Very-High-Temperature Materials and Heat Exchanger Testing in a Pilot-Scale Slagging Furnace

John P. Hurley
University of North Dakota Energy & Environmental Research Center
PO Box 9018
Grand Forks, ND 58202-9018

Charlene R. Crocker
University of North Dakota Energy & Environmental Research Center
PO Box 9018
Grand Forks, ND 58202-9018

Manuscript

INTRODUCTION

The University of North Dakota Energy & Environmental Research Center (EERC) is working with Oak Ridge National Laboratory (ORNL) 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 was built under the U.S. Department of Energy (DOE) Combustion 2000 Program as a testing facility for advanced high-temperature heat exchanger (HTHX) subsystems. It is a 2.5-MMBtu/hr solid-fuel combustion system with exit temperatures of 1500° to 1600°C to ensure the ash in the main combustor is molten and flowing. Sample coupons may be exposed in the system either within the slagging zone, near the convective air heater at 1000°C, or in an elbow following a heat exchanger at 700°C. The results of coupon exposures and analyses are presented in the first part of this paper.

Two main configurations of a single radiant heat exchanger have been tested extensively in the slagging combustor. The heat exchanger is composed of three 6-foot-long by 2 ½-inch-OD tubes of MA 754 and nickel/chrome-based oxide-dispersion-strengthened alloy. The first configuration is that developed by the United Technologies Research Center (UTRC) during Combustion 2000 testing. This "tubes-in-a-box" design has the three tubes held within a ceramic brick-lined box to prevent the products of combustion from direct contact with the alloy. Process air at 950°C and 150 psig was routinely produced with this configuration for over 2000 hours of testing. For a short time, conditions of up to 1100°C and 100 psig were reached. However, the ceramic tiles forming the face of the heat exchanger were prone to corrosion and thermal shock. Therefore, the EERC performed laboratory corrosion tests on the alloy which indicated very low surface recessions when the alloy was exposed directly to ash and gas at up to 1150°C. Based on these results, the EERC has begun testing the heat exchanger in a second configuration, exposing the alloy tubes directly to the products of combustion. The results of the initial tests of this bare-tube heat exchanger are described in the second part of this paper.

The Pilot-Scale Slagging Furnace System

Figure 1 is a simplified illustration of the pilot-scale slagging furnace system (SFS). It was constructed with funding from the DOE Combustion 2000 Program through a subcontract with UTRC to support testing and development of subsystems to be used in a high-temperature advanced furnace. It consists of eight main components: 1) slagging furnace, 2) slag screen/slag tap, 3) dilution-quench zone, 4) process air 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 1480°–1590°C to maintain the desired heat transfer to the RAH panel and slag flow. The furnace has a nominal firing rate of 2.6×10^6 kJ/hr and a range of 2.1 to 3.2×10^6 kJ/hr using a single burner. The furnace design was based on Illinois No. 6 bituminous coal (25,800 kJ/kg) and a nominal furnace residence time of 3.5 s. The EERC oriented the furnace vertically (downfired) so that slag would not interfere with the operation of the burner. Internal dimensions are 119 cm in diameter by roughly 4.9 m in total length. It is lined with three layers of refractory totaling 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.

Material sample coupons can be inserted into the system either through ports in the main combustor, in the slag screen, on racks in the convective pass downstream of the CAH, or in an elbow following the first tube-and-shell heat exchanger. Most samples were inserted downstream of the CAH. Near that

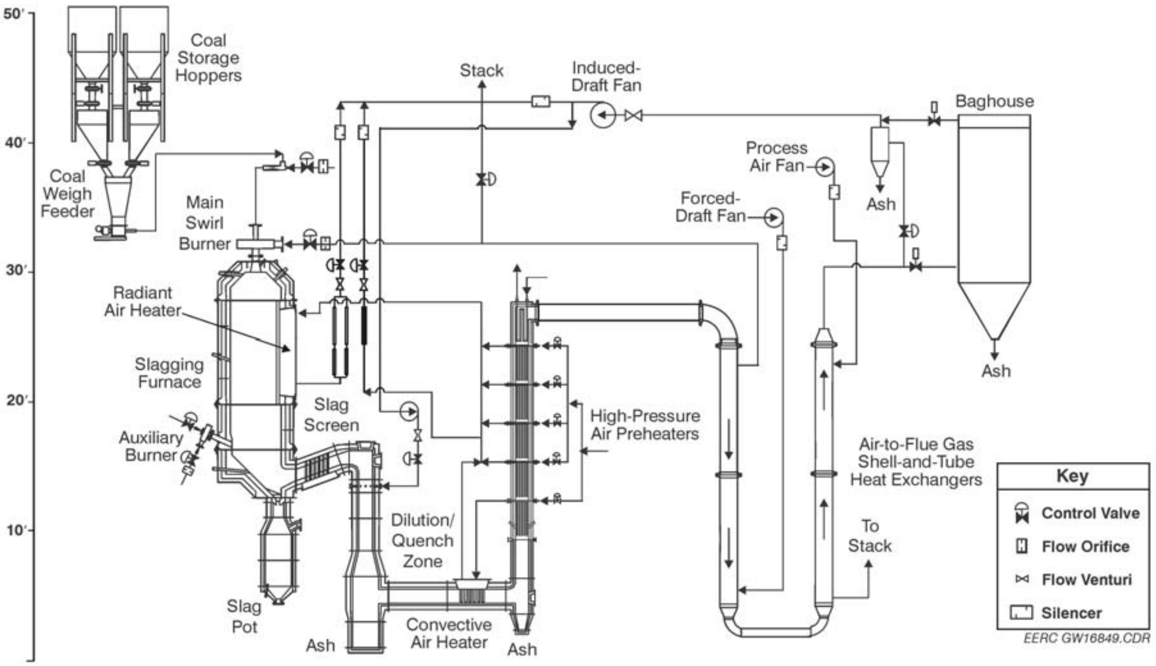

Figure 1. The EERC slagging furnace system.

subsystem, gas temperatures are maintained at 980°C, but they drop farther back in the system to approximately 175°C as the gas enters the exit stack. To be included in SFS tests, materials coupons should be no more than 5 cm wide and be able to slip onto a 1.2-cm-thick Inconel support rod.

COUPON TESTING

The EERC performed two 200-hour tests under separate DOE funding in the SFS in March and June of 2000,, during which ceramic and alloy samples were exposed to coal combustion conditions.

March 2000 Test

ORNL provided ten pure mullite ceramic rings which were installed in the convective pass of the SFS for the March test. Several of the samples were analyzed after the test, and several others were left in the system for the June test. The rings included five samples that were light grey because of contamination during processing. All rings were approximately 2.5 cm high and 6.3 cm in diameter with a wall thickness of 0.8 cm. Eight metal coupons were also installed in the SFS for the March test. They were duplicate samples of four metal alloys reportedly composed of iron (Fe) chromium (Cr), and silicon (Si); Fe with aluminum (Al); Fe, nickel (Ni), and Cr; or Ni, molybdenum (Mo), and Cr. The samples were 3.7 cm square and 1.3 cm thick.

Honeywell Advanced Composites, Inc., provided eight ceramic rings to be exposed in the SFS during both the March and June tests. Four were white ceramic rings composed of the trade material PRD-66 which contained mullite, alumina, and cordierite. The other four were charcoal gray 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 6.0 cm in diameter, and the fourth was 5.4 cm. All four SiC–SiC rings were 2.5 cm high and had a wall thickness of 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 2 shows the samples from the upstream side in position prior to the system being sealed for the March test. After gradual heating of the system, 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_2, 530 ppm NO_x, 30 ppm CO, 4.9% O_2, and 13.4% CO_2 with N_2 as the remainder. The average temperature was 965°C. Measurements during subsequent runs indicate that temperature variation across the duct was no more than 2°C. The appearance of the upstream sides of the samples, after the March 2000 test, is shown in Figure 3.

EERC JH17761.CDR

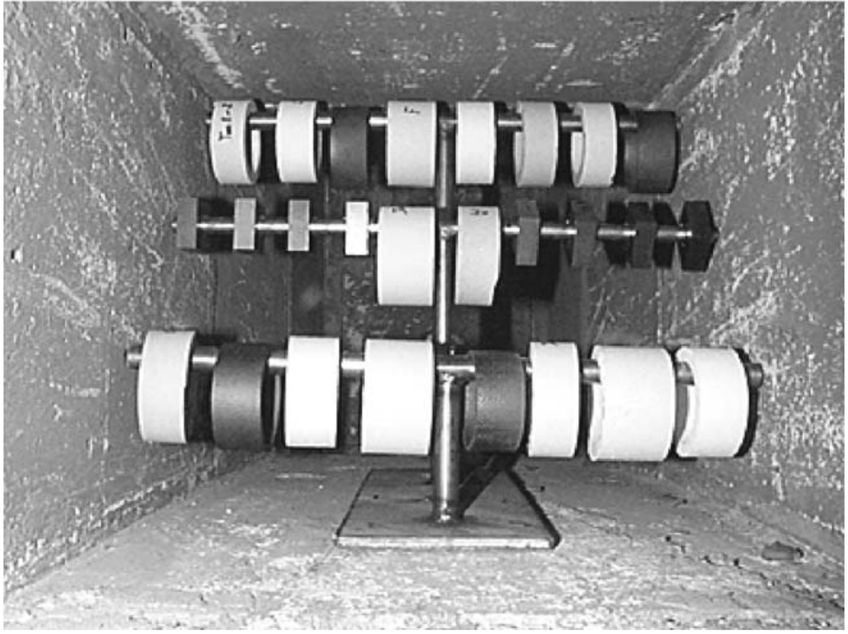

Figure 2. Material coupons in the convective pass of the SFS, viewed from the upstream side, before the March 2000 test.

EERC JH17762.CDR

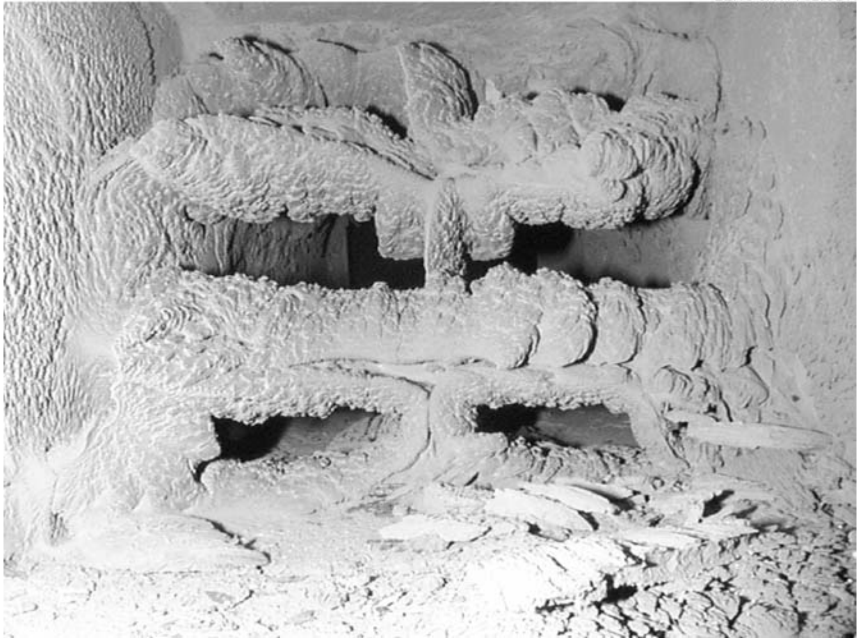

Figure 3. Material coupons in the convective pass of the SFS, viewed from the upstream side, after the March 2000 test.

June 2000 Test

Additional samples were received prior to the June 2000 test run. ORNL personnel sent 19 metal alloy samples and 12 ceramic rings. Fourteen duplicate samples of metal alloys were approximately 32 mm square and 1 to 3.4 mm thick. An exposure temperature below 700°C in the SFS was requested for these samples. Five additional alloy coupons contained Cr, tantalum (Ta), and Mo. These included a 9-mm-diameter rod 152 mm long and four identical cylinders 24 mm in diameter and approximately 12.5 to 12.8 mm high. The 12 ceramic rings were approximately 59–63.5 mm in diameter and 15–31 mm long, with a wall thickness ranging from 8 to 13.5 mm. All samples were described as mullite, gelcast. Four were thinner-walled white rings, and eight were thick-walled gray rings.

Special Metals Corporation (SMC) sent six alloy samples for inclusion in the June test. They included duplicate sample disks 48 mm in diameter and 5.5–9 mm thick and two duplicate samples approximately 46–50.5 mm square. The metal content of these samples has not been disclosed. All alloy samples, except for the rod, included a 12-mm-diameter hole for mounting.

The 19 metal alloys from ORNL, three alloys from SMC, and 12 ceramic samples were installed in the SFS for the June test, along with several samples exposed during the SFS operation in March. Fourteen duplicate ORNL samples were installed in an elbow between process air heaters and the first set of shell-and-tube heat exchangers. The Cr–Ta alloy rod was partially embedded in the refractory just downstream of the slag screen to be exposed to slag, ash, flue gases, and temperatures in excess of 1510°C. The other four Cr–Ta alloy coupons, all 12 new ceramic rings, and the ceramic rings and two alloys previously exposed in the SFS but not analyzed were installed on the three-tiered Iconite rack in the convective pass of the SFS 330 mm beyond the CAH.

Once the gradual heating of the system using natural gas was accomplished, the samples were exposed to an initial 14 hours of combustion conditions while an eastern Kentucky bituminous coal was fired. The high ash fusion temperature of this coal forced the EERC to add limestone to the coal feed to reduce the viscosity of the ash depositing in the slag screen. However, this measure was not sufficient to prevent an operation shutdown after the initial 14 hours of operation because of plugging of the slag screen. The remains of the Cr–Ta alloy rod were removed during maintenance of the slag screen area after the initial 14 hours of operation. The rod had succumbed to the intense temperature (approximately 1510°C) and corrosive effects of the slag and flue gas. One of the three pieces of sample recovered during maintenance of the slag screen was embedded in epoxy and analyzed by scanning electron microscopy (SEM). The results of this analysis follow this section. The remaining ceramic and alloy samples were exposed to an additional 150 hours of combustion conditions while another eastern Kentucky bituminous coal from the Prater Creek Mine was fired that had a lower ash fusion temperature.

The Prater Creek coal contained 1.7 wt% moisture, 5.1 wt% ash, and 0.94 wt% sulfur. The heating value was 31,459 kJ/kg on an as-fired basis. These data are similar to the eastern Kentucky bituminous coals previously fired. Coal ash was analyzed for ash fusion properties under oxidizing conditions. Results indicate a softening temperature of 1372°C and a fluid temperature of 1411°C. The fluid temperature of the Prater Creek coal ash was slightly lower than values observed for previously fired eastern Kentucky bituminous coals successfully fired and comparable to the high end of the temperature range observed for the Illinois No. 6 fuel previously fired.

The average flue gas flow rate through the slag screen and convective pass/elbow during the first 14 hours of coal firing was 685 and 948 scfm, respectively. The composition of the gas (on a dry basis) near the slag screen was 143 ppm SO_2, 458 ppm NO_x, 59 ppm CO, 3.1% O_2, and 14% CO_2 with N_2 as the remainder. The composition at the baghouse exit was 374 ppm SO_2, 575 ppm NO_x, 59 ppm CO, 4.5% O_2, and 12.9% CO_2 with N_2 as the remainder. The flue gas to which the coupons were exposed had a composition between these two points of analysis. Measurements during subsequent runs indicate that temperature variation across the duct is no more than 2°C. The temperature ranged from about 910° to about 960°C; average temperature was 950°C. The gas temperature near the samples at the elbow between process air heaters and the first set of shell-and-tube heat exchangers ranged from about 660° to about 710°C; average temperature was 690°C.

Once the system was repaired after the initial 14 hours of coal firing, the test run resumed for 150 hours of coal firing using the Prater Creek eastern Kentucky bituminous coal. The average flue gas flow rate through the convective pass and elbow during this portion of the test was 948 scfm. The composition of the gas (on a dry basis) at the baghouse exit was 336 ppm SO_2, 504 ppm NO_x, 19 ppm CO, 5.4% O_2, and 12.6% CO_2 with N_2 as the remainder. The gas temperature near the convective pass samples ranged from about 870° to about 995°C; average temperature was 930°C. The gas temperature near the elbow samples ranged from about 676° to about 750°C; average temperature was 708°C. For a full description of all materials coupons, test conditions, and coal and ash compositions, the reader is referred to the final report for the project ORNL/Sub/94-SS112/06 submitted in September of 2001.

Results of SEM Analyses of the Coupons

The 15 metal alloys and two ceramic composites were divided based on scale formation, and their general performances during the two combustion tests, as determined by SEM, were compared. Most samples exposed in the CAH pass and elbow formed one of four main types of scale: alumina, chromia, silica, or tantala. The Cr–Ta alloy sample exposed to high temperatures (1510°C) and corrosive flue gas constituents just downstream of the slag screen dissolved into the slag. No scale formation occurred.

Samples Exposed at 950°C in the CAH Pass

Ceramic and alloy samples exposed to flue gas and ash deposition in the CAH pass formed all four types of scale listed above and exhibited various general trends with respect to ash interaction and corrosion penetration.

Alumina. The mullite ceramic rings, Alloy 956, ORNL 17682, and ORNL 17433, formed alumina-rich or pure alumina scales. The alumina scales tended not to interact with ash constituents except Ca and Si. The low level of interaction was indicated by the fact that the ash layers tended to separate from the oxide scales upon sample cooling. Any ash constituents dissolved into the sample formed a corrosion product separate from the alumina scale. Some alumina scales formed good barriers to subsurface corrosion, but some did not, most likely due to the differences in the concentration of aluminum in the alloy.

Chromia. ORNL 17681, Alloy 803, Alloy 020, and the Cr–Ta alloy formed chromia scales. The chromia scales were much more bonded to the ash deposits than were the alumina scales. SEM analyses showed that all chromia scales forming on the CAH pass alloys underwent some interaction with ash constituents. Most of these samples exhibited either shallow subsurface corrosion or hollow pores, indicating loss of alloy material.

Silica. The only samples that formed a relatively exclusive silica scale were the SiC/SiC rings. ORNL 17681, exposed during both tests, formed silica–chromia scale. In all cases, the scale interacted with ash constituents more than did the alumina scales, but less than the chromia scales. The most common interaction was incorporation of Ca, Al, and Fe into the scale. Neither composite sample examined exhibited signs of ash penetration into the sample. The alloy sample suffered some subsurface pitting that took place during either or both tests. Silica was also incorporated into the scale of the Cr–Ta alloy. The behavior of that sample differed substantially and is discussed in the tantala section.

Tantala. In addition to an outer chromia scale, the Cr–Ta alloy formed a separate tantala scale, which incorporated some chrome and silica. The tantala scale underlying the chromia scale did not react with ash constituents. The sample exhibited limited surface pitting and no subsurface corrosion or alloy constituent loss.

Heterogeneous scales. Two samples in the CAH pass formed heterogeneous scales. Alloy 803 formed a uniform titania–chromia scale beneath the outer chromia scale. The scale, which included no ash constituents, did not appear sticky nor was it well attached to the sample. ORNL 17638 formed heterogeneous nickel oxide and nickel–chromia scales. This nonuniform scale was ineffective at maintaining a bond with the underlying sample surface.

Samples Exposed at 708°C in the Elbow

The alloy samples exposed to flue gas and ash deposition in the elbow between process air heaters and the first set of shell-and-tube heat exchangers formed two types of scale and exhibited various general trends with respect to ash interaction and corrosion penetration.

Chromia. Five of the elbow samples—three 310 alloy mixtures, 12RN72, and 625— formed chromia scales. Chromia-scale-forming samples in the elbow tended less to incorporate ash constituents into their scale than at the higher temperature of the CAH pass. Ash particles, however, were seen enveloped by several of the chromia scale on these samples. Few of these samples exhibited subsurface corrosion. However, sequential pitting and scaling were common on several samples.

Heterogeneous scales. Three alloys in the elbow formed heterogeneous nickel oxide, nickel–chromia, and/or iron nickel chromium oxide scales: 625, NF709, and RA253MA. Ca and Ba were the two ash constituents incorporated in the corrosion product of Alloy 625. Spherical ash particles, similar to those enveloped in some of the chromia scales on other samples in the elbow, were present in the corrosion product as well. The iron nickel chromium oxide scales were not consistent in their interaction with ash constituents. Although analysis of both scales suggests sulfidation, only one analysis included Ca and Al among the corrosion product components. Both scales were discontinuous; neither sample included signs of subsurface corrosion.

In general, for the elbow samples, no particular scale outperformed all others, but each produced characteristic ash constituent interactions. Temperature had a great effect on scale formation and ash interaction, and some samples withstood corrosive attack despite interaction with ash constituents.

HIGH-TEMPERATURE HEAT EXCHANGER TESTING

To determine if the HTHX built into the wall of the SFS combustion chamber could be operated without the original front ceramic panels, the EERC performed laboratory tests to determine if the MA754 alloy could be exposed directly to the products of coal combustion. Figure 4 shows the surface recessions of coupons of the MA754 exposed to Illinois No. 6 coal ash and flowing gas at 1000° and 1150°C. The data indicate that as long as the surface temperature of the alloy is kept below the solidus temperature of the fuel slag, corrosion rates of the MA754 could be commercially acceptable and the bare alloy tubes could be directly exposed to the products of coal combustion. Although the Combustion 2000 Program has ended, DOE is continuing the development of the very-high-temperature heat exchanger concept, both through funding the EERC directly for continued testing and through other programs such as the DOE Vision 21 Program.

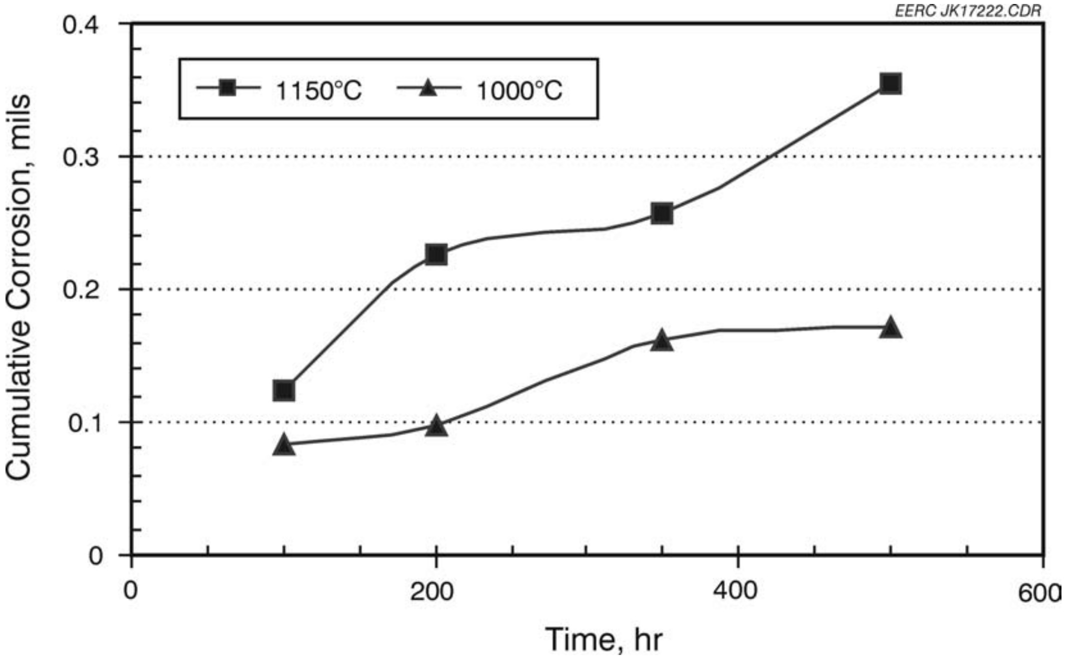

Figure 4. Surface recession rates for MA754 exposed to Illinois No. 6 ash and flowing gas.

Initial tests of the bare-tube configuration showed that heat exchange coefficients were so high without the ceramic panels that not enough cooling air could be provided with the existing equipment. Therefore, the initial tests were done while the SFS was fired at much lower rates than the normal operation as changes were made to the system to allow firing at higher rates while still cooling the surface temperature of the alloy to 1100°C. The changes culminated in reducing the surface area of the exposed tubes by encasing the bottom half of the HTHX in alumina insulation and refractory. The HTHX is typically operated with process air flow rates of 350–365 scfm at 150 psig. Inlet process air temperatures are 540°–550°C and alloy tube surface temperatures 750°–1100°C. The low end of the alloy tube surface temperature range represents the back side of the tubes at the process air inlet, with the high end of the range representing the front side of the tubes at the center of the HTHX. Process air temperature at the outlet ranged from 765° to 860°C. Heat recovery rates ranged from 206,000 to 241,000 Btu/hr.

The longest test of the HTHX while firing coal at the maximum level was made in November and December of 2001. The heat recovered by the HTHX decreased as a function of time, nominally from 241,000 to 209,000 Btu/hr, or 13%, during the first 70 hr of coal firing. Heat recovery appeared to be stable during the last 30 hr. Therefore, if adequate process air were available and half of the HTHX was not insulated, the resulting heat recovery rate would be 410,000–420,000 Btu/hr at a nominal furnace temperature of 1540°–1555°C.

HTHX heat removal data as a function of furnace temperature are summarized in Figure 5 on an equivalent-surface-area basis for select test periods completed in 1999 and 2000 and all of the test periods completed in 2001. The data for the June, August, and November/December 2001 tests of the

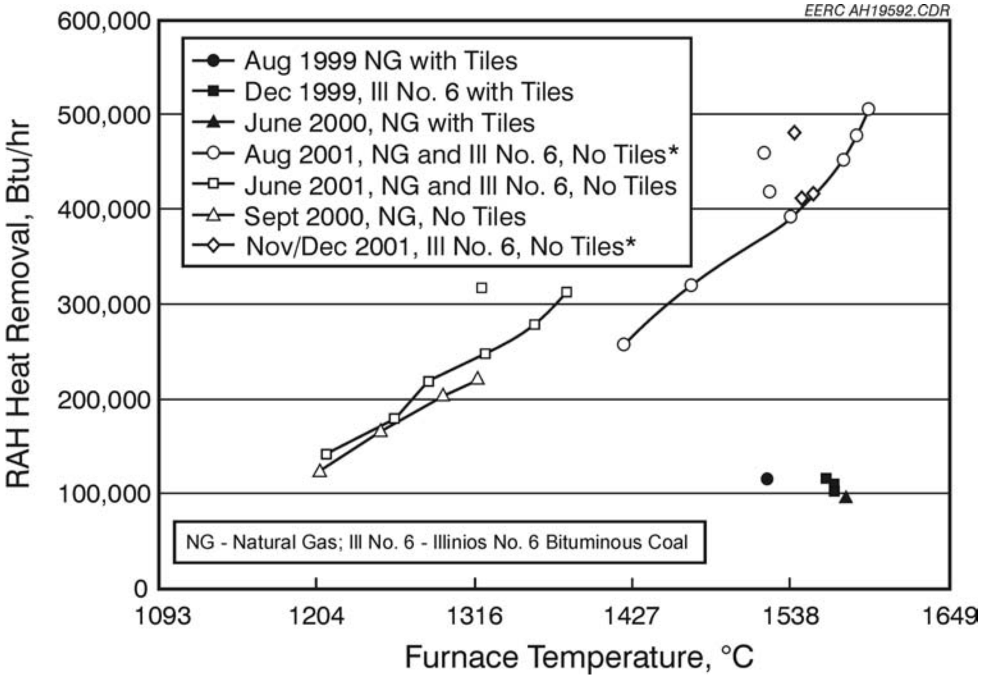

Figure 5. HTHX heat removal data as a function of furnace temperature.

bare-tube design are represented by open symbols and are connected by lines for natural gas-fired tests. Data resulting from coal-fired tests are simply an open symbol. The 2001 data are compared to data in the lower right of the graph, represented by closed symbols, for tests performed in 1999 and 2000 in which the original ceramic panels were in place. The data clearly show that for a given furnace temperature, removing the ceramic panels from the heat exchanger increases the heat removal rate by nearly a factor of five. This means the heat exchanger could be as small as one-fifth of that originally proposed. Factoring in the price reduction by not requiring the panels and the unprotected heat exchanger panel, the cost could be as little as one-tenth as much as the original tubes-in-a-box design.

Measurements of the MA754 tube diameters after coal firing indicated no recession or significant dimensional variations compared to the measurements before the test. Ash depositing on the tube formed a sintered powder layer of fly ash between a brittle slag layer and the alloy surface. Total thickness of the sintered powder was several tenths of a millimeter, while the slag layer varied from 2 to 5 millimeters thick. The lightly sintered nature of the inner layer indicated that its corrosivity toward the alloy should be low, while the slag layer formed running drips, indicating that it had reached its maximum thickness and begun to flow off of the tube. The brittle fused slag/sintered ash layer was easily removed from the alloy surfaces, indicating little interaction between the alloy and the ash.

The development of the sintered ash overlain by the slag layer was the primary reason for the 13% decrease in heat recovery during coal firing. This illustrates one of the main advantages to operating the HTHX at such high temperatures, which is that the ash develops only a very thin layer before becoming molten and flowing off. In essence, the tubes are self-cleaning, and the 13% drop is less than one-third of the typical 50% drop seen when much thicker sintered ash deposits develop on heat-transfer surfaces operating at lower temperatures. It is the insulating effect of the ash deposits that causes the need for up to twice as much heat exchange surface to be installed in a furnace than would be required if the ash did not insulate the tubes. Given the self-cleaning nature of the thin deposits forming on the bare-tube HTHX, the excess surface area needed would only be approximately 20% as compared to 100% excess for conventional heat exchangers operating at ash-sintering temperatures.