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Field Trial Results of an Improved Refractory Material for Slagging Gasifiers

James Bennett
U.S. Department of Energy, NETL, 1450 Queen Ave., SW, Albany, OR 97321
E-mail: james.bennett@netl.doe.gov; Telephone: (541) 967-5983; Fax: (541) 967-5845
Kyei-Sing Kwong, Art Petty, Cynthia Powell, Hugh Thomas
U.S. Department of Energy, NETL, 1450 Queen Ave., SW, Albany, OR 97321
H. David Prior
ANH Refractories Company, 1001 Pittsburgh-McKeesport Blvd., West Mifflin, PA 15122
Mark Schnake
Harbison-Walker Refractories Company, 111 West St. Eunice Rd., Fulton, MO

ABSTRACT

Gasifiers are used commercially to react a carbon feedstock with water and oxygen under reducing conditions; producing chemicals used as feedstock for other processes, fuel for power plants, and/or steam. A gasifier acts as a high temperature, high pressure reaction chamber, typically operating between 1250-1575°C, and with pressures between 300-1000 psi. Ash that originates from mineral impurities in the carbon feedstock becomes a by-product of gasification. In a slagging gasifier it melts, forming a liquid which flows down the gasifier sidewall; penetrating and wearing away the refractory liner by corrosive dissolution, abrasive wear, or by other mechanisms such as spalling. The refractory liner must withstand the severe service environment, protecting the steel shell against corrosive gases, temperature, slags, and material wear. Users have identified refractory service life as the most important limitation to sustained on-line availability of gasifiers, limiting gasifier acceptance and use by industry. The National Energy Technology Laboratory has developed and patented (US Patent # 6,815,386) a phosphate containing high chrome oxide refractory for use in slagging gasifiers. In cooperation with ANH Refractories Company, this refractory material has been commercially produced and is undergoing field tests in commercial gasifiers. An analysis of data from these field tests indicates that the phosphate containing refractory results in an improved service life over other refractory materials currently used as gasifier liners. Results from the post-mortem analysis of a field trial in relation to the failure mechanisms in a slagging gasifier will be presented.

INTRODUCTION/BACKGROUND

The gasification process used in today's chemical, petrochemical, and power industries was originally developed in the 50's and 60's [1] for use by the petroleum industry. The heart of the gasification process is a high temperature, high pressure reaction chamber, called a gasifier, which typically operates between 1250-1575°C, and with pressures between 300-1200 psi. A gasifier is used to react carbon, water, and oxygen (a shortage to cause a reducing environment) to produce CO and H_2 by the following reaction:

$$C + H_2O\ (gas) + O_2 \rightarrow CO + H_2 + CO_2 + \text{minority gases} + \text{by-products}$$

NOTE: by-products include mineral impurities in the carbon feedstock that become ash or slag

Gasification is one of several technologies expected to be utilized in the Advanced Fossil Fuel Power Systems of the future, and is considered a potential source of H_2 for fuel cells or the emerging hydrogen economy. The gasification process using an air cooled slagging gasifier (shown in figure 1) is able to produce a variety of products, from power to chemicals, and has the advantage of being able to capture pollutants such as H_2S and CO_2 because it is a closed circuit.

In the air cooled gasification process, ash impurities in the carbon feedstock become molten and flow down the sidewalls of the gasifier as a slag. As the slag flows, it interacts with the refractory lining through chemical dissolution or by infiltrating open porosity, causing surface spalling. In general, a relationship exists between refractory service life and thermal cycling of the air cooled slagging gasifier, gasifier feedstock throughput, ash chemistry and melting point, and the operating temperature of the gasifier. Attempts by gasifier users to enhance gasifier output and economics by operating at higher temperatures, with higher feedstock throughput, and/or with variable feedstock have put additional stress on liner materials, and typically result in a corresponding decrease in their useful service life. Because of interactions between the refractory and the molten slag, refractory service life can vary between 3 and 24 months. Repair of the hot face lining can take from 5-14 days, depending on the extent of repair. The long, and at times unscheduled, downtime due to refractory liner failure have caused poor system reliability and on-line availability of the gasifier. It is the reason gasifier users have identified refractory service life as one of their top research needs [2].

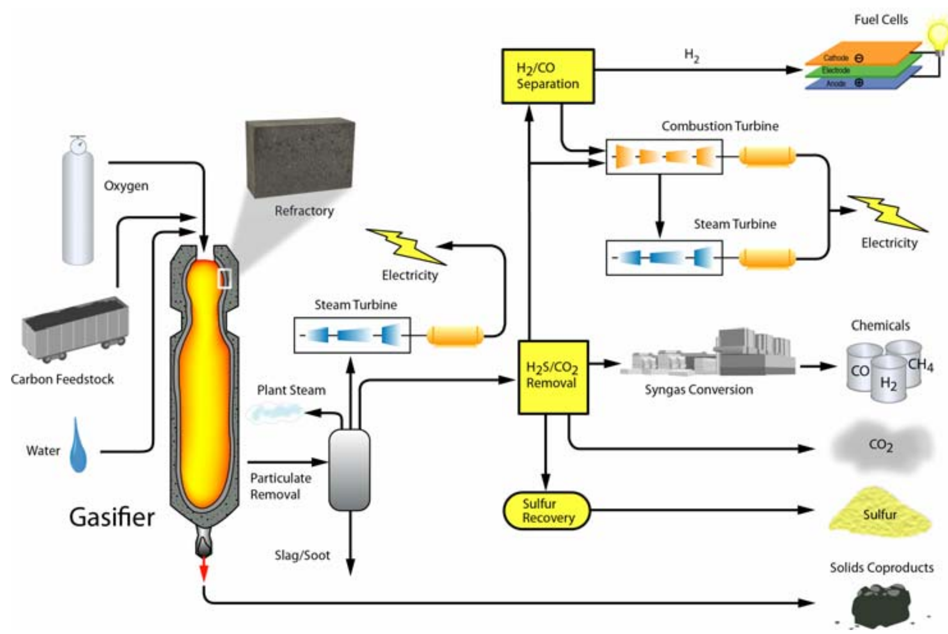


Figure 1: An air cooled slagging gasification facility

Air cooled slagging gasifiers use two primary feedstocks – coal and petroleum coke. The major impurities associated with ash in these feedstocks are oxides of Si, Fe, Ca, and Al in coal, and the additional oxides of V and Ni present in petroleum coke ash. Air cooled slagging gasifiers are lined with refractory materials that contain between 60-95 pct chrome oxide that evolved from research in the 1970-1980's funded by USDOE, EPRI, and private industry [3-11]. This early research indicated a minimum chrome oxide content of about 75 pct [12] was necessary to provide the best chemical resistance to gasifier slag corrosion. Since the early research of the mid 80's, three types of high chrome oxide refractory materials have been or are currently commonly used in gasifiers, and are listed in table 1; columns A, B, and C. Of these, the chrome oxide-alumina and chrome oxide-alumina-zirconia (brick types A and B) are used in the majority of air cooled slagging gasifiers as hot face liners, while usage of the chrome oxide-magnesia material (brick type C) has decreased or become historical in use.

In an air cooled slagging gasifier, zoning (the use of different refractory materials at different locations in a furnace) is practiced because of different wear mechanisms and wear rates at different locations in the gasifier, and because of high material costs. In general, chrome oxide content ranging from 60-95 pct are used to line the working face of a gasifier (figure 2), with lower chrome oxide content found in the low wear areas and higher chrome oxide content (approaching 95 pct) found in the higher wear locations. The backup lining is typically a high alumina/low chrome oxide refractory, which serves as an emergency lining to contain the gasifier environment in case of failure of the hot face lining. A third refractory layer, an insulating refractory, often backs up the hot face and backup linings, reducing thermal loss and controlling shell temperature.

Table 1 – Chemical composition of three classes of high chrome oxide refractories used in air cooled slagging gasifiers (wt pct)

Material (wt pct)	Brick Type			
	A	B	C	D
Cr_2O_3	95.1	87	81.0	92.0
Al_2O_3	4.3	3.0	0.4	4.7
MgO	0.1	NL	17.0	NL
ZrO_2	NL	6.5	NL	NL
P_2O_5	NL	NL	NL	3.3

Note: Data from manufacturer's technical data sheet
NL = Not listed

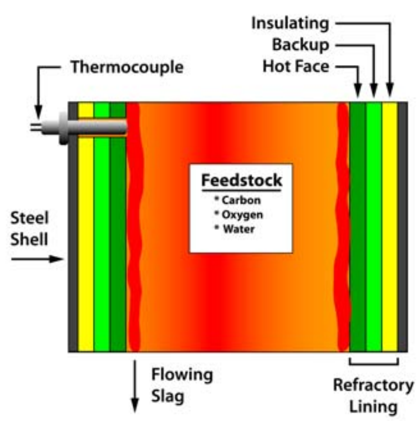


Figure 2 – Cross section of a gasification chamber.

As viewed from the interior of an air cooled gasifier on the hot face, an example of high chrome oxide refractory wear dominated by chemical corrosion and spalling is shown in figure 3. Chemical corrosion involves the dissolution of refractory into the slag as it flows over it, and is one of the main causes of wear. Corrosion can lead to the removal of large refractory particles or grains as the bond phase is weakened and/or removed. Chrome oxide can compose up to 90-95 wt pct of the hot face refractory composition, and is the main component because of its low soluble in the molten slag during normal gasifier operation and because it interacts with iron oxide in the slag, forming high melting phases (solid solutions or spinels). The hot face refractory liner is not fully dense, having a porosity between 12 and 15 pct, which improves thermal shock resistance. The porosity, however, along with the small thermal gradient across the working lining during use, allows slag to penetrate surface microstructure, setting up the basis for another major wear mechanism - spalling.

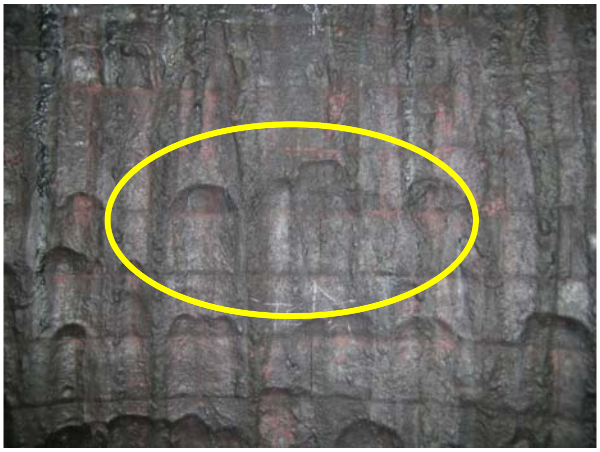
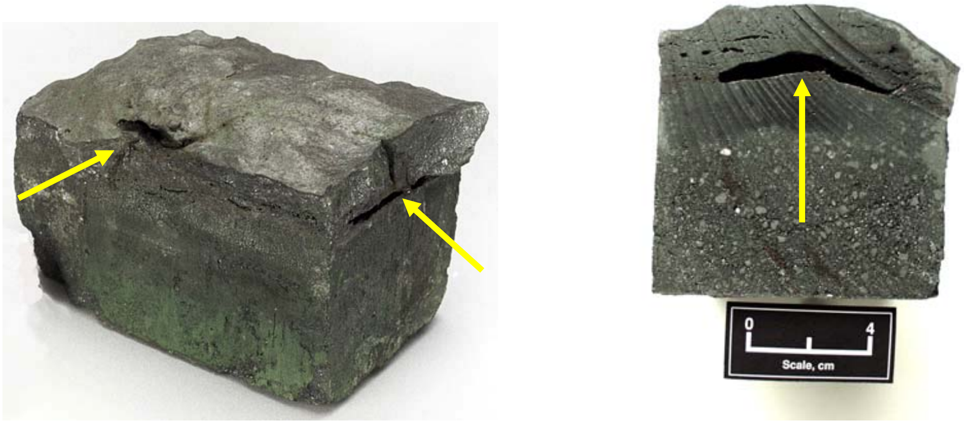


Figure 3 - Refractory surface wear dominated by chemical corrosive (dissolution). Evidence of surface spalling is shown by scalloped brick surface in circled area.

Refractory spalling in slagging gasifiers is a complex process involving factors such as slag chemistry, interactions between slag and the refractory grain, slag infiltration/penetration of interconnected porosity, thermal cycling with the associated thermal expansion mismatch, stresses resulting from gasifier design, and long term creep. Bakker [12] discussed how refractory spalling can incrementally remove large portions of a gasifier refractory thickness, rapidly shortening service life as material is physically removed versus a slow chemical dissolution of material in a slag.

Spalling, combined with chemical corrosion, are the predominant wear mechanisms, and are shown in figure 4 on a refractory brick removed from the sidewall of a gasifier. Chemical corrosion is evident on the surface of the refractory, while spalling is occurring on the surface and the interior, and is marked with arrows in figure 4-a. A cross section of the refractory brick, with visible slag penetration of approximately 4 mm into the hot face, is shown in figure 4-b. In this slag penetrated area, an internal void is opening parallel to the hot face, which is in the process of spalling.



a. b.

Figure 4 – Sidewall refractory brick removed from a gasifier. (a) chemical dissolution and severe spalling (yellow arrows point to spalled areas), (b) internal voids due to spalling (yellow arrow).

Many factors influence refractory wear in an air-cooled slagging gasifier using a high chrome oxide lining, which are summarized in figure 5 from observations/post-mortem analysis of spent refractories.

These factors include gasifier design (air versus water quench, gasifier size, and brick placement); refractory installation; and gasifier operation (carbon source, feedstock throughput, temperature of gasification, burner alignment, and the number of thermal excursions and/or cycles per campaign). Other wear factors include refractory issues (material type and quality) and material issues (including corrosion and physical wear that is a consequence of material properties). Of the material issues identified in figure 5, chemical corrosion and spalling are the primary causes of refractory failure.

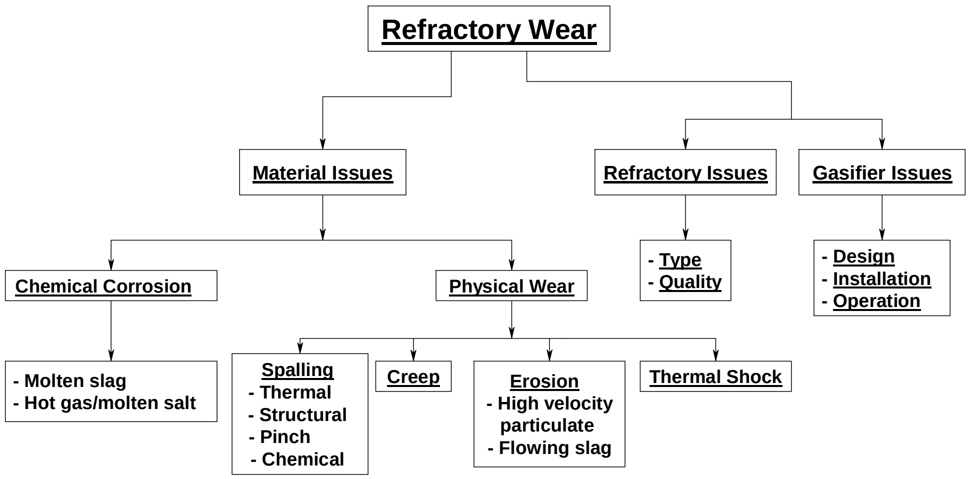


Figure 5 – Causes of refractory failure in a slagging gasifier.

Using the knowledge of refractory wear shown in figure 5, NETL developed and patented (US Patent # 6,815,386 [13]) a new phosphate containing refractory targeting the reduction or elimination of material wear by structural/chemical spalling in air cooled slagging gasifiers [14]. NETL worked with ANH Refractories Co. (Harbison-Walker Refractories Co.) to scale-up this refractory material from the laboratory into commercial production, and is working with them to conduct field trials in industrial slagging gasifiers using various carbon source and gasifier designs. This joint work is still on-going, with the results of sidewall tests at one gasification facility using coal as a carbon feedstock presented in this paper.

SIDEWALL PANEL FIELD TRIAL

Phosphate containing high chrome oxide refractory materials used in field tests were produced under commercial conditions by Harbison-Walker Refractories Co. at their Vandalia, MO plant using a general composition similar to that shown in table 1, column d. These materials were installed in an air cooled slagging gasification facility using bituminous coal as a feedstock during November of 2004. The test panel consisted of 24 test brick, and was installed in the upper portion of the gasifier sidewall during a complete gasifier reline. The test panel, after installation, is shown in figure 6–a, and is marked by red dots; while the conventional refractory material is marked by yellow dots.

The gasifier was put into standby mode after reline, than placed into service using a feed rate of approximately 1200 tons/day of bituminous coal. The gasifier operated at an approximate temperature of 1400°C, and was brought up/down in service several times over the next 14 month, during which the condition of the test panel was documented. The broad outline of the test panel after approximately 150 days of service is outlined in yellow in figure 6-b. Severe spalling in conventional refractory material without phosphate additions is evident underneath the test panel, while no spalling is observed in the phosphate containing refractory material.

In December of 2005, after 5688 hours (237 days) of service, the test panel was removed during a complete reline of the hot face lining of the gasifier. The appearance of the lining sidewall before removal, with the outline of the test panel marked in white, is shown in figure 7. Spalling is evident below the test panel. Also note the depth of spalling into the hot face compared to the phosphate containing refractory materials.

a b.

Figure 6. Sidewall test panel of phosphate containing refractory materials. (a) Test panel after installation and before use - test brick are marked by red dots, conventional refractory materials are marked by yellow dots. (b) Test panel after approximately 150 days of service. Test panel is in yellow boxed area.

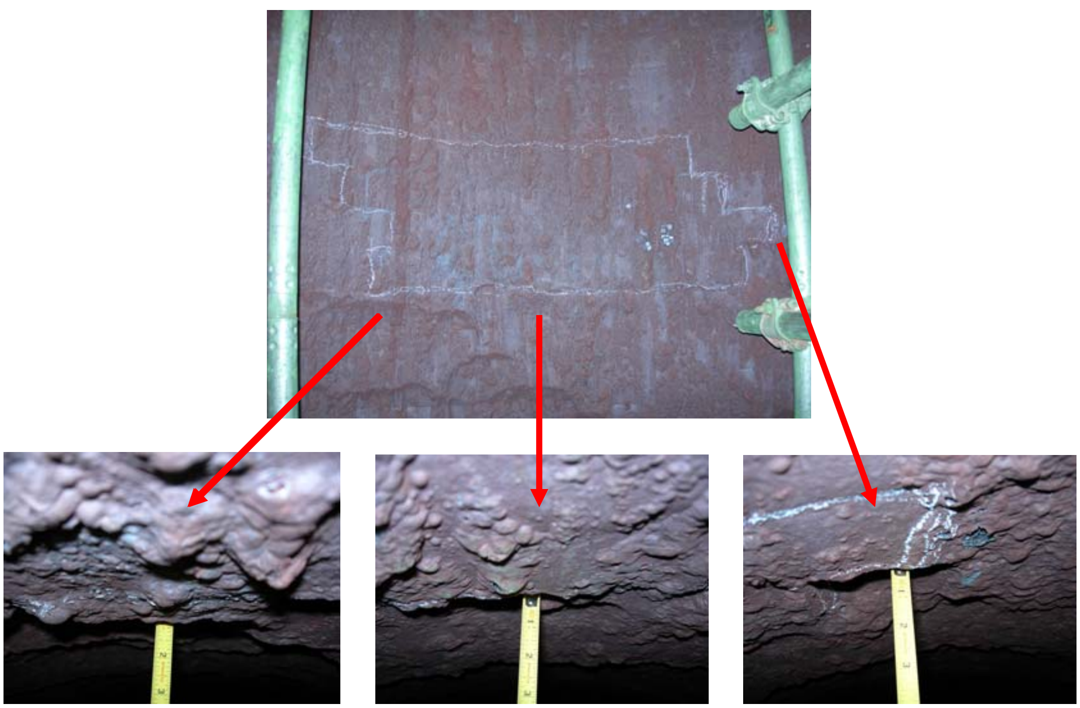


Figure 7. Test panel of phosphate containing refractories after 237 days of service prior to removal. Note the depth of wear caused by corroded and spalled material underneath the test panel.

The phosphate containing test brick removed from the test panel, along with conventional high chrome refractory brick surrounding them (brick above, below, left and right) were carefully marked for identification and location; and are shown in figure 8-a. Both the phosphate containing and non-phosphate containing brick were examined visually and cut in half to allow measurements of thickness and examination of the internal microstructure. The results, shown in figures 8-b to e, indicate the following:

1. Phosphate containing refractories (example shown in figure 8-c) did not contain internal cracks parallel to the hot face; while all surrounding commercial brick, regardless of location, did (examples shown in figures 8-b, d, and e). These internal cracks are indicative of the early stages of spalling.

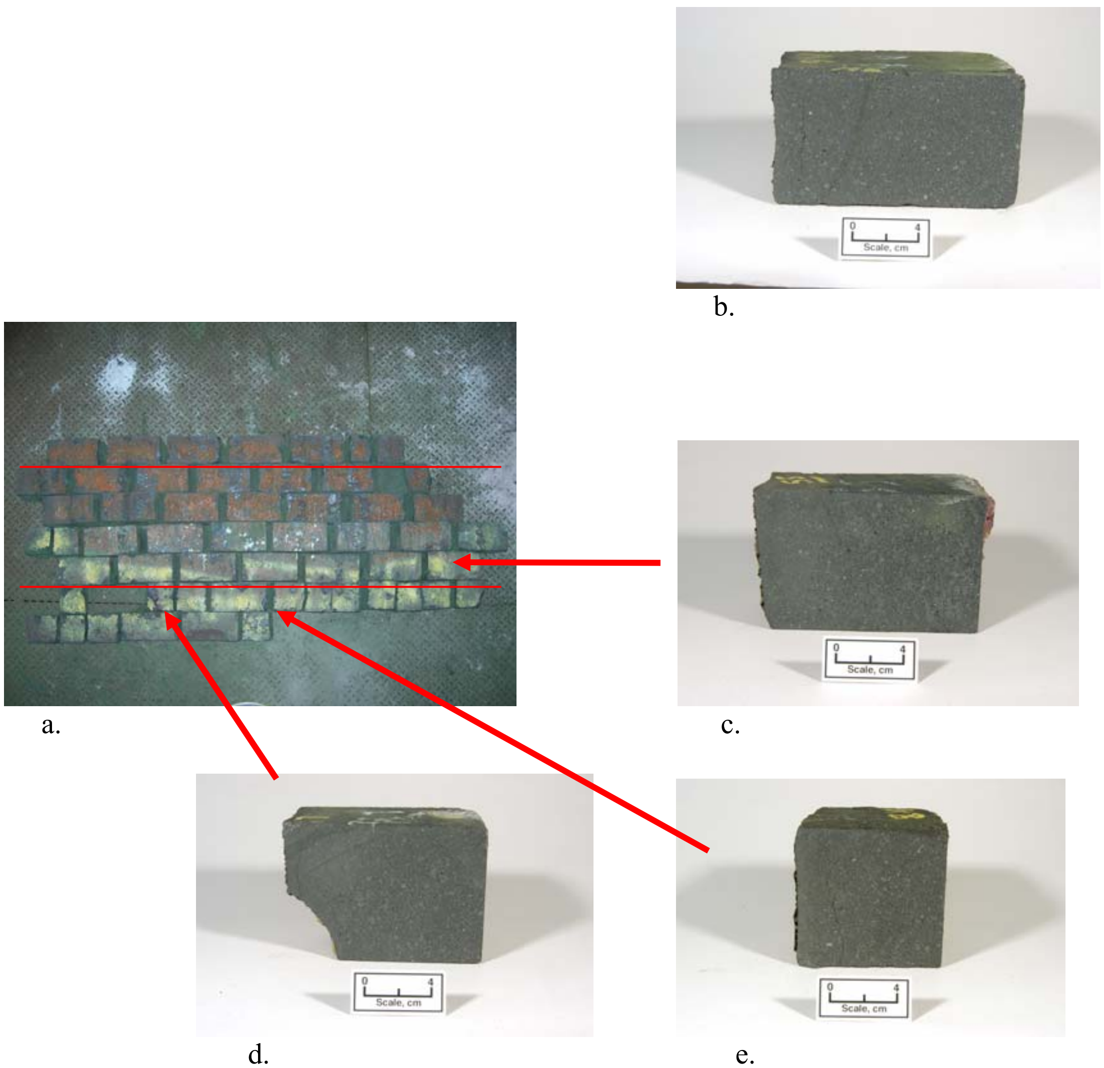


Figure 8. Cross section of test panel brick after 237 days of service. Conventional and test refractory brick as removed (a), conventional brick above phosphate test panel (b), phosphate containing test brick (c), and conventional brick below phosphate test panel (d and e).

2. Corrosive material loss from the non-phosphate containing brick located immediately above the test panel (example shown in figure 8-b) was approximately the same as from the phosphate containing test brick (example shown in figure 8-c). Corrosion loss was assumed to be related brick thickness remaining since surface spalling did not appear to have occurred on the surface of these brick. It is important, however, to note that the non-phosphate brick above the phosphate containing materials had large cracks parallel to the hot face, indicative of early-stage spalling.
3. Material loss from the non-phosphate containing brick located immediately below the test panel (figure 8-d and e) was substantially greater than for the phosphate containing brick (figure 8-c), as measured by brick thickness. The thinner non-phosphate materials had surface evidence of past spalling and of spalling in the process of occurring within the refractory.

Slag penetration, as measured by both x-ray fluorescence (XRF) and SEM wave dispersive spectroscopy (WDS), was approximately 5-10 mm into the phosphate containing refractory; while slag penetration into the conventional refractory was much greater, 22 to 45 mm. Research is being conducted on the refractory materials to determine the mechanism of why slag penetration is inhibited in the phosphate containing refractory. Phosphate additions appear to influence how slag Fe ions interact with chrome oxide in the refractory, reducing expansive behavior when a Fe-Cr spinel structure was formed.

Because of the thickness difference in the conventional versus phosphate containing refractory, preliminary data from this single sidewall panel test looks very promising for improved refractory performance in the phosphate containing refractory. The effects of spalling (and corrosive) wear on brick thickness in the gasifier is evident in figure 9, where a direct comparison between conventional brick and phosphate containing refractory materials was made. Note that the phosphate material has approximately one third greater thickness - which would equate to longer service life. Additional tests are underway at other gasifier locations that will help confirm the impact of phosphate additions on slag/refractory service life.

Figure 9. Comparison of conventional (left side) versus phosphate containing refractory (right side) after removal from sidewall test panel in an air cooled slagging gasifier.

SUMMARY

High chrome oxide refractories are used as liners in air cooled slagging gasifiers. These gasifiers use coal and/or petroleum coke as carbon feedstock, and have a short service life due to interactions between the refractory and the slag; resulting in spalling and chemical dissolution of the refractory, premature sample failure, and unpredictable gasifier shutdown. The premature gasifier shutdown impacts gasifier acceptance and use by industry. Because of this, NETL developed and patented (US Patent # 6,815,386) a new phosphate containing refractory material targeting the reduction or elimination of spalling wear. In conjunction with ANH Refractories Co. (Harbison-Walker Refractories Co.), this refractory was scaled-up from the laboratory into commercial production, and is undergoing field trials at a number of gasifiers. A sidewall panel of 24 full sized brick was installed in a commercial gasifier and left in service for 237 days before being removed. A post-mortem evaluation of the test panel indicated a reduction/elimination of surface spalling and internal cracking (that would result in spalling) in the phosphate containing refractory compared to surrounding conventional, non-phosphate containing refractory material. Phosphate additions in the high chrome oxide refractory appear to change how iron oxide in gasifier slags interact with chrome oxide in the refractory, decreasing surface expansion and slag penetration, and reducing refractory loss. The reduction in refractory material loss should translate into longer service life. Larger test panels and evaluation of the phosphate containing refractory at other gasification sites operating with different feedstock and under different gasifier conditions are underway to confirm these observations.

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