LOW CHROME/CHROME FREE REFRACTORIES FOR SLAGGING GASIFIERS

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ABSTRACT

Gasifiers are containment vessels used to react carbon-containing materials with oxygen and water, producing syngas (CO and H_2) that is used in chemical and power production. It is also a potential source of H_2 in a future hydrogen economy. Air cooled slagging gasifiers are one type of gasifier, operating at temperatures from 1275-1575º C and at pressures of 400 psi or higher. They typically use coal or petroleum coke as the carbon source, materials which contain ash impurities that liquefy at the gasification temperatures, producing liquid slag in quantities of 100 or more tons/day, depending on the carbon fed rate and the percent ash present in the feedstock. The molten slag is corrosive to refractory linings, causing chemical dissolution and spalling. The refractory lining is composed of chrome oxide, alumina, and zirconia; and is replaced every 3-24 months. Gasifier users would like greater on-line availability and reliability of gasifier liners, something that has impacted gasifier acceptance by industry. Research is underway at NETL to improve refractory service life and to develop a no-chrome or low-chrome oxide alternative refractory liner. Over 250 samples of no or low chrome oxide compositions have been evaluated for slag interactions by cup testing; with potential candidates for further studies including those with ZrO_2, Al_2O_3, and MgO materials. The development of improved liner materials is necessary if technologies such as IGCC and DOE's Near Zero Emissions Advanced Fossil Fuel Power Plant are to be successful and move forward in the marketplace.

INTRODUCTION

Gasifiers are the high temperature containment vessels used to react carbon-containing materials with oxygen and water using fluidized-bed, moving-bed, or entrained-flow system designs to produce syngas (CO and H_2) and/or other gases [1]. Sulfur compounds and ash in a powder or a molten slag form are the primary solid by-products of the gasification process, and are associated with impurities in the carbon feedstock. In air cooled slagging gasification systems, coal or petroleum coke is the typical carbon feedstock. Examples of two types of air cooled slagging gasifiers are shown in figure 1. Gasification in these processes is conducted at temperatures between 1275º and 1575º C, and with pressures of 400 psi or higher. The slagging gasifier shell is lined using refractory materials capable of withstanding the severe environment; protecting the outer steel shell from erosion, corrosion, and temperature (gasifier cross section is shown in figure 2). The refractory liner materials used in today's slagging gasifiers are typically fused or dense firebrick containing Cr_2O_3 (60 to 90 wt pct) with a second refractory oxide (typically Al_2O_3, ZrO_2, or MgO).

Early slagging gasification research concentrated on developing sound gasifier designs and on determining appropriate refractory liners for different systems under development. Refractory practices in industries thought to be similar to gasification; including petrochemical processing, blast furnaces for steel production, coke ovens, glass furnaces, and coal fired boilers; were evaluated for applicability to gasification. The high chrome oxide content of refractories used in today's slagging gasifier 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 [2-10]. Materials that were evaluated included alumina-silicate, high alumina, chromia-alumina-magnesia spinels, alumina and magnesia, alumina and chrome, and SiC materials – both sintered and fused cast shapes of many refractory compositions. Liner materials for high wear areas in today's gasifiers evolved from these materials to those utilizing high chrome oxide content, with a minimum of 75 pct chromia thought to be necessary for satisfactory performance [11]. Wear mechanisms considered in early gasifier research included gaseous corrosion, corrosion/erosion by molten slags, erosion/abrasion by particulates, thermal/mechanical failures, and condensation of acids or steam entrapment at the shell.

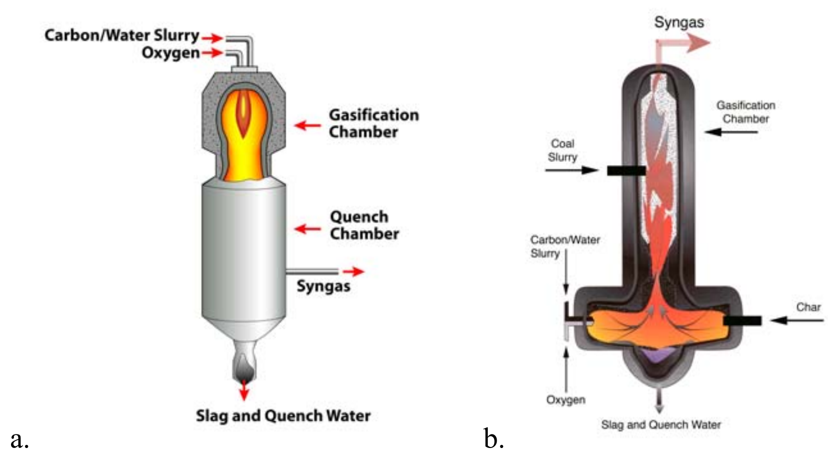

Figure 1 - Two types of air cooled slagging gasifiers; a) single injector GE type, and b) opposing flow dual injector ConocoPhillips type.

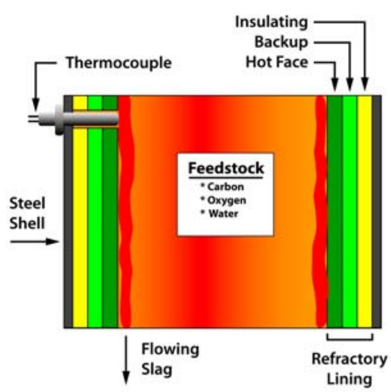

Figure 2 – General cross-section of an air cooled slagging gasifier.

Failure of today's refractory lining in a slagging gasifier is expensive, both in terms of refractory replacement costs (as high as $1,000,000 depending on shell size and the extent of rebuild necessary) and in terms of lost production. Re-lining a gasifier requires that the system be completely shut down, and under the best of circumstances takes 7 days for a partial rebuild. A rebuild involves cool-down (4-6 days), refractory tearout, and refractory installation (3 days for a partial reline, 7-10 days for a full reline). Some gasification facilities maintain a second gasifier for use while repairs are made to reduce downtime or off line availability. Even then, the time to switch gasifiers can vary from hours to days, depending on the spare gasifier availability and if it is pre-heated. Because of the long down time required for repair, gasifier operators would like to install refractory linings with a reliable service life of at least three years. The current generation high chrome oxide 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 short refractory service life, gasifier manufacturers and operators have identified it as the most important barrier to reliable and efficient gasification [12]. Users desire a gasifier availability of 85-95% for utility applications and more than 95% in applications such as chemicals, creating a roadblock if technology such as IGCC is to move forward in the marketplace [13]. Gasifiers are also a key component of new energy systems being developed as part of the Department of Energy's Near Zero Emissions Advanced Fossil Fuel Power Plant.

Several issues exist with Cr_2O_3 refractory materials used in air cooled slagging gasifiers, which include: 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 and their interaction with slags, c) the high cost associated with refractory materials containing high Cr_2O_3 content, and d) possible long-term domestic supply issues. To address these and other concerns, this research project will investigate and develop low-chrome/no-chrome oxide liner materials for use in slagging gasifiers. These goals will be achieved by:

1) investigating the role chrome oxide plays in gasifier refractories,
2) evaluating wear mechanisms that play a role in gasifier failure,
3) evaluating non-chrome or low-chrome high temperature refractory oxides with potential for use in combating known wear mechanisms in gasifier refractories,
4) developing and evaluating engineered refractory shapes containing low or no chrome oxide, and
5) conducting field tests of these engineered refractory materials.

Past refractory research conducted on spent high chrome oxide liners at NETL-Albany has indicated two major wear mechanisms, corrosion and spalling (see figure 3). The causes of gasifier refractory spalling are complicated, but are thought to include: time, gasifier feedstock, slag penetration and differential thermal expansion between slag penetrated/non-penetrated layers in the refractory, high temperature creep [14], reactions between Cr_2O_3 and FeO that cause different expansion between components in the refractory [15], and thermal cycling of the gasifier [16]. A refractory material with phosphate additions was developed, patented (US Patent # 6,815,386) by NETL, and is commercially produced by a refractory company. It is currently undergoing evaluation in plant trials at several gasification facilities. Preliminary results indicate this newly developed refractory material produces an incremental improvement in service life, but may not achieve that desired by industry.

This research focuses on non-chrome oxide refractory research efforts for slagging gasifier applications and outlines initial efforts to add low levels of Cr_2O_3 into the fine grain refractory microstructure of what would otherwise be a non-chrome oxide composition.

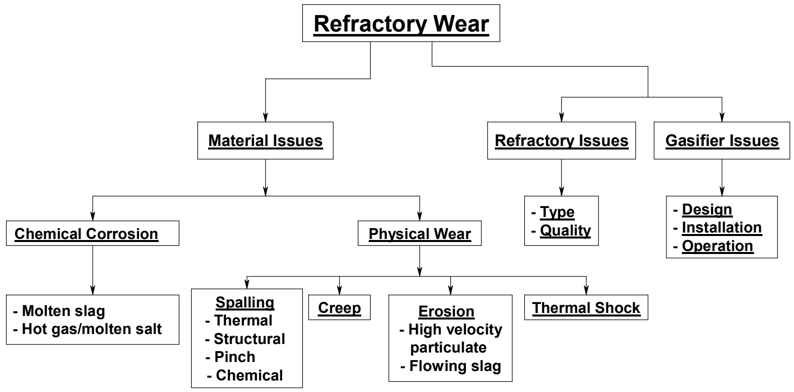

Figure 3 – Causes of refractory wear in air cooled slagging gasifier liner materials

NO/LOW CHROME OXIDE RESEARCH

The focus of no/low chrome oxide refractory research is on improving the resistance to chemical corrosion and spalling, identified as primary wear mechanisms in earlier research. The long range research goal is to develop no/low chrome oxide refractories for use in gasifiers with a service life of at least 3 years, or with a service life that matches the plant maintenance schedule for the gasification facility. All aspects of this research are being performed in close collaboration with commercial manufacturers and operators to ensure that refractories are developed that can be produced commercially and used in slagging gasifiers. Refractory material selection is based on thermodynamic considerations, phase diagram compatibility, laboratory research, and literature reviews.

In the past, non-chrome oxide refractory compositions did not show comparable performance to high chrome oxide refractory materials. Chrome oxide materials have low chemical solubility in gasifier slags and formed high melting spinels/solid solutions with iron oxides. It is important to remember that most coal slags are "acidic", being high in Al_2O_3 and SiO_2; and that petroleum coke slags contain other impurities, such as vanadium and nickel. Because only a few materials, including ZrO_2, have the potential to resist slag corrosion as well as chrome oxide, a refractory material must be designed with an engineered microstructure that helps to resist dissolution into the slag and slag penetration.

Compositions selected for testing were first evaluated in small scale lab cup tests (sample size less than 2.5 cm cube; test conditions of 1600°C for 1 hour in an Ar atmosphere) using a coal gasifier slag. An example of small cup test samples is shown in figure 4. Those samples identified for further testing based on slag penetration and corrosion resistance were evaluated as both single and multiple component mixtures in large sample cups (5.1 mm cube) under similar conditions. Both coarse and fine grain raw materials were used to make large cup samples and were blended to achieve an engineered microstructure of controlled porosity. An indication of the effect of controlling both the sample composition and microstructure in large sample cups is shown in figure 5. Over 250 slag cup tests have been evaluated using a variety of different raw materials. Those with the greatest potential are listed in table 1.

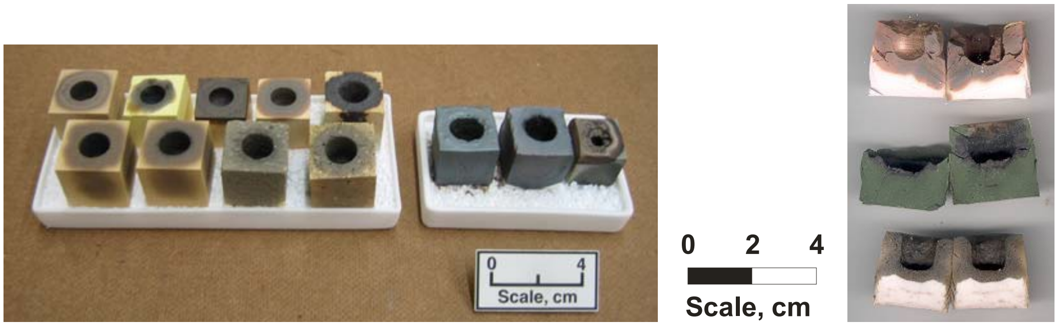

Figure 4 – Small 2.5 cm "cup" tests used to evaluate refractory/slag interactions at 1600°C in an Ar atmosphere. Once exposed, samples are cut in half to determine slag penetration.

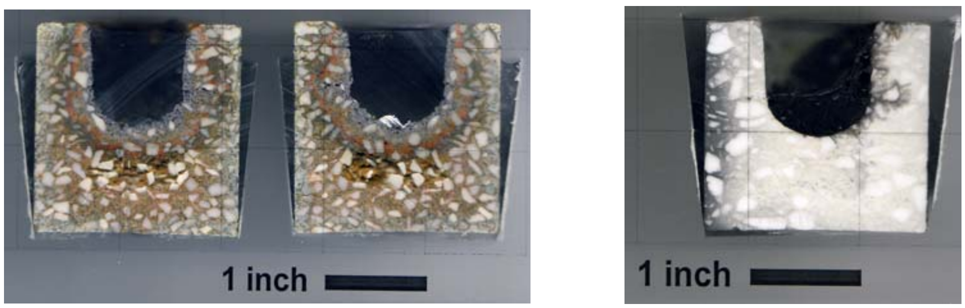

Figure 5 - Large 5 cm "cup" tests samples used to evaluate refractory/slag interactions at 1600°C in an Ar atmosphere. Once exposed, samples are cut in half to show slag penetration. a) slag penetrated refractory microstructure with typical microstructure, and b) improved refractory microstructure.

Table 1 – General composition being evaluated in non-chrome refractory research
(note that minor additions of Cr_2O_3 are being made to specific compositions)

- Refractory compositions
  - NETL focused compositional areas
    - Major component - Al_2O_3
    - Secondary component - ZrO_2, MgO, Cr_2O_3
    - Minor additives - CaO, MgO, rare earths, TiO_2, SiO_2, Cr_2O_3
  - Commercial submitted compositions
    - Major component - Al_2O_3, ZrO_2
    - Secondary additives - MgO, SiC
    - Minor additives - CaO, MgO, others (unknown)
- Target Properties/considerations
  - Porosity - 15 pct
  - Mechanical strength (CCS) - 45 N/mm2 (or higher)
  - Corrosion resistance - approaching high Cr_2O_3 (probably not equal)
  - Slag penetration - equal or better to high Cr_2O_3
  - Thermal shock resistance - expect better than high Cr_2O_3
  - Cost - targeting lower than chrome oxide

Samples of commercially produced refractories have been submitted for gasification slag evaluation by several companies, with negotiations underway with one company for evaluating specific zirconium oxide based materials. A general listing of refractory materials with potential for use as a substitute for high chrome oxide gasifier refractories that were developed at NETL or that are commercially produced are listed in table 1. Specific information on compositions is not given because of patent potential and because of the proprietary nature of the commercial compositions. Besides focusing on refractory compositions with minimal interaction with gasifier slag; research is also focused on grain sizing/particle packing, on the correct use of coarse and fine grained materials to limit slag penetration, and on the use of minor additives to impact slag penetration into the refractory matrix. Promising materials identified in cup testing are being targeted for rotary slag testing, which simulates the slagging gasifier environment better than the isothermal environment of a cup test. Rotary slag testing exposes samples to a thermal gradient, has a constant replenishment of slag preventing slag saturation, and has a constant slag flow over the surface of a sample that can release refractory grains into the slag.

CONCLUSIONS

NETL is researching no/low chrome oxide refractory materials for use in slagging gasifiers to increase their performance and reliability. These materials are being researched because high chrome oxide refractories currently used by industry do not meet its needs. Two wear mechanism identified in high chrome oxide materials will play a critical role in the wear of no/low chrome oxide materials; chemical corrosion and spalling. No/low chrome oxide research has focused on refractory compositions containing ZrO_2, Al_2O_3, MgO, and Cr_2O_3; although other minor additives are being considered, with encouraging results obtained in both NETL developed and commercially produced materials. Research has focused on 2.5 cm and 5 cm cube cup tests using commercial coal slag, with over 250 samples being evaluated. Slag penetration into the refractory structure appears to be a critical factor in controlling refractory wear. Larger scale testing using the rotary slag test is underway to evaluate encouraging compositions in a flowing slag environment.

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