Refractory Improvement

Background

Gasification of coal and coal-petcoke blends produces a hot gas mixture consisting primarily of hydrogen and carbon monoxide called synthesis gas (syngas). The syngas is used for production or co-production of power, fuels, and chemicals. Development of the gasification process as a fuel- and product-flexible energy conversion system that can, in addition to other purposes, enable power plants to be competitive with conventional pulverized coal power plants is a goal of the U.S. Department of Energy (DOE). Specific DOE targets include cost-effective increase in refractory service life and the control of gasifier slag viscosity through slag management, regardless of the feedstock used. Slag management in combination with refractory development has been shown to improve refractory material service life in laboratory tests. Achieving this target will increase the reliability, availability, and maintainability of facilities such as integrated gasification combined cycle (IGCC) power plants, while maintaining highest environmental standards.

One aspect of this effort focuses on improving the performance of refractory liners through better slag management. Ash originating from impurities in gasifier carbon feedstock liquefies at the high temperatures of gasification, leading to refractory wear by corrosion and spalling. The result of refractory wear is unplanned shutdowns for repair, replacement, or cleaning, which impact gasifier service life. Coal, a common carbon feedstock in slagging gasifiers, is typically high in mineral impurities containing silicon, calcium, iron, and aluminum—the elements controlling slag viscosity and refractory interactions. Mixed carbon feedstock, including petcoke, further complicates refractory performance because of its unknown effects on gasifier linings. Questions also exist concerning the use of new or mixed carbon feedstock containing western coals and/or biomass, both of which are high in alkali/alkaline earth components, creating the potential for a viscous slag.

The Gasification Team at the U.S. Department of Energy National Energy Technology Laboratory (NETL) is addressing these issues using an integrated approach that leverages the expertise of the NETL-Regional University Alliance. The approach combines theory, computational modeling, laboratory experiments, and industry input to develop physics-based methods, models, and tools to support the development and deployment of advanced gasification based devices and systems.

Project Description

Researchers will improve gasifier service life through both refractory development and research on additives to carbon feedstock that affect ash behavior. These research efforts focus on six areas of interest: (1) increasing the service life and performance of gasifier refractory material (liner and thermocouple filler) with consideration given to evaluating and improving carbon feedstock flexibility; (2) developing a fundamental understanding of slag and refractory behavior and interactions, i.e., spalling and chemical dissolution of refractory material, which will be used to improve refractory service life; (3) developing an understanding of slag behavior in a gasifier and of refractory/slag interactions during gasification so as to allow for carbon feedstock flexibility and control of ash phases as they impact material performance; (4) developing carbon feedstock

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ash models to predict and control slag formation/refractory interactions; (5) determining the fundamental impact of carbon feedstock additives on slag viscosity and refractory wear during gasification; and (6) obtaining thermodynamic information on vanadium oxides in petcoke and coal/petcoke slag mixtures.

**Goals and Objectives**

The goal of this project is to increase the gasifier service life, reliability and availability in order to lower the cost of electricity via refractory development/improvements.

The objectives are to (1) develop new refractory materials or improve the performance of existing gasifier refractory liner materials through studies of material wear and failure of both laboratory and commercial refractory materials, and (2) target ash/slag management to improve the service life of gasifier liner materials while controlling slag fluid flow viscosity within the ranges desired by gasifier operators, and to reduce carbon feedstock ash interactions with refractories and downstream materials that impact gasifier performance (e.g., fouling of syngas coolers).

**Accomplishments**

**Refractory Development**

The team completed an analysis of approximately 90 percent by weight high-chrome gasifier refractory samples with and without phosphate additions. The thickness of the samples with phosphate additions was approximately 33 percent greater after gasifier slag exposure than the samples without phosphate additions, a result that corresponds to an increase in refractory service life (see figure below).

Joint monitoring efforts occurred at one gasifier site, and plans have been completed to evaluate test materials at a second site where a different carbon feedstock of the phosphate-containing high-chrome oxide is used. These trials would be significant as wear mechanisms are different at different gasifier sites because of temperature, carbon throughput, and carbon feedstock ash differences. Microstructures of phosphate containing refractories removed from a gasifier in Jan of 2012 using a mixed feedstock of both coal and petcoke are being studied. These samples are being compared to samples removed from the gasifier site 4 years ago to determine how slag wear occurs. The study is focused on the migration of phosphate compounds because evidence of limited spalling was noted and because the improved performance of the phosphate refractories may result in further improvements in refractory service life if the mechanism of phosphate migration can be understood.

Characterization of slag penetrated/non-penetrated areas in commercial high chrome oxide refractory samples is also being conducted to determine the causes of differences in structural spalling.

Computed tomography imaging of refractory samples taken from gasifiers that use both coal and coal/petcoke blends indicates that cracks form in materials due to firing shrinkage, and that mismatches between structural materials occur at the hot face, creating pathways for slag penetration.

**Ash Management**

Laboratory exposure of synthetic coal/petcoke slag compositions at 1425, 1500, and 1575 degrees Celsius under an oxygen partial pressure of 10^-8 atm was completed, with the phases in the samples now being analyzed. Nanophase vanadium oxide particles with specific sample chemistries have been found in the samples.

Slag modeling to control refractory wear, slag viscosity, and minimize downstream material effects continues, with current emphasis on inputting published literature and laboratory data into the models, and on determining which software predictions using existing slag models are most accurate.

Thermodynamic data of different vanadium compounds in coal/petcoke slag mixtures at high temperatures and low-oxygen partial pressures can be used to predict properties of molten coal/petcoke carbon feedstock ash. This is the first time this phase diagram information has been modeled. This research, though in its early stages, was recognized by the American Ceramic Society (http://ceramics.org/acers-community/award-winners-resources) as the most important phase diagram work of 2012. The award, given in 2012, was for work published in 2011.

**Benefits**

Research products will provide knowledge and process insights contributing to the improvement of refractory service life through material development, and will enable the modeling and control of slag chemistry. Slag modeling will allow gasifier operators to control slag viscosity, maximize refractory service life, and, where applicable, minimize downstream material issues such as syngas fouling. The slag model will also input known carbon feedstock impurities to predict for the first time key slag properties at desired gasification temperature ranges and, if necessary, use additives to achieve desired slag properties. High-temperature thermodynamic information on vanadium phases existing at low oxygen partial pressure and high temperature will become part of FactSage™ databases, allowing for greater accuracy in predictive models used in modeling petcoke slags in gasifiers.