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

Ash behavior in power systems can have a significant impact on the design and performance of advanced power systems. The Energy & Environmental Research Center (EERC) has focused significant effort on ash behavior in conventional power systems that can be applied to advanced power systems. This initiative focuses on filling gaps in the understanding of fundamental mechanisms of ash behavior that has relevance to commercial application and marketable products. This program develops methods and means to better understand and mitigate adverse coal ash behavior in power systems and can act to relieve the U.S. reliance on diminishing recoverable oil resources, especially those resources that are not domestically available and are fairly uncertain.

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 and reducing operation and maintenance costs. The specific objectives of this initiative are focused 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.
- Determine fundamental ash properties (viscosity) in the temperature range at which fouling and wall slagging occurs (10^5 to 10^8 poise).
- 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.
- Verify and improve the predictive ability of ash-modeling programs currently used to evaluate slagging behavior and thermodynamic equilibrium.
- 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, will provide excellent focus and direction to this project. A committee of experts will be appointed to periodically review the status of this program and provide direction and guidance. Key questions that will be answered in this task are as follows:

- What are the critical issues in 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?
- What is the current status in the understanding of ash deposition mechanisms in advanced power systems?

3.1.2 Task 1 - Results

The EERC has generated a wealth of data through several research projects in the last several years that needs to be summarized and reported concisely and distributed to key personnel. The summary report and a selective survey of key literature performed on 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 that may have critical information pertaining to ash deposition mechanisms in gasification or reducing environments are

given in Table 1. Some of the project information which 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 a single key issue is currently in the process of being assembled.

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 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 are based on lower viscosities at higher temperature 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 a synthesis that quantitatively relates fundamental ash properties, chemistry, and mineralogy to actual ash deposition behavior in both conventional and gasification systems. The ability to better predict fouling and slagging behavior under oxidizing and reducing conditions from coal and ash mineral composition will significantly enhance the ability of the EERC to assist commercial clients with urgent problems related to ash deposition.

Some of the key questions that will be 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, and can the resultant multiphase slag viscosity be predicted?
- To what extent do the size and shape of the solid phases affect flow characteristics?
- Does the amount of crystalline phase present regulate the viscosity, or does the resultant residual glassy material describe the viscosity?
- What methods can be used to determine viscosity of slag and ash in low-temperature, high-viscosity regions (10^5 to 10^8 poise), and can this viscosity range be predicted?

3.2.2 Task 2 – Results

Measurements of fundamental ash properties (viscosity) in the range of interest for fouling (10^5 to 10^8 poise) will be performed. Experimentally this will be done by using the Instron compression tester to determine stress-strain curves for several different ashes. Sintered ash pellets will be prepared, and determination of viscosity from the stress-strain curves will be calculated from the following:

$$\epsilon = \epsilon_f + \sigma(1 - 2\nu)/3\eta \quad [1]$$

where ϵ is the strain rate, ϵ_f is the thermal strain rate, σ is the compressive stress, ν is Poisson ratio, and η is viscosity. The ashes studied would be from coals for which detailed mineral chemistry and rheologic behavior are known and for which plant operating data are available. A computer program will be developed to extract the pertinent data from the Instron and place it into a workable format. The impacts of crystallization on viscosity will be determined. The samples will be melted under reducing and oxidizing conditions. Quenched samples will be taken below the T_{cv} , at the T_{cv} , and above the T_{cv} . These samples will be subjected to x-ray diffraction (XRD) and scanning electron microscopy (SEM) to determine the crystalline phases present, their size and shape, as well as the chemical composition of the residual glassy phase.

This portion of the project has been delayed due to flood-related damage to the Instron instrument, which is currently under repair.

In conjunction with the Instron tests, HSM will be used to measure the rate and extent of neck growth between the particles at various temperatures. These measurements will be used to verify Frankel's model of viscosity in sintering particles. The predictions and calculated viscosity will be correlated with the low-temperature viscosity work.

The heated-stage microscope has been assembled and shaken down for performing sintering measurements. A literature search was also performed on the use of HSM in sintering and viscosity, with approximately 20 significant references found. Temperature calibration and preliminary sintering tests indicated the need for more precise control of the heated stage. A controller has been purchased and is being incorporated into the HSM electrical heating system prior to further sintering experiments.

Two materials were selected for the HSM sintering experiments. The first is a commercial glass of uniform composition with viscosity and surface tension available from the literature, already in the form of spheres which will be sieved to obtain a size cut in the 20–38 μm range. The second material is a slag produced from an Illinois No. 6 coal, which has been previously characterized at the EERC.

The slag was crushed to nominal size ranges of 53–90 and 38–53 μm and fed into two separate preparation experiments through a bench-scale drop-tube furnace with a 2-second residence time at 1300°C to produce spherical particles for use with the HSM. These slag spheres were sieved to obtain a size cut in the 20–38- μm range. Examination of the slag spheres by SEM in Figure 1 indicated that good sphericity had been obtained by the drop-tube furnace preparation technique. The chemistry of spheres selected for microprobe analysis (Table 2) showed a rather wide variation in composition. Further, it was noted that the spheres appeared to be enriched in iron at the surface, apparently as a result of segregation of material as the molten slag spheres cooled. The segregation of iron was somewhat unexpected, and HSM experiments may require SEM microprobe analysis after sintering to determine particle and neck compositions. The two materials will be complementary, with the glass samples being an idealized system and the slag sample providing information on a real-world ash system.

Figure 1. Slag spheres produced in the drop-tube furnace.

The experimental ash properties will be compared to the predictions of existing models to ascertain the validity of current predictions. Improved predictive algorithms will be developed to correlate the fundamental properties with detailed coal chemistry and mineralogy.

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 (1), the mechanisms of sulfide formation in gasification are not well understood. Work by Benson and Sondreal (2) 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 (2) 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

TABLE 2

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

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

Ash deposits have been collected from the riser section during a run of the EERC pilot-scale pressurized fluidized bed, also called the transport reactor demonstration unit (TRDU), and submitted for SEM analysis to determine deposit chemistry with particular emphasis on the possible presence of sulfides. Additional process information and deposits will be obtained from new TRDU runs planned for fiscal year 1997. Ash deposits from gasification systems such as the unit at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama, and the Piñon Pine IGCC (integrated gasification combined-cycle) Clean Coal V project in Tracy, Nevada, may be acquired to compare the EERC pilot-scale ash deposits with those acquired from larger-scale gasification systems. The interactions between sulfides and silicate or oxide materials, which can lead to serious ash deposit formation, will be investigated in this effort.

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 which is 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 specific studies of alloys. Table 3 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.

TABLE 3

Candidate Tube Materials							
Material	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

One of the samples has been received and the others are expected in the near future. An AGFA digital scanner and 35-mm macro lens have also been purchased. These will allow corrosion photographs to be placed into reports more efficiently and the 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 purchased in the near future.

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.

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