IMPROVED REFRACTORIES FOR SLAGGING GASIFIERS IN IGCC POWER SYSTEMS

James P. Bennett
U.S. Department of Energy Albany Research Center,
1450 Queen Ave., SW, Albany, OR 97321
E-mail: jbennett@alrc.doe.gov; Telephone: (541) 967-5983; Fax: (541) 967-5845

Kyei-Sing Kwong, Cynthia Powell Dogan and Richard E. Chinn
U.S. Department of Energy Albany Research Center, 1450 Queen Ave., SW, Albany, OR 97321

ABSTRACT

Most gasifiers are operated for refining, chemical production, and power generation. They are also considered a possible future source of H_2 for future power systems under consideration. A gasifier fulfils these roles by acting as a containment vessel to react carbon-containing raw materials with oxygen and water using fluidized-bed, moving-bed, or entrained-flow systems to produce CO and H_2, along with other gaseous by-products including CO_2, CH_4, SO_x, HS, and/or NO_x. The gasification process provides the opportunity to produce energy more efficiently and with less environmental impact than more conventional combustion processes. Because of these advantages, gasification is viewed as one of the key processes in the U.S. Department of Energy's vision of an advanced power system for the 21st Century. 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 (ARC) is to develop improved refractory liner materials capable of withstanding the harsh, high-temperature environment created by the gasification reaction. Current generation refractory liners in slagging gasifiers are typically replaced every 3 to 18 months at costs ranging up to $1,000,000 or more, 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 refractory repair/exchange. The goal of this project is to develop new refractory materials or to extend the service life of refractory liner materials currently used to at least 3 years.

Post-mortem analyses of refractory brick removed from slagging commercial gasifiers and of laboratory produced refractory materials has indicated that slag corrosion and structural spalling are the primary causes of refractory failure. Historically, refractory materials with chrome oxide content as high as 90 pct have been found necessary to achieve the best refractory service life. To meet project goals, an improved high chrome oxide refractory material containing phosphate additions was developed at ARC, produced commercially, and is undergoing gasifier plant trials. Early laboratory tests on the high chrome oxide material suggested that phosphate additions could double the service life of currently available high-chromium oxide refractories, translating into a potential savings of millions of dollars in annual gasifier operating costs, as well a significant increase in gasifier on-line availability. The ARC is also researching the potential of no-chrome/low-chrome oxide refractory materials for use in gasifiers. Some of the driving forces for no-chrome/low-chrome oxide refractories include the high cost and manufacturing difficulties of chrome oxide refractories and the fact that they have not met the performance requirements of commercial gasifiers. Development of no/low chrome oxide refractories is taking place through an examination of historical research, through the evaluation of thermodynamics, and through the evaluation of phase diagram information. This work has been followed by cup tests in the laboratory to evaluate

slag/refractory interactions. Preliminary results of plant trials and the results of ARC efforts to develop no-chrome/low chrome refractory materials will be presented.

INTRODUCTION

Gasifiers are operated for refining, chemical production, and power generation, and are being considered as a possible source of H_2 for some future power systems. They act as a containment vessel to react carbon-containing raw materials with oxygen and water using fluidized-bed, moving-bed, or entrained-flow systems to produce CO and H_2, along with other gaseous by-products including CO_2, CH_4, SO_x, HS, and/or NO_x (1). Gasification provides the opportunity to produce energy more efficiently and with less environmental impact than more conventional combustion processes.

Ash originating from impurities in the carbon-containing raw materials (primarily coal, petroleum coke, or combinations of them) is considered one of the primary by-products of the gasification process, forming molten slag in the combustion chamber of slagging gasifiers. Amounts of slag exceeding 5 or more tons per hour can be generated in a slagging gasifier. The gasification chamber typically operates at temperatures between 1250º and 1550ºC, at pressures of 400 psi or higher, and is lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and temperature. The ash from the carbon feedstock is liquefied into slag in the gasification chamber and can corrode, penetrate, and interact with the refractory liner at the elevated temperatures, severely limiting refractory service life and gasifier operation. Reactions can occur between refractory materials and slag oxides of Fe, Si, and/or V; or with H_2 and CO gasification products (2). Other slag components such as Ca and Al will play a role in slag fluidity and penetration. Refractory materials used as liner materials in a gasifier are typically dense firebrick composed of chromium oxide as the primary component, along with smaller quantities of other refractory oxides (typically aluminum and/or zirconium oxide).

Because of the severe environment in a slagging gasifier, the material challenges for a refractory liner are many, and include: elevated temperature; large and/or rapid changes in temperature; erosion by particulates; molten slag attack; variable slag composition resulting from the feed stock; attack by hot corrosive gases; alkali vapor attack; and variable oxidizing and/or reducing conditions (3-5). Refractory materials that can withstand these environments for long periods of time are necessary for a continuous, efficient, and reliable gasification process. The high chrome oxide material used today evolved through industrial efforts to develop an improved performance material, through plant trials conducted by industry, and through DOE and Electric Power Research Institute funded efforts traceable back to the 70's and 80's (3-11). This research and industrial experience indicated that only $Cr_2O_3 – Al_2O_3$, $Cr_2O_3 – Al_2O_3 –ZrO_2$, and Cr_2O_3 – MgO compositions could withstand these conditions long enough to be economically feasible (3,12), although refractory materials with improved performance and lower material costs are desired. Bakker indicated that a minimum level of 75 pct Cr_2O_3 in a refractory material is necessary for sustained material performance in slagging gasifiers (13).

Failure of the refractory lining in a gasifier is expensive, both in terms of refractory replacement costs (up to $1,000,000 USD or higher, depending on gasifier size and the extent of rebuild required) and production down time. Re-lining a gasifier requires that the system be taken out of service, and under the best of circumstances takes about 10 days for a partial rebuild, longer for a complete rebuild. A rebuild involves cooldown (5-7 days) and teardown and repairs (3 days for a partial rebuild and 7-10 days or longer for a full rebuild - depending on the extent of repairs necessary). Some gasification facilities maintain a second gasifier for use while repairs are being made, reducing system downtime and increasing on-line service and availability of the gasification system. Even then, the time to switch gasifiers can vary from hours to days, depending on if the spare gasifier is in pre-heat mode and if it is available. Because of the long down times required for repair, gasifier operators would like to install refractory linings with a reliable life of at least three years. The current generation refractory liners installed in gasifier systems have yet to meet this requirement, failing in as little as 3 months in high wear areas. Because of the short refractory service life and because of the importance of gasifiers in areas such as future power generation, the Albany Research Center of the U.S. Dept. of Energy (ARC) is researching hot face liners for integrated gasification combined cycle (IGCC) gasifiers. This paper discusses efforts to increase refractory service life on the hot face refractory walls of the gasifier through the use of an improved, chromium-oxide-based refractory containing phosphate additions and through the development of no-chrome/low-chrome oxide refractory liner materials. Improvements in refractory service life would lead to both enhanced gasifier reliability and economics, helping to give gasifier users extended periods of continuous, trouble-free gasifier operation.

CURRENT STATUS

CHROME BASED REFRACTORIES

A strategy was adopted by the Albany Research Center to develop new or improved high chrome-oxide refractory liner materials for the hot face of slagging gasifiers based on limiting refractory corrosion and on limiting slag penetration into a refractory material. This strategy was adopted after examining spent materials removed from slagging gasifier environments and determining their failure mechanisms. From the forensic analyses, it was noted that two primary causes of refractory failure occur; dissolution of the refractory in the molten slag and spalling of the refractory. These and other causes are shown in figure 1. Other gasifier issues that impact refractory wear, such as gasifier design, how a gasifier is operated, or factors involving refractory installation, were not evaluated in this study.

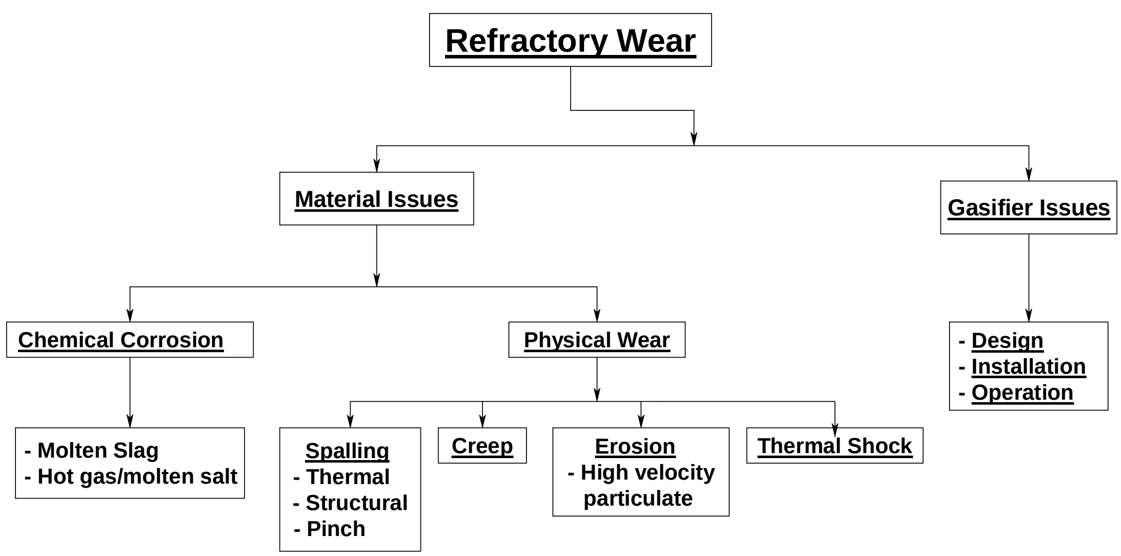


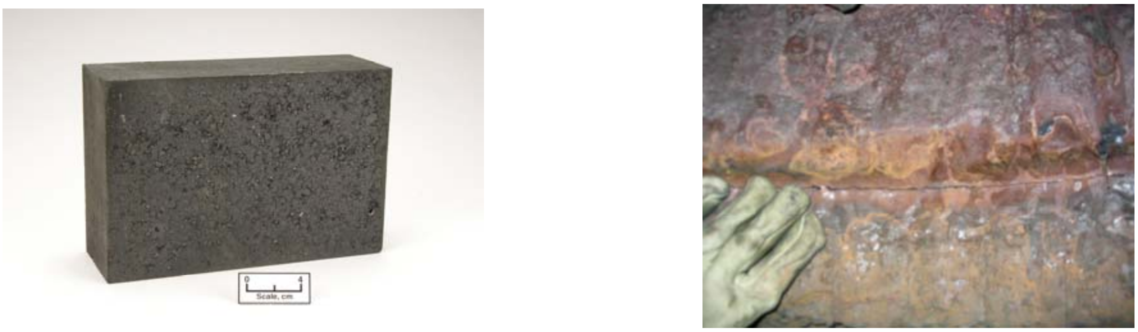
Figure 1 – Causes of refractory wear in a slagging gasifier.

Chemical corrosion as a refractory wear mechanism is caused by molten slag dissolution of the refractory as it flows down the refractory sidewall. During flow, a molten slag dissolves refractory material and releases some grains of refractory material into the slag as bond phases are removed. Both the dissolution and grain removal produce a gradual and predictable refractory wear. Spalling is caused by slag penetration and attack of the refractory hot face, leading to large "chunks" of the refractory material being removed as layers, and causing unpredictable and incremental refractory wear. Spalling starts with slag that has penetrated the refractory surface, a process that is followed by small crack formation parallel to the hot face in or near the slag-penetrated/virgin refractory interface. These cracks link-up, a processes accelerated by sudden or large changes in gasifier operating temperature. Different expansion characteristics in the slag penetrated/non-penetrated layers, thermal cycling of the gasifier, stresses within the refractory and within the gasifier, and/or other possible factors contribute to spalling. Slag corrosion and spalling of a gasifier sidewall are shown in figure 2. Corrosion caused the gradual wearing away of refractory and is noted over all the gasifier sidewall, while the circled area indicates spalled material sliding down the gasifier hot face. Over time, the corrosion/spalling cycle repeats itself, leading to a rapid thinning of the gasifier sidewall.

Figure 2. Slagging gasifier refractory sidewall showing corrosive wear and spalling (circled material).

Analysis of the spent refractory failure mechanism was used to develop a phosphate containing high chrome oxide refractory material better able to withstand the severe service environment (14). Phosphate material additions were found to significantly reduce slag corrosion and slag penetration of the microstructure in laboratory tests, properties that should improve spalling resistance.

Under a cooperative research and development agreement with ANH Refractories, full-sized phosphate containing high chrome oxide refractory brick of several formulations were scaled-up by ANH using laboratory processes that simulated commercial production. These materials were tested at ARC. Test results indicated good material properties, so samples were produced commercially by ANH for field testing in a commercial gasifier. One of the test refractory materials produced by ANH is shown in figure 3a. Unfortunately, the commercial gasifier containing the test refractory materials was shut down after 17 days of service due to gasifier problems unrelated to the test materials. Because preliminary evaluation of the test samples indicated good service results, additional testing of these materials in a gasifier are scheduled. Photographs of the test material before removal from service are shown in figure 3b.



a. b.

Figure 3. Phosphate containing high chrome oxide refractory materials for gasifier testing: a) as manufactured, and b) after 17 days of trial service.

NON-CHROME BASED REFRACTORIES

Refractory liner materials currently utilized in slagging gasification systems are composed of dense firebrick with a composition of Cr_2O_3 (60 to 95 wt pct) and a second (or third) refractory oxide (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.

Several issues, however, 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 the following: a) current high Cr_2O_3 containing refractories do not meet the performance requirements of gasifier users, b) perceived/real long term safety concerns associated with the use of Cr_2O_3 refractory materials, c) the high cost associated with refractory materials containing Cr_2O_3, d) the difficulity in sintering high chrome oxide materials, and e) possible long term domestic supply issues with high Cr_2O_3 refractories. Because of these issues, gasifier refractory research efforts at ARC are also centered on 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 will be used to identify potential non-chrome materials for laboratory testing.

The sequence of material testing is to evaluate small "cups" of materials first, which are used to study interactions between slag and refractory material at elevated temperatures. Scale-up testing to larger cup tests is next conducted to evaluate materials identified as having good refractory/slag interactions in the small sample studies. Cup tests are used to evaluate coarse grained microstructures and different matrix material for particle packing , densification, and the microstructure interaction with the gasifier slag. Samples that have encouraging properties from the larger cup tests will be scaled-up into full sized test brick for additional physical property testing and composition refinement. Physical property testing will include density, porosity, crushing strength, creep under load at elevated temperature, and slag resistance testing in the rotary slag test.

A review of historical research on non-chrome slagging gasifier refractories indicated problems with slag corrosion and/or reactions between the slag and refractory raw material as service limiting issues. Several refractory compounds have been identified as potential liner materials for use in gasifiers. As mentioned earlier, material selection has been restricted through a combination of literature reviews, phase diagram research and by an evaluation of the thermodynamic interactions between slag, gas, and potential materials under gasifier operation conditions. It must be kept in mind that thermodynamic studies evaluate only potential refractory oxide/non oxides as hot-face liner materials. Data generated must be used with caution because it does not indicate reaction kinetics, only what material combinations are thermodynamically stable. Specific candidate material could appear unstable for use, but may be kinetically stable. Some of the specific oxide compounds identified as having potential as either aggregate or matrix materials meriting further evaluation include Al_2O_3, CaO, MgO, SiO_2, SrO_2, TiO_2, phosphates, and/or mixtures of them. The goal of this research is to form new or improved refractory compounds or controlled advanced microstructures that can provide longer service life than high chrome oxide refractories currently used in slagging gasifiers. Samples with low Cr_2O_3 content (less than 30 wt %) will be evaluated only after materials without chrome oxide have been considered.

Limited fabrication and testing of several compositions identified as having potential for use as a gasifier liner is underway. Samples have been manufactured in the laboratory or have been obtained from refractory manufacturers. Results of two types of slag tests (cup and rotary slag) are shown in figure 4. Some of the candidate material evaluated included MgO/Al_2O_3 spinel refractories and high Al_2O_3 refractory materials with/without SiC. Preliminary tests indicated that high wear occurred in refractory materials containing spinel materials and that reactions occurred between SiC containing refractories and the FeO in slag, producing metallic Fe and CO gas. Refinements are being made to the microstructure of these and other materials to control grain size and bond matrix materials with the goal of improving slag resistance.

a.

b.

Figure 4. Examples of gasifier slag resistance tests conducted on no-chrome materials by: a) cup tests, and b) rotary slag test results.

CONCLUSIONS

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. The Albany Research Center has developed a high chrome oxide refractory containing phosphates that has been produced commercially and is being evaluated in a commercial gasifier. Preliminary testing of this material produced encouraging results, with additional field tests planned. Investigations to develop a non-chrome oxide refractory material are in the early research stages, 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 is critical to developing a refractory material with superior performance.

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