U.S. Department of Energy • Office of Fossil Energy National Energy Technology Laboratory

Advanced Materials

Successes

0

Improved Refractory and Thermocouple Materials for Commercial Slagging Gasifiers

Advanced Research

To support coal and power systems development, NETL's Advanced Research Program conducts a range of pre-competitive research focused on breakthroughs in materials and processes, coal utilization science, sensors and controls, computational energy science, and bioprocessing—opening new avenues to gains in power plant efficiency, reliability, and environmental quality. NETL also sponsors cooperative educational initiatives in University Coal Research, Historically Black Colleges and Universities, and Other Minority Institutions.

ACCOMPLISHMENTS

- ✓ **Process improvement**
- ✓ Cost reduction
- ✓ **Greater efficiency**
- Innovative materials



Description

High-performance coal gasification systems are crucial to the success of advanced, zero-emissions power plants of the future, such as the FutureGen prototype plant for hydrogen and electricity production. Refractory linings and thermocouples currently used in slagging gasifiers employed in integrated gasification combined-cycle power systems have unacceptably short service lives, limiting the efficiency, reliability, on-line availability, and cost-effectiveness of power generation systems using gasification. Improving these components is critical for greater marketplace acceptance of gasification systems as an alternative to conventional coal-fired combustion plants.



A test panel of phosphate-containing, high chrome oxide refractory (brick marked in red) installed in a commercial slagging gasifier

Premature failure of refractory brick results from the extreme environment inside an operating gasifier, where the materials used to contain the high-temperature gasification reaction are attacked by molten slag from the residual ash from the carbon feedstock, and by corrosive gases from the gasification reaction. The best refractory liner materials heretofore available have a predicted service life of no more than two years, with actual service life tending to be shorter in duration. Liner failure can result in complete shutdown of the gasifier island, and therefore the entire plant, to allow for material replacement. Unless there is a second gasifier available, these one to two week shutdowns result in stoppage of synthesis gas (syngas) production, which can cost millions of dollars in lost opportunity costs.

Thermocouple life in a gasifier is even shorter than that of the refractory lining, with a typical service life less than four months. As a result, long-term reliable temperature measurement within a gasifier is problematic, making process control difficult. Like the refractory lining, thermocouple failure is typically the result of slag attack of thermocouple components.

In research sponsored by the U.S. Department of Energy's Office of Fossil Energy (DOE-FE), scientists at DOE's National Energy Technology Laboratory (NETL) have pursued a multiyear project to identify scenarios under which materials fail, and to develop ways to extend the

PROJECT DURATION

Start Date 10/01/98

End Date 09/30/06

Соѕт

Total Project Value \$4,646,600

DOE/Non-DOE Share \$4,593,600 / \$50,000

INDUSTRIAL PARTNERS

ANH Refractories Co./ Harbison-Walker Refractories Co. Moon Township, PA http://www.hwr.com/

ConocoPhillips Company Houston, TX http://www.conocophillips.com

Eastman Chemical Company Kingsport, TN http://www.eastman.com/

TECO Energy/Tampa Electric Company Tampa, FL http://www.tecoenergy.com/ lifetimes of primary refractory liners and thermocouple assemblies. Funding for this joint effort comes through NETL's Advanced Research Materials and Advanced Gasification Technologies programs. Leading refractory suppliers are participating, along with commercial gasification system owners and operators.

Project Goals

The goals of the project are to identify material failure mechanisms; develop primary refractory liners with extended lifetimes of at least 50 percent in slagging gasifier systems; shorten system downtime caused by refractory repair and maintenance; develop



Laboratory test of refractory performance under extreme operating conditions

repair materials that can reduce installation time and cost; and develop improved thermocouples/ temperature-monitoring techniques. The overall materials program is part of a larger DOE goal to provide gasifier operators with a system capable of achieving an online availability of greater than 90 percent.

Refractory Material Research Accomplishments

The causes of refractory brick failure have been identified. Post-mortem analyses of refractory brick removed from commercial gasifiers, combined with laboratory studies of refractory behavior in simulated gasifier environments, indicate that corrosion and repeated penetration of slag into the porous brick lead to a phenomenon called spalling. The spalling or cracking is accelerated by sudden or large changes in gasifier operating temperature, ultimately leading to large-scale loss of surface material. Spalling then begins again with renewed chemical corrosion by the slag and penetration of the freshly exposed refractory surface.

Based on the above analyses, NETL scientists developed and patented a new gasifier refractory material (U.S. Patent # 6,815,386) designed specifically to reduce slag penetration and spalling in order to extend the useful life of the material. The new material was produced in collaboration with Harbison-Walker Refractories Co., a major industrial supplier of refractories. The improved refractory has an altered microstructure accomplished through small additions (< 10 weight percent total) of phosphate- and oxide-based materials. As a result of these additions, the damage and volume of refractory material loss in a gasifier environment are significantly diminished.

The photos below show a comparison between commercially used refractory and the improved materials, once both were exposed to a rotary slag flow typical of a coal gasifier. Field tests of this new refractory are currently under way at several commercial gasifier sites in the United States. Field tests to date have been conducted at Eastman Chemical Company, Kingsport, TN; Tampa Electric Company's (TECO Energy) Polk Power Station, Lakeland, FL; and Wabash River Power Station, Terre Haute, IN. Simultaneously, development work continues at NETL to design refractory linings without chromium oxide that can match or beat current refractory performance at a lower cost and with less environmental impact.



Refractory brick following exposure in the rotary kiln test: To the left are commercially produced high-chromium oxide refractories; to the right are the improved refractories

Thermocouple Research Accomplishments

In addition to the improved refractory, NETL has worked with gasifier users to improve thermocouple performance through material and design changes, with the goal of providing gasifier operators better gasifier control. Post-mortem analyses of spent thermocouples removed from commercial gasifiers indicated that, as with the refractory materials, slag penetration and corrosive attack are principal mechanisms causing rapid thermocouple failure in gasifiers. Current-generation thermocouples are very susceptible to the harsh operating environment inside the slagging gasifier and often fail within hours of gasifier start-up, leaving the operator with no accurate real-time means to measure temperatures.

To reduce thermocouple susceptibility to slag attack, NETL designed and began testing thermocouple assemblies that incorporate a more slag-resistant thermocouple sheath and filler material. NETL has also worked on improved fabrication and installation methodologies to provide an enhanced ceramic protection system — one that can better shield thermocouples from corrosive components of molten slag. Field tests to prove the concept in a commercial coal-fed gasifier are ongoing.



NETL-engineered thermocouple protection system for gasifier systems



Test thermocouples being installed in a commercial gasifier

"This project will benefit gasification technology development and deployment by improving materials to contain and monitor gasification processes."

STATES AND LOCALITIES IMPACTED

Tampa, FL Terre Haute, IN Moon Township, PA Kingsport, TN

Benefits

This project will benefit gasification technology development and deployment by improving materials to contain and monitor gasification processes. Results of laboratory and field tests suggest that the improved refractory material should result in much longer and more reliable service lifetime than the materials currently used. These extended lifetimes translate into the possibility of millions of dollars in annual gasifier operating costs savings, as well as a significant increase in gasifier on-line availability. Commercial availability of the improved refractory lining, for example, could save up to \$4 million every three years, depending on the size of the gasifier and a plant's production schedule. In addition, down-time for refractory relining could be cut in half. Providing such improved components in advanced generation plants such as FutureGen also could be critical to greater acceptance of gasification systems as an alternative to conventional coal-fired combustion technology.



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