FIELD TRIAL RESULTS OF NETL'S PHOSPHATE-MODIFIED HIGH CHROME OXIDE REFRACTORY MATERIAL FOR SLAGGING GASIFIERS

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ABSTRACT

An improved performance, high chrome oxide refractory for slagging gasifier applications has been developed, evaluated in field trials, and placed in commercial production. This refractory was conceived and engineered by the NETL, and produced and evaluated in collaboration with Harbison-Walker Refractories Company. Developed with the goal of reducing slag penetration and the subsequent spalling caused by slag penetration and thermal cycling, this material represents a major step forward in improving the service life of slagging gasifier refractories, and should reduce gasifier downtime caused by this type of failure. Field trial results of the NETL refractory will be discussed, along with a discussion of the known wear mechanisms in this material. The progress of NETL's current research program to develop an alternative, non-chrome oxide refractory liner for slagging gasifiers will also be discussed.

INTRODUCTION

Gasification of carbon containing materials for the production of CO and H_2 (called syngas) has become an important aspect of process generation, feedstock for chemical production, and an environmentally acceptable way of processing low-value wastes from industries such as petroleum refinement. It is a leading candidate for the production of H_2 in a hydrogen based economy that would include fuel cells; and is considered a critical component of advanced power generation technologies such as Integrated Gasification Combined Cycle (IGCC) power production or in the U.S. DOE's near Zero Emissions Advanced Fossil Fuel Power Plants. The gasification process is as follows: $C + H_2O + O_2 \rightarrow H_2 + CO + CO_2 + H_2S$ + minority gases + by products. The primary carbon feedstock materials used in gasification are coal and petroleum coke, or combinations of the two.

Air cooled slagging gasifiers are among the leading technologies used to process these materials, with two examples shown in Figure 1. These types of gasifiers operate in a reducing environment (oxygen partial pressures about 10^{-9}), at temperatures as high as 1575°C, and at pressures that can range up to 7 MPa. A typical slagging gasifier is lined with high chrome oxide refractory materials to protect it from the severe service environment of gasification. The refractory may contain up to 95 pct chrome oxide, and typically last no more than 2 years, with high wear areas failing within 3 months. Refractory failure is usually by slag corrosion/dissolution of the refractory or by slag penetration of the refractory, followed by spalling. Slag originates from impurities (ash) in the carbon feedstock that liquefy during gasification, and are often high in oxides of Si, Fe, Al, and Ca in coal or petcoke feedstock. The slag may also contain elevated levels of K, Na, Mg, Ni, and V; depending on the carbon source (Ni and V tends to originate from petcoke). Slag impacts and can severely limit refractory service life.

Gasifier operators have identified refractory service life as a key barrier to widespread commercialization of gasification technology. Failure of the refractory lining is expensive, both in terms of material replacement costs (as high as $1,000,000) and in lost production (due to gasifier shutdown). Downtimes can range from 5-14 days for lining repair. Users desire a gasifier availability of 85-95 pct for utility applications and more than 95 pct in applications such as chemical feedstock production, with service life of at least 3 years. Failure to meet these goals has impacted the utilization of gasification technology.

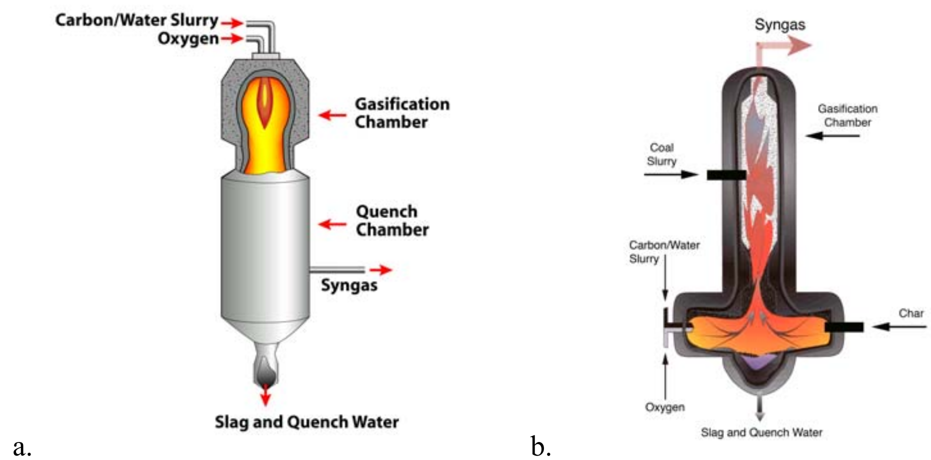


Figure 1 – Two types of air cooled slagging gasifier: a) General Electric design, and b) ConocoPhillips design.

Although refractory liner life is a key roadblock to this technology, only a limited number of research studies have been published recently on the failure of refractories used for slagging gasifiers[1-4]. Operating conditions that effect refractory service life include material throughput, temperature, and oxygen partial pressure. During gasification, ash liquefies at the high temperatures to form slag, which flows down the interior of the gasification chamber, interacting with and infiltrating open porosity in the high chrome oxide refractory liners. This interaction leads to failure of the refractory. The high chrome oxide refractory materials currently used in gasifiers and listed in Table 1 evolved from research in the 1970-1980's funded by U.S. DOE, EPRI, and private industry[1]. This research indicated a minimum of 75 pct Cr_2O_3[3] was necessary to provide the best chemical resistance to gasifier slag corrosion.

Table 1 – Chemical composition of two types of high chrome oxide refractories commonly used in air cooled slagging gasifiers

Property*	Brick Type	
	A	B
Chem. (wt %) - Cr_2O_3	60.4 – 95.1	64 - 87
- Al_2O_3	37.9 – 4.3	3.0 - 15.5
- ZrO_2	NL	6.5 – 11.5
Bulk Density (g/cc)	3.84 – 4.29	4.83 – 4.15
Porosity (pct)	15.1 – 16.7	NL
CCS (MPa)	48.3 – 75.9	NL

* Data from manufacturer's technical publication
NL = Not listed

In this study, post-mortem examination, of refractory bricks removed from service in slagging gasifiers was used to determine interactions between slag components and the Cr_2O_3 and Al_2O_3 in the refractory. These interactions were used to identify and understand phase and microstructural changes that occur in service, and were the basis for developing an improved high chrome oxide refractory material. Emphasis was placed on microstructural changes that occur at the refractory hot face leading to refractory failure. An evaluation is made in this study of the NETL developed and patented phosphate containing high chrome oxide material, and its performance in field trials. Research efforts on developing non-chrome oxide refractories at NETL are also discussed.

EXPERIMENTAL PROCEDURE/RESULTS AND DISCUSSION

Post Mortem Analysis of Conventional Refractory Materials

In cooperation with gasifier operators and refractory manufacturers, NETL conducted post-mortem analyses of refractories removed from commercial gasifiers to determine causes of failure and service life issues needing research focus, as shown in Figure 2.

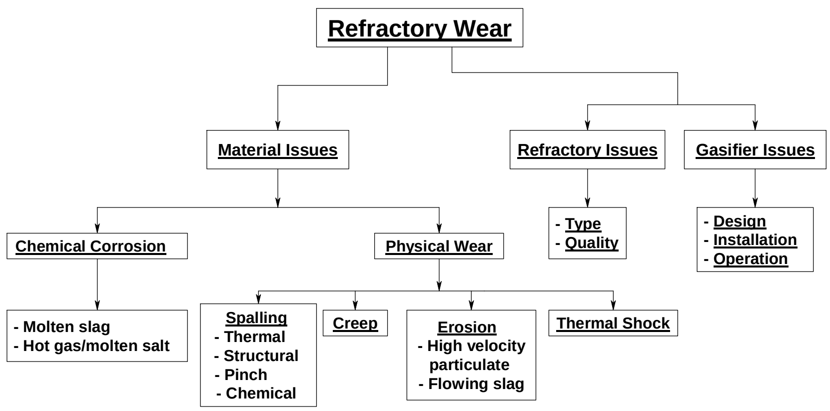


Figure 2 - Cause of failure in slagging gasifiers identified through post-mortem analysis in hot face refractory liners.

Two primary causes of refractory failure were determined from post-mortem studies: 1) refractory corrosion, and 2) spalling. Figure 3 shows the hot face refractory lining located on the sidewall of a gasifier, with widespread surface corrosion and spalling circled (Figure 3a); and with the cross section (interior) of a brick showing deep slag penetration (Figure 3b) and a void associated with spalling in progress (indicated by the arrow on Figure 3b).

Chemical corrosion of a refractory is caused by slag attack at the refractory surface. It is shown in Figure 4 for a SEM backscatter image of a slag/refractory interface after approximately 2000 hrs of exposure to a gasifier slag around 1500^{o}C. Slag is located at the far right of the image in Figure 4 (point 1), and has infiltrated the pores of the refractory (point 5). FeO in the slag interacts with Al_2O_3 from the refractory to form a crystalline phase ($FeAl_2O_4$) on the refractory surface (point 2), which impacts future slag/refractory interactions. Point 3, on the surface of the refractory grain in contact with slag, is in a diffusion zone, with elevated Fe (from the slag) and Cr, and a depletion of Al versus the starting chromia/alumina spinel (point 4). An iron-chrome spinel of fixed Fe/Cr ratio is formed in zone 3.

Corrosive wear is impacted by the relationship between points 2 and 3 at the slag/refractory interface. The surface flow of slag provides a constant source of FeO for the formation of $FeAl_2O_4$ (zone 2), which appears to act as diffusion barrier at the refractory surface, limiting further Fe interaction with the chromia/alumina spinel of the refractory. When the iron oxide/chromia spinel layer at point 3 becomes thicker than about 5-10 mm, it appears to experience chemical spalling, which may accelerate breakup of the grain surface into the slag (observed in the thicker areas of Figure 4). The stability of the layer at zones 2 and 3 are important to refractory wear, and inpact corrosion. The depletion of FeO in the slag as it penetrates pores of the refractory is important because it causes slag viscosity to increase and decreases the ability of the slag to chemically interact with refractory grains.

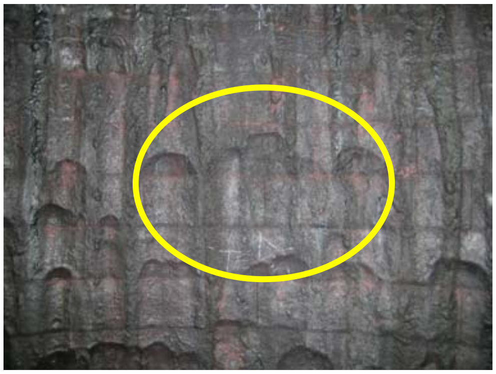
a.  b. 

Figure 3 – Causes of refractory failure in a slagging gasifier. a) Gasifier sidewall with spalling [section circled] and corrosive wear [over the refractory liner surface]. b) Cross section of refractory with a spalling void [see arrow] and deep slag penetration [dashed line].

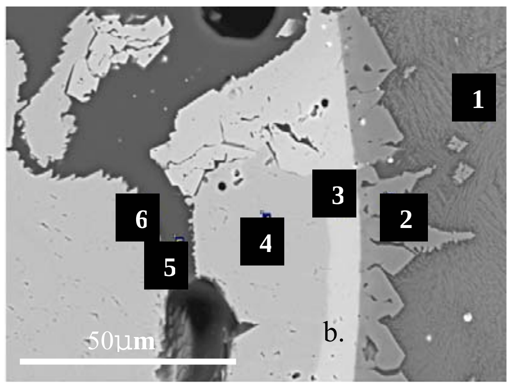
a. 

Figure 4 – SEM micrograph (backscatter) of the slag/refractory interface after approximately 2000 hrs of exposure to a gasifier slag at about 1500^{o}C in a slagging gasifier.

Of the two wear mechanisms shown in Figures 2-4, spalling brings about rapid and unpredictable removal of the refractory surface layer versus the "slow", predictable surface corrosion caused by slag. Spalling wear is most pronounced in specific gasifier locations, such as the sidewalls, and is caused by: 1) slag penetration within the refractory pores and the resulting material property differences between the penetrated versus un-penetrated areas; and 2) by thermal cycling of the gasifier. Spalling leads to the removal of surface material in thicknesses up to 25 mm, and is a cycle that repeats itself, resulting in premature refractory failure. For this reason, the focus of initial NETL research was to improve the spalling resistance by limiting slag penetration in existing types of high chrome oxide refractories.

Phosphate Containing High Chrome Oxide Development

An evaluation of materials to limit slag penetration was conducted using 50 mm cubes. Static cup tests of the porous refractory (12-15 pct porosity) indicated phosphate additions dramatically decreased slag penetration. A 25 mm hole was drilled in the center of samples to a depth of approximately 35 mm, and filled with a granulated gasifier slag. Testing was conducted from 1500-1600^{o}C in an argon environment to approximate the reducing conditions of a slagging gasifier. Figure 5 shows the results of initial cup tests and changes in slag penetration resistance with phosphate additions at 1600^{o}C. Phosphate additions to the chrome oxide refractory were also found to decrease internal cracking, which is visible in the refractory material in Figure 5 (see Figure 5a and 5b, without and with phosphate treatment).

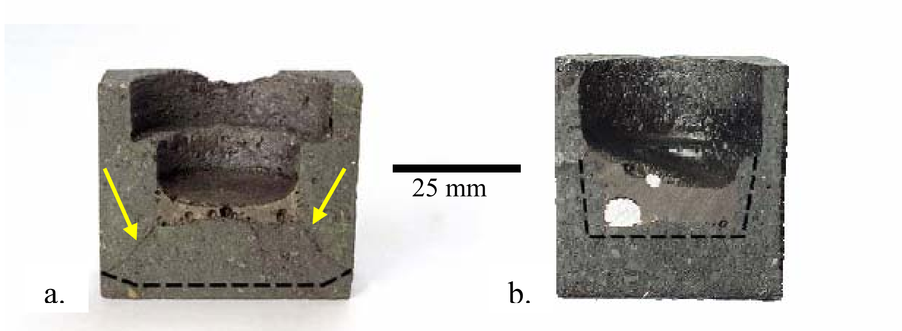


Figure 5 – Cup test results of gasifier slag penetration in high chrome oxide refractories without (a) and with (b) phosphate additions after sample exposure at 1600°C for one hour in an Ar atmosphere. The dashed line indicates slag penetration depth, arrows internal cracking.

Because the cup test is run with everything at a set temperature (isothermal), and used a static rather than a dynamic slag environment, further material evaluation and refinement in a flowing slag with a thermal gradient across the brick was conducted in the rotary slag test[5]. Information from the cup test was used as a tool to eliminate materials or compositions that did not have promise, while rotary slag testing was used to rank materials based on slag penetration and wear. Full sized brick (22.9 cm by 11.4 cm by 7.6 cm) of the phosphate compositions were fabricated at ANH Refractories Company (Harbison-Walker Refractories Company) of Pittsburgh, PA, for rotary slag testing, which was conducted with an inner furnace temperature of 1675°C. Data on the refined phosphate containing NETL and commercial brick compositions is listed in Table 2, and indicates improved slag penetration resistance, improved thermal shock resistance, and comparable slag corrosive wear resistance in the NETL developed refractory versus commercially used liner materials. All other physical properties in the NETL developed material were comparable to, or better than, commercial materials. The improved performance of the phosphate containing high chrome oxide material led NETL to apply for, and be granted, a patent on this material (US Patent # 6,815,386).

Table 2 – Chemical (from product data sheets) and physical properties (from laboratory testing) of Commercial (Com) and NETL developed high chrome oxide refractories

BRICK TYPE:	Com A	Com B	NETL
*Chemistry**			
(Wt %) - Cr_2O_3	90.1	87	92.0
Al_2O_3	9.3	3.0	4.7
ZrO_2	NL	6.5	NL
P_2O_5	NL	NL	3.3

	Com A	Com B	NETL
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	+ 5.2	+5.8	+0.6
– mm penetration	5.2	4.8	1.8

NL = Not Listed
* Chemistry from product data sheets

*[1]= 1550ºC, 50 hr hold
*[2] = 1550ºC, 50 psi, 50 hr hold
*[3] = 1667ºC, 5 hrs of slag feed, 2 ½ rpm

Field Trials of Phosphate Containing High Chrome Oxide Refractory

Because the NETL developed refractory showed comparable-to-superior physical properties to commercial materials, the decision was made for commercial field testing in air cooled slagging gasifiers. Testing targeted the lower cone/throat/slope areas (high corrosive wear, low-to-no spalling) and the sidewall areas (high corrosive wear/high-to-low spalling wear) in two types of gasifies. Test materials were commercially manufactured by Harbison, with installation and material performance documented. A summary of field trials and their status is shown in Table 3, with material testing and evaluation still on-going. The duration of the tests were determined by issues unrelated to the test material performance.

Table 3 – Summary of gasifier field trials on NETL developed, phosphate containing high chrome oxide refractory

Gasifier Type, Feedstock	**Test Sample Location**	**Days Testing***	**Field Trial Status**	**Test Results**
Type A, coal	Lower Cone	17	Completed	Run prematurely ended – inconclusive testing
Type A, coal	Lower Cone	82	Completed	Comparable or slightly better corrosion resistance
Type A, coal	Sidewall	237	Completed	Superior spalling, comparable or slightly better corrosion
Type A, coal/petcoke	Slope	275 +	Underway	Visual – comparable corrosion, unknown spalling
Type A, coal/petcoke	Throat	275 +	Underway	Visual – comparable corrosion, unknown spalling
Type B, petcoke	Unknown	300 +	Completed	Evaluation underway

*Test duration was determined by issues unrelated to test material performance.

Preliminary physical data from field trials indicates the phosphate containing high chrome oxide refractory has superior performance in preventing surface spalling, and has slag resistance equaling, or slightly better than, conventional high chrome oxide refractories. Laboratory examination of these materials following field trials has indicated possible mechanisms by which phosphate additions improve high chrome oxide performance in a gasifier. These mechanisms are as follows: 1) phosphate additions decrease porosity, contributing to a decrease in slag penetration; 2) phosphates promote the formation of a dense Cr_2O_3-FeO spinel solid solution layer at the refractory/slag interface that inhibits slag penetration; 3) phosphate additions promote the formation of an immiscible $Ca_3(PO_4)_2$ phase in the slag, increasing slag viscosity and decreasing slag corrosivity; and 4) phosphates promote the formation of lower melting bond phases that aid in thermal shock resistance.

The sidewall test panel dramatically demonstrates the influence of phosphate additions on high chrome oxide material performance, as shown in Figure 6. The 24 brick test panel area, faintly outlined in Figure 6a, had no spalling and appeared to have a protective effect on the refractories above it, whereas severe spalling occurred below the test panel. A direct comparison of the remaining thickness of brick removed from the gasifier in Figures 6b (conventional refractory with no phosphate additions outside the test panel) and 6c (phosphate containing refractory within the test panel) illustrates the improved performance of the phosphate containing refractories, which had no internal cracking and were much thicker than conventional refractories, indicating longer potential service life.

Spalling and internal cracking of the conventional versus the improved refractory in the test panel is shown in Figure 7, which shows the cross section (from the hot face to the cold face – left to right) of the phosphate containing test panel brick and surrounding conventional refractory. Internal cracking leading to spalling was observed in all conventional high chrome oxide materials shown, in addition to the irregular surface resulting from spalling in many brick. Conventional refractory materials below the test panel were observed to be much thinner and contained internal cracks, both evidence of spalling. Conventional refractory materials above the test panel contained only the internal cracks. The test panel materials containing the phosphate additions showed no evidence of internal cracks or spalling, and were much thicker than conventional refractory materials below the test panel.

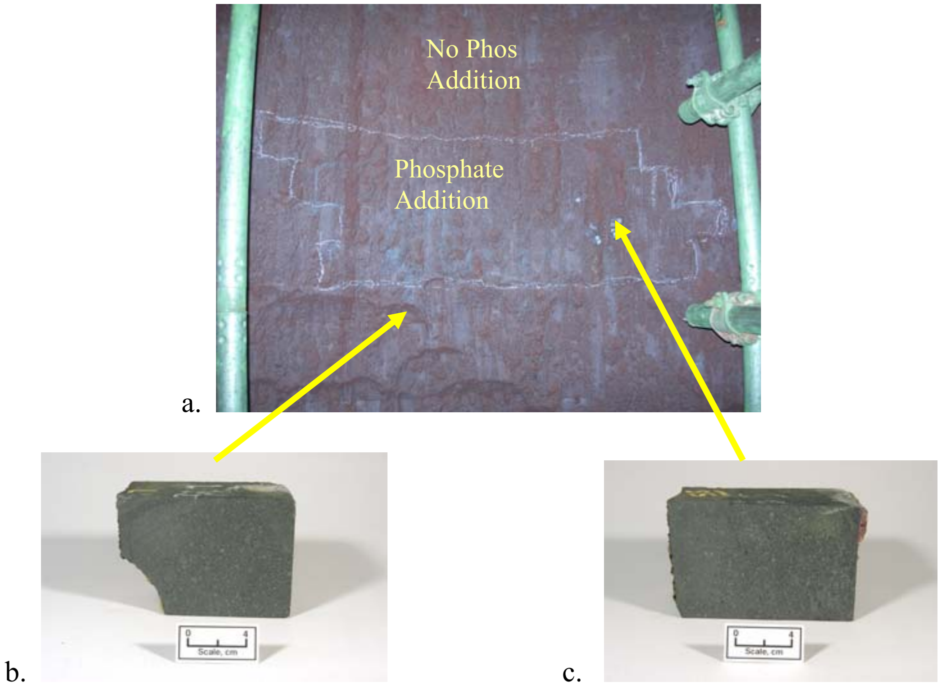


Figure 6 - Sidewall test panel (24 brick circled in white) after 237 days of service in an air cooled coal slagging gasifier environment. a) Test panel prior to removal. Note spalling below the test panel. b) Cross section of traditional refractory below the test panel. Brick had no phosphate additions. c) Cross section of phosphate containing refractory. Note refractory is thicker, has no internal cracking or spalling.

In gasifier zones where spalling is the major refractory wear mechanism, the results of field trials indicate that the phosphate containing high chrome oxide refractory could improve service life by 50 pct or greater over conventional refractories, based on the remaining thickness of test materials. This would increase refractory service file from 2 to 3 years, for example. The observed improvement in performance has resulted in Harbison-Walker Refractories Company signing a licensing agreement with NETL to manufacture and market the novel refractory composition, which is being produced under the product name of Aurex® 95P.

Non-Chrome Oxide Refractory Development

Non-chrome refractory research is being conducted at NETL because it is highly unlikely that one type of refractory will have comparable or suitable performance in all gasifier environments and because a re-evaluation of low-chrome or no-chrome oxide refractories from research conducted in the 70's and 80's is also merited for possible gasifier liner materials. Gasifier feedstock of the future may include mixed carbon sources such as biomass, which is high in alkali and alkaline earths, and which could cause the formation of +6 Cr in the high chrome oxide refractories currently used as gasifier liners. This hazardous material is not known to be an issue with current gasifier carbon feedstock, but could become an issue with biomass additions. It is important to note that many improvements in refractory technology have occurred since gasification research was conducted in the 70's and 80's, when high Cr_2O_3 refractories were identified as the liner material of choice. Raw materials of higher purity and of controlled grain size are now available, and significant improvements have occurred in refractory bonding technology since the earlier work. In addition, low or no chrome oxide refractories have an advantage over the high chrome oxide materials currently used in that they can be installed as monolithic cast or gunned linings – greatly reducing gasifier downtime.

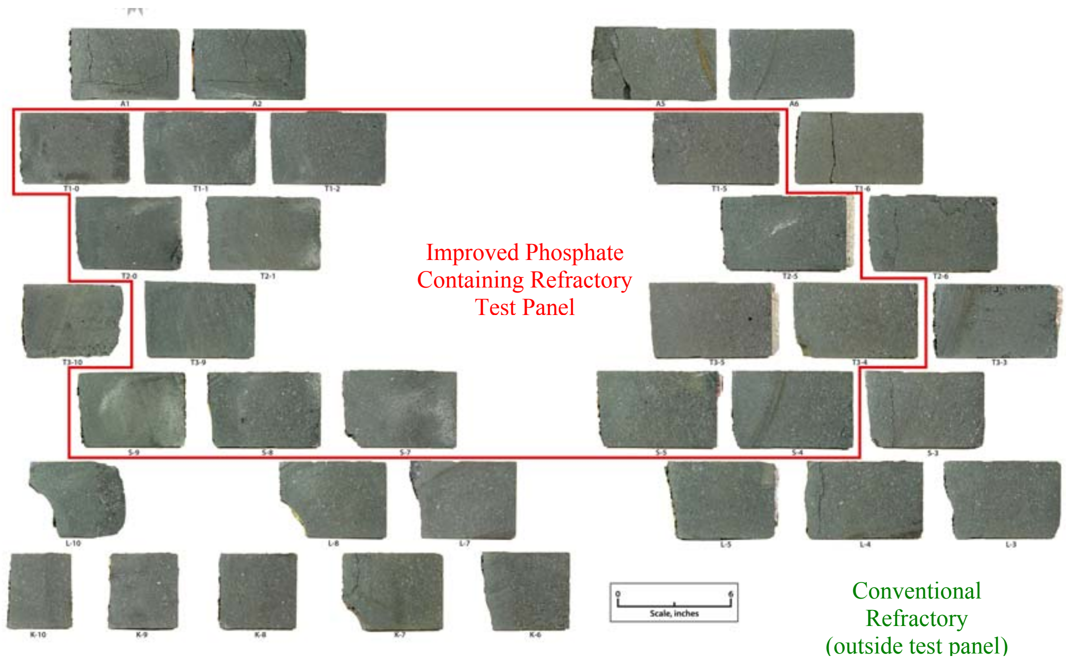


Figure 7 – Cross section of refractory materials in sidewall test panel. Test panel is composed of phosphate containing high chrome oxide refractory (surrounded by red) versus conventional high chrome oxide refractory materials. Brick are cut in half going from the hot face (on the left) to the cold face of the test refractory materials. The conventional refractory materials are thinner and have internal cracks or have spalled versus the phosphate refractory materials.

Non-chrome oxide research at NETL has based material selection on thermodynamic considerations, phase diagram compatibility, laboratory research, and a review of past research. It is important to remember that most coal slags are "acidic", being high in Al_2O_3 and SiO_2; and that only a few non-chrome materials, including ZrO_2, have the potential to resist slag corrosion as well as Cr_2O_3. A refractory material must be designed with an engineered microstructure that helps to resist material dissolution into the slag and slag penetration in the microstructure. At NETL, over 250 slag cup tests have been conducted to evaluate a variety of different raw materials or refractory compositions. Cup tests using 25 mm cubes of two materials, one developed at NETL and a commercial material, are shown in Figure 8. Sample testing was conducted at 1600°C for one hour using coal slags in an argon (non-oxidizing) environment. A total of three compositions developed at NETL and three commercial compositions are undergoing scale-up for evaluation in a flowing slag using the rotary slag test[5].

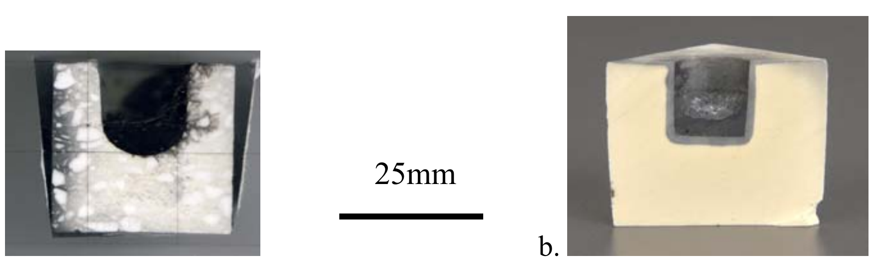
a.  b.

Figure 8. Non-chrome oxide 25 mm "cup" tests samples exposed to gasifier slag at 1600°C in an argon atmosphere for one hour. Once exposed, samples are cut in half to show slag penetration. a) NETL developed microstructure showing slag penetration. b) Commercial microstructure shown slag penetration.

CONCLUSIONS

The mechanisms of failure in high chrome oxide refractory materials removed from slagging gasifiers were evaluated through post mortem analysis. The major failure causes were corrosion and/or spalling of the refractory hot face surface. NETL targeted the reduction or elimination of spalling in the refractory materials as a way to reduce wear, and developed a phosphate composition with improved spalling resistance. In cooperation with Harbison-Walker Refractories Company, full size brick of this refractory composition were produced and installed in commercial gasifiers for field trails. Testing was conducted in two different types of gasifiers; and used coal, petcoke, or combinations of the two as carbon feedstock. Test materials were evaluated in a number of gasifier locations, with the most comprehensive study conducted on a sidewall for 237 days. Results indicated the phosphate containing refractory had at least a 50 pct improvement in service life over conventional materials in this sidewall application (where spalling was the primary wear mechanism) based on an estimation of remaining refractory material. The improved refractory material has been licensed to Harbison-Walker Refractory Company for commercial production. Potential non-chrome oxide refractory compositions are under development for use in slagging gasifiers, with several indicating promise in early laboratory testing.

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