Preliminary Results from Field Testing an Improved Refractory Material for Slagging Coal Gasifiers

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ABSTRACT

Slag attack of refractory materials used to line the hot face of slagging gasifiers limits their service life to between 3 and 24 months. These gasifiers use coal, petroleum coke, or combinations of them as raw materials to produce chemicals, liquid fuel, and/or electricity; with future consideration being given to the use of other abundant, low cost feedstock such as biomass. The ash from these materials generate liquid slags during gasification at temperature between 1300 - 1575°C and pressures up to 1000 psi, leading to severe slag attack of a vessel lining and causing unacceptable gasifier reliability and on-line availability. To maximize refractory life and provide protection of the gasifier metal shell, the best liners have contained a minimum of 60-70 pct chromia in combination with alumina, alumina/zirconia, or magnesia. The Albany Research Center of DOE has developed a phosphate containing high chrome oxide refractory liner that indicates potential for increased service life over currently used materials. This new liner has been produced commercially by a refractory company and installed in a gasifier for performance evaluation. Refractory issues in slagging gasifiers, the development and properties of the phosphate containing high chrome oxide material, and the preliminary results from the plant trial of this material will be presented.

INTRODUCTION

Gasifiers are operated for chemical production and power generation, and are being considered as a possible future source of H_2 if power systems based on this gas are developed. 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 products/by-products that include 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 entrained-flow gasifiers. Slagging gasifiers can operate at temperatures between 1300° and 1575°C and pressures of 400 psi or higher, and can generate slag quantities in excess of 5 or more tons per hour depending on material throughput and carbon source impurities. The gasifier is lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and temperature. The slag by-product is liquefied 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. Specific reactions can occur between the refractory liner and slag oxides such as Fe, Si, Ca, Al, or V; or can occur with gasification products such as H_2 and CO[2]. Slag fluidity and penetration can also have a large impact on refractory service life. Refractory materials used as liners in a gasifier are typically dense firebrick composed of chromium oxide as the primary component, along with smaller quantities of other refractory oxides (typically alumina or alumina and zirconia).

Because of the severe environment in a slagging gasifier, the material challenges for the 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], with a minimum level of 75 pct Cr_2O_3 reported as necessary by Bakker[13] for sustained material performance.

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 completely shut down, and under the best of circumstances takes about 7-10 days for a partial rebuild, longer for a complete rebuild. A complete rebuild involves cooldown (4-7 days) and teardown and repair (7-10 days or longer, 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 available in the pre-heat mode. 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 this 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 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. Post-mortem analysis of spent refractory material is discussed, the development and properties of a phosphate containing high chrome oxide material are presented, and the preliminary results from a plant trial of this material are discussed. 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.

CAUSES OF CHROME BASED REFRACTORY FAILURE

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 based on limiting slag penetration into a refractory material. This strategy was developed after examining spent refractory materials removed from slagging gasifier environments and determining their failure mechanisms. From the forensic analyses of refractory brick removed from commercial gasifiers, it was noted that two primary causes of refractory failure occur, dissolution of the refractory in the molten slag and spalling. These and other causes of refractory failure are shown in figure 1. Other refractory and gasifier issues that impact refractory wear; such as the refractory type and quality, and the gasifier design, how it is operated, and factors involved in refractory installation; were not evaluated in this study. These other areas are indicated by dashed lines in figure 1.

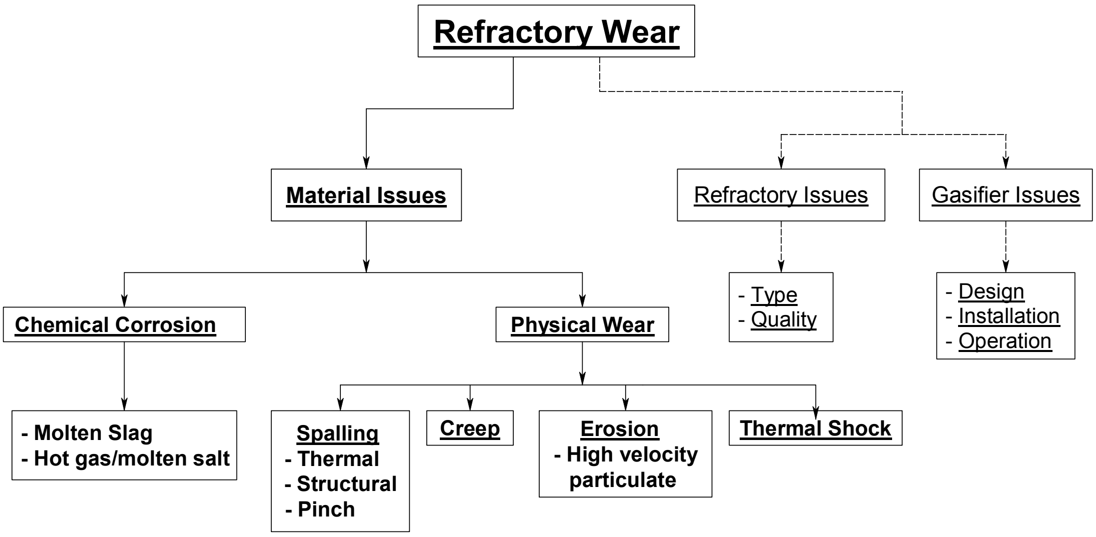


Figure 1 – Causes of refractory wear in a slagging gasifier.

Chemical corrosion as a refractory wear mechanism is caused by molten slag dissolution of the refractory as it flows down the refractory sidewall. As a slag dissolves a refractory material, it can also remove grains from the surface of the refractory material, producing a gradual and predictable wear. Spalling is caused by slag penetration and attack of the refractory, causing large "chunks" of the refractory hot face to be removed in layers. The removal of large surface portions from a refractory surface leads to unpredictable and incremental refractory wear. Spalling starts with slag that has penetrated the refractory's surface, and is initiated by cracks that form parallel to the hot face near the slag-penetrated/virgin refractory interface. These cracks link-up, a processes accelerated by sudden or large changes in gasifier operating temperature. Thermal cycling of the gasifier, stresses within the refractory and within the gasifier, and other factors can also contribute to spalling. Slag corrosion and spalling of a gasifier sidewall are shown in figure 2. The circled area is spalled material sliding down the inside of a gasifier. Over time, the spalling cycle repeats, with renewed slag corrosion, penetration and attack of the freshly exposed refractory surface. Analysis of the spent refractory lining failure mechanisms was used to develop/re-design a high chrome oxide refractory material that is better able to withstand the causes of failure, as reported earlier[14].

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

REFRACTORY TESTING AND DEVELOPMENT

Refractory Materials

The approach taken to improve the performance of high chrome oxide materials was to minimize slag dissolution and slag penetration of the refractory by controlling refractory microstructure. The addition of phosphate materials was found in earlier cup tests [15] to restrict molten slag infiltration into the refractory, tying up many slag elements as high melting compounds, solid solutions, or glass. By limiting/reducing slag penetration, the refractory should have improved spalling resistance and a longer refractory service life. Maintaining the high chrome oxide level in the refractory with the phosphate addition helped to created both good slag resistance and good spalling resistance in laboratory test materials, both properties important to a long service life.

Under a cooperative research and development agreement with a commercial refractory producer, full-sized brick of phosphate containing materials were made in a commercial setting for laboratory testing and comparison with commercial chrome based refractory materials that are or were historically used as hot-face gasifier liners. The chemical composition of these refractories is given in table 1. Note that the elemental Cr levels in all compositions are high (above 80 oxide wt pct), with three of the materials (compositions A, B, and C) containing alumina as a part of the refractory composition. The fourth material (composition D) is a high chrome/magnesia refractory. One sample, composition B, has ZrO_2 additions, and one composition, C, has phosphate additions, and is the test material manufactured by a refractory company.

Table 1 Chemical Composition of Test Samples (elemental wt %)

Element	Composition			
	A	B	C	D
Cr	\$55.0	\$55.0	\$55.0	\$55.0
Al	#5.0	#5.0	#5.0	#0.3
Zr	#0.1	#5.0	#0.1	NA
Mg	NA	NA	NA	\$10.0
P	#0.05	#0.05	#8.0	NA
Fe	#0.05	0.41	#0.05	#0.3

NA = Not analyzed

Experimental Procedure

Table 2 contains the general physical properties of compositions listed in table I.

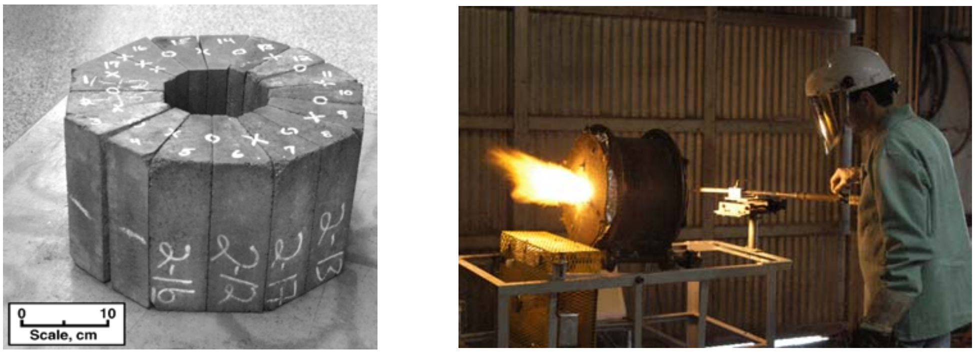
Density and porosity were measured using ASTM C-20[16]; cold crushing strength was measured using ASTM C-133[17]; thermal expansion under load was measured using ASTM C-832[18], with only the final percent length change is reported; and dynamic slag attack was measured using the rotary slag techniques established and reported by the US Bureau of Mines[19]. Rotary slag testing was conducted to simulate the dynamic environment of a flowing gasifier slag.

Table 2 Physical Properties of Refractory Materials Tested

	A	B	C	D
Bulk Density (g/cc)	4.27	4.07	4.20	3.89
Apparent Porosity (%)	14.8	16.5	12.7	10.2
CCS (MPa)	65.5	66.9	63.1	19.8
Reheat expansion *[1]	+0.64	-0.08	+0.11	NA
Creep deformation*[2]	+0.18	-1.98	- 0.24	NA
Rotary slag *[3]				
- % area change	+2.3	+2.3	+6.5	+1.4
- mm slag penetration	3.5	6.0	1.8	7.0

*[1] = 1550ºC, 50 hr hold
*[2] = 1550ºC, 345 kPa, 50 hr hold
*[3] = 1657ºC, 5 hrs of slag feed, 2 ½ rpm.
NA = Not analyzed

The rotary slag apparatus was heated to a target temperature range of 1650-1675ºC in 2 ½ hrs, held in this temperature range for 1 hour, than slag fed at a rate of 400 grams every 10 minutes for the first hour and 200 grams every 10 minutes for the next 4 hours. The oxygen-propane flame used in rotary slag testing was burnt under reducing conditions to simulate the gasifier environment. During the test, excess slag flowed from the rotating test unit as slag was added to the test drum. When slag feed was discontinued, the drum was emptied of slag and cooled to room temperature naturally. Drum rotational speed during heat-up, testing and cooling was 2 ½ rpm. The effects of molten slag on the refractory during the rotary slag testing was measured by evaluating the change in surface area dimension of the brick and by evaluating the depth of slag penetration into the hot face of the refractory. Samples prepared for testing and being evaluated in the rotary slag drum are shown in figure 3. The results of these tests are noted in table 2.



a. b.

Figure 3 - Refractory samples tested for molten slag resistance in the rotary slag test, a) samples prepared for mounting in test drum, and b) samples during rotary slag testing.

Slag chemistries in a gasifier can vary greatly depending on the carbon source. The chemistry of the slag used during rotary slag testing is similar to one that may be encountered at a gasifier, and is listed in table 3.

Table 3 Chemistry of Slag Used in Rotary Slag Testing (elemental %)

Element	Amount
Al	#15
Ca	#2
K+Na	#2
Cr	< 0.1
Fe	#20
Si	#25

Discussion of Results

1. Physical Properties

The bulk density of A and C compositions in table 2 are similar, however, the C composition, with the phosphate addition, had a lower porosity, which would assist in the goal of decreasing slag infiltration. Composition B had the highest porosity of the materials tested, which may account for the lower bulk density, even though it had lower alumina additions than compositions A and C, and had zirconia additions. The material with the lowest porosity, the Cr_2O_3/MgO refractory, also had the lowest cold crushing strength, about one third the value of compositions A, B, or C. This reason for this low strength was not determined. In general, low porosity is difficult to achieve in high Cr_2O_3 materials. Phosphate additions to composition C helped achieve lower porosity, but caution should be exercised in targeting low porosity alone to reduce slag infiltration because it can contribute to thermal shock tendencies, something that could contribute to crack growth and/or spalling.

As mentioned, all chrome/alumina compositions (A, B, and C) had comparable cold crushing strengths. Their creep deformation after 50 hours of a 345 kPa load was near zero for two of the compositions (A and C), with B being a nearly 2 pct deformation. The high iron content indicated in table I for composition B may account for some of this large deformation under load. The B composition also had a slight contraction when its reheat expansion was measured, indicating densification or crystal structure changes may still be occurring in the sample. The slight increase in sample length (+ 0.18 pct) for the A composition during creep deformation testing along with the large unconstrained reheat expansion for this sample (+ 0.64 pct increase) may be due to reactions still occurring in the sample that did not finish during sintering. A smaller unconstrained expansion occurred in composition C.

2. Rotary Slag

Note the high elemental content of Fe, Al, and Si in the slag used for rotary slag testing (table 3). Iron has been found to be tied up as oxide spinels or as solid solutions with chrome oxide on the refractory surface. Analysis of the dispersal of Al in the slag-infiltrated microstructure of composition A by energy dispersive x-ray analysis (scanning electron microscopy) indicated Al might be removed from refractory grains into the slag, although more work is necessary to clarify what may be occurring. Si and Ca have been found to penetrate the porous microstructure of the high chrome/alumina brick, while Fe is tied up on the brick's surface.

Wear data of samples evaluated by the rotary slag test shown in figure 3 is listed in table 2. Data from table 2 indicated that no measurable wear occurred with any of the samples during the 5 hours of rotary slag testing at 1657°C. Given the high levels of chrome oxide in all samples, this result is not surprising. Slightly positive changes in slag wear measurements were observed with all samples and indicated an area increase, which may be due to slag adherence on the surface of samples or to reheat expansion that occurred in compositions A and C (see reheat expansion data shown in table 2).

It is of interest to note that slag penetration in all compositions tested was lowest in the phosphate containing material, composition C. As noted earlier, the additions of phosphates to composition C resulted in a lower porosity than A and B chromia/alumina compositions. During service, it is expected that the lower porosity in the C composition along with the interaction of chromia and phosphates in the refractory with slag would result in higher melting phases (such as calcium phosphate), causing an increase in slag viscosity and a lower slag penetration. These interactions would result in lower potential for corrosion/spalling. Improved thermal shock resistance was also noted in early tests conducted on phosphate containing refractory material[14]. Because of this good lab test data, field testing of composition C was targeted in a commercial gasifier using refractory materials produced by a refractory company.

COMMERCIAL TESTING OF PHOSPHATE CONTAINING REFRACTORY MATERIALS

Samples of the high chrome oxide refractory material that contained phosphates (composition C) and whose chemical and physical properties are indicated in tables 1 and 2 was produced commercially by a refractory company for field testing in a commercial gasifier. An example of the test refractory material is shown in figure 4a. Unfortunately, the gasifier containing the test refractories was shut down after 17 days of service due to problems unrelated to this refractory composition. During the shutdown, the gasifier had a complete rebuild and the phosphate containing test samples were removed. Because preliminary evaluation of the test samples indicated good service results, additional testing of these materials in a future gasifier run is scheduled. Photographs of the test material after 17 days of service but before removal from the gasifier are shown in figure 4b.

a. b.

Figure 4. Phosphate containing high chrome oxide refractory materials for gasifier testing: a) as manufactured, and b) after 17 days of trial service.

CONCLUSIONS

Gasifier refractories currently used by industry contain high levels of chrome oxide. These materials have not met the needed service requirements, failing 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 a phosphate material in the laboratory. This refractory composition has been produced by a refractory company and has been evaluated in a commercial gasifier. Although the phosphate containing test material had only 17 days of service, preliminary evaluation of it indicated good performance, with additional field tests planned in the future.

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