Improved Refractories for Slagging Gasifiers in IGCC Power Systems

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Abstract

The gasification of coal and other carbon-containing fuels 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 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 viewed as one of the key processes 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 enhanced reliability and economics is the development of materials with longer service lives in gasifier systems that can provide extended periods of continuous, trouble-free gasifier operation.

The focus of the Advanced Refractories for Gasification project at the Albany Research Center is to develop improved refractory materials capable of withstanding the harsh, high-temperature environment created by the gasification reaction, and includes both the refractory lining that protects and 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 four to 18 months, at costs ranging up to $2,000,000, depending upon the size of the gasification vessel. Compounding materials and installation costs are the lost-opportunity costs for the time 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 routine operation. Reliable, efficient, and economical gasifier operation that includes the 90 to 95% on-line availability desired by the industry clearly requires improvements in refractory liner materials and in thermocouple protection strategies. 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 gasifier operation.

Current Status

Refractories

The strategy adopted by the Albany Research Center to develop improved materials for this application is to examine spent materials exposed to slagging gasifier environments to determine their failure mechanisms, and then to re-design the material to better withstand those specific stresses. Forensic analyses of refractory brick removed from commercial gasifiers utilizing a variety of feedstocks, combined with laboratory studies of refractory behavior in simulated gasifier environments, indicate that slag penetration and attack of the refractory is a primary cause of the rapid degradation of the refractory lining in slagging gasifiers.(1-8) Once slag infiltrates the refractory, changes in the mineralogy and/or physical characteristics of the material relative to the virgin material 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 freshly exposed refractory surface.

When structural spalling is the principal failure mechanism for a refractory, there is the potential for large volumes of material to be removed as the result of single fracture events. In this case the volume of material removed is defined by the depth of slag penetration, since changes induced in the refractory as a result of interaction with the slag lead to crack initiation near the interface. Therefore, one of the keys to improving the performance of refractories in slagging gasifier environments where structural spalling is a problem, is to reduce the depth 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 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.

The Albany Research Center (ARC) has explored each of these methodologies as possible routes to improved refractory service life in slagging gasifier environments and has determined that the last is the most likely to provide the biggest improvement. As reported last year,[3] the ARC is developing improved refractory materials for this application by designing a refractory chemistry and microstructure that can effectively reduce slag penetration and attack. By altering the chemistry of the high chromium oxide refractory matrix through the addition of a small amount (< 10 weight percent total) of phosphate- and oxide-based materials, we can significantly reduce slag penetration into the refractory brick and enhance its mechanical durability. As a result, the degree of damage and the volume of material loss that exposure to the gasifier environment causes to the refractory are significantly diminished. Over the course of the past year, we have focused on optimization of matrix chemistry and "proof of concept" of these materials through continued laboratory performance tests. Under a cooperative research and development agreement with ANH Refractories in West Mifflin, PA, we have produced full-sized brick of several test compositions in a commercial setting. Results of a rotary slag exposure test of these brick (Fig. 1) indicate that under the conditions of this test, they outperform the best high-chromium oxide refractory materials currently utilized by the industry. In the rotary slag test, the brick were exposed to a flowing coal slag for five hours at a temperature in excess of 1650º C. As is clear in Fig. 1, the commercial high-chromium oxide refractory materials cracked severely during the test (Fig. 1a), whereas the ARC-ANH material showed no evidence of fracture (Fig. 1b). In addition, there was relatively less interaction with the slag in the ARC-ANH refractory and no evidence of spalling-type fracture (Fig. 2). While the conditions of the rotary slag test do not exactly reproduce those experienced in an operating gasifier, the results do suggest that the ARC-ANH improved refractory has the potential to have a much longer service life than the materials currently used, translating into the possibility of millions of dollars in savings in annual gasifier operating costs, as well as a significant increase in gasifier on-line availability. Work continues in our laboratory to finalize performance tests, in preparation for placing test panels of this material in commercial gasifiers in the Fall.

Figure 1. Refractory brick following exposure in the rotary kiln test. To the left are commercially-produced high chromia refractories; to the right are the ARC-ANH developed refractories.

While not currently an issue, there is some concern that the future use and disposal of chrome-bearing materials will be subject to more-stringent environmental regulations. The Albany Research Center is also looking to this future by beginning the development of a non-chrome based refractory material that will have the requisite stability for long service life in a

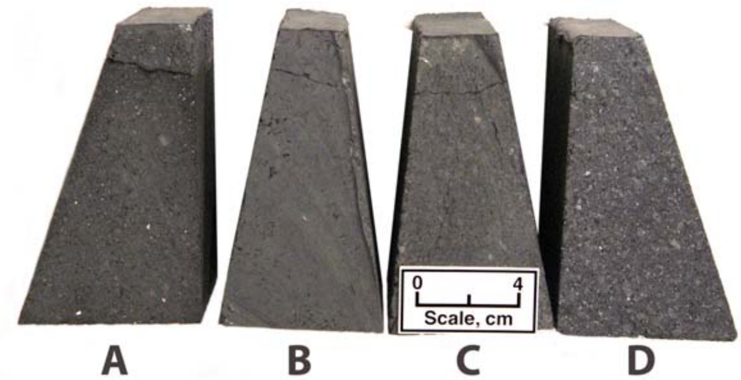

Figure 2. Cross-section view of the four types of refractories tested in the rotary kiln test. “A,” “B,” and “C” are commercially-produced refractories currently used by the gasifier industry, and “D” is the ARC-ANH refractory. Note the spalling-type fracture near the hot face in “A,” “B,” and “C,” that is missing in “D.”

gasifier environment. We have screened several candidate material systems utilizing laboratory exposure tests and will be working in collaboration with a commercial refractory manufacturer to further develop a spinel-based material for this application.

Thermocouples

Post-mortem analyses of spent thermocouples removed from commercial gasifiers indicate that as with the refractories, slag penetration and attack is one of 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 both of the following protection strategies: a more slag-resistant thermocouple sheath and a more slag-resistant filler material.

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 or Cr_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 gasifier 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 to extend thermocouple life, ARC, in collaboration with scientists at Ames Laboratory and Oak Ridge National Laboratory, have examined the feasibility of utilizing several techniques to modify the outer protection sheath to slow the rate of slag attack. Several barrier coating compositions (W, $LaCrO_3$, La_2S_3, Cr_2O_3, and several commercial refractory glazes) and coating methodologies (vapor deposition, spraying, and dip coating) were tested; however, the difficulties in producing a fully-dense, defect-free coating, combined with the reactivity of the coatings with the coal slag, resulted in the coated materials performing no better, or in some cases worse, than the uncoated materials in laboratory exposure tests. ARC also utilized ORNL’s high-density infrared (HDI) heating facility[8] in an attempt to produce a fully dense refractory surface for enhanced slag resistance. However, preliminary results indicate that until problems with thermal shock of the ceramic matrix during processing and uniformity of the finished surface are resolved, this last will not be a viable methodology to enhance slag resistance of ceramic materials.

To complement an improved thermocouple sheath, ARC has also developed an economical method to manufacture dense thermocouple filler materials, with a composition similar to that of the improved refractory material previously described (Fig. 3). This improved filler material is expected to have both increased physical and chemical resistance to attack by most gasifier slags. Once the optimum sheath is identified it will be combined with ARC’s filler material, and the prototype

Figure 3. ARC-engineered thermocouple protection system for gasifier systems.

thermocouple assembly will be tested in the laboratory to confirm its relative resistance to slag penetration and attack. After the laboratory exposure tests are completed, fully instrumented prototypes will be produced in collaboration with our partner thermocouple manufacturers, for testing in commercial gasifiers.

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