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AN ANALYSIS OF THE CAUSES OF FAILURE IN HIGH CHROME OXIDE REFRACTORY MATERIALS FROM SLAGGING GASIFIERS

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ABSTRACT

High Cr_2O_3 refractory materials are used to line the hot face of slagging gasifiers. Gasifiers are reaction chambers that convert water, oxygen, and a carbon feedstock into CO, H_2, and methane at temperatures as high as 1575°C and pressures up to 1000 psi. Ash in the carbon feedstock liquefies, erodes and corrodes the gasifier's refractory liner, contributing to liner failure within a few months to two years. The failure of a refractory liner decreases a gasifier's on-line availability and causes costly system downtime and repairs. Many factors contribute to refractory lining failure, including slag penetration and corrosion, thermal cycling, gasifier environment, and mechanical loads. The results of refractory post-mortem failure analysis and how observations relate to gasifier service life 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 Vision 21 Fossil Fuel Power Plant. Gasifiers are also used to produce chemicals that serve as feedstock for other industrial processes, and are considered a potential source of H_2 in applications such as fuel cells. An IGCC gasification chamber 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. An example of an IGCC gasification system with an air cooled slagging gasifier is shown in Figure 1. IGCC systems are expected to play a dominant role in meeting the Nation's future energy needs. A distinct advantage of gasifiers is their ability to meet or exceed current and anticipated future environmental emission regulations. Also, because gasification systems are part of a closed circuit, gasifiers are considered process ready to capture CO_2 emissions for reuse or processing should that become necessary or economically feasible in the future.

The service life of refractory liners for slagging gasifiers has been identified by users as a critical barrier to IGCC system economics and to gasifier reliability and on-line availability[1]. The refractory lining contains the harsh, high temperature/pressure gaseous environment, an environment that includes molten slag originating from impurities in the carbon source. Coal, petroleum coke, and mixtures of them are the primary carbon sources, although other materials such as biomass waste and black liquor are also being explored as carbon feedstock.

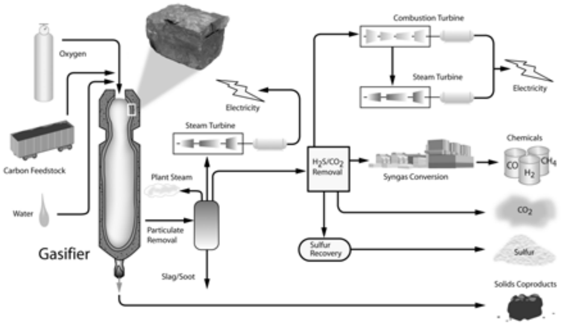


Fig. 1: Integrated Gasification Combined Cycle gasification system.

Refractory liners for slagging gasifiers are typically of two types, 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, which indicated high chromia content in a refractory (75 wt pct or higher) gave superior performance to all other refractory materials tested[2].

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 the environment for refractory spalling to occur. Refractory dissolution and spalling are thought to be the two primary wear mechanisms of refractories. The current generation of refractory liners used in a gasifier must be replaced within 3 to 24 months of installation because of wear. Refractory wear by dissolution is highly dependent on gasifier carbon feedstock, material throughput, gasification temperature, usage time, and system maintenance. Wear by spalling is influenced by slag composition and penetration depth, gasifier cycling, and rapid temperature changes; and leads to portions of a liner peeling from the working face lining.

Predicting when a refractory lining needs replacement is difficult, with the cost of replacing all or part of the lining exceeding $1M, depending on the extent of the necessary repairs. Compounding material 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 that the system be completely shut down, and under the best of circumstances takes about 12 days; involving cool down (5-7 days) and teardown and repairs for a partial reline (3 days) or a full reline (7-10 days). Industry would like refractory materials that have a predictable and improved service life of 50 pct.

ARC's program goal is to attain improved service life and reliability in refractory liners through materials research. This paper discusses post-mortem analysis of gasifier refractories, information which can be used to improve gasifier service life.

EXPERIMENTAL PROCEDURE/RESULTS

Postmortem refractory material failure analysis was conducted on hot face gasifier materials and compared to typical high chromia refractory materials used in gasifiers and listed in table 1. Porosity in these materials is about 12 -15 pct.

Table 1 Chemical composition of two high chromia refractories used in slagging gasifiers (wt %)

	Brick Type	
Element	A	B
Cr_2O_3	90.3	87.3
Al_2O_3	7.0	2.5
SiO_2	0.3	0.2
ZrO_2	0.01	5.2
$Fe^{+2 \text{ and } +3}$	0.23	0.28
CaO	0.28	0.03
MgO	0.28	0.12

A general evaluation of the causes of refractory wear based on studies of samples removed from slagging gasifiers is shown in figure 2. Other issues not listed may cause refractory wear. Gasifier issues impacting wear include temperature, slag chemistry, slag viscosity, carbon feedstock throughput, and gasifier cycling. Of the causes listed, chemical corrosion (dissolution of the slag) and spalling have been found to be the predominant cause of wear that can be controlled through engineered refractory composition. Wear related to thermal cycling is typically caused by maintenance or repair of the gasifier or downstream components of the gasification system.

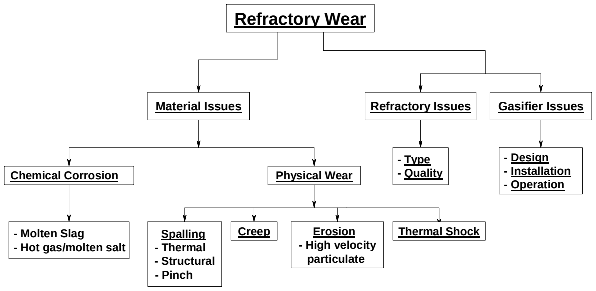


Fig. 2: Causes of refractory wear.

As viewed from the interior of a gasifier on the hot face, an example of wear dominated by chemical corrosion is shown in figures 3. Chemical corrosion involves the dissolution of the refractory in the slag as it flows over and/or penetrates within the refractory pores, and is thought to be one of the main wear components. It can also lead to the removal of large refractory particles or grains as the bond phase between them is weakened or removed. Chrome oxide can make up to 95 wt pct of the hot face refractories (due to zoning), and is considered to be an excellent refractory material because it ties up some of the gasifier slag components as high melting phases (solid solutions or spinels) and because it is highly insoluble in the molten slag during normal gasifier operation. The refractories used to line a gasifier are not fully dense, in part because of thermal shock associated with the refractory material in the application. Because of the porous nature of chrome oxide refractories and the small thermal gradient across them during service, slag can penetrate deeply within the refractory, setting up the basis for refractory wear by spalling and by chemical corrosion. If the bond phase between grains is attacked by slag, slag penetration into the refractory can cause dissolution or weakening of grain bonds, allowing the possible release of refractory material into the surface flowing slag.

Fig. 3: Refractory surface wear dominated by chemical corrosive (dissolution).

Refractory wear by several types of spalling in a gasifier is shown in figure 4. The pinch spalling (a) probably originates from compressive hoop stress due to the vessel steel shell. Thermal spalling (b) visible on the edge of a is caused by rapid temperature fluctuation in the vessel, and structural spalling (c) may be due to a complex combination of such factors as shell stress loading, slag infiltration, thermal cycling, or long term creep. As shown, pinch spalling and thermal spalling occur in isolated areas of the gasifier. Structural spalling can occur throughout the gasifier, and is one of the common wear mechanisms.

Fig. 4: Spalling examples in gasifier refractory; a) pinch spall along refractory joint, b) thermal spall, and c) structural spall.

Bakker[3] discussed how spalling can incrementally remove large portions of a gasifier refractory, rapidly shortening refractory service life as large pieces of material are physically removed versus a slow material dissolution in slag. The effect of both chemical dissolution and spalling on the wear of a refractory is shown in figure 5. Factors such as the gasifier operational temperature, thermal cycling of the gasifier, and slag infiltration into a refractory have a pronounced influence on refractory spalling.

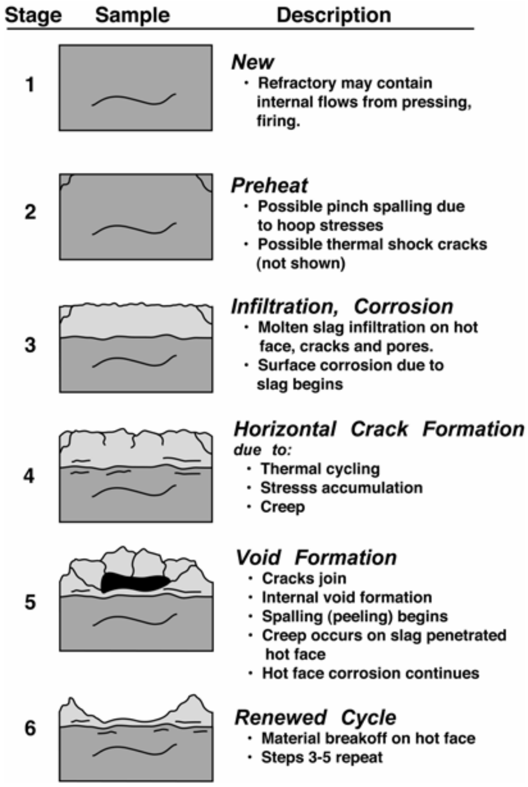


Fig. 5: Stages of refractory wear

The degree of spalling in a refractory can be quite large, as is shown in figure 6. Note that slag has penetrated to a depth of almost 4 cm from the hot face, and that a large interior void is present approximately approximately 1.5 cm from the surface – a void that was not visible from the gasifier interior. Schott[4] explained some of the variables causing spalling in his stress analysis of a cylindrical vessel with a constrained refractory lining. As noted earlier, besides the cycling of a vessel which contributes to the spalling, factors such as the heating and cooling rate of a gasifier, slag penetration depth, long term creep, and the oxidation/reduction of a furnace atmosphere play significant, but different roles in refractory performance. The degree of spalling varies from gasifier to gasifier based on plant operation practices.

Fig. 6: Spalling in a refractory material

A cross section of a refractory removed from a gasifier was evaluated by SEM microstructural analysis and for chemistry, crystalline phases, and thermal expansion characterization. This sample is shown in figure 7. Chemistry and crystalline phases were analyzed on a large core approximately 3 cm in diameter and 8 cm in depth. The large core was taken from the hot face (slag exposed surface) through the cold face, where no slag had penetrated. This cored sample was cut into discs parallel to the hot face at approximate 5 mm intervals, which were used for the analysis. Thermal expansion samples were also cored parallel to the hot face of the refractory in two areas, where the slag had infiltrated (labeled hot face) and at the cold face, where the slag had not infiltrated (labeled cold face).

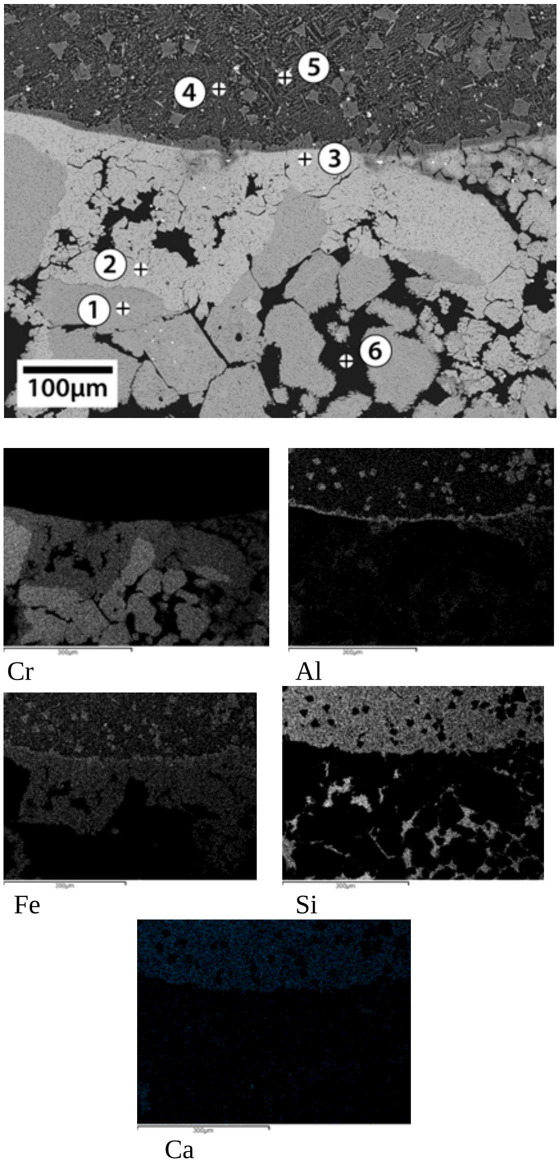
Fig. 7: Location of test samples removed from a Gasifier refractory sample

The chemistry of the high chrome oxide refractory versus depth from the hot face to the cold face is shown in table 2. Eskolaite (Cr_2O_3) was the primary crystalline phase present in all layers except for the hot face (HF to 2.3 mm section), which had a crystalline $(Fe_{0.6},Cr_{0.4})_20_3$ spinel phase present. In evaluating the chemistry of table 2, it is of interest to note that iron is predominately tied up on the hot face of the refractory, although smaller amounts are found to have penetrated the porous refractory to a depth of 38.9 mm. Evidence of the surface reaction of iron is also shown in a hot face to cold face cross section of the slag/refractory analyzed by SEM and shown in figure 8. The concentration of CaO in table 2 increases with depth, peaking in concentration from about 25-39 mm, than decreasing to background concentration at approximately 48.0 mm. SiO_2 decreases in the sample from the hot face to a depth of about 53 mm, after which it is present at a background concentration in the sample. These compounds are carried by the slag into the porous refractory, which reacts with some components in it. It is thought that the viscosity of the slag increases with depth of penetration as it reacts with the refractory, limiting slag penetration. Further evaluation of the different layers of slag is underway to confirm this.

Distance from Hot Face (mm)	Bulk Chemistry (wt pct)				
	Cr_2O_3	Al_2O_3	SiO_2	CaO	Fe
H.F. to 2.3	80.0	10.8	5.4	0.3	1.6
6.9	84.2	10.2	3.9	0.3	0.4
11.4	83.9	10.7	3.2	0.4	0.4
16.0	87.7	10.3	3.5	0.5	0.3
20.6	83.9	10.3	3.0	0.5	0.3
25.1	83.5	10.7	0.2	0.6	0.3
29.7	84.3	10.4	2.7	0.6	0.3
34.3	83.5	10.4	2.8	0.6	0.4
38.9	82.7	10.0	1.6	0.6	0.3
43.3	83.9	9.3	2.3	0.5	0.2
48.0	85.4	9.6	0.6	0.1	0.2
52.7	85.7	10.5	0.9	0.2	0.2
57.2	86.1	10.5	0.2	0.0	0.2
61.7	86.1	10.6	0.2	0.0	0.2
127	87.4	9.4	0.2	0.2	0.2

Table 2. Chemistry of high chromia refractory versus depth (from the hot face to the cold face).

The SEM backscatter image and elemental maps in figure 8 indicate that chrome and iron interact at the refractory surface; that alumina builds up a concentrated layer at the slag/refractory interface; and that the slag that penetrates into the refractory contains silicon, aluminum, and calcium. The reason for the buildup of alumina on the slag/refractory interface is being studied. It is of interest to note that where the slag interacts with the high chromia/alumina refractory, a fractured surface appears to form. The compound formed is probably a solid solution of Cr_2O_3 and FeO. The impact of this on slag wear is being evaluated.



Point	Element (wt pct)				
	Cr	Al	Fe	Si	Ca
1 – ref. grain	63.8	5.7	-	-	-
2 – ref. grain	37.8	5.6	25.2	-	-
3 – ref. grain	39.9	3.5	24.0	-	-
4 - slag	-	7.2	21.1	23.2	3.5
5 – crystal slag	-	27.0	31.1	-	-
6 – interior slag	1.3	8.0	1.4	32.7	1.6

Fig. 8: SEM backscatter imaging and elemental mapping of a cross section of spent refractory.

Thermal expansion of samples taken from the hot face (slag infiltrated area) and cold face (non-slag infiltrated area) of the refractory in figure 7 had the following linear slopes between 100^o and 1300^oC when run in an inert gas of He:

Hot face: 8.18 x 10^{-6} mm/mm/^{o}C
Cold face: 7.68 x 10^{-6} mm/mm/^{o}C

The difference between these two is 6.5 pct, which could contribute to the spalling, along with other factors previously noted. The effect of changes in the oxidation/reduction behavior of sample on expansion is also being investigated because of the known problems with valance changes of iron in chrome/magnesite refractories[5].

CONCLUSIONS

The wear of high chromia/alumina refractories used as the hot face liners in air cooled slagging gasifiers is predominately caused by surface corrosion and spalling of the refractory. Iron present in the slag interacts with chrome oxide in the refractory, with a slag rich in silica, alumina, and calcia penetrating into the interior of the refractory, setting up the basis for spalling to occur. A number of possible variables impacting spalling were identified, including thermal cycling, heating rate, thermal expansion mismatches between the slag penetrated/not penetrated layers, long term creep during service, and oxidation/reduction. Additional research to identify these variables is underway.

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