DOE/ARC-2002-014

Improved Refractories for IGCC Power Systems

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Manuscript

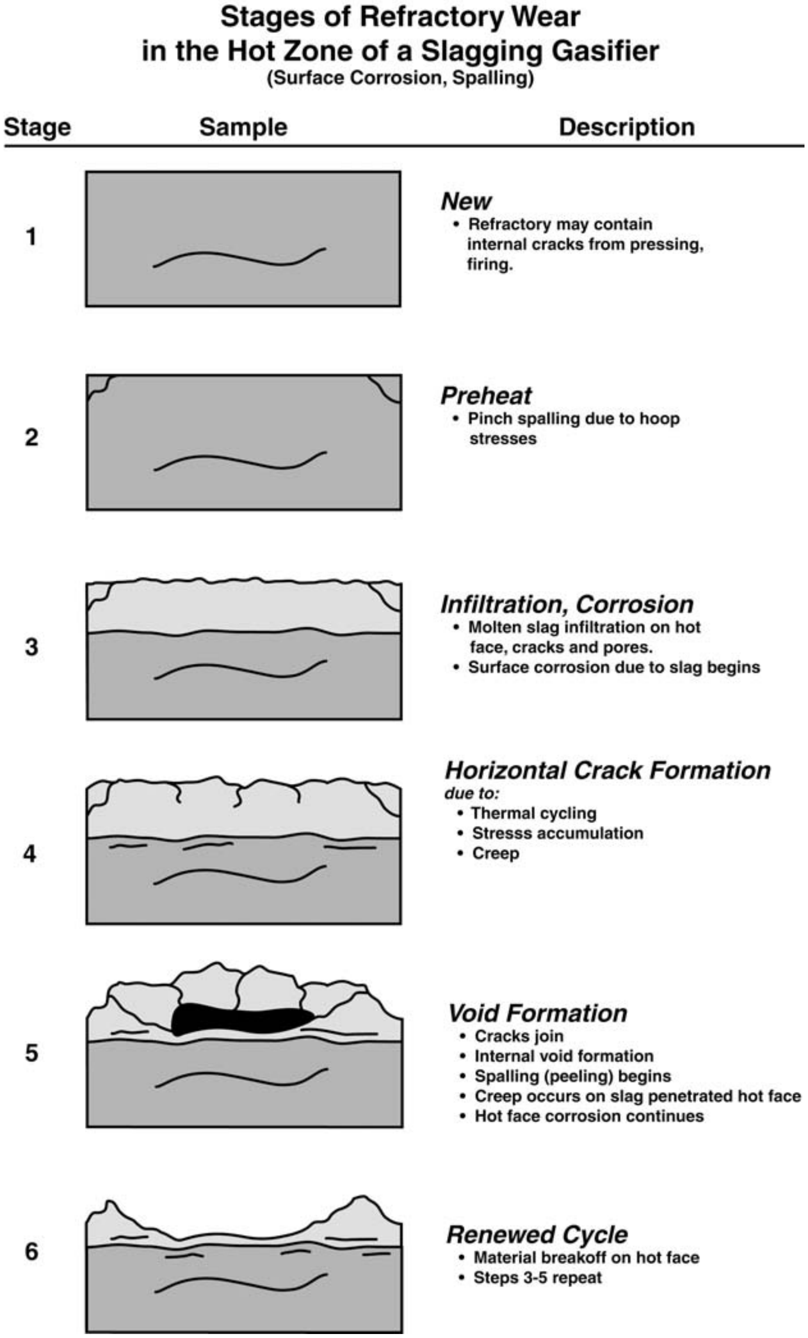
The gasification of coal, petroleum residuals, and biomass provides the opportunity to produce energy more efficiently, and with significantly less environmental impact, than more-conventional combustion-based processes. In addition, the synthesis gas that is the product of the gasification process offers the gasifier operator the option of "polygeneration," i.e., the production of alternative products instead of power should it be economically favorable to do so. Because of these advantages, gasification is a key element in the U.S. Department of Energy's Vision 21 power system. However, issues with both the reliability and the economics of gasifier operation will have to be resolved before gasification will be widely adopted by the power industry. Central to both increased reliability and economics is the development of materials with longer service lives in gasifier systems that can provide extended periods of continuous gasifier operation.

The focus of the Advanced Refractories for Gasification project at the Albany Research Center is to develop improved materials capable of withstanding the harsh, high-temperature environment created by the gasification reaction, and includes both the refractory lining that insulates the slagging gasifier, as well as the thermocouple assemblies that are utilized to monitor gasifier operating temperatures. Current generation refractory liners in slagging gasifiers are typically replaced every 10 to 18 months, at costs ranging up to $2,000,000. Compounding materials and installation costs are the lost-opportunity costs for the three to four weeks that the gasifier is off-line for the refractory exchange. Current generation thermocouple devices rarely survive the gasifier start-up process, leaving the operator with no real means of temperature measurement during gasifier operation. As a result, the goals of this project include the development of a refractory liner with a service life at least double that of current generation refractory materials, and the design of a thermocouple protection system that will allow accurate temperature monitoring for extended periods of time.

Current Status

Extensive *post-mortem* analyses of refractory brick removed from commercial gasifiers, combined with laboratory studies of refractory behavior in simulated gasifier environments, indicate that slag penetration and attack of the refractory is the primary cause for the rapid degradation of the refractory lining in slagging gasifiers.(1-6) The mechanisms leading to material loss are illustrated schematically in Figure 1. *Post-mortem* analyses suggest that stresses generated as the brick expand during heat-up of the gasifier may lead to some initial cracking and subsequent pinch spalling at the brick corners. As the feedstock is introduced into the gasifier and slag begins to flow down the refractory wall, the slag immediately penetrates the refractory and corrosion of the material begins. Because the thermal gradient within the hot-face brick is relatively flat (~ 4° C/cm) and the viscosity of the slag is typically low at the gasifier operating temperature, the slag moves deeply (> 4 cm) into the refractory via the interconnected porosity and along matrix grain boundaries. The presence of cracks vertical to the hot face will also facilitate slag penetration. The resulting changes in mineralogy and/or physical characteristics of the slag-penetrated region result in the formation of cracks parallel to the hot face near the slag-penetrated/virgin refractory interface. Link-up of this crack system, which is accelerated by sudden or large changes in gasifier operating temperature, ultimately leads to large-scale material removal. The cycle then begins again with renewed slag penetration and attack of the fresh refractory.

When structural spalling is the principal failure mechanism for a refractory, as is the case in slagging gasifiers, there is the potential for large amounts of material to be removed as the result of single fracture events. The actual volume of material removed is defined by the depth of slag penetration, since changes induced in the material as a result of interaction with the slag lead to crack initiation behind the hot face. Therefore, the key to improving the performance of refractories in slagging gasifier environments where structural spalling is a problem, is to reduce the ease of slag penetration into the material. This can be achieved in a number of ways, including changing the wetting characteristics of the slag by altering the slag



New
- Refractory may contain internal cracks from pressing, firing.

Preheat
- Pinch spalling due to hoop stresses

Infiltration, Corrosion
- Molten slag infiltration on hot face, cracks and pores.
- Surface corrosion due to slag begins

Horizontal Crack Formation
due to:
- Thermal cycling
- Stresss accumulation
- Creep

Void Formation
- Cracks join
- Internal void formation
- Spalling (peeling) begins
- Creep occurs on slag penetrated hot face
- Hot face corrosion continues

Renewed Cycle
- Material breakoff on hot face
- Steps 3-5 repeat

Figure 1. Sequence of slag penetration and attack in the gasifier refractory.

chemistry, reducing the wettability of the refractory, reducing the level of interconnected porosity in the refractory, changing the pore size distribution within the refractory, and/or inducing an *in-situ* change in the refractory microstructure that effectively seals the refractory surface. Any changes made to the refractory must be effective in reducing slag penetration while retaining the other beneficial properties of the material.

At the Albany Research Center, we are developing improved refractory materials for this application by applying the last of these strategies to reduce slag penetration and attack. By adding a small amount (< 5 weight percent) of a phosphate-based material ($AlPO_4$, $CrPO_4$, etc) to the matrix of a high-chrome refractory, we can reduce slag penetration to less than one-fifth that observed in an unmodified high-chrome refractory under identical conditions in laboratory exposure tests.(7) As a result, the amount of damage and the volume of material loss that slag penetration causes to the refractory is significantly diminished. The results of a laboratory cup exposure test comparing the performance of a commercial high-chrome refractory with the ARC-modified material is illustrated in Figure 2. In this test, a "cup" is drilled into each refractory brick and filled with a coal ash slag with the composition (in weight percent) 51% SiO_2, 21% Al_2O_3, 20% Fe_2O_3, 6% CaO, and 2% MgO. The slag filled cups are then placed in a furnace and heated to 1600ºC for 24 hours in an argon environment. Following the exposure test, the refractories are cross-sectioned and examined for evidence of slag penetration and attack. As indicated by the dotted lines in Figure 2, the level of slag penetration in the phosphate-modified refractory is limited to within one millimeter of the refractory-slag interface. This is compared with almost complete penetration by the slag to the bottom of the "cup" (a depth greater than two centimeters) in the unmodified refractory control. Microstructural and microchemical analyses by scanning electron microscopy indicate that where slag penetration occurs in the modified material, it is along matrix grain boundaries and via the interconnected porosity. However, there is very little evidence of slag interaction with either the fine-grained matrix or the aggregate phases. A chemical map of the presence of silica (a major component of the slag) in the near surface regions of the modified refractory, provided in Figure 3, illustrates the limited depth of penetration and attack. The mechanisms for improved refractory performance in the phosphate-modified materials have not been fully confirmed; however, we believe that the reaction between constituents in the slag, the phosphate, and the refractory causes the slag to "freeze" much more quickly within the refractory, limiting penetration to a narrow surface region and therefore reducing the potential for large volumes of material loss by structural spalling. An added benefit to the phosphate-modified material is that the relatively small change in chemistry required by this process will likely not result in a large scale change in the mechanical and thermal performance of the refractory product.

If the results of these laboratory exposure tests are any indication, ARC's improved refractory material will have at least double the service life of currently available high-chrome refractories, translating into a potential savings of millions of

Figure 2. Cross sections of (a.) a conventional 90% chrome refractory, and (b.) ARC's modified refractory following exposure to a coal slag at 1600º C. The depth of slag penetration is marked in each case.

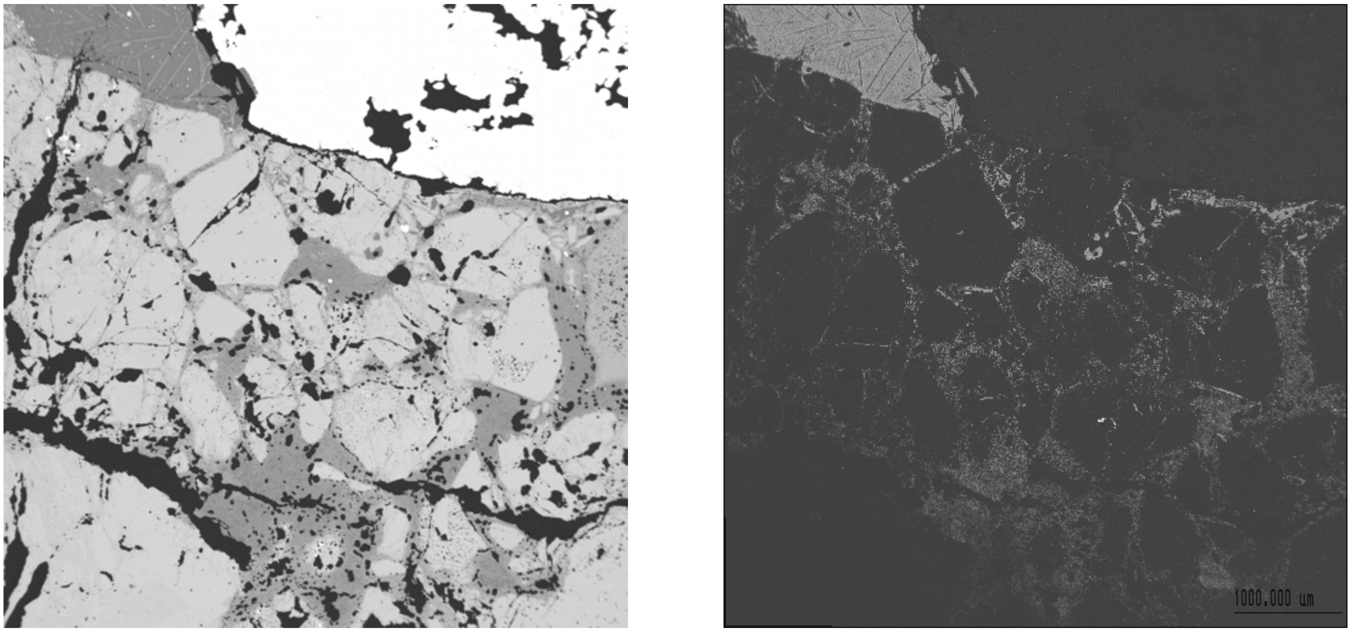


Figure 3. (a) Back-scattered electron micrograph of the slag-refractory interface following exposure of the improved material to 1600ºC for 1 hour, and (b) an Si X-ray map of the same region.

dollars in annual gasifier operating costs, as well a significant increase in gasifier on-line availability. Work continues in our laboratory to further optimize this refractory and to prepare materials in collaboration with a commercial refractory manufacturer for expanded pilot-scale and field tests.

Post-mortem analyses of spent thermocouples removed from commercial gasifiers indicate that as with the refractories, slag penetration and attack are the principle mechanisms of rapid thermocouple failure in the gasifier environment. In this case elements of the slag penetrate quickly into the thermocouple protection assembly, react with the thermocouple wire, and result in rapid failure of the device. To reduce thermocouple susceptibility to slag attack, we are currently designing and testing thermocouple assemblies that incorporate one or more of the following protection strategies: a slag-resistant coating of the thermocouple sheath; a more slag-resistant filler material; and a slag-resistant assembly end cap.

The purpose of most of the thermocouple assembly is to provide protection to the thermocouple wire in the service environment. This assembly usually consists of an outer sheath or sheaths (frequently Al_2O_3 or SiC), a filler material (usually Al_2O_3), and the individual thermocouple wires encased in a final Al_2O_3 protection tube. However, because most molten gasifier slags are undersaturated with respect to Al_2O_3 at the operating temperature, the high-Al_2O_3 protection tubes and filler materials are particularly susceptible to attack by the slag. Similarly, the reducing operating conditions combined with the presence of iron in the molten slag result in rapid degradation of SiC components. As a result, direct contact of the thermocouple device with the molten slag results in a rapid breach of the protection system. As a possible method of extending thermocouple life, ARC, in collaboration with scientists at Ames Laboratory and Oak Ridge National Laboratory, is examining the feasibility of utilizing several coating techniques on the outer protection sheath to slow the rate of slag attack. Several coating compositions, including Cr_2O_3 and tungsten, will be tested to determine their relative resistance to the molten slag under gasifier operating conditions. In addition, ARC is also developing an economical method to manufacture dense thermocouple filler materials, with a composition similar to that of the improved refractory material previously described. This improved filler material is predicted to have both increased physical (because of the higher density) and chemical resistance to attack by most gasifier slags. Once this manufacturing technique is perfected, the filler will be tested to confirm its relative resistance to slag penetration and attack. After the exposure tests are completed, an optimum thermocouple protection assembly will be designed, and prototypes will be produced in collaboration with Engelhard-Clal, a thermocouple manufacturer, for testing in commercial gasifiers.

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