



**Energy &  
Environmental  
Research  
Center**

**ORNL/Sub/94-SS112/05**

---

**SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES**

---

**Final Annual Technical Progress Report**

**June 28, 2000**

**Report Prepared by  
John P. Hurley and Charlene R. Crocker  
Energy & Environmental Research Center  
University of North Dakota  
PO Box 9018  
Grand Forks, North Dakota 58202-9018  
under  
Subcontract No. 19X-SS112V**

**for**

**OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831**

**Managed by  
UT-BATTELLE, LLC**

**for the  
U.S. DEPARTMENT OF ENERGY  
under contract DE-AC05-96OR22464**

**This report has been reproduced directly from the best available copy.**

**Available to DOE and DOE contractors from the Office of Scientific and Technical Information, PO Box 62, Oak Ridge, TN 37831; prices available from (865) 576-8401.**

**Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.**

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

## TABLE OF CONTENTS

LIST OF FIGURES .....	ii
LIST OF TABLES .....	ii
ABSTRACT .....	iii
1.0 INTRODUCTION .....	1
2.0 FACTORS AFFECTING THE COMPOSITIONS OF ASH DEPOSITS .....	1
2.1 Coal-Related Factors .....	1
2.2 Factors Related to Ash Deposition Mechanisms .....	2
2.3 Factors Related to the Temperature of the Material .....	3
3.0 MATERIALS TESTING IN PILOT-SCALE SYSTEMS .....	5
3.1 The EERC Slagging Furnace System .....	5
3.2 The EERC Transport Reactor Development Unit .....	7
3.3 Samples Exposed at the EERC This Year .....	9
3.4 The NETL CERF Reactor .....	13
4.0 SUMMARY .....	14
5.0 REFERENCES .....	14

## LIST OF FIGURES

1	Comparison of the compositions ( $\text{SO}_3$ -free) of the aerodynamically sized entrained ash particles and an upstream enamel deposit .....	3
2	Temperature-dependent concentrations of silicon, sulfur, and calcium (reported as oxides) in deposits collected from the convective pass of a pulverized coal-fired utility boiler burning a subbituminous coal from the western United States .....	4
3	Viscosity-versus-temperature plot for a slag produced in a boiler firing Illinois No. 6 bituminous coal to which limestone has been added to reduce slag viscosity .....	5
4	The EERC slagging furnace system .....	6
5	TRDU and HGFV in the EERC gasification tower .....	8
6	Upstream view of samples installed in the SFS convective pass .....	10
7	Temperature profile downstream of the samples .....	11
8	Upstream view of samples with ash deposition .....	11
9	Downstream view of samples with ash deposition .....	12

## LIST OF TABLES

1	Composition of the Bulk Cordero Rojo Coal Ash and the Convective Pass Deposits .....	13
---	--	----

## **SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES**

### **ABSTRACT**

Structural and functional materials used in solid- and liquid-fueled energy systems are subject to gas- and condensed-phase corrosion and erosion by entrained particles. For a given material, its temperature and the composition of the corrodents determine the corrosion rates, while gas flow conditions and particle aerodynamic diameters determine erosion rates. Because there are several mechanisms by which corrodents deposit on a surface, the corrodent composition depends not only on the composition of the fuel, but also on the temperature of the material and the size range of the particles being deposited. In general, it is difficult to simulate under controlled laboratory conditions all of the possible corrosion and erosion mechanisms to which a material may be exposed in an energy system. Therefore, with funding from the Advanced Research Materials Program, the University of North Dakota Energy & Environmental Research Center (EERC) is coordinating with NCC Engineering and the National Energy Technology Laboratory (NETL) to provide researchers with no-cost opportunities to expose materials in pilot-scale systems to conditions of corrosion and erosion similar to those occurring in commercial power systems.

The EERC has two pilot-scale solid-fuel systems available for exposure of materials coupons. The slagging furnace system (SFS) was built under the DOE Combustion 2000 Program as a testing facility for advanced heat exchanger subsystems. It is a 2.5-MMBtu/hr ( $2.6 \times 10^6$  kJ/hr) solid-fuel combustion system with exit temperatures of 2700° to 2900°F to ensure that the ash in the main combustor is molten and flowing. Sample coupons may be exposed in the system either within the slagging zone or near the convective air heater at 1800°F (980°C). In addition, a pilot-scale entrained-bed gasifier system known as the transport reactor development unit (TRDU) is available. Also operating at approximately 2.5 MMBtu/hr ( $2.6 \times 10^6$  kJ/hr), it is a pressurized unit built to simulate the Kellogg entrained-bed gasifier in use at the Southern Company Services Wilsonville facility, but at 1/10 of the firing rate. At the exit of the unit is a large candle filter vessel typically operated at approximately 1000°F (540°C) in which coupons of materials can be inserted to test their resistance to gasifier ash and gas corrosion. The system also has ports for testing of hydrogen separation membranes that are suitably contained in a pressure housing.

In addition, NETL is operating the combustion and environmental research facility (CERF). In recent years, the 0.5 MMBtu/hr ( $0.5 \times 10^6$  kJ/hr) CERF has served as a host for exposure of over 60 ceramic and alloy samples at ambient pressure as well as at 200 psig (for tubes). Samples have been inserted in five locations covering 1700°–2600°F (930°–1430°C), with exposures exceeding 1000 hours. In the present program, the higher priority metals are to be tested at 1500°–1600°F (820°–870°C) in one CERF location and near 1800°–2000°F (980°–1090°C) at other locations to compare results with those from the EERC tests.

# **SUPPORT SERVICES FOR CERAMIC FIBER-CERAMIC MATRIX COMPOSITES**

## **1.0 INTRODUCTION**

To increase national self-sufficiency for the near future, energy systems will be required to fire low-grade fuels in a more efficient manner than currently possible. The typical coal-fired steam cycle used at present is limited to a maximum steam temperature of 1000°F (540°C) and a conversion efficiency of 35%. Higher-working-fluid temperatures are required to boost efficiency, exposing subsystems to much more corrosive environments. Issues of special concern to materials developers are corrosion and warping of hot-gas particulate filters and corrosion and erosion of high-temperature heat exchangers.

The University of North Dakota Energy & Environmental Research Center (EERC) is working in conjunction with NCC Engineering Inc. and the National Energy Technology Laboratory (NETL) to provide technical and experimental assistance to the Fossil Energy Advanced Research Materials (ARM) Program investigating materials failure in fossil energy systems. The main activities of the EERC are to provide technical expertise concerning appropriate corrosion test conditions, to assemble coal slag and hot-gas filter ash samples for use in laboratory corrosion tests, and to assist in providing opportunities for realistic tests of advanced materials in pilot-scale fossil energy systems.

In this report, fuel and operational factors that affect the corrosion rates of advanced materials in coal-fired combustor systems are described. Particular attention is focused on two subsystems: hot-gas particulate filtration and high-temperature heat exchangers. In addition, facilities at the EERC and NETL that can be used by researchers for realistic testing of materials are described.

## **2.0 FACTORS AFFECTING THE COMPOSITIONS OF ASH DEPOSITS**

All surfaces of a coal-fired combustor upstream of particulate removal systems are quickly covered with ash. The composition of the ash deposits depends on the composition of the coal, the mechanisms of ash deposition, and the temperature of the deposits.

### **2.1 Coal-Related Factors**

Coal is composed primarily of carbon with lesser amounts of heteroatoms such as hydrogen, oxygen, sulfur, and nitrogen and ash-forming constituents such as mineral matter and organically associated alkali and alkaline-earth cations. Coals from the eastern United States are typically higher in rank and form ash from microscopically observable mineral grains. The most prevalent minerals in U.S. coals are quartz ( $\text{SiO}_2$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5[\text{OH}]_4$ ), other aluminosilicate clays such as montmorillonite ( $[\text{Al,Mg}]_8[\text{Si}_4\text{O}_{10}]_3[\text{OH}]_{10} \cdot 12\text{H}_2\text{O}$ ) and illite ( $\text{KAl}_3\text{Si}_7\text{O}_{20}[\text{OH}]_4$ ), and pyrite ( $\text{FeS}_2$ ). These minerals are rich in silicon, aluminum, and iron, so the coal ash formed from them is acidic. Coals from the western United States also contain these minerals, but they are primarily lower-rank coals that have undergone less lithification than the

eastern coals and so contain much more oxygen in their organic structures. The oxygen is commonly present in carboxylic acid functional groups. During interaction with groundwater, these acids can undergo ion exchange to fix sodium, potassium, magnesium, and calcium in an atomically disbursed form within the organic structure. The addition of the alkali metal and alkaline-earth elements to the ash makes it much more basic than eastern coal ash.

## **2.2 Factors Related to Ash Deposition Mechanisms**

In addition to the type of coal that may be used in the energy system, the materials researcher must consider which fractions of the ash will come in contact with the structure of interest. This information is best obtained experimentally, although approximations can be made based on extensive testing performed at utility boilers. During combustion of the coal, the minerals can vaporize, fragment, or coalesce, depending on the initial associations of the mineral, the temperature and composition of the local combustion environment, and the morphology of the original mineral grains (1-6). In general, mineral grains that are included within coal particles will experience temperatures 300°–500°F (170°–280°C) higher and much more reducing conditions than the excluded mineral grains. The included minerals commonly fuse with other mineral grains in the coal particle to form larger, more compositionally complex ash particles. The excluded mineral grains are much less likely to interact with other mineral grains and may also fragment to form smaller ash particles.

In contrast to the mineral grains, the organically associated elements vaporize during combustion and become extremely reactive. The alkaline-earth elements rapidly oxidize to form micron-sized ash particles on the surface of the burning char particle. These can be shed as oxide particles or coalesce with quartz- and clay-derived ash to form complex aluminosilicates (1, 2). In contrast, the vaporized alkali metals exist as gaseous sulfates, hydroxides, and chlorides that can condense far downstream of the fireball. The vaporization and subsequent condensation of the organically associated elements cause them to concentrate in smaller ash particles.

The size and composition interdependence in the ash means that the ash depositing on and possibly corroding the material of interest may be very different from the bulk ash. If the object of interest is placed directly in the gas flow, then ash particles with aerodynamic diameters of over 10 microns will separate from the gas and strike the upstream side of the tube as the gas diverges around it (7). Smaller ash particles stay entrained with the gas which often forms eddies on the downstream side of the tube. Because of this, deposits formed on the downstream sides of tubes are enriched with particles having aerodynamic diameters of less than 10 microns. A third type of deposit forms on the upstream sides of tubes at gas temperatures less than 1700°F (930°C). At these low temperatures, the larger particles are relatively hard, and because of their high kinetic energy, they often bounce off of the tubes. However, smaller particles trapped in the boundary layer approach the tube with low velocities through thermophoresis or Brownian motion. These particles often sinter and form an enamel-like layer that can be soft at temperature. As this type of deposit builds, it acts as a cushion into which larger particles can become stuck, so that the diameters of the depositing particles increase with time.

Figure 1 shows the composition of an enamel-like deposit formed in a utility boiler along with the compositions of four aerodynamically sized particulate ash samples collected from the gas stream in the vicinity of the deposit (7). The boiler was firing a high-calcium subbituminous coal at the time. The figure illustrates the striking variations in elemental concentration versus ash particle size that occur for silicon and calcium in this ash. The average concentration of silicon is much greater in the larger particles, whereas the average concentration of calcium is much greater in the smaller. This characteristic of the ash is typical of most high-calcium U.S. coals. The bulk composition of the enamel-like deposit shows that it is formed primarily from particles with aerodynamic diameters of less than 3 microns. Materials such as silicon-based ceramics which are prone to calcium corrosion would be much more severely attacked by this type of deposit than deposits formed from larger particles. In addition, the figure shows that the deposit contains a high level of sulfur and that the sulfur condenses after ash deposition. These condensed sulfates can be very corrosive towards ferritic alloys.

### 2.3 Factors Related to the Temperature of the Material

The temperature of the subsystem affects not only the kinetics of reaction but the composition and physical nature of the ash deposit as well. Figure 2 shows the concentrations of silicon, calcium, and sulfur in ash deposits collected from steam tubes in a boiler firing a high-calcium coal. It shows that the sulfur concentration in the deposits increases dramatically at temperatures below 2000°F (1090°C). Laboratory experiments show that the mechanism of increase is chemical vapor deposition caused by the conversion of calcium in either oxides or

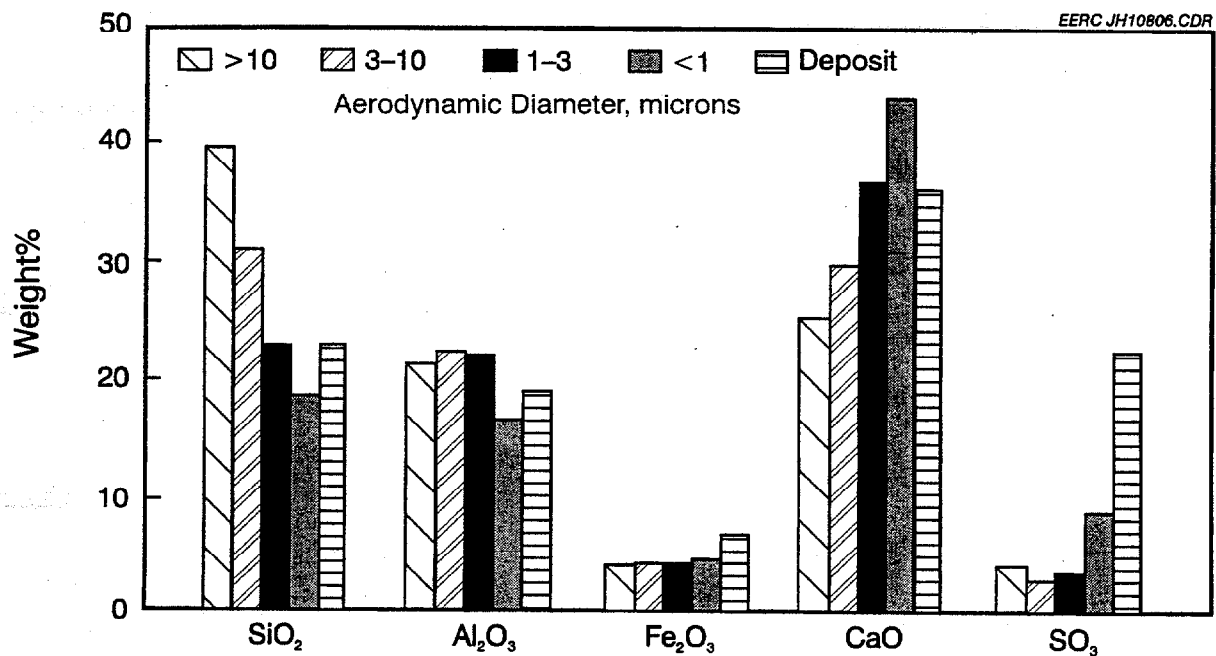


Figure 1. Comparison of the compositions (SO<sub>3</sub>-free) of the aerodynamically sized entrained ash particles and an upstream enamel deposit.



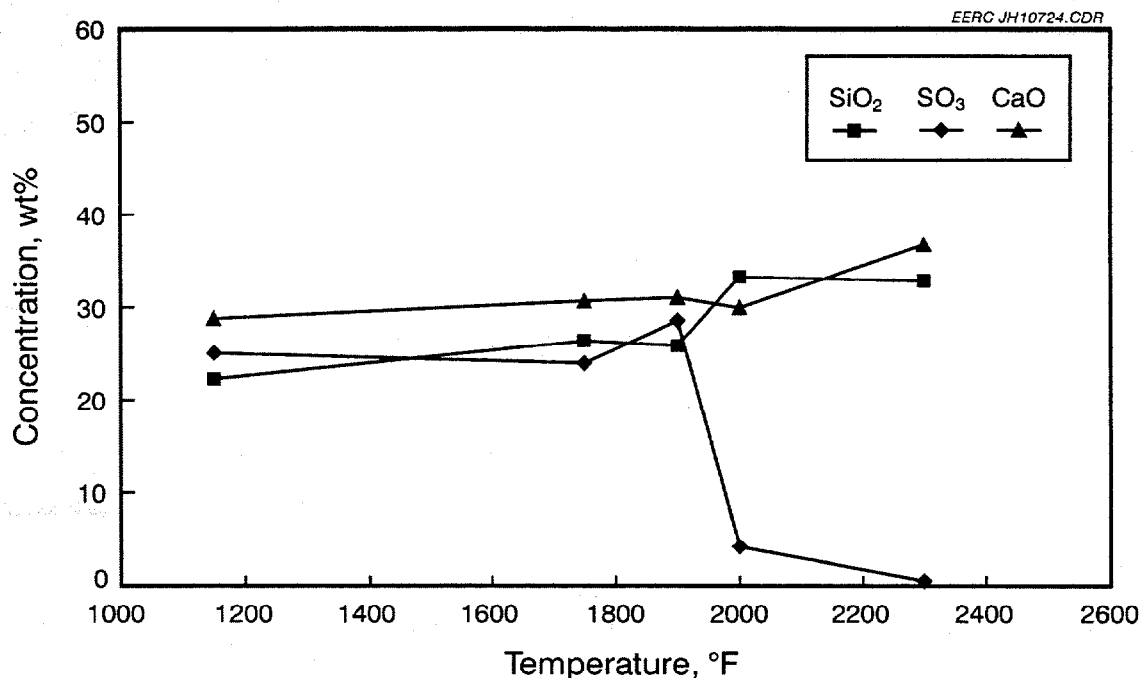


Figure 2. Temperature-dependent concentrations of silicon, sulfur, and calcium (reported as oxides) in deposits collected from the convective pass of a pulverized coal-fired utility boiler burning a subbituminous coal from the western United States.

aluminosilicates to calcium sulfate (8). The concentrations of sodium, potassium and phosphorus also increase significantly, but not as much as that of the sulfur. The sodium concentration increases primarily through physical vapor deposition, or condensation, of sodium sulfate. This indicates that in the presence of ash, materials cooled to below approximately 2000°F (1090°C) will be subjected to alkali sulfate corrosion, whereas those at higher temperatures will not. Therefore, materials such as ferritic ODS alloys that are creep resistant but prone to sulfate corrosion may have much longer lifetimes if used above 2000°F (1090°C) than if used below that temperature.

In addition to affecting composition, temperature will affect the physical nature of the deposits. Figure 3 shows a viscosity-versus-temperature plot for fused slag formed in a Central Illinois Public Service Coffeen Plant boiler while burning Illinois No. 6 bituminous coal to which limestone has been added to reduce the viscosity of the slag. The measurements were made in air and in a reducing environment in the presence of 10% water vapor. At temperatures above 2500°F (1340°C), the slag has a viscosity below 250 poise, implying that it will flow and be erosive as well as corrosive. These liquid slags dissolve the protective oxide scale on most ceramic materials, causing the corrosion rate to be linear rather than parabolic with time. Corrosion by flowing slag is expected to result in a uniform recession rate of the surface, while pitting is seen in corrosion by static slag or with sintered ash. At still lower temperatures, the ash may sinter but does not dissolve the protective oxide layer. Therefore, a comparison of Figures 2 and 3 indicates that a temperature window exists, from approximately 2000°F (1090°C) to

2300°F (1380°C), which is coal dependent but over which the products of coal combustion may be less corrosive to certain materials than at lower or higher temperatures.

### 3.0 MATERIALS TESTING IN PILOT-SCALE SYSTEMS

The wide range of factors affecting the composition of corrodents deposited on structures within coal-fired energy systems illustrates the difficulty in accurately simulating corrosion conditions on small scales. A simpler, if less available, method of corrosion testing is to expose coupons of materials in systems built to simulate full-scale power systems. Through the Fossil Energy Materials AR&TD program, coupons of materials can be exposed in pilot-scale combustion and gasification systems in operation at the EERC and NETL with no cost to the materials researchers. The systems available are described in the following sections.

#### 3.1 The EERC Slagging Furnace System

Figure 4 is a simplified illustration of the pilot-scale slagging furnace system (SFS). It was constructed with funding from the Department of Energy Combustion 2000 Program through a subcontract to the United Technologies Research Center to support testing and development of subsystems to be used in a high-temperature advanced furnace (HITAF). It consists of eight main components: 1) slagging furnace, 2) slag screen/slag tap, 3) dilution-quench zone, 4) process air

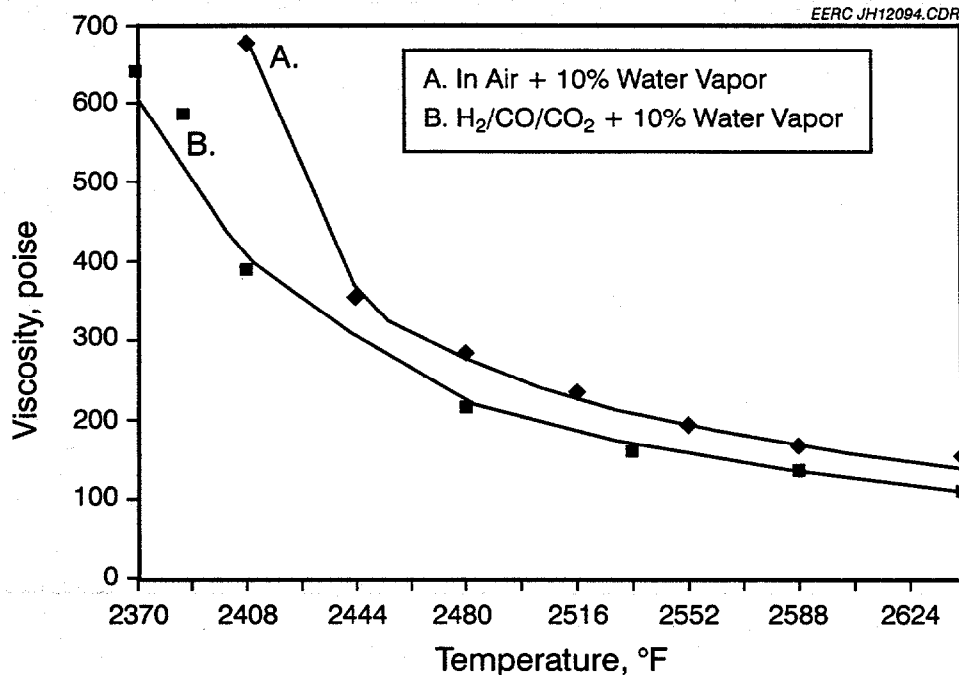


Figure 3. Viscosity-versus-temperature plot for a slag produced in a boiler firing Illinois No. 6 bituminous coal to which limestone has been added to reduce slag viscosity.

preheaters, 5) convective air heater (CAH) section, 6) radiant air heater (RAH) panel, 7) tube-and-shell heat exchangers, and 8) pulse-jet baghouse. The SFS design is intended to be as fuel-flexible as possible, with maximum furnace exit temperatures of 2700° to 2900°F (1480° to 1590°C) to maintain the desired heat transfer to the RAH panel and slag flow. The furnace has a nominal firing rate of 2.5 MMBtu/hr ( $2.6 \times 10^6$  kJ/hr) and a range of 2.0 to 3.0 MMBtu/hr ( $2.1$  to  $3.2 \times 10^6$  kJ/hr) using single burner. The EERC oriented the furnace vertically (downfired) so that slag would not interfere with the operation of the burner. Internal dimensions are 47 in. (119 cm) in diameter by a roughly 16 ft (4.9 m) in total length. It is lined with three layers of refractory totaling 12 in. (30 cm) thick to minimize heat loss. This insulation keeps the wall surface temperature near that of the gas stream. The inner layer is composed of an alumina castable, developed by the EERC in cooperation with the Plibrico Company, that has been shown in bench and pilot tests to be extremely resistant to slag corrosion at the high wall temperatures.

Sample coupons can be inserted into the system either through ports in the main slagging combustor or on racks in the convective pass downstream of the CAH where the ash is less corrosive. Gas temperatures downstream of the CAH are maintained at 1800°F (980°C). To be included in SFS tests, materials coupons should be no more than 2 in. wide and able to be slipped onto a ½-inch-thick (1.3-cm) Inconel support rod. A standard test with this system usually lasts 200 hours.

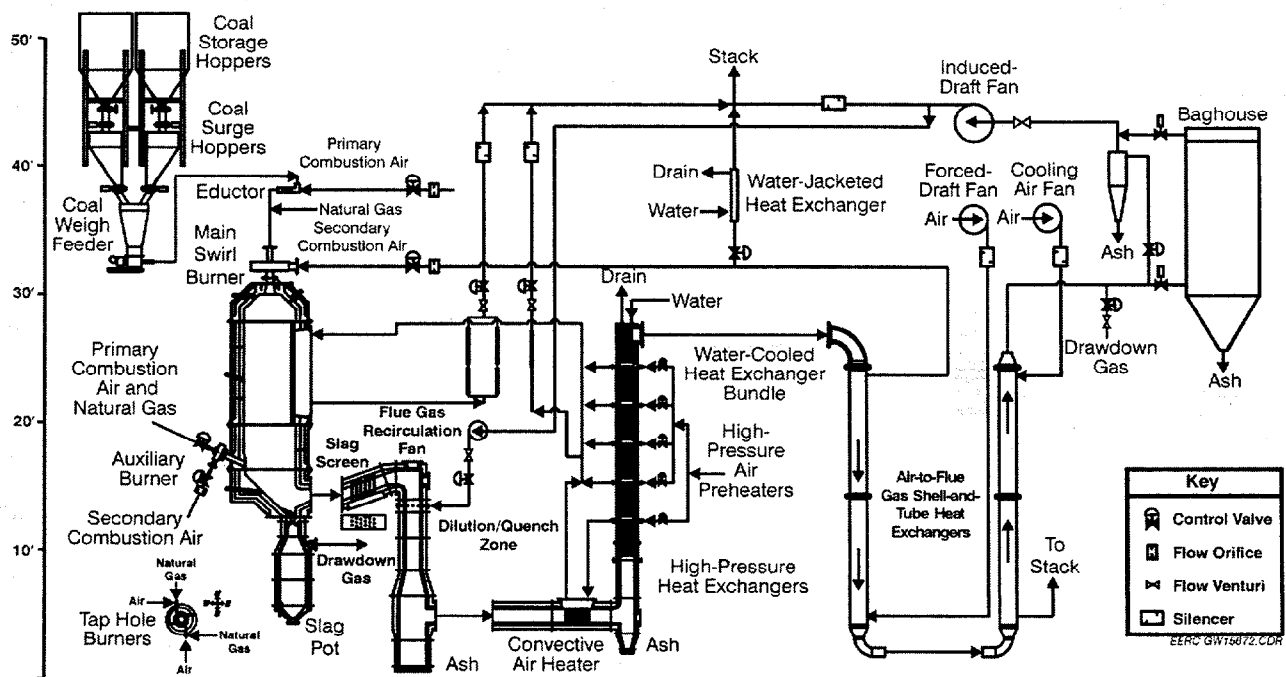


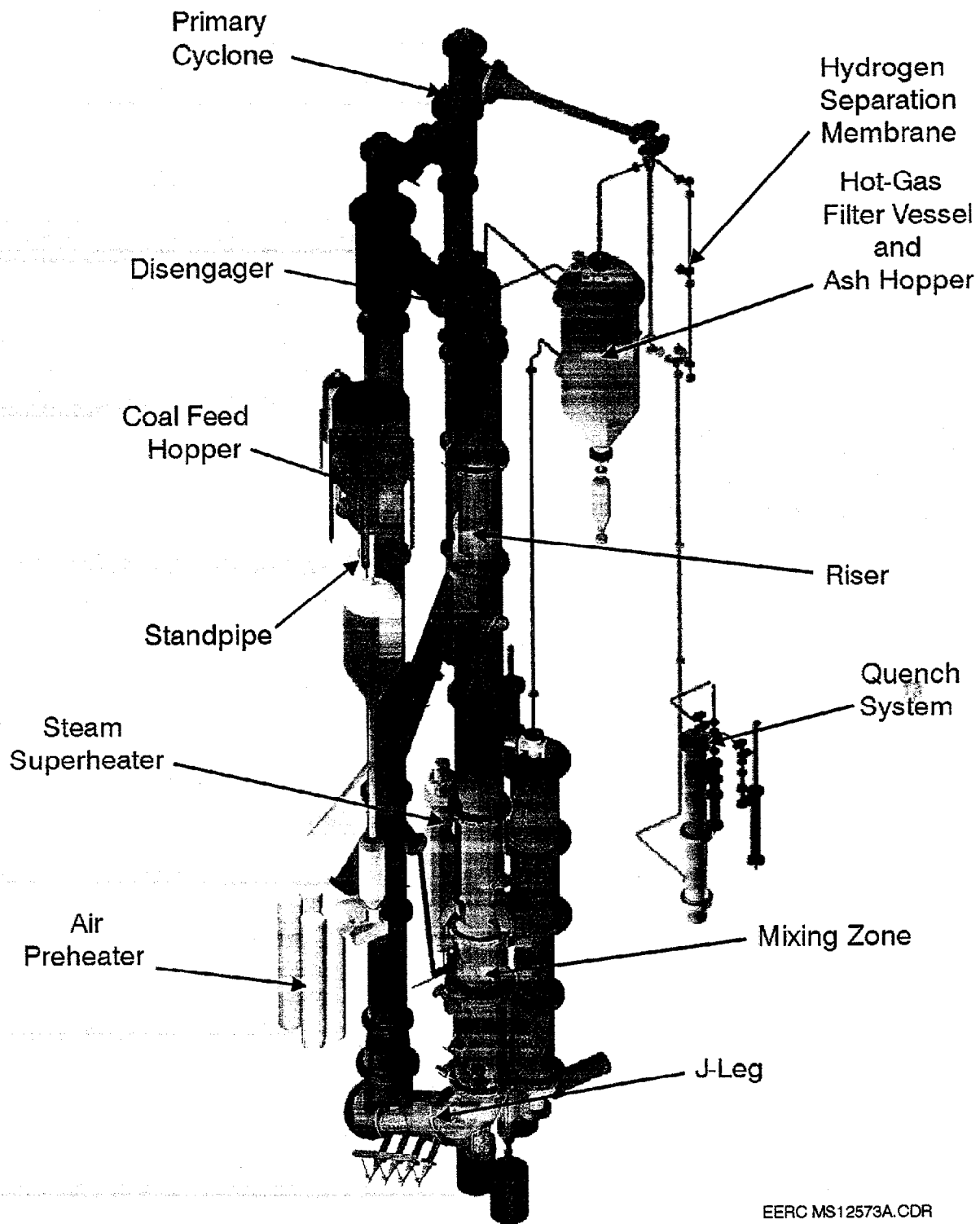
Figure 4. The EERC slagging furnace system.

### 3.2 The EERC Transport Reactor Development Unit

In addition to exposure to combustion conditions in the SFS, materials coupons can also be exposed to gasification gas and dust in the hot-gas filter vessel of the transport reactor development unit (TRDU). The TRDU is a 2.5-MMBtu/hr ( $2.6 \times 10^6$ -kJ/hr) pressurized circulating fluid-bed gasifier similar to the gasifier being tested at the Southern Company Services (SCS) Wilsonville, Alabama, facility. The system is illustrated in Figure 5. It has an exit gas temperature of up to 1800°F (980°C), a nominal gas flow rate of 18,000 ft<sup>3</sup>/hr (510 m<sup>3</sup>/hr), and an operating pressure of 9.2–11.2 atm (0.93–1.1 MPa). The TRDU system can be divided into three sections: the coal feed section, the TRDU, and the product recovery section. The TRDU proper 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 11.2 atm (1.1 MPa) and an internal temperature of 2000°F (1090°C).

The premixed coal and limestone fed to the transport reactor can be admitted through one of three nozzles, which are at varying elevations. 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 oxidant and the steam, which is injected into the J-leg. This feature enables spent char to contact oxidant and steam prior to the fresh coal feed. Gasification or combustion and desulfurization reactions are carried out in the riser, as coal, sorbent, and oxidant (with steam for gasification) flow up the riser. The solids circulation into the mixing zone is controlled by the solids level in the standpipe. 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 at an appropriate level. Gas exiting the disengager enters a primary cyclone that has been modified to provide variable particulate collection performance. Solids from the dipleg of the primary cyclone are collected in a lock hopper. Gas exiting this cyclone enters a jacketed pipe heat exchanger before entering the HGFV (hot-gas filter vessel). The cleaned gases leaving the HGFV enter a quench system before being depressurized and vented to a flare.

This vessel is designed to handle all of the gas flow from the TRDU at its expected operating conditions. The vessel is approximately 4.0 ft (1.2 m) inner diameter (ID) and 15 ft (4.7 m) long and is designed to handle gas flows of approximately 19,000 ft<sup>3</sup>/hr (550 m<sup>3</sup>/hr) at temperatures up to 1800°F (980°C) and 9.8 atm (0.99 MPa). The refractory has a 2.3 ft (0.71 m) ID with a shroud diameter of approximately 1.8 ft (0.56 m). The vessel is sized such that it could handle candle filters up to 4.9 ft (1.5 m) long; however, 3.3 ft (1.0 m) candles are being used in the initial 1000°F (540°C) gasification tests. Candle filters are 2.4 in (60 mm) outer diameter (OD) with a 4.0 in (10 cm) center line-to-center line spacing. The total number of candles that can be mounted in the current geometry of the HGFV tube sheet is 19.



EERC MS12573A.CDR

Figure 5. TRDU and HGFV in the EERC gasification tower.

Standard TRDU tests consist of 200 hours of operation under gasification conditions with the HGFV operating at temperatures of 1000°–1200°F (540°–650°C), 9.2 atm (0.93 MPa). Materials coupons are exposed in the system by sliding them over ½ in.- (1.3-cm)-diameter stainless steel rods in the free space below the candle filters. Samples up to 2 in. (5.1 cm) wide can be included. The composition of the gas to which the materials coupons would be exposed in the HGFV is approximately 8%–14% H<sub>2</sub>O, 6%–9% each of CO and H<sub>2</sub>, 8%–10% CO<sub>2</sub>, 1.0%–2.5% CH<sub>4</sub>, with the balance being N<sub>2</sub> and other trace constituents.

### 3.3 Samples Exposed at the EERC This Year

Personnel from Oak Ridge National Laboratory (ORNL) provided ceramic rings and alloy coupons to be exposed in the SFS under oxidizing conditions or in the TRDU under gasification conditions. Ten pure mullite ceramic rings were installed in the convective pass of the SFS for a 200-hour test of a Powder River Basin coal in March 2000. The rings included five samples that were light grey because of contamination during processing. Eight white ceramic rings with a composition of 2Al<sub>2</sub>O<sub>3</sub>–3SiO<sub>2</sub> (mullite) will be installed in the HGFV of the TRDU next month. All rings were approximately 1 in. (2.5-cm) high, 2.5 in. (6.3-cm) in diameter, with a wall thickness of 0.3 in. (0.8 cm). The eight metal coupons were also installed in the SFS for the March test. They were duplicate samples of four metal alloys composed of iron with chromium and silicon or nickel, iron with aluminum, and nickel with molybdenum and chromium. The samples are 1.2 in. (3.7 cm) square and 0.5 in. (1.3 cm) thick.

Personnel from Honeywell Advanced Composites, Inc., provided eight ceramic rings to be exposed in the SFS under oxidizing conditions. Four were white ceramic rings composed of the trade material PRD-66 which contained mullite, alumina, and cordierite. The other four were charcoal grey rings of enhanced silicon carbide fibers in a silicon carbide matrix (SiC–SiC). The PRD-66 rings were similar in dimensions to the ceramic rings received from ORNL. Three of the SiC–SiC rings were 2.4 in. (6.0 cm) in diameter, and the fourth was 2.3 in. (5.4 cm). All four SiC–SiC rings were 1 in. (2.5 cm) high and had a wall thickness of 0.1 in. (0.3 cm).

The metal alloys and the 18 ceramic samples were placed on a three-tiered Iconite rack and installed in the convective pass of the SFS 13 in. beyond the CAH. Figure 6 indicates the upstream appearance of the samples in position prior to the system being sealed for the March test. Once the gradual heating of the system was accomplished, the samples were exposed to 200 hours of flue gas generated by combustion of a Powder River Basin subbituminous coal from the Cordero Rojo mine. The average flue gas flow rate through the convective pass was 940 scfm. The composition of the gas (on a dry basis) to which the coupons were exposed was 300 ppm SO<sub>2</sub>, 530 ppm NO<sub>x</sub>, 30 ppm CO, 4.9% O<sub>2</sub>, and 13.4% CO<sub>2</sub>, with N<sub>2</sub> as the remainder. The average temperature was 1770°F (965°C). Figure 7 shows a profile of the flue gas temperature just downstream of the sample rack during the run. The temperature ranged from about 1740°F to about 1800°F (949°–982°C). The temperature variability is due to the control thermocouple (TC) upstream of the CAH tubes. This temperature is used to control the amount of cold flue gas entering the quench zone. As this TC gets exposed to ash, it becomes either covered with deposits so that it gives an artificially low reading, resulting in a too-low quench flow rate and higher downstream temperatures, or it simply deteriorates as a result of exposure to ash. The TC

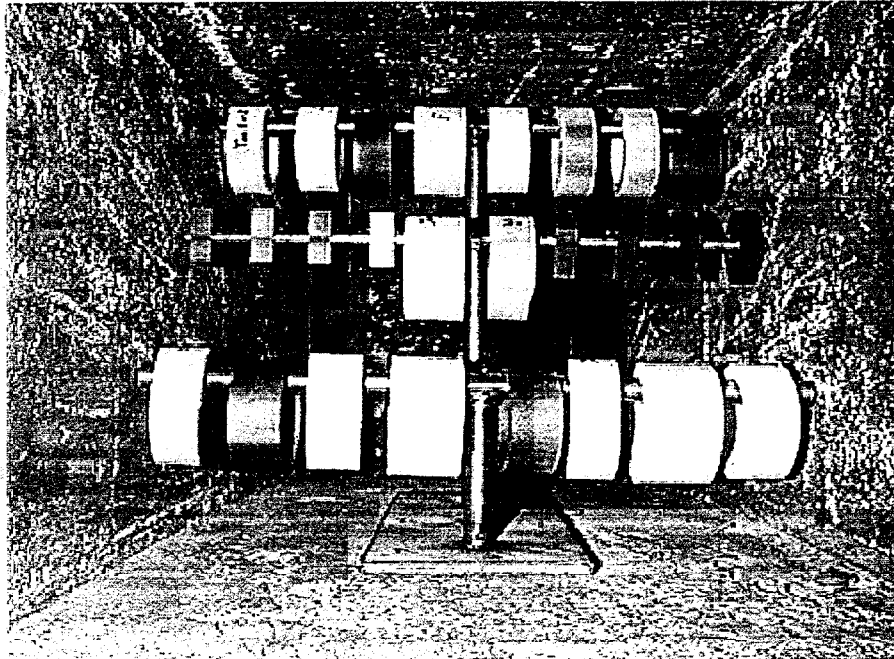


Figure 6. Upstream view of samples installed in the SFS convective pass.

was replaced twice during the run. The six vertical lines on the chart indicate when coal feed stopped and started during the run. Excess slag buildup at the slag tap forced coal feed shutdown twice during the run. As the graph indicates, temperature was relatively unimpaired during this process.

Two activities that affected temperature in the convective pass during operation of the SFS were quench zone cleaning and cleaning of the CAH (sootblowing). Cleaning of the quench zone (just upstream of the convective pass) was performed as needed, approximately every 6 hours. A port must be opened during cleaning, with the result that the flue gas temperature drops and the gas velocity increases. Also, sootblowing of the front tubes on the CAH occurred every 8 hours with pressurized room temperature  $N_2$ . The results of this activity were temporary temperature decreases and higher concentrations of ash blown against the coupons.

During the run, the samples were observed via site ports located throughout the SFS convective pass. The samples, which initially swung in the force of the flue gas, became cemented in place by the ash deposits by Day 4 of the 9-day test. Figure 8 shows the extent of ash deposition on the upstream surfaces of samples at the end of the test. In addition, ash filled the open areas in the center of each ceramic ring. Downstream deposition on the samples, shown in Figure 9, was thinner.

After the combustion test, the sample rack was carefully removed from the SFS. The coupons were separated from each other and the rack, maintaining as much ash on the samples as possible. Each sample was examined and photographed, with care being taken not to dissociate

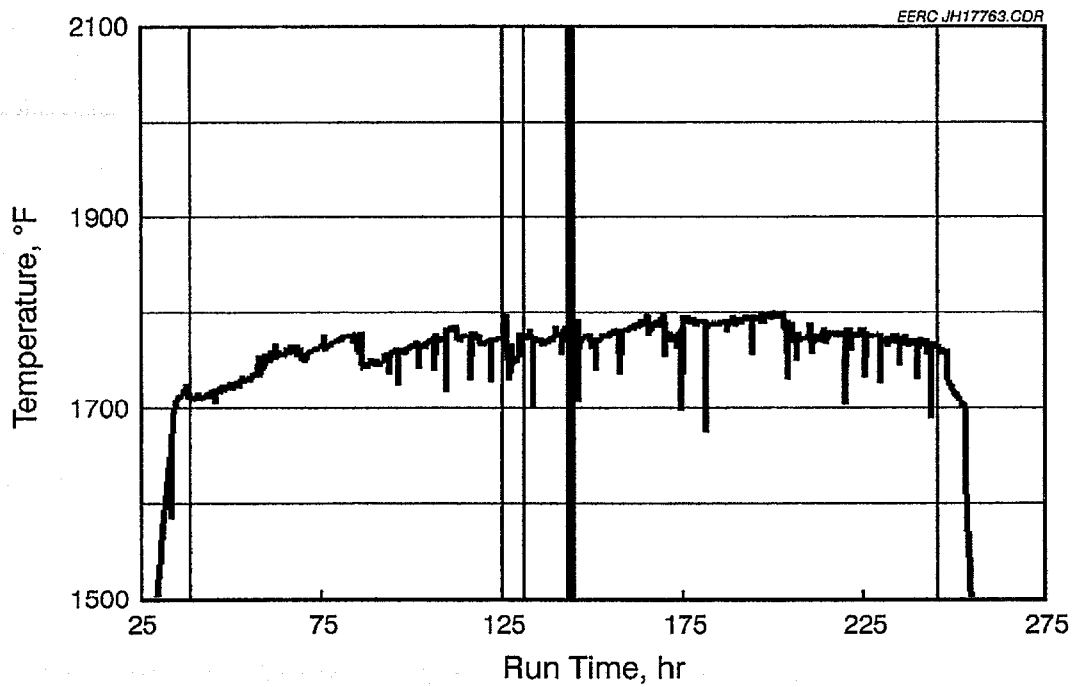


Figure 7. Temperature profile downstream of the samples.



Figure 8. Upstream view of samples with ash deposition.



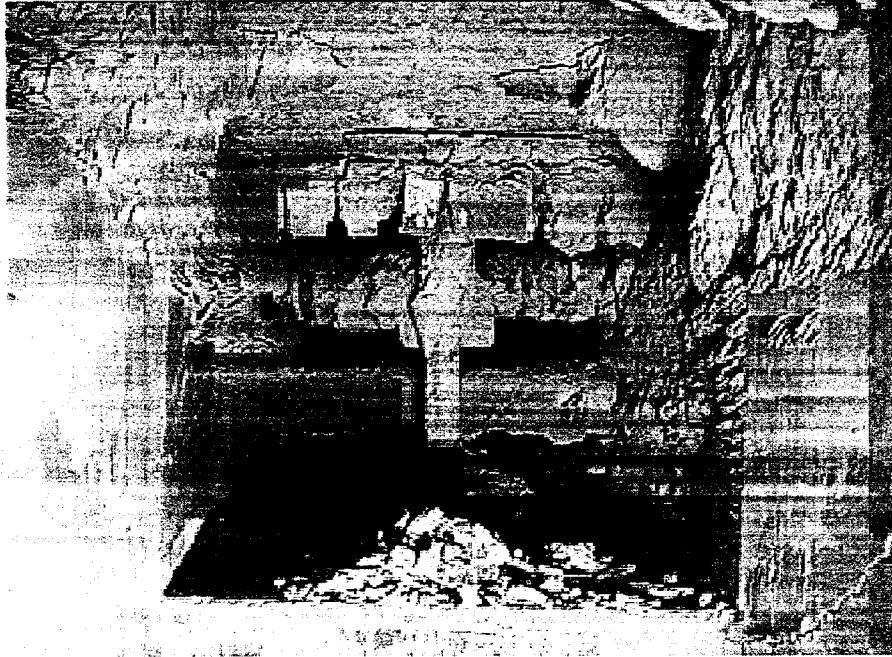


Figure 9. Downstream view of samples with ash deposition.

the ash from the coupon. Visual inspection of the rings revealed no changes because of the exposure. Some rings will undergo SEM (scanning electron microscopy) analysis to determine corrosion and erosion effects not visible to the eye. The remainder of the samples will be returned to the submitter or cleaned and reinstalled in the SFS for further high-temperature exposure during an upcoming run.

In contrast to the ceramic rings, the metal coupons exhibited effects of both corrosion and erosion. Visual inspection showed discoloration of all metal sample surfaces. Four sample surfaces included blotchy white patches. Two samples were severely corroded, turning green, and flecking off layers of material. These samples are visible on the center right of Figure 9. At least one sample from each pair will be analyzed by SEM.

As shown in Table 1, the compositions of the deposits that formed in the convective pass on the SFS coupons contained much less silicon and much more calcium than the bulk coal ash. Computer-controlled scanning electron microscope (CCSEM) analyses of the minerals in the coal indicate that the mineral matter in the coal is composed primarily of silica-rich clays. Approximately  $\frac{1}{2}$  of the mass of the clay is composed of particles with diameters over  $10\text{ }\mu\text{m}$ . These particles would be expected to be collected with relatively high efficiency in the slag screen upstream of the convective pass, leaving the ash particles reaching the sample coupons relatively deficient in silica. In contrast, only small amounts of calcium-rich minerals are found in the coal, even though the coal ash contains over 30% calcium on a sulfur-free oxide basis. This implies that the calcium occurs in the coal primarily as the salt of an organic acid, highly dispersed and able to form micron-sized calcium-rich ash particles upon combustion of

the coal. This size range of particle is inefficiently captured in the SFS slag screen, leaving the ash reaching the materials coupons relatively enriched in calcium. SEM point count analyses indicate that the calcium in the deposits primarily occurs as calcium oxide, much of which is partially sulfated, and calcium aluminosilicates, a portion of which is also partially sulfated.

TABLE 1

Composition of the Bulk Cordero Rojo Coal Ash and the Convective Pass Deposits (normalized sulfur-free oxide basis)

Oxides, wt%	Cordero Rojo Coal	Convective Pass Ash Deposit
SiO <sub>2</sub>	29.5	20.7
Al <sub>2</sub> O <sub>3</sub>	19.1	20.2
Fe <sub>2</sub> O <sub>3</sub>	6.9	8.9
TiO <sub>2</sub>	1.9	2.1
P <sub>2</sub> O <sub>5</sub>	1.0	2.1
CaO	33.3	38.5
MgO	6.6	5.9
Na <sub>2</sub> O	1.2	1.3
K <sub>2</sub> O	0.5	0.3
SO <sub>3</sub> <sup>1</sup>	15.2	5.9

<sup>1</sup> Normalized with other oxides.

### 3.4 The NETL CERF Reactor

The materials coupon exposures at the EERC are being coordinated with tests of the same materials being conducted at NETL. The NETL tests are being performed in the combustion and environmental research facility (CERF) with one of the same coals that will be used at the EERC, except in the CERF the tests will be for more variable times and at different temperatures. The CERF is a state-of-the-art pilot-scale combustor with a nominal rating of 0.5 MMBtu/hr (0.5 × 10<sup>6</sup> kJ/hr) used to conduct a wide range of combustion and pollution control studies of most solid, liquid, and gaseous fuels.

Typically, the CERF R&D involves outside parties that bring fuels, concepts, or materials for evaluation. The CERF has served as a host site for exposure of over sixty ceramic and alloy samples from materials researchers at temperatures from 1700°–2600°F (930°–1430°C).

Within the convective pass of the CERF, materials coupons are typically clamped to a water-cooled probe for exposure. In the main furnace, the samples can be welded directly to an air-cooled slag probe. In past tests, materials coupons have been exposed for over 1000 hours in five locations (1700°–2600°F [930°–1430°C]), with exposures exceeding 1000 hours. In the present program, the higher-priority metals are to be tested at 1500°–1600°F (820°–870°C) in one CERF location and near 1800°–2000°F (980°–1090°C) at other locations to compare results with those from the EERC tests.

#### 4.0 SUMMARY

The composition of corrodents present on a specific surface within an energy conversion system are functions of the fuel composition, the material temperature, and the size range of the particles being deposited. In addition, erosion is often a major contributor to the failure of a structure within the system. It is difficult to simulate under controlled laboratory conditions all of the possible corrosion and erosion mechanisms to which a material may be exposed in an energy system. Therefore, the EERC is coordinating with NETL, NCC Engineering Inc., and Oak Ridge National Laboratory to provide materials scientists with no-cost opportunities to expose materials in pilot-scale systems to conditions of corrosion and erosion similar to those in occurring in commercial power systems.

The EERC has two pilot-scale solid-fuel systems available for exposure of materials coupons. The slagging furnace system is a 2.5-MMBtu/hr ( $2.6 \times 10^6$ -kJ/hr) solid-fuel combustion system with exit temperatures of 2700°–2900°F (1480°–1590°C). Sample coupons may be exposed in the system either within the slagging zone or near the convective air heater at 1800°F (980°C). A pilot-scale entrained-bed gasifier system known as the transport reactor development unit is also available. Similarly operating at approximately 2.5 MMBtu/hr ( $2.6 \times 10^6$  kJ/hr), it is a pressurized unit built to simulate the Kellogg entrained-bed gasifier in use at the Southern Company Services Wilsonville facility, but at 1/10 of the firing rate. At the exit of the unit is a large candle filter vessel typically operated at approximately 1000°F (540°C) in which coupons of materials can be inserted to test their resistance to gasifier ash and gas corrosion. The system also has ports for testing of hydrogen separation membranes that are suitably contained in a pressure housing.

In addition, NETL is operating the Combustion and Environmental Research Facility. It is a 0.5-MMBtu/hr ( $0.5 \times 10^6$ -kJ/hr) downfired combustor. Materials coupons have been exposed for over 1000 hours in five locations 1700°–2600°F (930°–1430°C), with exposures exceeding 1000 hours. In the present program, the higher-priority metals are to be tested at 1500°–1600°F (820°–870°C) in one CERF location and near 1800°–2000°F (980°–1090°C) at other locations to compare results with those from the EERC tests.

#### 5.0 REFERENCES

1. Hurley, J.P.; Schobert, H.H. *Energy & Fuels* **1992**, 6 (1), 47–58.

2. Hurley, J.P.; Schobert, H.H. *Energy & Fuels* **1993**, 7, 542–553.
3. Walsh, P.M.; Sayre, A.N.; Loehden, D.O.; Monroe, L.S.; Beér, J.M.; Sarofim, A.F. *Prog. Energy Combust. Sci.* **1990**, 16, 327–346.
4. Benson, S.A.; Jones, M.L.; Harb, J.H. In *Fundamentals of Coal Combustion for Clean and Efficient Use*; Smoot D., Ed.; Elsevier: Amsterdam, 1993; p 299.
5. Baxter, L.L.; DeSollar, R.W. *Fuel* **1993**, 72, 1411.
6. Wibberley, L.J.; Wall, T.F. *Fuel* **1982**, 61, 93–99.
7. Hurley, J.P.; Benson, S.A. *Energy & Fuels* **1995**, 9, 775–781.
8. Hurley, J.P.; Nowok, J.W.; Beber, J.A.; Dockter, B. A. *Prog. Energy Combust. Sci.* **1998**, 24, 513–521.

## DISTRIBUTION

ALLISON GAS TURBINE DIVISION  
P.O. Box 420  
Indianapolis, IN 46206-0420  
P. Khandelwal (Speed Code W-5)  
R. A. Wenglarz (Speed Code W-16)

ARGONNE NATIONAL LABORATORY  
9700 S. Cass Avenue  
Argonne, IL 60439  
K. Natesan

BRITISH COAL CORPORATION  
Coal Technology Development Division  
Stoke Orchard, Cheltenham  
Gloucestershire, England GL52 4ZG  
J. Oakey

DOE  
DOE OAK RIDGE OPERATIONS  
P. O. Box 2001  
Oak Ridge, TN 37831  
Assistant Manager for Energy Research and  
Development

DOE  
DOE OAK RIDGE OPERATIONS  
P. O. Box 2008  
Building 4500N, MS 6269  
Oak Ridge, TN 37831  
M. H. Rawlins

DOE  
NATIONAL ENERGY TECHNOLOGY  
LABORATORY  
3610 Collins Ferry Road  
P.O. Box 880  
Morgantown, WV 26507-0880  
R. C. Bedick  
D. C. Cicero  
R. A. Dennis  
W. J. Huber  
T. J. McMahon  
J. E. Notestein

DOE  
OFFICE OF FOSSIL ENERGY  
FE-72  
19901 Germantown Road  
Germantown, MD 20874-1290  
F. M. Glaser

DOE  
OFFICE OF BASIC ENERGY SCIENCES  
Materials Sciences Division  
ER-131, GTN  
Washington, DC 20545  
H. M. Kerch

DOE  
NATIONAL ENERGY TECHNOLOGY  
LABORATORY  
626 Cochrans Mill Road  
P.O. Box 10940  
Pittsburgh, PA 15236-0940  
A. L. Baldwin  
N. T. Holcombe  
G. V. McGurl  
U. Rao  
L. A. Ruth  
T. M. Torkos

ELECTRIC POWER RESEARCH INSTITUTE  
P.O. Box 10412  
3412 Hillview Avenue  
Palo Alto, CA 94303  
W. T. Bakker  
J. Stringer

EUROPEAN COMMUNITIES JOINT RESEARCH  
CENTRE  
Petten Establishment  
P.O. Box 2  
1755 ZG Petten  
The Netherlands  
M. Van de Voorde

FOSTER WHEELER DEVELOPMENT  
CORPORATION  
Materials Technology Department  
John Blizzard Research Center  
12 Peach Tree Hill Road  
Livingston, NJ 07039  
J. L. Blough

IDAHO NATIONAL ENGINEERING  
LABORATORY  
P. O. Box 1625  
Idaho Falls, ID 83415  
A. B. Denison

**Distribution****Revised: June 9, 2000**

LEHIGH UNIVERSITY  
Materials Science & Engineering  
Whitaker Laboratory  
5 E. Packer Avenue  
Bethlehem, PA 18015  
John N. DuPont

NATIONAL MATERIALS ADVISORY BOARD  
National Research Council  
2101 Constitution Avenue  
Washington, DC 20418  
K. M. Zwilsky

OAK RIDGE NATIONAL LABORATORY  
P.O. Box 2008  
Oak Ridge, TN  
P. T. Carlson  
J. M. Crigger (3 copies)  
R. R. Judkins  
D. P. Stinton  
P. F. Tortorelli  
I. G. Wright

SHELL DEVELOPMENT COMPANY  
WTC R-1371  
P.O. Box 1380  
Houston, TX 77251-1380  
W. C. Fort

TENNESSEE VALLEY AUTHORITY  
Energy Demonstration & Technology  
MR 2N58A  
Chattanooga, TN 37402-2801  
C. M. Huang

WESTERN RESEARCH INSTITUTE  
365 N. 9th Street  
P.O. Box 3395  
University Station  
Laramie, WY 82071  
V. K. Sethi

WESTINGHOUSE ELECTRIC CORPORATION  
Research and Development Center  
1310 Beulah Road  
Pittsburgh, PA 15235  
S. C. Singhal