Development of Improved Performance Refractory Liner Materials for Slagging Gasifiers

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ABSTRACT

Refractory liners for slagging gasifiers used in power generation, chemical production, or as a possible future source of hydrogen for a hydrogen based economy, suffer from a short service life. These liner materials are made of high Cr_2O_3 and lower levels of Al_2O_3 and/or ZrO_2. As a working face lining in the gasifier, refractories are exposed to molten slags at elevated temperature that originate from ash in the carbon feedstock, including coal and/or petroleum coke. The molten slag causes refractory failure by corrosion dissolution and by spalling. The Albany Research Center is working to improve the performance of Cr_2O_3 refractories and to develop refractories without Cr_2O_3 or with Cr_2O_3 content under 30 wt pct. Research on high Cr_2O_3 materials has resulted in an improved refractory with phosphate additions that is undergoing field testing. Results to date of field trials, along with research direction on refractories with no or low Cr_2O_3, will be discussed.

INTRODUCTION

Gasifiers are the heart of Integrated Gasification Combined Cycle (IGCC) power system currently being developed as part of the DOE's Advanced Fossil Fuel Power Plant and are being considered by electric power producers for future plants. They are expected to play a dominant role in meeting the Nation's future energy needs because of their ability to meet or exceed current and anticipated future environmental emission regulations, and have demonstrated a great degree of fuel flexibility. IGCC systems are one of the few proposed for power generation that are expected to easily meet future environmental regulations impacting CO_2. This is because IGCC plants are a closed circuit, making them process ready to capture CO_2 emissions for reuse or processing, should that become necessary or economically feasible in the future. Gasifiers have been used for over 20 years to produce chemicals serving as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. An example of an IGCC system with an air cooled slagging gasifier is shown in figure 1.

An IGCC gasification chamber (gasifier) is a high pressure/high temperature reaction vessel used to contain a mixture of O_2, H_2O, and coal (or other carbon-containing materials) while it is converted into thermal energy and chemicals (H_2, CO, and CH_4). In a slagging gasifier, the reaction chamber operates at temperatures between about 1250º-1550ºC, at pressures up to 1000 psi, and is lined with refractory materials to contain the severe environment and to protect the outer steel shell from erosion, corrosion, and temperature.

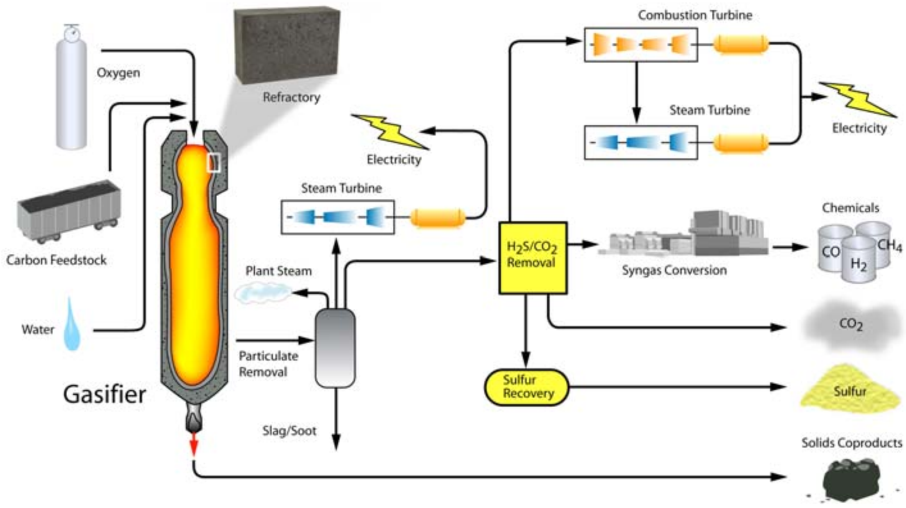


Figure 1: One type of Integrated Gasification Combined Cycle system showing refractory placement in the gasifier.

A number of issues in gasifiers cause system downtime; including refractory service life, that has limited their wider usage in industry. Gasification manufactures and operators point out that increased gasifier reliability and on-line availability are key issues to moving IGCC technology forward, with refractory service life being the top research need [1]. The refractory lining contains the harsh gasifier environment that includes molten slag originating from impurities in the carbon source. Coal, petroleum coke, and mixtures of them are the primary carbon feedstock in gasifiers, with other carbon containing materials such as biomass waste and black liquor being explored. Two types of refractory liners are widely used in slagging gasifiers, high chromia-alumina, and high chromia-alumina-zirconia; with some historical use of chromia-magnesia linings. The use of high chromia refractories evolved from gasifier research in the mid 70's to 80's [2-11], research which indicated high chromia content in a refractory (75 wt pct or higher) gave superior performance to all other refractory materials tested [12].

During gasification, molten slag from ash in the carbon source flows over the refractory surface and penetrates it, causing refractory dissolution in the slag, and setting up a situation where refractory spalling can occur. Refractory dissolution and spalling are thought to be the two primary wear mechanisms of refractories, with the current generation of refractory liners requiring replacement or repair within 3 to 24 months of installation. In general, refractory wear by dissolution is slow and is highly dependent on gasifier carbon feedstock, material throughput, gasification temperature, usage time, and system maintenance. Wear by spalling is periodic and is influenced by slag composition, slag penetration depth, gasifier cycling, and rapid temperature changes. It leads to rapid removal of portions of a liner and greatly reduces refractory service life.

Predicting when a refractory lining needs replacement is difficult, with the cost of replacing all or part of a gasifier lining exceeding $1M, depending on the extent of repairs. Compounding refractory repair and installation costs are lost opportunity costs that occur when a gasifier is off-line for refractory replacement or repair. Re-lining a gasifier requires it to be completely shut down, and under the best of circumstances takes about 12 days; involving gasifier cool down (3-7 days) and lining removal/installation when doing a partial rebuild (3 days) or longer for a full reline (7-10 days). Industry would like refractory materials that have a predictable and improved service life, something that has not been achieved. The high cost and the downtime associated with replacing the refractory liner, along with other gasifier issues will impact the future of gasification technology in power generation through cost comparisons against other technologies such as natural gas and conventional pulverized coal power plants. A targeted gasifier availability of 85-95% is needed for utility applications and more than 95% for other applications if IGCC technology is to move forward in the marketplace [1]. Refractory performance will be a key part of gasifier on-line performance.

The goal of the Albany Research Center is to attain improved service life and reliability in refractory liners through materials research. This paper discusses its research efforts to develop improved performance high chrome oxide and no/low chrome oxide materials for slagging gasifiers.

HIGH CHROME OXIDE REFRACTORY LINERS

COMMERCIAL TESTING OF PHOSPHATE CONTAINING REFRACTORY

The approach taken at Albany to develop improved performance high Cr_2O_3 refractory materials was to limit slag penetration in the refractory and to limit refractory corrosion (dissolution of the refractory in the slag). Examples of spalling and dissolution causing refractory failure in a gasifier are shown in figure 2. A spalled refractory material flowing down the hot face of a gasifier is circled in yellow in figure 2 (a). This spalled material from figure 2 (a), along with a different spalled refractory piece removed from a different gasifier, is shown in figures 2 (b) and (c), respectively. Note that the spalled refractory shown in figure 2 (c) is much thicker and more defined in shape than figure 2 (b).

A refractory sample in the process of spalling was removed from a gasifier lining and is shown in figure 3. Note that this refractory sample has two locations in the process of spalling, a thin layer on the surface (indicated by the upper arrow) and a thick lower area indicated by the lower arrow points. It is not know why the thickness of these two materials is so different other that corrosive wear. Factors such as the temperature of operation, the length of uninterrupted service, and the speed of a gasifier shutdown or heat up will influence how much spalling and corrosion occurs and when a material is released from the refractory surface, creating the differences shown in figure 2 (a) and (b) and figure 3. Spalling is exacerbated by rapid cycling of the gasifier, which causes large portions of the refractory hot face lining to be incrementally removed from the gasifier, decreasing refractory service life as large pieces of material are physically removed from a lining versus a slow material wear through dissolution into slag [13]. Refractory wear by corrosion and spalling is shown in figure 4. The mechanism of refractory slag attack on a high chrome oxide refractory that causes corrosion and spalling and how the cycle is thought to repeat itself is shown in figure 5.

Phosphate additions to a high chrome oxide refractory composition targeting a reduction in slag penetration were made and patented by Albany (US patent No. 6,815,386). This material has been described previously [14], with chemical and physical properties summarized in table 1. The phosphate containing refractory was commercially produced and has undergoing testing at in a commercial gasifier using coal as a carbon feedstock. The first testing of this new refractory was for 17 days in the lower cone of a gasifier (a test that of limited duration) and was terminated for non-refractory reasons. The appearance of the test panel after the 17 days of service indicated performance as good as or better than the current utilized high chrome oxide refractory materials. Because of this performance, the decision was jointly made between the gasifier user and Albany to expand testing into the gasifier sidewall and to retest the refractory in the lower cone area. Test materials have been produced by the refractory company, installed in the gasifier sidewalls, and put in service; with installation of the lower cone materials scheduled for a future gasifier repair. The sidewall test panel after installation but before service is shown in figure 6 (a); with the same test section (yellow circled area) after 130 days of service shown in figure 6 (b). Preliminary evaluation of this material indicates performance that equals or exceeds the existing gasifier liner. Spalling was noted to occur in comparable areas of the hot face gasifier lining (above, below, or at the same height as the test material), but not in the enclosed yellow square that contained the test material. It is important to note that one other area in the gasifier near the test brick also was observed where spalling was not found. Because of this observation, additional comparison of the phosphate containing test refractory with surrounding material will be made during future shutdowns. Although visual evaluation of the test panel is encouraging, future information is needed to reach conclusions on the test brick performance. It is important to note that through 130 days of gasification service; the phosphate containing refractory has performed as designed - showing good spalling and corrosion resistance.

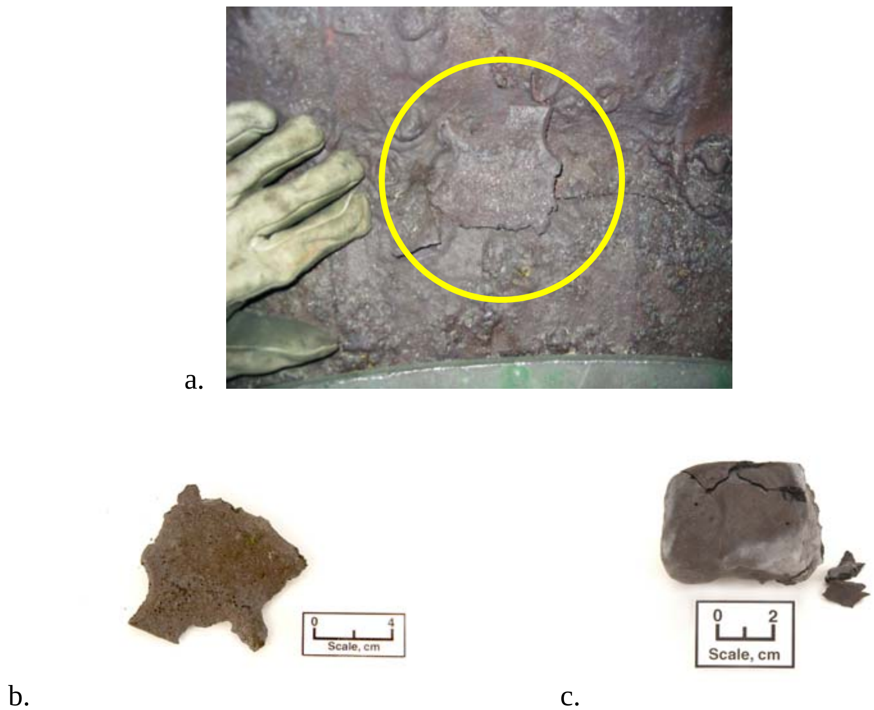


Figure 2: Examples of refractory wear caused by slag dissolution and spalling: a) Flowing slag is causing chemical dissolution of the refractory sidewall and refractory material spalling (circled fragment). b) Thin spalled refractory shown fig 2 (a). c). Thick spalled refractory.

Figure 3: Refractory surface in the process of spalling (yellow arrows point to spalled material).

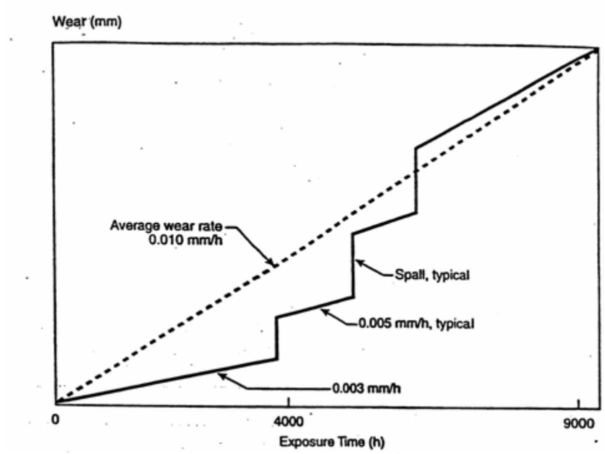


Figure 4: Incremental wear of a refractory brick lining by spalling in a slagging gasifier [13]

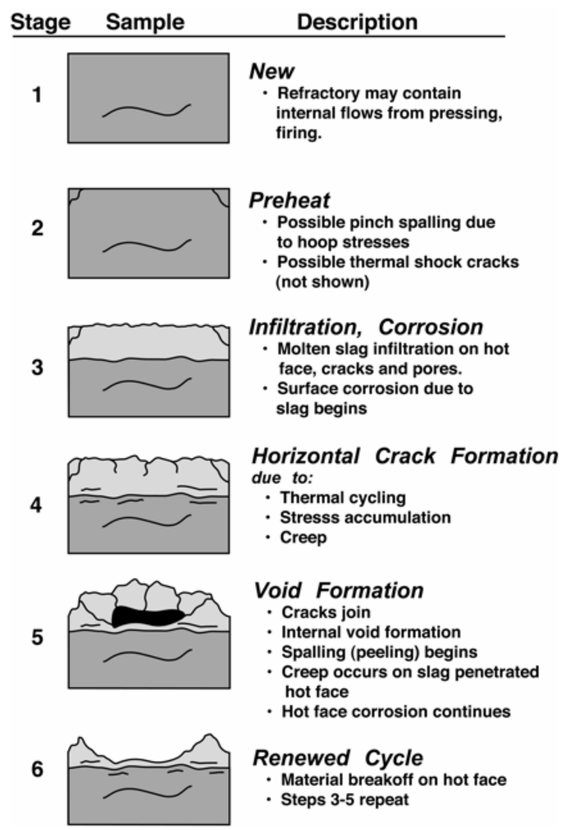


Figure 5: Stages of refractory wear in high chrome oxide refractories used in slagging gasifiers

Table 1 Chemical and physical properties of high Cr_2O_3 phosphate containing test refractory developed at ARC

Chemical Composition

Element	Elemental wt pct
Cr	≥55.0
Al	≤5.0
Zr	≤0.1
Mg	NA
P	≤8.0
Fe	≤0.05

Physical Properties

Bulk Density (g/cc)	4.20
Apparent Porosity (%)	12.7
CCS (MPa)	63.1
Reheat expansion *[1]	+0.11
Creep deformation*[2]	- 0.24
Rotary slag *[3]	
- % area change	+6.5
- mm slag penetration	1.8

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

a.

b.

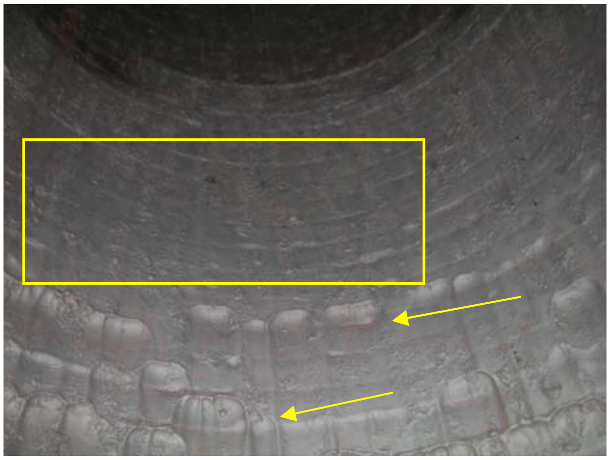


Figure 6: Sidewall test panel of phosphate containing high chrome oxide undergoing testing in a commercial gasifier. a) Test refractories after installation. Refractory samples marked with red dots are test materials and yellow dots are the traditionally used refractory material. b) Test panel (surrounded by the yellow square) after 130 days of service. Yellow arrows point to spalling in traditional refractory lining material.

Because current refractory testing of the phosphate containing high chrome oxide refractory is in a gasifier using coal as a feedstock, additional testing in gasifiers using petroleum coke and mixtures of petroleum coke/coal as feedstock are planned. Testing of carbon feedstock originating from petroleum coke is important as it may contain higher amounts of vanadium, nickel, or other elements not in coal to an appreciable level. These compounds may influence gasifier refractory wear, leading to possible modifications in the composition of the phosphate containing refractory material.

NO/LOW CHROME OXIDE REFRACTORIES

A strategy to develop no/low chrome oxide refractories for hot face linings in slagging gasifiers centers on making materials able to withstand slag corrosion and minimize spalling caused by slag penetration. This is being accomplished through control of raw materials and brick porosity. For purposes of this research, no-chrome refractories contain no intentional chrome oxide additions while low chrome oxide refractories are defined as containing less that 30 wt pct chrome oxide. The emphasis of this research is currently directed towards developing a no-chrome oxide engineered refractory material, with selection of the coarse, intermediate, and fine grain matrix components made using the following input:

- Evaluation of corrosive slag and spalling wear mechanisms determined from past gasifier studies
- Phase diagram interactions predicted to occur between refractory and slag materials
- Relative acidity/basicity rankings of candidate materials that indicate the potential of a material to withstand gasifier slags [15].
- Thermodynamic studies of the interactions predicted to occur between slag, gas, and potential refractory materials in a gasifier (Caution must be exercised when using thermodynamic data as it does not indicate reaction kinetics, only what material combinations are thermodynamically stable. Candidate material could appear thermodynamically unstable for use, but may be kinetically stable in practice.)
- SEM microstructural evaluation of test samples exposed to gasifier conditions.

Because many promising materials that were identified using the above criteria are often not commercially available; factors such as the ability of industry to produce a specific material and the projected costs of the material were also taken into consideration. Using this information, several refractory materials were identified as candidates for possible gasifier use. These materials included Al_2O_3, CaO, MgO, SiO_2, SrO, TiO_2, phosphates, and/or mixtures of them in the coarse and fine grained microstructure.

The sequence used to test/determine material properties was to prepare small "cups" of potential materials or compositions and study the interactions between a gasifier slag and the refractory containment vessel at elevated temperatures. The small scale cup test samples were made from fine powders (less than 325 mesh US Series), and were approximately 25 mm in diameter and 25 mm in height. Samples had a shallow depression in the top, making a “cup” able to hold a small quantity of gasifier slag. Once filled with slag, a cup was heated to 1600^oC in an Ar atmosphere and held for one hour. Interactions between the slag and the test material were evaluated by visual observations (degree of slag/refractory interaction), by measuring slag penetration, and by x-ray crystalline phase identification of the phases present. Slag/refractory interactions and the depth of penetration into the crucible are shown in figure 7.

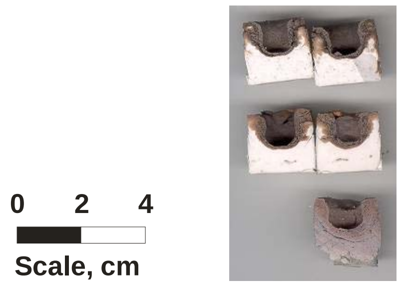


Figure 7: Cross section of small “cup” tests evaluating refractory/slag interactions at 1600°C in an Ar atmosphere. Different materials are evaluated in the “cup” cut in half to show slag penetration.

Materials identified as having potential from the small scale cup tests were fabricated into larger cups for evaluating slag interactions. These cups were approximately 65 mm in diameter and 65 mm in height. A recession in the cup, similar to that used in the smaller cup tests, held the test gasifier slag. Testing was conducted using the same heating schedule as smaller cup samples (1600°C in an Ar atmosphere using a gasifier slag with a one hour soak at the test temperature). The larger cup samples were made using coarse and fine grained matrixes, most with different compositions of the coarse and fine aggregate in the same sample to begin engineering specific properties in the refractory. The goal was to produce a microstructure that would control slag corrosion and penetration through particle packing, porosity, and fired density. An example of the larger cup test is shown in figure 8.

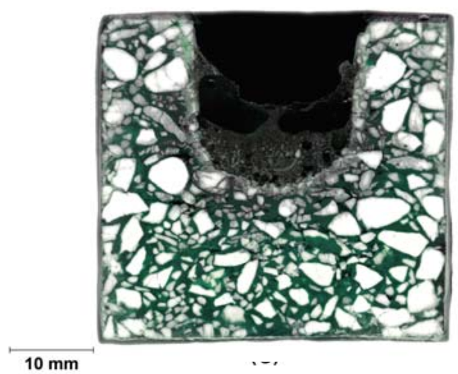
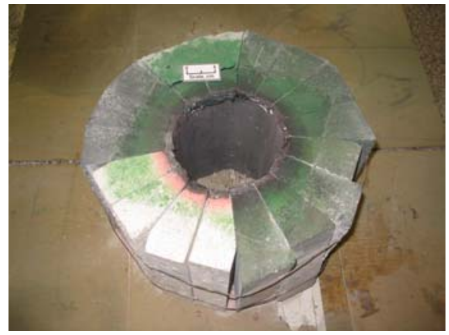


Figure 8: Cross section of larger cup test sample evaluating slag attack of coarse and fine grained microstructure in Ar at 1600°C.

Small and large cup tests are a way to quickly evaluate different materials (over 100 different compositions have been tested), but have the drawback that they do not introduce a thermal gradient across a sample. Because gasifier refractories have a thermal gradient, further testing of materials that looked promising are being evaluated in the rotary slag test which introduces a gradient. This test requires 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. Rotary slag testing of a non-chrome oxide refractory and of high chrome oxide refractories are shown in figure 9. Testing was conducted for four hours at near 1650°C using a gasifier slag feed of 200 grams every 10 minutes and a rotational speed of 1.5 rpm. Refinements are being made to the microstructure of test materials based on rotary slag testing to control grain size and bond matrix materials with the goal of improving slag and wear resistance. Research to develop non-chrome materials for slagging gasifier applications has produced compositions meriting additional research, leading Albany to begin soliciting the involvement of refractory producers for input in this research.



a. b.

Figure 9: Refractory samples tested for molten slag resistance in the rotary slag test, a) samples during rotary slag testing, and b) non-chrome and chrome based refractories after rotary slag testing. Testing was for 4 hours of exposure to a coal gasifier slag at 1667^{o}C.

CONCLUSIONS

The wear of high chromia/alumina refractories used to line the hot face of slagging gasifiers is predominately caused by refractory surface corrosion and spalling. An improved high chrome oxide refractory composition containing phosphates has been patented, produced commercially, and is undergoing field testing in a commercial gasifier. Phosphate containing samples have completed field testing for 17 and 130 days successfully, with continued material evaluation underway. Preliminary field test data indicates spalling wear that is less than traditionally used refractory materials. Further analysis of the test samples must be made upon completion of gasifier testing before final conclusions can be reached. Additional testing at other gasifiers using different carbon feedstock is scheduled. Research and development of gasifier refractory liner materials containing no chrome oxide is also underway at Albany. Using information from the literature, phase diagrams, thermodynamic data, and other sources; an improved performance refractory material is being developed in the laboratory. Promising materials are being scaled up from small cup tests to larger cup tests, than to the rotary slag tests. This information is being used to determine potential field test compositions. Work has begun with refractory producers to evaluate these and other potential refractory materials.

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