ranged in volatile matter from 12.8 to 49.2 percent, dry basis, and had grindability indexes ranging from 35 to 121. A restricted model applicable to bituminous coals having grindabilities in the 40-to-110 range was developed from the proximate analysis and the petrographic composition of the coal. The prediction of coal grindability within a seam was also investigated. The results support the belief that mechanical properties of the coal are related to both chemical and petrographic features of the coal.

Cho, H.; Luckie, P.T. "Grinding Behavior of Coal in a Standard Ball-and-Race Mill," *Energy & Fuels* **1995**, *9*, 59-66.

An investigation was carried out to predict size-composition makeup of the product of a coal blend ground in a ball-and-race mill using the breakage characteristics of the individual components. The composition of the product size intervals is generally different

from the weighted sum of the two products from separate grinding. An empirical equation was used to predict the change in breakage parameters as a function of the blending ratio and the difference between the relative strengths of the two materials. A locked-cycle simulation for grinding a binary mixture shows that the content of the mill charge becomes richer in the stronger component. The system attains steady state when the absolute production rates of both materials are the same, although the ratio of materials in the mill charge is not necessarily the same as the ratio in the feed. As a result, the production rate can be lower than expected based on the feed ratio.

“Development of a Coal-Blending Model,” final report for ESEERCO, CQ Inc.; Aug., 1994.

This project developed models for engineers to use in calculating blend properties for coal blends and also investigated blending volatile matter. It was found that the HGI for a blend can be approximated by a weighted average of the parent coal HGI values. However, this blended HGI may not be the most important property related to grindability for a coal blend. The hardest coals are concentrated in the coarsest fractions of the pulverized blend, while the softest coals are concentrated in the finest fractions. This segregation causes variations in the volatile matter, sulfur, ash composition, and ash fusion temperature by size and can affect performance in the boiler. This segregation is masked by evaluating only the composite values for these properties.

ISSUE: COAL ORGANIC MINERAL ANALYSIS

EERC Expertise (0-5): 5

Research Priority (0-5): 2

Summary: Determination of organically bound coal mineral content is a mature analysis method. It is of particular importance with subbituminous and lignite coals that contain substantial amounts of Ca and Na attached to coal carboxylic acid groups. Some questions remain with the technique, including the effect of pH change during extractions, methods to account for extractable Si, and the significance of possible ammonium acetate-soluble Fe and Al in tropical coals.

Unanswered Research Questions:

- The amount and effect of soluble Si species on the chemical fraction normalization
- The effect of pH changes during extractions on the chemical fractionation results
- The role of water and ammonium acetate-soluble Al and Fe species in soils and coals mined in a tropical setting.

Applicable EERC Research and Reports:

S.A. Benson et al. "Project Sodium," final technical report; July, 1988

The project final report contains a description of the chemical fractionation procedure along with the mineral species expected to be removed at each step. The chemical fractionation analysis (CHF) procedure has been modified to include an initial water extraction to remove water-soluble minerals prior to extraction with ammonium acetate.

Combustion Inorganic Transformations

The chemical fractionation technique was further refined and developed in this project and with the combination of computer controlled scanning electron microscopy (CCSEM) mass balances of total coal inorganic constituents were performed. Over ten different U.S. coals were part of this inorganic characterization.

Advanced Combustion Engineering Research Center – Brigham Young University and University of Utah

Chemical fraction and coal mineral inorganic mass balances were performed and the information and data were used in devising predictive ash transformation models as supplemental algorithms for the Advanced Combustion Engineering Research Center (ACERC) computational fluid dynamics codes termed PCGC-2 and PCGC-3.

Zygarlicke, C.J.; McCollor, D.P. "Fouling Assessment of Coal and Soil-Waste Blends Phase I," final report to Duke Power Validation of Fireside Performance Indices Project; Sept., 1995

Three samples of soil-waste (soil contaminated with organics) were examined by CHF analysis as part of a program to determine the slagging and fouling impacts of cofiring the soil-waste with coal in a cyclone-fired utility boiler. It was noted that the bulk chemistry calculated from CCSEM data differed significantly from the x-ray fluorescence bulk chemistry of two of the soils. The CHF analysis of these soils gave very high levels of aluminum and iron extraction by ammonium acetate. The soils appear to be laterites, with high concentrations of iron and aluminum hydroxides present. Although not stated, similar behavior may appear in coals mined in tropical locations.

Key Literature Information:

Benson, S.A.; Fegley, M.M.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D. P.; Miller, B.G.; Miller, S.F.; Steadman, E.N.; Schobert, H.H.; Weber, B.J.; Weinmann, J.R.; Zobeck, B.J. "Project Sodium: A Detailed Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report, EERC Publication, July, 1988.

Benson, S.A.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D.P.; Ness, S.R.; Nowok, J.; Puffe, W.; Ramanathan, R.; Steadman, E.N.; Toman, D.L.; Zygarlicke, C.J. "Project Sodium: Follow-on Work to the Original Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report, EERC Publication, Jan., 1992.

Zygarlicke, C.J.; Katrinak, K.A. "Combustion Inorganic Transformations," final technical progress report for the period April 1, 1986 – Dec. 31, 1992, for U.S. DOE DE-FC21-86MC10637; EERC publication, 1992.

Zygarlicke, C.J.; Jones, M.L.; Steadman, E.N.; Benson, S.A. "Characterization of Mineral Matter in ACERC Coals," Prepared for Brigham Young University and the University of Utah Advanced Combustion Engineering Research Center; EERC Publication, 1990, 32 p.

Miller, R.N.; Given P.H., "Variations in Organic Constituents of Some Low-Rank Coals, from Ash Deposits and Corrosion Due to Impurities in Combustion Gases," *In* R.W. Bryers, Ed.; The Engineering Foundation, 1977, pp. 39–50.

Twenty to thirty elements were determined in four drill cores. The elements Ca, Na, K, Sr, Mg, and Mn are present in ion-exchangable form bound to carboxylic acid groups in the coal. Al, Ti, Be, and V are present as chelated organometallic complexes. The paper contains a description of the CHF procedures and mineral associations.

Benson S.A.; Holm, P.A. "Comparison of Inorganic Constituents in Three Low-Rank Coals," *Industrial and Engineering Chemistry Product Research and Development* **1985**, 24, 184-189.

The association of fourteen elements (Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Si, Sr, and Ti) in a North Dakota lignite, a Texas lignite, and a Montana subbituminous coal were examined by chemical fractionation. Ion-exchangeable elements associated with carboxylic acid groups and extracted by 1 M ammonium acetate were Ba, Ca, Mg, Mn, Na, and Sr. Al, Ba, Cr, Cu, Fe, Ni, Sr, and Ti were extracted by 1 M HCl and are present either as coordination complexes or as acid-decomposable minerals. Remaining inorganics are present as quartz, clays, and sulfides. The three coals show significant differences in the amounts and mode of occurrence of the elements present.

Karner, F.R.; Zygarlicke, C.J.; Brekke, D.W.; Steadman, E.N.; Benson, S.A. "New Analysis Techniques Help Control Boiler Fouling," *Power Engineering* **1994**, 98, 35-38.

A good applied approach to using chemical fractionation data, CCSEM mineralogy, and scanning electron microscopy analysis on coal boiler ash fouling deposits is demonstrated in this paper. The mechanics of how organically bound inorganics interact with aluminosilicate clays to form tenacious fouling deposits in the convective pass region of a boiler are described.

Benson, S.A.; Jones, M.L.; Harb, J.N. "Ash Formation and Deposition," In *Fundamentals of Coal Combustion for Clean and Efficient Use*; Smoot, L.D. Ed.; New York: Elsevier, pp. 299-374.

This is a fairly good summary of the development and application of chemical fractionation and CCSEM techniques for determining inorganic quantities in several different types and ranks of coal. The CCSEM technique is described as a research tool for characterization coal and ash by-products and as an important technique for providing sound modeling input data.

ISSUE: CCSEM DETERMINATION OF COAL MINERAL CONTENT

EERC Expertise (0-5): 5

Research Priority (0-5): 3

Summary: The CCSEM technique has provided a significant advancement in the understanding of ash transformation processes in coal combustion systems. Early work by Huggins et al. (1980) has been refined and applied by others, including the EERC, to provide a necessary technique for acquiring detailed analysis of coal minerals for model predictions. Some refinement is still needed, particularly in standardization of procedures and improvement in agreement between laboratories. CCSEM provides size and inference of mineral species from point elemental analyses for mineral particles routinely between 1 and 100 μ m. A special fine-particle technique has been developed for analysis in the 0.1-1- μ m size range.

Applicable EERC Research and Reports:

Zygarlicke, C.J.; Katrinak, K.A. "Combustion Inorganic Transformations," final technical progress report for the period April 1, 1986 - Dec. 31, 1992, for DOE Contract No. DE-FC21-86MC10637; EERC publication, 1992.

The development and improvement of the CCSEM technique to quantify coal minerals is reviewed. Improvements included standards, three magnification protocols, image analysis to determine mineral grain juxtaposition, and atomic number, absorption, and fluorescence (ZAF) correction. A small-particle analysis method was also developed to quantify particles as small as 0.1 μ m.

Unanswered Research Questions:

- Development of standardized CCSEM calibration procedures

Key Literature:

Benson, S.A.; Fegley, M.M.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D. P.; Miller, B.G.; Miller, S.F.; Steadman, E.N.; Schobert, H.H.; Weber, B.J.; Weinmann, J.R.; Zobeck, B.J. "Project Sodium: A Detailed Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report; EERC Publication, July, 1988.

Benson, S.A.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D.P.; Ness, S.R.; Nowok, J.; Puffe, W.; Ramanathan, R.; Steadman, E.N.; Toman, D.L.; Zygarlicke, C.J. "Project Sodium: Follow-on Work to the Original Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report; EERC Publication, Jan., 1992.

Zygarlicke, C.J.; Katrinak, K.A. "Combustion Inorganic Transformations," final technical progress report for the period April 1, 1986 – Dec. 31, 1992, for DOE Contract No. DE-FC21-86MC10637; EERC publication, 1992.

Zygarlicke, C.J.; Jones, M.L.; Steadman, E.N.; Benson, S.A. "Characterization of Mineral Matter in ACERC Coals," Prepared for Brigham Young University and the University of Utah Advanced Combustion Engineering Research Center; EERC Publication, 1990, 32 p.

Galbreath, K.A. et al. "Collaborative Study of Quantitative Coal Mineral Analysis Using Computer-Controlled Scanning Electron Microscopy," *Fuel* **1997**, 75 (4), 424–430.

Six laboratories participated in a comparative study of CCSEM analysis of coal minerals. Five analyses were performed by most laboratories on Pittsburgh No. 8, Illinois No. 6, and Prince bituminous coals. Repeatability relative standard deviation was <20% for calcite, pyrite, kaolinite, and quartz. Reproducibility of kaolinite was the poorest, and that of pyrite was the best. Although pyrite determination was the most precise, mineral calculations indicate that the results are overbalanced. A standardized calibration procedure is needed to improve agreement between laboratories.

Kong, L.; Zygarlicke, C.J.; Benson, S.A. "Computer-Controlled Analyses of Minerals in Coal," *In Proceedings of the 13th Annual International Pittsburgh Coal Conference: Coal-Energy and the Environment*, Sept. 2–7, 1996; Chiang, S.H. Ed.; Vol. 1, pp. 228–233.

The paper describes the precision and accuracy of CCSEM results from two different laboratories. Quartz, kaolinite, are some of the coal minerals were compared for size and quantity between the two laboratories for two different coals. It was concluded that CCSEM methods for quantifying coal minerals have improved greatly since the inception of the method and are an excellent tool for providing input into predictive coal and ash evaluation models.

Katrinak, K.A.; Zygarlicke, C.J. "Size-Related Variations in Coal Fly Ash Composition as Determined Using Automated Scanning Electron Microscopy," *Fuel Processing Technology* **1995**, 44, 71–79.

The CCSEM capabilities for examining fly ash particles that are below 1 micron in average diameter are described in this paper. Normal coal and fly ash analysis of mineral and ash particles using CCSEM is limited to about 1 micron or greater because of beam spot sizes and the need to obtain accurate chemical information. A new technique minimizes the SEM beam spot size while optimizing chemical information gained by adjusting SEM acceleration voltage and beam current. Results include calibration of the technique on known compounds. The technique has far-reaching applications with the increased interest in reducing levels of fine particulate in the less-than-2.5-micron range from the earth's atmosphere.

Huggins, F.E.; Kosmack, D.A.; Huffman, G.P.; Lee, R.J. "Coal Mineralogies by SEM Automatic Image Analysis," *Scanning Electron Microscopy* 1980, 1, p. 531-540.

Procedures for using SEM automatic image analysis to obtain quantitative mineral descriptions are delineated. Experimental tests indicate that the precision and accuracy are comparable to other methods, but that pyrite is overestimated. The technique is more sensitive to minor components than other methods and also provides mineral particle size information. Results are summarized describing the effects of coal washing and the reconstruction of paleoenvironments for coal quality determination.

Jones, M.L.; Kalmanovitch, D.P.; Steadman, E.N.; Zygarlicke, C.J.; Benson, S.A. "Application of SEM Techniques to the Characterization of Coal and Coal Ash Products," In *Advances in Coal Spectroscopy*; Meuzelaar, H., Ed.; Plenum: New York, 1989.

The book article is a good synopsis of a the variety of CCSEM, point count, and SEM morphological analyses that were used for understanding the mechanisms of ash and deposit formation during coal combustion. Several ACERC program coals were part of the study, and much of the data were used for developing predictive fouling and slagging models in conjunction with the ACERC PCGC codes.

Zygarlicke, C.J.; Steadman, E.N. "Advanced SEM Techniques to Characterize Coal Minerals," *Scanning Microscopy* 1990, 4 (3), 579-590.

The paper describes some of the earlier work performed at the EERC using SEM methods for coal mineral analysis. Much effort is put forth describing the technical aspects of CCSEM and the methods for pigeonholing minerals chemically using the energy-dispersive spectral data.

Skorupska, N.M.; Carpenter, A.M. "Computer-Controlled Scanning Electron Microscopy of Minerals in Coal," *IEA Coal Research Perspectives*, IEAPER/07; Dec. 1993.

The paper is a summary report of CCSEM technique at the time, covering methods, reproducibility, and the analysis results and their significance in predicting coal ash deposition behavior.

Benson, S.A.; Jones, M.L.; Harb, J.N. "Ash Formation and Deposition," In *Fundamentals of Coal Combustion*; Smoot, L.D., Ed.; Elsevier: New York, 1993; pp. 299-373.

This is a fairly good summary of the development and application of chemical fractionation and CCSEM techniques for determining inorganic quantities in several different types and ranks of coal. The CCSEM technique is described as a research tool for characterization of coal and ash by-products and as an important technique for providing sound modeling input data.

ISSUE: HIGH-TEMPERATURE COMBUSTION DEPOSITION (>1050°C)

EERC Expertise (0-5): 5

Research Priority (0-5): 3

Summary:

There has been a plethora of research and published results from the EERC and other research institutions over the last century pertaining to high-temperature-zone (>1050°C) silicate- and sulfate-based ash deposition. Research in the area of slag formation in the radiant portion of a conventional combustion system has probably been more prevalent than for research in fouling deposits that are more associated with the convective heat-absorbing sections of a boiler. Lower-rank coals and U.S. PRB coals have by far the least amount of published and studied information; however, the last 25 years have seen a great increase in research in ash fouling deposition for western U.S. coals. In general, the mechanisms of ash transformation from coal minerals to fly ash, ash transport to deposition surfaces, ash sticking and surface viscosity development, and deposit strength development have been studied the most intensely for high-temperature regimes. Various models or algorithms have been proposed to help predict the behavior of ash from coals, but a reliable, all-inclusive model has yet to be configured.

Unanswered Research Questions:

- A major unanswered question is the actual relationship of calculated viscosity and percentage of liquid-phase material to ash deposition behavior, particularly in the high-viscosity regime of 10^7 poise where conventional rotating-bob viscosity measurements are not possible.
- A second major unanswered question is the prediction of ash removability by sootblowing from fundamental coal ash chemistry.

Applicable EERC Research:

U.S. Bureau of Mines and U.S. DOE Grand Forks Energy Technology Center Low-Rank Coal Research

The research conducted under the U.S. Bureau of Mines and the U.S. Department of Energy involved extensive pilot-scale testing of lignites and, to a lesser extent, subbituminous coals. Additional information was obtained from field testing at utility sites. A key result was the elucidation of the initial "inner white layer" of sodium sulfate condensing on heat-exchange surfaces and its role in initiating deposition. The role of sodium in deposition was examined, and the importance of sodium and other organically bound minerals in increasing ash deposition recognized. The differences between western and eastern ashes were noted, and some of the first fouling mechanisms for western coals proposed.

Project Sodium

Project Sodium dealt with deposition issues specifically related to high-sodium lignite coals. Results were obtained from laboratory studies, pilot-scale testing, and limited full-scale testing. In the high-temperature regime, deposit initiation by the classic sodium sulfate inner white layer on the tube surface, followed by transition to a silicate-based deposit was reaffirmed. A key finding was that the chemical association of sodium was crucial to the degree of fouling experienced. Early chemical fractionation experiments indicated that organically bound sodium contributed to severe deposition, while sodium aluminosilicate clays were relatively benign. In the deposits, sodium was found to be associated with amorphous glass phases, indicative of sodium having formed low-melting-point eutectics with aluminosilicate ash material.

ACERC Project

Studies were performed to examine factors that influence initiation of ash deposition. Five coals, including lignite, subbituminous, and bituminous, were combusted and the initial deposits formed, and the bulk fly ash was examined using SEM techniques. Initial adhering particles consisted primarily of iron-iron-calcium- and iron-silica-aluminum-rich particles. The enriched particles were common to all the initial deposits, with abundance determined by concentration in the original coal ash. The great majority of particles clustered in groupings above a certain critical mass and below a critical viscosity regardless of individual compositions. The propensity for initial ash deposition could be related to the fraction of bulk fly ash particles with sufficient kinetic energy to inertially impact the substrate and with sufficiently low viscosity to adhere on impact.

Coal Beneficiation Project

A DOE Clean Coal project involving ABB-CE and the EERC focused on coal beneficiation using flotation methods. The EERC performed coal mineral and deposit characterization using CCSEM and other advanced methods of inorganic analysis. Fly ash and deposits were generated from several baseline and beneficiated fuels, and the properties of the ash components were correlated to the coal processing. In some instances, coal cleaning reduced the amount of ash but concentrated coal inorganics, that are notorious for causing tenacious fouling deposits.

Development of Fireside Performance Indices Project

Ash deposition indices (slagging and high-temperature fouling) were formulated from existing bench-, pilot-, and full-scale combustion-testing data and knowledge of inorganic transformations, entrained ash formation, and ash deposition. Additional bench-scale testing in drop-tube furnaces (DTFs) was performed on eight PRB subbituminous coals to refine and verify the ash deposition indices and to develop ash removability indices (slag tapping and sootblowing). Slagging and conventional and low-NO_x high-temperature fouling were simulated. Deposit growth rates, sticking coefficients, in situ adhesion

strengths, crushing strengths, initial slagging temperatures, porosities, and chemical and phase compositions were determined. In general, the low-NO_x combustion conditions produce high-temperature fouling deposits that have less adhesion and crushing strengths relative to those produced in conventional combustion conditions.

Development of Fouling Algorithms for the Coal Quality Expert

Dynamic fouling algorithms were developed to predict ash transformations during conventional coal combustion, ash transport to convective pass fouling heat exchange surfaces, rate of fouling deposition, deposit strength development, and deposit shedding or sootblowing effectiveness. The algorithms were developed based in part on ash deposition theory and empirical data and were part of a comprehensive coal quality impact model for conventional boilers called the Coal Quality Expert (CQE). Coal mineral data and boiler design and dynamic operating data were used as inputs. The models were hooked to a boiler engine in the CQE so that ash deposition occurred in a particular region of the boiler, flue gas temperatures would also increase in that temperature and ash deposit mechanisms could be updated.

Key Literature:

Sondreal, E.A.; Tufte, P.H.; Beckering, W. "Ash Fouling in the Combustion of Low-Rank Western U.S. Coals," *Combustion Science and Technology* 1977, 16, 95-110.

Honea, F.I. "Studies of Ash-Fouling Potential and Deposit Strength in the GFTEC Pilot Plant Test Furnace," In *Fouling and Slagging Resulting from Impurities in Combustion Gases*, Bryers, R.W.; Cole, S.S., Eds.; Proceedings of the Engineering Foundation Conference, Henniker, NH, July 12-17, 1981; pp 117-142.

Honea, F.I. "Survey of Ash-Related Losses at Low-Rank Coal-Fired Utility Boilers," In *Fouling and Slagging Resulting from Impurities in Combustion Gases*, Bryers, R.W.; Cole, S.S., Eds.; Proceedings of Engineering Foundation Conference, Henniker, NH, July 12-17, 1981; pp 527-539.

Rindt, K.K.; Jones, M.L.; Schobert, H.H. In *Fouling and Slagging Resulting from Impurities in Combustion Gases*, Proceedings of the Engineering Foundation Conference, Bryers, W.R.; Cole, S.S., Eds.; July 12-17, 1981, Henniker, NH; pp. 17-35.

Tufte, P.H.; Beckering, W. "A Proposed Mechanism for Ash Fouling Burning Northern Great Plains Lignite," *Journal of Engineering for Power* 1975, July, 407-412.

Sondreal, E.A.; Kube, W.R.; Elder, J.L. "Analyses of the Northern Great Plains Province Lignites and Their Ash: A Study of Variability," Bureau of Mines RI 7158; 1968, 94 p.

Benson, S.A.; Fegley, M.M.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D. P.; Miller, B.G.; Miller, S.F.; Steadman, E.N.; Schobert, H.H.; Weber, B.J.; Weinmann, J.R.; Zobeck, B.J. "Project Sodium: A Detailed Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report; EERC Publication, July, 1988.

Benson, S.A.; Hurley, J.P.; Jones, M.L.; Kalmanovitch, D.P.; Ness, S.R.; Nowok, J.; Puffe, W.; Ramanathan, R.; Steadman, E.N.; Toman, D.L.; Zygarlicke, C.J. "Project Sodium: Follow-on Work to the Original Evaluation of Sodium Effects in Low-Rank Coal Combustion Systems," final technical report; EERC Publication, Jan. 1992.

Hurley, J.P.; Zygarlicke, C.J. "Physical and Chemical Changes in Fly Ash and Deposits Caused by Coal Beneficiation," In *Inorganic Transformations and Ash Deposition During Combustion*; Benson, S.A., Ed.; American Society of Mechanical Engineers: New York, 1992; pp 345-366.

Zygarlicke, C.J.; Katrinak, K.A. "Combustion Inorganic Transformations," final technical progress report for the period April 1, 1986 - Dec. 31, 1992, for DOE Contract No. DE-FC21-86MC10637; EERC publication, 1992.

Benson, S.A.; Jones, M.L.; Harb, J.N. "Ash Formation and Deposition," In *Fundamentals of Coal Combustion*; Smoot, L.D. Ed.; Elsevier: New York, 1993; pp. 299-373.

An excellent explanation of the physical and chemical transformations of mineral and organically bound inorganics into entrained ash and ash deposits and the associated mechanisms of formation and deposition are given in this book chapter. Ash formation and deposition results for several different U.S. coals are given based on laboratory- and pilot-scale combustion testing. This work was primarily based on the DOE Clean Coal Technology and ACERC projects.

Srinivasachar, S.; Helble, J.J.; Boni, A.C. "An Experimental Study of the Inertial Deposition of Ash Under Coal Combustion Conditions," In *Proceeding of the 23rd Symposium (International) on Combustion*; The Combustion Institute, 1990; pp 1305-1312.

The study identified particle viscosity as the dominant ash variable in determining inertial deposition of ash. A critical viscosity for adhesion was identified that is dependent on particle kinetic energy. The critical viscosity range was several orders of magnitude higher than currently used to predict slagging propensity in boilers. Deposition experiments were conducted with a San Miguel lignite coal to verify the applicability to coal ash deposition.

McCollor, D.P.; Zygarlicke, C.J.; Allan, S.E.; Benson, S.A. "Ash Deposition Initiation in a Simulated Fouling Regime," *Energy & Fuels* **1993**, 7, 761-767.

The paper describes the significant results of work performed under the ACERC project.

Allan, S.E.; Erickson, T.A.; McCollor, D.P. "Modeling of Ash Deposition in the Convective Pass of a Coal-Fired Boiler," In *Application of Advanced Technology to Ash-Related Problems in Boilers*, Baxter, L.; DeSollar, R., Eds.; New York: Plenum Press; 1996, pp 451-470.

Bryers, R.W. "Fireside Behavior of Mineral Impurities in Fuels from Marchwood 1963 to the Sheraton Palm Coast 1992," In *Inorganic Transformations and Ash Deposition During Combustion*; Benson, S.A., Ed.; American Society of Mechanical Engineers: New York, 1992; pp 3-70.

His summary of recent work in understanding the impact of coal impurities on boiler systems revealed that most of the work performed in ash deposition behavior is in response to critical boiler events or catastrophic events and little study is actually performed methodically. Areas identified as needing more attention include coal mineral variability; coal beneficiation, blending, and switching; in situ remedial measures; age hardening of deposits; and loss in thermal effectiveness and thermal properties in general.

Zygarlicke, C.J.; Benson, S.A.; Borio, R.W.; Mehta, A.K. "Examination of Ash Deposition in Full-, Pilot-, and Bench-Scale Testing," Presented at the 3rd International Conference on the Effects of Coal Quality on Power Plants, San Diego, CA, Aug. 25-27, 1992.

Zygarlicke, C.J.; Benson, S.A.; Borio, R.W. "Pilot- and Bench-Scale Combustion Testing of a Wyoming Subbituminous/Oklahoma Bituminous Coal Blend," In *Coal-Blending and Switching of Low-Sulfur Western Fuels*; Bryers, R.W.; Harding, N.S., Eds.; American Society of Mechanical Engineers: New York, 1994; pp 281-300.

McCollor, D.P.; Zygarlicke, C.J.; Benson, S.A. "Mechanisms of Ash Fouling During Low-Rank Coal Combustion," In *Applications of Advanced Technology to Ash-Related Problems in Boilers*; Baxter, L.; DeSollar, R., Eds.; Plenum Press: New York, 1996; pp 223-235.

ISSUE: LOW-TEMPERATURE COMBUSTION DEPOSITION (<1050°C)

EERC Expertise (0-5): 5

Research Priority (0-5): 3

Summary: Low-temperature deposition in combustion systems is primarily the result of calcium deposition by thermophoresis and impaction followed by subsequent sulfonation, although other alkali and alkaline-earth elements may also contribute. Measurements have been made that allow estimates of deposition rate and sulfate strength development.

Unanswered Research Questions:

- Definition of the temperature range most favorable for sulfonation and sulfate strength development producing the most problematic deposits.
- Calcium in silicate structures and impaction on sulfation.
- Methods for mitigation of sulfation and bridging in hot-gas filters.

Applicable EERC Research:

Project Calcium

The project involved field tests at five full-scale utility boilers, combined with coal and deposit analysis, and bench-scale studies of calcium sulfate-based low-temperature deposition. Four types of low-temperature deposits were identified: upstream massive, upstream enamel, upstream double-crested, and downstream powder deposits. All contain large amounts of sulfur fixed from the gas stream by alkali and alkaline-earth elements, particularly calcium. The massive deposits form as fins windward of the lead tubes of the reheat steam banks, sulfonate, and become hard rapidly and are difficult to remove by sootblowing. Upstream enamel deposits comprise particles < 3µm diameter and are highly enriched in calcium. The deposits remain relatively thin, but are very difficult to remove either by sootblowing or off-line cleaning. The double-crested deposits are similar to the enamel deposits. The downstream powder deposits form as a result of gas eddies downstream of the tubes. These deposits are powdery and quite easy to remove and shed because of their own weight at a thickness of approximately 1 cm. However, these deposits cause the greatest reduction in heat transfer of the low-temperature type, and their location in the economizer often does not permit effective sootblower coverage. Estimates of deposit growth rates at full-scale utility boilers and lab-scale sintering strength development were developed for use in the LEADER program.

Development of Fireside Performance Indices Project

In the course of the project, low-temperature fouling deposits were produced from three subbituminous coals under conditions simulating conventional and low-NO_x combustion conditions. The low-temperature fouling deposits generally did not show a significant difference between the conventional and the low-NO_x condition. This was ascribed to sulfonation of the calcium-rich deposits, which is in contrast to the melting and sintering mechanism of deposit strength development that dominates in the high-temperature fouling deposits. The low-temperature fouling deposits were generally depleted in SiO₂ and Na₂O but enriched in CaO and MgO. Apparently the amount of organically bound Ca and Mg in a coal is an important variable to consider in predicting low-temperature fouling propensity. The low-temperature fouling deposits are also enriched in SO₃, as evidenced by the relatively high concentrations of anhydrite. It appeared that deposit porosity was unrelated to deposit crushing or adhesion strength.

Hot-Gas Filter Project

The EERC performed chemical and physical analysis of ash bridges formed between candle filters in advanced particulate filters. The purpose of the analysis was to quantify the changes in the ash that led to the reduction in bridging. Analysis included advanced SEM techniques to determine the size and composition of ash particles down to 0.1 microns in diameter and high-temperature tensile strength testing. Ash bridges between filters showed greater age and quantities of sulfur, and sulfation is one proposed mechanism by which hard bridging deposits form and force apart filter structures, causing failure.

Key Literature:

Hurley, J.P.; Benson, S.A.; Erickson, T.A.; Allan, S.E.; Bieber, J. "Project Calcium," final report; 1992

Project Calcium involved field tests at five full-scale utility boilers, combined with coal and deposit analysis and bench-scale studies of calcium sulfate-based low-temperature deposition. Four types of low-temperature deposits were identified: upstream massive, upstream enamel, upstream double-crested, and downstream powder deposits. All contain large amounts of sulfur fixed from the gas stream by alkali and alkaline-earth elements, particularly calcium. The deposits tend to be very difficult to remove either by sootblowing or off-line cleaning. Estimates of deposit growth rates at full-scale utility boilers and lab-scale sintering strength development were developed for use in the EERC LEADER program.

Zygarlicke, C.J.; Galbreath, K.C.; McCollor, D.P.; Toman, D.L. "Development of Fireside Performance Indices," final topical report for DOE Contract No. DE-FC21-93MC30098, Nov. 1995.

In the course of the project, low-temperature fouling deposits were produced from three subbituminous coals under conditions simulating conventional and low-NO_x combustion conditions. The low-temperature fouling deposits generally did not show a significant difference between the conventional and the low-NO_x condition. This was ascribed to sulfonation of the calcium-rich deposits, which is in contrast to the melting and sintering mechanism of deposit strength development that dominates in the high-temperature fouling deposits. The low-temperature fouling deposits were generally depleted in SiO₂ and Na₂O but enriched in CaO and MgO. Apparently, the amount of organically bound Ca and Mg in a coal is an important variable to consider in predicting low-temperature fouling propensity. The low-temperature fouling deposits are also enriched in SO₃, as evidenced by the relatively high concentrations of anhydrite. It appeared that deposit porosity was unrelated to deposit crushing or adhesion strength.

Hurley, J.P.; Erickson, T.A.; Benson, S.A.; Brobjorg, J.N. "Ash Deposition at Low Temperatures in Boilers Firing Western U.S. Coals," Presented at the International Joint Power Generation Conference, San Diego, CA, 1991, 8 p.

Benson, S.A.; Hurley, J.P.; Zygarlicke, C.J. "Studies on Calcium-Based Deposition in Utility Boilers," *In* Proceedings of the Conference on Effects of Coal Quality on Power Plants, St. Louis, MO, Sept. 1990.

Benson, S.A.; Hurley, J.P.; Zygarlicke, C.J.; Steadman, E.N.; Erickson, T.A. "Predicting Ash Behavior in Utility Boilers: Assessment of Current Status," Presented at the Conference on Effects of Coal Quality on Power Plants, Electric Power Research Institute, San Diego, CA, Aug. 1992.

Hurley, J.P.; Watne, T.M.; O'Keefe, C.A.; Katrinak, K.A.; Nowok, J.W.; Roling, T.A.; Dockter, B.A. "Chemical and Physical Analysis of Tidd Hot-Gas Filter Ash," *In* Proceedings of the 13th Annual Pittsburgh Coal Conference, Pittsburgh, PA, Sept. 3-7, 1996; Vol. 1, pp 241-246.

APPENDIX B

COMPUTED VARIABLES FOR HOPPER MODEL AND MODIFIED FRENKEL MODEL

TABLE B-1

Computed Variables for Hopper Model

$(\gamma t)/(\eta r_f)$	(x/r_f)
0	0
0.00135	0.00355
0.00297	0.0071
0.00860	0.0181
0.01986	0.0372
0.0331	0.0574
0.0483	0.0787
0.0656	0.1013
0.0851	0.1253
0.1071	0.1509
0.1321	0.1782
0.1604	0.2075
0.1927	0.2391
0.2299	0.2734
0.2731	0.3106
0.3239	0.3515
0.3848	0.3967
0.4595	0.4472
0.5542	0.5046
0.6809	0.5713
0.8660	0.6520
1.1946	0.7577
1.4426	0.8147
1.6417	0.8501
1.9845	0.8955
2.5839	0.9438
3.1325	0.9676
3.7342	0.9825
4.2836	0.9900
5.4348	0.9968
	1.0000

TABLE B-2

Computed Variables for Modified Frenkel Model

$(\gamma t)/(\eta r_0)$	(x/r)
0.0001	0.0100
0.01	0.0979
0.02	0.1396
0.03	0.1713
0.04	0.1984
0.05	0.2210
0.06	0.2419
0.07	0.2609
0.08	0.2786
0.09	0.2949
0.10	0.3109
0.20	0.4274
0.30	0.5060
0.40	0.5736
0.50	0.6242
0.60	0.6721
0.70	0.7062
0.80	0.7403
0.90	0.7666
1.00	0.7910
1.50	0.8767
2.00	0.9241
4.00	0.9872
6.00	0.9976
8.00	0.9995