THE IMPROVEMENT OF SLAGGING GASIFIER REFRACTORIES

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ABSTRACT

Refractories play a vital role in slagging gasifier on-line availability and profitability for the next clean power generation system. A recent survey of gasifier users by USDOE indicated that a longer service life of refractories is the highest need among gasifier operators. Currently, Cr_2O_3 based refractories, the best of commercially available materials for use in slagging gasifiers, last between 3 and 24 months. Researchers at Albany Research Center (ARC) have identified structural spalling, caused by slag penetration, as one of the major failure mechanisms of Cr_2O_3 refractories through postmortem analysis. New Cr_2O_3 refractories with phosphate additives have been developed by ARC to decrease slag penetration and thus structural spalling. Laboratory physical property tests indicated that ARC developed refractories are superior to other commercial bricks. One of the ARC developed phosphate containing refractories has been installed in a slagging gasifier. Preliminary results of the performance of this refractory in the gasifier will be reported along with research to develop non-chromia refractories.

INTRODUCTION

IGCC (Integrated Gasification Combined Cycle) processing is a commercially proven technology, providing an exceptionally clean environment, fuel flexibility, CO_2 sequestration-ready processes, cost effective and high efficiency means to make poly-generation products which include electrical power, hydrogen, fuel, diesel oil, fertilizers, and chemicals. Gasifiers have been commercialized to make profit for more than two decades by chemical producers. Currently, major electrical power producers are considering adopting IGCC technology because of environment regulations, CO_2 sequestration issues, and future natural gas price. Gasification manufactures and operators point out that increased reliability of operation is one of the keys to moving this technology forward. Surveys from gasifier operators indicated that the service life of refractory is the most critical issue affecting the gasifier reliability[1]. Refractories have been used to line gasifiers to protect the steel vessel from molten slag attack and to insulate the heat for preventing the energy loss. Currently, the actual refractory lifetime ranges between 3 and 24 months. The high costs and the downtime associated with replacing the refractory liner may decide the future of gasification technology in power generation when competiting against natural gas and pulverized coal power plants. A gasifier availability of 85-95% for utility applications and more than 95% for other applications is required to move IGCC technology forward in the marketplace[1]. However, since the late 1970's, when Cr_2O_3 refractories were developed, no major improvement in these refractories has occurred because of small market and the complex technical issues in the gasifier. Extensive research efforts are needed to overcome the challenges from a gasifier's operational environment. However, the service life of gasifier refractories must be extended in order to move the IGCC technology forward and make it profitable. To address this issue, the US Department of Energy's Office of Fossil Energy and the Albany Research Center are exploring ways to extend the service life of the refractory liner by improving the currently available commercial chromia (Cr_2O_3) refectories and by developing new, low or no chromia, gasifier refractories.

GASIFIER OPERATION AND CONDITIONS

The slagging gasifier is a pressurized vessel lined with multi-layers of chromia-containing refectories that protect against large amount of flowing molten slag which can be more than 10 tons/hour of ash originating from coal, petcoke, or other carbon source feedstock supplied by high speed slurry injected in the gasifier[2, 3]. Depending on the melting point and viscosity characteristics of the residual gasifier ash, typical gasifier operation temperature ranges between 1300 and 1600 °C and at pressures up to 400 psi or higher.

The hot-face refractory lining inside a slagging gasifier must be able to withstand challenges from

- High temperature operation
- Aggressive low melting, low viscosity and high acidic coal slag attack
- Variation of feedstock
- Particle erosion from the injected slurry
- Alternating oxidized and reduced atmosphere
- Erratic operating conditions such as frequent of shutdowns and aberrant temperature control
- Material stability under load at high temperature (creep)
- Flame impingement.

Refractory bricks located in different portions of a gasifier may not have the same wear mechanisms; for example, the bottom refractories may experience higher flow speed of molten slag and the top refractories may have alkali vapor attack. Hence, the service life of refractory brick in different areas of a gasifier may be different.

FAILURE MECHANISMS OF GASIFIER REFRACTORIES

The performance of gasifier refractories has a very close relationship to coal/petcoke slag chemistry, as well as refractory material and microstructure. Before doing any improvement or development of a gasifier refractory, researchers should understand gasifier slag chemistry and industrial gasifer operation conditions. Gasifier operators have guidelines to select the coal or other carbon source by cost, availability, coal consistence, and operational ability[4]. For example, in comparison to Pittsburgh #8 or Illinois #6, the western low-rank coal is not suitable for slagging gasifier because of its lower solid concentration to feed into the slagging gasifier and costs more to generate the same amount of electrical power[5]. Hence, most slags from slagging gasifiers contain high silica, low calcium oxide and high iron oxide; typical of eastern coals. The characteristics of these slags are low melting, low viscosity, and high corrosion. One more example, petcoke slags contain high vanadium oxides and nickel oxides which both have multiple valence states. The viscosity of slag can be affected by the operational atmosphere and temperature of a gasifier because of different valence states of oxide components in the slag. Therefore, the service life of gasifier refractory is not only a material issue but also other issues. For simplification, this paper focuses only on material issues.

Chemical Corrosion

Because the gasifier slag directly contacts with refractory lining, it must have a good chemical corrosion resistance. In general, the concept of bases and acids reactions in chemistry can also be applied to the reaction of slag and refractory materials. Understanding the slag characteristics and the selection of correct refractory are very important to minimize chemical corrosion. A number of studies conducted during the 1980's at the cool water demonstration plant and subsequently at other slagging gasifier facilities indicated that high-chrome refractories are viable for this application.[6,7] The Albany Research Center has performed extensive post-mortem analyses of spent refractories from commercial gasifier which utilize coal as the major feedstock. Analyses found that chromium oxide does not react with calcium silicate and only reacts with iron oxide on the hot face of refractory, forming new components which have good high temperature properties[8]. The iron oxide ties up the chromium oxide refractory having a very low dissolution rate of the refractory. However, the inertness of chrome refractory allows calcium silicates slag to penetrate into its pores. Detailed fundamental studies on slag and refractory reaction in the laboratory also support the above post mortem analyses[9]. The coal slag contains both acidic and basic oxides, making it difficult to find any refractory material that will not react with components in the gasifier slag. By studing the reaction of high temperature oxides and any component in the slag, especially iron oxide, provides us an understanding to develop a new type refractory.

Slag Penetration and Structural Spalling

Ceramic materials, especially chromium oxide, don't have good thermal stability; suffering from the fast change of temperature. Pores in the refractory are not only for insulation, but also are a way of avoiding long cracks which may be caused by sudden temperature change. However, pores also provide channels that allow molten slag penetration into chromia bricks, forming a 3 to 5 centimeter dense layer which can be lost by spalling during a gasifier shutting down. Gasifiers used to shut down at about every 30-45 days for non-refractory issues such as system maintenance or down-stream problems. Every time, a gasifier cycle increases the chance of crack formation and growth because of slag filling up the pores of refractory (structural spalling). Eventually, a chunk of refractory pieces falls off exposing a fresh refractory surface for slag attack. Spent refractories, collected from commercial gasifier, show evidence of structural spalling (figure 1). Figure1 shows a void formation about 12 centimeters wide and 12 centimeters deep. Figure 2 shows that refractory material loss during a commercial gasifier operation. This figure indicates that sudden material loss occurs every 1300-1500 hours. The service life of a refractory could be doubled if structural spalling can be prevented.

Other Failure Mechanisms

Refractory bricks in some area of gasifers are worn by flowing molten slag, high injected slurry stream, and flame impingement. Harder or denser the refractory material also offers better physical wear resistance in these areas. Cr_2O_3 has a similar hardness (knoop value) to SiC, which is known as a good wear resistance material[10]. It seems that Cr_2O_3 may have proper wear resistance.

Some gasifiers are operated in an oxidized atmosphere during warm-up and start-up stages and in a reduced atmosphere during operation. It has been known that Cr_2O_3 refractory is susceptible to the cycle of oxidized/reduced environment than other refractories[11].

The gasifier may not be operated at a constant pressure. The pulsation by the changing of pressure may help to loosen cracked refractory pieces and promotes structural spalling. Certainly, the sudden pressure and temperature changes during emergency shut downs will severely decrease the service life of a refractory.

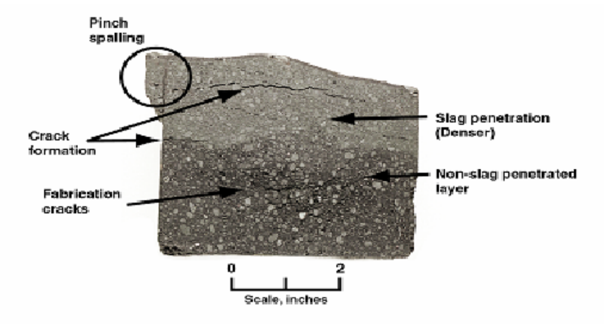

Fig. 1: Spent refractory brick from a commercial gasifier

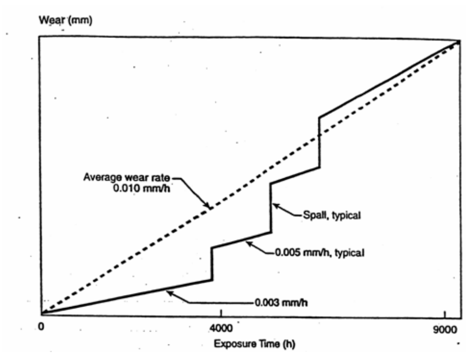

Fig. 2: Wear Rate of Refractory Brick Lining in Slagging Gasifier[12]

RESEARCH TO IMPROVE CHROMIA REFRACTORIES

Based on the above failure mechanisms, it is obvious that some issues are not directly related to the refractories such as gasifier design and operation, the nature and limitation of materials, and business decisions. Post-mortem analyses showed that structural spalling is a major factor on the prematural failure of hot face refractory. This problem can be improved by engineering refractory materials in the laboratory to decrease the depth of slag penetration.

Researchers at ARC have conducted numerous trials to solve the spalling problem, such as improving the microstructure of hot face refractory, adding non-wetting materials, promoting sintering, and adding phosphates. ARC researchers found phosphate additives decreased slag penetration. Phosphate additives have been commonly used in the refractory industry, especially in ramming mixes or castable, for enhancing the bonding strength from room to high temperatures. Phosphate additives in Cr_2O_3 refractory are designed to react with molten penetrated slag, calcium silicates, with the goal of forming highly siliceous melts that stop or slow slag penetration. In addition, some phosphate additives provide other benefits, such as decreasing the porosity of Cr_2O_3 refractory and improving its thermal shock resistance. Extensive laboratory tests, from small size to brick size samples, confirmed the benefits of phosphate additives.

Figure 3 shows a section profile of phosphate containing high Cr_2O_3 refractory sample after high temperature cup testing. It showed that phosphate additives reduced slag penetration verus commercial refractories. Rotary slag drum tests were performed to compare the corrosion and slag penetration resistance of ARC-developed refractories (brick D) with other similar high chromia containing commercial gasifier refractories (brick A &B) (Figure 4). These tests indicated that ARC developed refractory has better slag penetration and thermal shock resistance. Table 1 lists the comparison of physical properties among ARC-developed refractory and commercial bricks. Cup, rotary slag drum, and physical tests indicated that ARC-developed refractory should provide better performance than other commercial bricks.

Detailed studies by SEM and XRD have been conducted to understand the real mechanism of improving slag penetration resistance by phosphate additives. Unfortunately, conclusive evidence of the mechanism has not been found and further studies are needed to investigate it.

A commercial refractory company has produced bricks of the phosphate containing material for field trials. Test bricks of the first trial were removed from the gasifier after a short service for non-refractory related reasons (Figure 5). A second trial is underway and has been in the test panel of gasifier for several months. A patent on phosphates added to chromium refractory for gasifier operation has been issued[13].

Fig. 3: Cross sections (a) a conventional 90% chrome refractory, and (b) ARC improved refractory following exposure to a coal slag at 1600°C. The depth of slag penetration is marked in each case.

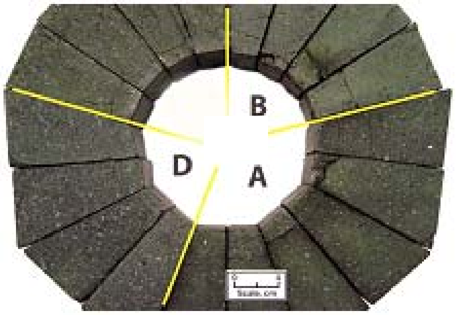

Fig. 4: A section of refractory brick after a rotary slag drum test (A: commercial brick 1, B: commercial brick 2, D: ARC-developed brick)

Table 1. Physical Properties of High Cr_2O_3 Gasifier Refractories.

	A	B	D
Bulk Density (g/cc)	4.27	4.07	4.20
Apparent Porosity (%)	14.8	16.5	12.7
CCS (MPa)	65.5	66.9	63.1
Reheat expansion *1	+0.64	-0.08	+0.11
Creep deformation*2	+0.18	-1.98	- 0.24
Rotary slag *3			
- % area change	+2.3	+2.3	+6.5
- mm slag penetration	3.5	6.0	1.8

*1 = 1550ºC, 50 hr hold
*2 = 1550ºC, 345 kPa, 50 hr hold
*3 = 1657ºC, 5 hrs of slag feed, 2 ½ rpm.

Fig. 5: Field Trial of Test Material after 17 days service

STRATEGIES TO DEVELOP NEW NON-CHROMIA REFRACTORIES

The goal of this non-chromia refractory research is to develop a new refractory which can perform comparable to chrome refractory at a reasonable cost. In order to achieve this goal, five major tasks were identified: 1) to explore the potential candidate material systems and to understand the basic properties of each material, 2) to make small refractory samples and to determine critical problems under static test conditions, 3) to scale-up potential materials size and to evaluate their performance under dynamic tests, 4) to cooperate with refractory companies commercially produce tested bricks and 5) to conduct field tests and continue improve bricks.

The first step is to find a material system able to withstanding the chemical corrosion from different feedstock slags. Fundamental scientific methods were adopted to identify potential candidates using thermodynamic calculations, phase diagram studies, material property investigation, and literature reviews. Laboratory analyses were performed to verify potential candidates by visual inspection, optical microscopy, X-ray diffractometer (XRD), thermogravimeter (TGA), differential thermal analysis (DTA), and scanning electronic microscopy (SEM) from designed mixture samples after high temperature treatments. Issues related to chemical corrosion resistance, age deterioration, steam reaction, hardness, vapor pressure, sintering ability, cost, health, environment, and others have been examined. Samples evaluated at this stage are in a powder form (matrix material), which is a key component in the refractory, and is susceptible to chemical corrosion. Sample mixtures were formed as cups, disks, and pellets depending on the need of studies. All samples were less than 2.5 centimeters in diameter. Several potential candidates were selected after this first primary stage study.

Several commercially available aggregates, with potential matrix materials, were adopted to make 5 centimeter refractory cups. Coal slags from several gasifier operators were used to conduct cup tests which heated to high temperature. Cup tests can reveal problems such as the reactivity of aggregates, slag penetration, particle bonding, and microstructure defects. Most of the research effort was focused on decreasing slag penetration by modifying microstructure, adding additives, selecting aggregate, and using other practical methods. Improvement on slag penetration resistance has been made (figure 6). Each component's function in the refractory has been designed and engineered from the fundamental studies and laboratory tests.

More dynamic and physical property tests will be conducted on these potential compositions including rotary slag tests, creep tests, hot and cold strength, and thermal expansion. The Albany Research Center is planning to produce small batches of bricks for these laboratory dynamic and physical tests and for panel tests in gasifiers. Depending on the laboratory test results and equipment conditions, it will target the production of potential non-chrome refractories for a panel test in a gasifier in the future.

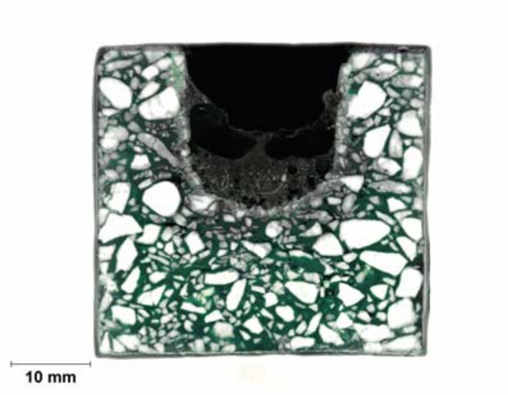

Fig. 6: A cup test showing a potential non-chromia refractory to resist slag penetration

SUMMARY

The commercial adaptation of slagging gasifier technology to produce power will depend on the technology's ability to prove itself as both economic and reliable. Refractory service life is one of major factor affecting the economic of gasifier. Phosphate-containing Cr_2O_3 refractories have been developed , patented and are being evaluated to increase the service life by improving slag penetration resistance. Currently, new low-chrome/chrome free refractory materials are being developed and evaluated.

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