ENGINEERED REFRACTORIES FOR SLAGGING COAL GASIFIERS

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ABSTRACT

The widespread commercial adaptation of slagging gasifier technology to produce power, fuel, and/or chemicals from coal will depend in large measure on the technology's ability to prove itself both economic and reliable. Improvements in gasifier reliability, availability, and maintainability will in part depend on the development of improved structural materials with longer service life in this application. Current generation refractory materials used to line the gasifier vessel, and contain the gasification reaction, often last no more than three to 18 months in commercial applications. The downtime required for tear-out and replacement of these critical materials results in gasifier on-line availabilities that fall short of targeted goals. In this talk we will discuss the development of improved refractory materials engineered specifically for longer service life in this application, with emphasis on the design of new refractories that contain little or no chrome.

INTRODUCTION

Refractory liner materials currently utilized in air-cooled slagging gasification systems are typically composed of dense firebrick with a composition of Cr_2O_3 (60 to 95 wt pct) and one or more secondary refractory oxides (typically Al_2O_3, ZrO_2, or MgO). Experience has indicated that the high Cr_2O_3 content is necessary for the best refractory service life, with severe wear areas requiring a minimum of 75-wt pct Cr_2O_3. Refractory failure is typically by spalling and/or corrosive wear. Early attempts to develop non-chrome oxide refractories were hampered by a lack of understanding of the failure mechanisms in slagging gasifiers, by raw material purity issues, and by the superior performance of Cr_2O_3 refractories.

However, several issues exist with the Cr_2O_3 refractory materials currently used in slagging gasifiers that act as driving forces for new material development. These issues include: a) current generation high Cr_2O_3 containing refractories do not meet the performance requirements of gasifier users, b) possible long term safety concerns associated with the use of Cr_2O_3 refractory materials, c) the high cost of refractory materials containing Cr_2O_3, d) the difficulty in sintering high chrome oxide materials, and e) possible long term supply issues with high Cr_2O_3 refractories. Because of these issues, gasifier refractory research efforts at the Albany Research Center are directed toward investigating and developing low-chrome/no-chrome oxide liner materials. These goals will be achieved by evaluating wear mechanisms of chrome oxide based refractories in gasifiers and by evaluating non-chrome or low-chrome high temperature refractory oxides with potential for use in combating these and other material specific wear mechanisms. A review of the literature, thermodynamic studies, and a review of phase diagram behavior is being used to identify potential non-chrome materials for laboratory testing.

DISCUSSION

The strategy to develop low chrome/no-chrome materials for lining the hot face of slagging gasifiers centers on making the refractories capable of withstanding the severe operating environment through the control of raw materials and brick microstructure. Initially material compatibility, oxidation/reduction behavior, and melting temperature are used to suggest potential alternative materials. Relative acidity/basicity of candidate materials is also used to give an indication of the ability of materials to withstand the corrosive slag environment in the gasifier. Material selection criteria is also based on an evaluation of the thermodynamic interactions between slag, gas, and the candidate materials under typical gasifier operating conditions, as well as their reaction kinetics. Finally, the cost, availability, and/or the ability to produce candidate materials are also considered.

Based on these selection criteria, several refractory material systems have been identified as candidates for possible use as gasifier refractories. These materials included Al_2O_3, CaO, MgO, SiO_2, SrO, TiO_2, phosphates, and/or mixtures of them.

Once identified, candidate materials must go pass a series of laboratory tests before they will be considered for scale-up and field testing. In the first stage of material testing and evaluation, small "cups" of the target compositions are prepared to study the interactions between the slag and refractory material at elevated temperatures. These small-scale cup test samples are made with a fine grained matrix of the targeted compound, and are approximately 25 mm in diameter and 30 mm in height. Samples are made with a recession in the top to contain a gasifier slag and are heated to 1600^{o}C in an Ar atmosphere for one hour. Interactions between the slag and the test material are evaluated by direct observation of the degree of slag/refractory interaction, by the level of slag penetration, and by X-ray diffraction identification of any new crystalline phases that are created. Experimental results are compared with those predicted by thermodynamic analyses. Examples from this first stage of testing are shown in Figure 1.

Materials identified as having potential in the small-scale cup tests are fabricated into larger cups measuring approximately 65 mm in diameter and 65 mm in height. A recession in the cup, similar to that used in the smaller cup tests, again holds the gasifier slag, and exposure tests are conducted using the same conditions described previously. The larger cup samples provide opportunity to evaluate microstructural, as well as compositional, impact on slag resistance, with the goal of engineering the best possible material for extended service life in a gasifier environment. In this stage of analysis, particle packing, green and fired density, and the ability of the material to resist gasifier slag penetration and interaction are evaluated (Figure 2).

Figure 1. Small "cup" tests conducted to evaluate refractory/slag interactions at 1600^oC in an Ar atmosphere.

Figure 2. An example of large cup test to evaluate refractory/slag interaction and slag penetration at 1600°C in air.

While cup tests are an effective way to quickly evaluate different materials quickly (over 50 different compositions have been tested in our lab so far), they have several serious drawbacks, including the facts that they are static and they do not introduce a thermal gradient across the test material. As a result, a third stage of laboratory testing that is more dynamic in nature is required before a candidate material can be considered for field trial. Rotary slag tests expose a material to both a thermal gradient and a flowing slag, and while they do not exactly simulate a gasifier environment, they are recognized as providing a good indication of relative refractory performance in such environments. The rotary slag test utilizes samples measuring 229 mm by

115 mm by 64 mm, a sample size that can also used to evaluate porosity, crushing strength, and creep under load at elevated temperature. Post rotary slag test results of a non-chrome oxide refractory and several high chrome oxide refractories are shown in Figure 3. Testing was conducted for four hours at 1667^{o}C using a gasifier slag feed of 200 grams every 10 minutes and a rotational speed of 1.5 rpm. In spite of very good results in the cup tests, the non-chrome sample, a spinel material, shows a very high wear rate compared to the high chrome/alumina refractory, which showed no measurable wear. Based on these results, refinements are being made to the microstructure of these materials to control grain size and bond matrix materials with the goal of improving slag resistance. Research into other non-chrome oxide systems also continues.

Figure 3 – Chrome and non-chrome based refractory samples tested for molten slag resistance in the rotary slag test. Test conditions included 4 hours of exposure to a coal gasifier slag at 1667^{o}C.

SUMMARY

Slagging gasifier refractories currently used by industry contain high levels of chrome oxide and have not met the service requirements of industry. They fail by two primary mechanisms, slag attack that leads to corrosion, and by spalling. After the research on improving chrome refractory by phosphate additives, the Albany Research Center is developing a non-chrome oxide refractory material with a number of compounds being considered. Early testing of slag resistance has indicated that the bond phase (intergranular material) and the interaction of grains with components in the slag are critical to developing a refractory material with superior performance.