REFRACTORY FAILURE IN IGCC FOSSIL FUEL POWER SYSTEMS

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ABSTRACT

Current generation refractory materials used in slagging gasifiers employed in Integrated Gasification Combined Cycle (IGCC) fossil fuel power systems have unacceptably short service lives, limiting the reliability and cost effectiveness of gasification as a means to generate power. The short service life of the refractory lining results from exposure to the extreme environment inside the operating gasifier, where the materials challenges include temperatures to 1650°C, thermal cycling, alternating reducing and oxidizing conditions, and the presence of corrosive slags and gases. Compounding these challenges is the current push within the industry for fuel flexibility, which results in slag chemistries and operating conditions that can vary widely as the feedstock for the gasifier is supplemented with alternative sources of carbon, such as petroleum coke and biomass. As a step toward our goal of developing improved refractory materials for this application, we have characterized refractory-slag interactions, under a variety of simulated gasifier conditions, utilizing laboratory exposure tests such as the static cup test and a gravimetric test. Combining this information with that gained from the post-mortem analyses of spent refractories removed from working gasifiers, we have developed a better understanding of refractory failure in gasifier environments. In this paper, we discuss refractory failures in slagging gasifiers and possible strategies to reduce them. Emphasis focuses on the refractories employed in gasifier systems which utilize coal as the primary feedstock.

INTRODUCTION

Integrated Gasification Combined Cycle (IGCC) power production is one of the cleanest and most efficient means of producing electricity from coal, petroleum residues, and other low- or negative-value feedstocks. Gasification of the carbon-containing feed results in the formation of synthesis gas (primarily a combination of carbon monoxide and hydrogen), which can be converted to electricity using a combination of gas and steam turbine technology. In addition to producing power with thermal efficiencies that are significantly higher than those obtained in conventional coal power plants, IGCC systems are also more environmentally friendly, with air emissions that exceed U.S. Clean Air Act standards.

The gasifier at the heart of the IGCC system acts as a containment vessel for the reaction of carbon-containing materials with oxygen and water to form syn-gas. Heat, ash, and sulphur compounds are the principal by-products of this reaction. Because the environment inside an operating gasifier is typically severe, the chamber is lined with refractory materials that protect the outer steel shell from erosion, corrosion, and temperature. Gasifiers may either be dry ash or slagging systems, but the most severe environments occur in the slagging gasifiers, where operating temperatures can range from 1300° to 1600°C, depending upon the melting point and viscosity of the residual ash. In addition to high temperature, the refractory lining inside a slagging gasifier must also be able to withstand a number of other materials challenges, including: large and sometimes sudden variations in temperature; alternating oxidizing and reducing environments; corrosive slags and gases; erosion by residual particulates; and high pressures. Several studies have indicated that because of the severity of these challenges, high-chrome bricks are the only commercial materials that are viable for this application.(1) However, the best chrome-based refractory materials that are commercially available today have a predicted service life of less than two years. Actual service life is often much shorter, and in severe cases, excessive refractory loss can force the unscheduled shutdown of the gasifier. With the price of relining the gasifier exceeding one million dollars in materials costs alone, it is apparent that cost-effective operation and process reliability require that refractory performance be improved in slagging gasifier systems. To address this need, it is the goal of the current project to develop improved materials and techniques that will reliably extend the lifetime of refractory liners in slagging gasifier systems to at least three years.

CURRENT STATUS

Our primary research effort in this project has focused thus far on understanding how refractory materials behave in gasifier environments, with the goal of utilizing this understanding to develop improved materials and processes that can significantly extend refractory service life for this application. Characterization of materials behavior in the gasifier environment has included both post-mortem examination of spent refractory brick removed from commercial gasifiers, and laboratory exposure tests aimed at understanding how changes in slag chemistry and gasifier environment affect refractory performance. Utilizing the knowledge gained from these studies, several new materials have been produced in our laboratory that demonstrate reduced slag penetration when exposed to simulated coal slags.

LABORATORY EXPOSURE TESTS

The laboratory exposure tests utilized in this project include both a modified cup test that is a proven method of simulating gasifier slag-refractory interactions,[2] and a recently-developed gravimetric technique that can provide direct information on the dynamic processes that occur during refractory-slag interactions.[3] With the exception of some recent materials development work that will not be discussed in detail here, all laboratory exposure tests to date have employed commercially-produced, high chrome materials as the refractory samples.

Typical coal ash contents range between five and 15 weight percent, with a composition that varies depending on where the coal was mined. Nonetheless, most coal slags can be described to a first approximation as a five-component oxide system, with an average composition (in weight percent) of 50% SiO_2, 25% Al_2O_3, 16% Fe_2O_3, 7% CaO, and 2% MgO. In our laboratory cup exposure tests, we have investigated the role of each of these oxide components, both individually and in combination, on refractory-slag interactions in a simulated gasifier environment. In addition, refractory-slag interactions utilizing a bottom slag removed from a commercial gasifier, and an artificial slag based on the bottom slag composition (but without the high carbon content), have also been studied using the cup test.[4] The more important results of this suite of studies can be summarized as follows:

- Coal slags penetrate rapidly into the refractory brick.
- It is the SiO_2 and CaO components of the slag that penetrate the most deeply into the refractory brick.
- The Fe_2O_3/FeO components of the slag react with the refractory to form a spinel phase at the hot face surface.
- Severe cracking of the refractory can result from slag penetration.

In addition to the cup test, refractory-slag interactions are also being studied using an accelerated gravimetric technique. Developed utilizing the principals of wetting and capillary flow, this gravimetric test provides direct information on the dynamic wetting, penetration, and dissolution of refractories by molten slags. Our studies to date utilizing this technique have examined the influence of temperature and atmosphere on refractory-coal slag interactions. Three tests have been completed so far, with the following conditions:

Test 1: T = 1550°C; atmosphere: $CO/CO_2 = 2$
Test 2: T = 1490°C: atmosphere: $CO/CO_2 = 2$
Test 3: T = 1550°C; atmosphere: air

Each of the three experiments utilized the same 90% Cr_2O_3 refractory material and an artificial coal slag with the composition (in weight percent) of 50% SiO_2, 25% Al_2O_3, 16% Fe_2O_3, 7% CaO, and 2% MgO. The results from these experiments, presented graphically in Fig. 1, confirm our previous observations from the cup tests that the slag penetrates rapidly into the high-chrome refractories, and that the degree of penetration depends both upon the atmosphere and the temperature of the system. Oxidizing conditions, such as those that can occur in an operating gasifier, enhance the wettability of the high-chrome refractory by the coal slag, increasing the level of slag penetration. An increase in temperature for a given atmosphere (in this case CO/CO_2) will also increase the amount of slag penetration, through a decrease in slag viscosity. As is apparent in Fig. 1, refractory wettability decreases after the first five minutes of the test, as an iron-chrome spinel forms at the refractory hot face, slowing slag penetration. It is interesting to note, however, that in spite of significant slag penetration, large-scale dissolution of the refractory does not occur during these tests, suggesting that dissolution is not a major source of material removal under these conditions.

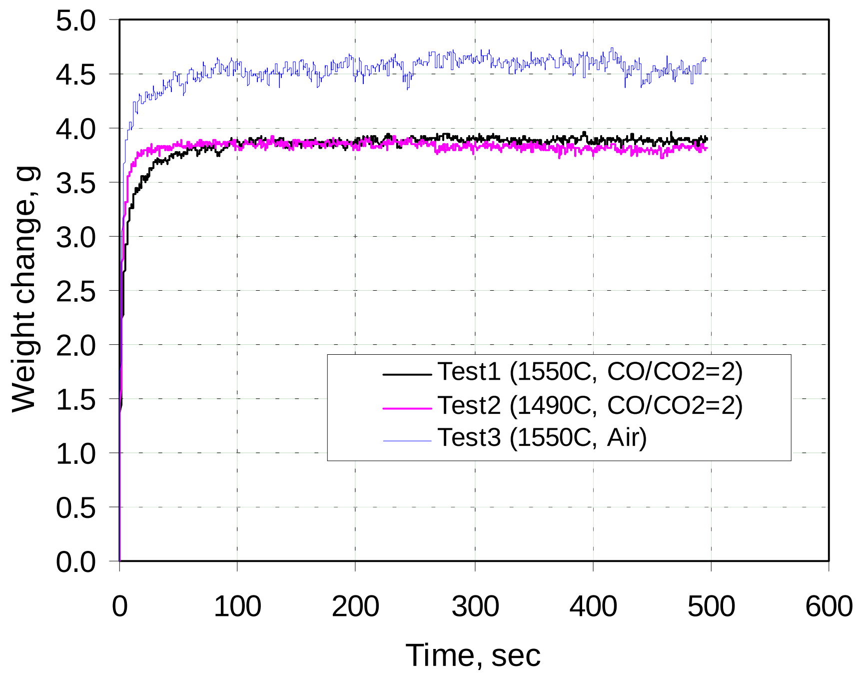

Fig. 1. Results from the first 8 minutes of the Gravometric test.

POST-MORTEM ANALYSES

Post-mortem characterization of refractory bricks removed from service in commercial gasifiers provides a wealth of information about refractory-slag interactions in the working environment, as well as offers a reality-check for the simulated exposure tests performed in the laboratory. The spent refractory brick that we have examined to date have all come from commercial gasifiers in which coal is the primary feedstock. Their service life in each case was approximately 18 months; however, the exact conditions of service (i.e., the temperature, environment, number of cool-down cycles, etc.) are not known. Figure 2 provides a look at the external surface and cross section of a spent refractory brick that consists of 90% Cr_2O_3. Material loss, resulting from a combination of corrosion and spalling, has been extensive during the lifetime of this brick, and the presence of horizontal cracks parallel to the hot face indicate that further material loss was imminent, had the refractory remained in service. The cross section of the refractory illustrates the deep level of slag penetration into the brick, and the horizontal cracks that form and link-up in the refractory as a direct result of the microstructural changes that occur with slag penetration. Note that these cracks are different in character from the fabrication flaws that can be occasionally observed in the virgin material. In addition to material loss as a result of slag penetration, there is also evidence of pinch spalling at the hot face corners of the refractory. Such spalling occurs most often as the result of hoop stresses that develop as the refractory liner is heated to the working temperature.

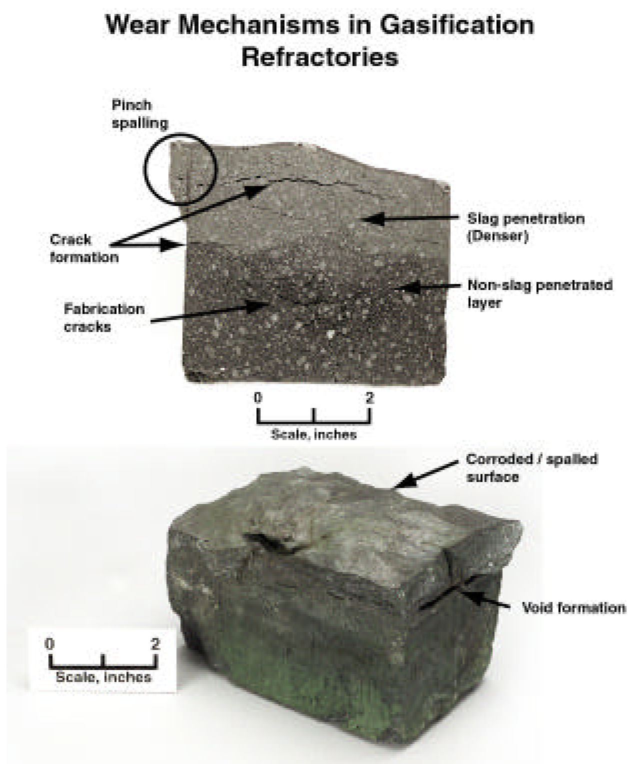

Fig. 2. Wear mechanisms observed in the spent refractory.

Chemical analyses of the penetrated slag in the spent refractories corroborates the results of the laboratory exposure tests, as illustrated by the plot of chemistry as a function of distance from the hot face in Fig. 3. As in the cup exposure tests, it is the SiO_2 and CaO components of the coal slag that penetrate most deeply into the refractory brick, whereas the Fe_2O_3/FeO reacts with the Cr_2O_3 at the refractory surface to

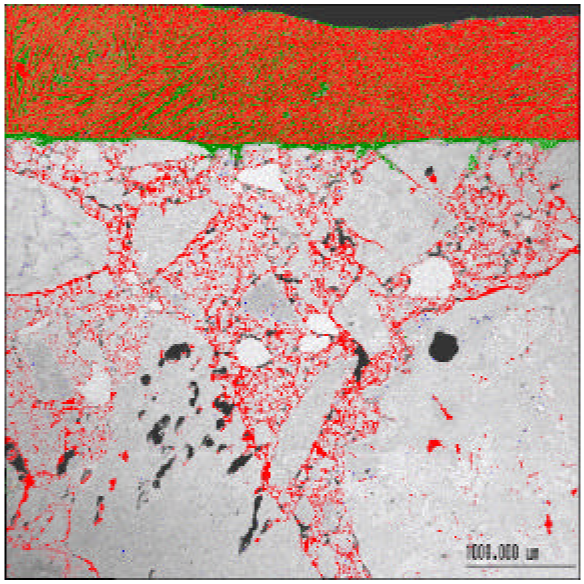

Fig. 3. X-ray map of the slag-hot face region of the spent refractory. In this image, red is Si, green is Fe; and blue is Ca.

form a spinel phase. The X-ray map of the hot-face region in Fig. 4 indicates that the slag penetrates primarily through the matrix, with only minor dissolution of the aggregate grains in the near surface region.

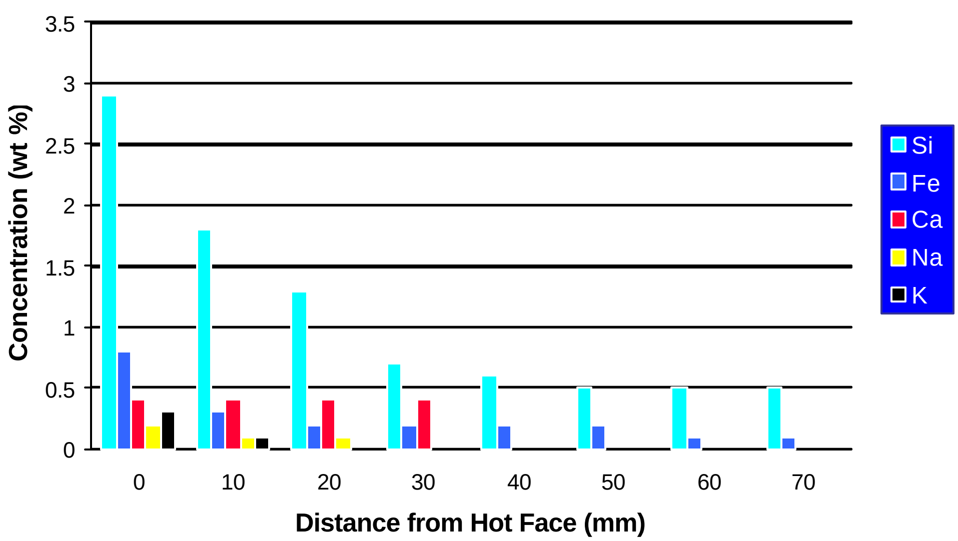

Fig. 4. Composition of penetrated slag as a function of distance from the hot face of the spent refractory.

IMPROVED REFRACTORY MATERIALS

Material loss resulting from refractory-slag interactions usually occurs as the result of one, or some combination, of the following processes:

- Corrosion
- Erosion
- Spalling

The combined results of our laboratory-exposure tests and post-mortem analyses of spent refractories indicate that the primary mechanism of material loss in slagging coal gasifiers is the spalling that occurs as the result of rapid and extensive slag penetration. Thus our efforts at developing an improved refractory material for this application are focused on incorporating mechanisms that will reduce slag penetration in these systems. These mechanisms include (1) reducing the volume of interconnected porosity; (2) reducing the pore sizes; and/or (3) inducing in-situ microstructural changes that either seal the refractory surface, preventing slag penetration, or reduce penetration by causing the slag to solidify more rapidly inside the refractory. Utilizing this approach, a refractory material has been developed at the Albany Research Center that demonstrates good resistance to simulated coal slag in laboratory exposure tests. Work continues to further characterize this material and confirm its ability to better withstand gasifier environments.

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