THE WEAR AND CORROSION OF HIGH CHROME OXIDE LININGS USED IN AIR-COOLED SLAGGING COAL GASIFIERS

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ABSTRACT

Gasifiers are high temperature, high pressure containment vessels used to convert carbon feedstock; such as coal or petcoke, into a synthesis gas (also called syngas) composed primarily of H_2 and CO. Syngas produced by gasification is used as a fuel in energy production, as a raw material feedstock for chemical synthesis, and can be a source of H_2 for a hydrogen based economy. Air cooled slagging gasifiers, one of several gasifier types used in industry, typically operate at temperatures between 1325-1575^{o}C, and at pressures between 300-1000 psi. They are lined on the hot face with high chrome oxide refractory materials; which may contain up to 95 wt pct chrome oxide, with possible additives of zirconia and alumina also present. Impurities in the carbon feedstock exist in many forms, and can be oxides of Si, Fe, Ca, Al, Na, and S in coal; with additional elements, such as Ni and V, present in petcoke. Depending on the feedstock source, the quantities of impurities generally range from one to over ten pct; leading to ash waste quantities reaching 100 tons/day, or more, in the operation of a single gasifier. Because of the high temperatures used during gasification, the ash by-products liquefy and react with, or penetrate the refractory liner pores; leading to refractory wear and corrosion, and ultimately, premature brick failure. This paper will discuss interactions between slag components and gasifier refractories, with post-mortem analysis of refractory liner failure being presented from systems using coal as a carbon feedstock.

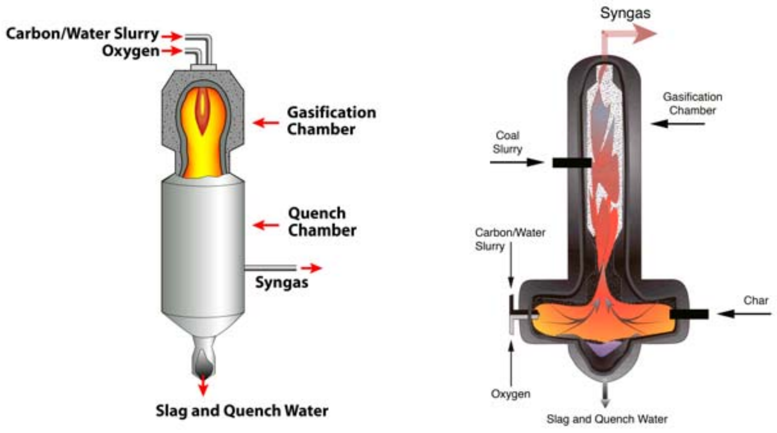
INTRODUCTION

Gasification as a modern high temperature, high pressure industrial process was first used by the oil industry in the 50's to process low value petroleum and by-products from petroleum processing into a usable product[1]. Since that time, gasification has expanded to other uses; including power generation, the production of CO and H_2 feedstock for use by the chemical industry (for applications including the production of fertilizer or Fischer Tropsch liquids), and as a leading candidate for H_2 production in a hydrogen based economy. As a process, gasification converts a carbon feedstock (typically methane, coal, or by-products from petroleum processing such as petcoke) into CO and H_2 (called synthesis gas or syngas). Several types of gasifiers are used by industry for gasification; and include dry ash gasifiers (slag does not fuse due to the low temperature of operation), water cooled entrained bed slagging gasifiers (operate at temperatures that create a molten slag from ash this is contained by a water cooled refractory liner), and the air cooled entrained bed slagging gasifiers (these types operate at temperatures were ash liquidifies into molten slag that but slag flows on an air cooled versus a water cooled refractory liner surface). Variables in gasification include the type of carbon feedstock and the associated impurity levels, the required syngas composition, and operational parameters of the gasifier (i.e. related to the gasifier design). Two types of air cooled slagging gasifies used in industry are shown in figure 1; the GE* gasifier (1a) and ConocoPhillips* gasifier. Figure 2 is a generic cross section of a gasifier showing molten slag (originating from mineral impurities) flowing down the hot face refractory lining and interacting with it.

In practice, a gasifier is a high temperature reaction vessel used to contain reactions between carbon feedstock, oxygen, and water (steam). Gasification occurs in a pressurized environment (typically between 400 and 1000 psi) with a shortage of oxygen necessary for theoretical combustion (gasification occurs in a reducing environment with an oxygen partial pressure between 10^{-7} and 10^{-9} atm) at high temperature (typically between 1325 and 1575°C). The general gasification reaction is as listed below:

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

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



a) b)

Figure 1: Two types of air cooled slagging gasifier used for syngas production. a) GE* design. b) ConocoPhilips* design.

(*Use of manufacturer's names in this paper does not constitute endorsement, and is for identification purposes only.)

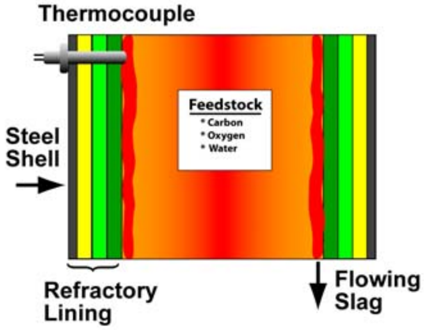


Figure 2: Cross section of a gasification chamber showing molten slag flow down the sidewall.

The hot face of an air cooled slagging gasifier is lined with high chrome oxide refractory material of the types listed in table 1. This environment involves not only hot corrosive gases, but includes slag formed from impurities within the carbon feedstock that liquefy into slag at the elevated processing temperatures. The liners for air cooled slagging gasifiers are based on research conducted during the mid 70's to mid 80's that was a combined effort of DOE, EPRI, the refractory industry, and gasifier users[2-5]. This research identified high chrome oxide refractories as the liner material of choice. Unfortunately these materials have not met the service life requirements of the gasification industry, failing between 3 and 24 months, after which the gasifier is taken out of service for between 4 and 21 days while a new lining is installed or repairs are made.

Gasifier slag originates as impurities in the carbon feedstock that become molten slag at the gasification temperature, and are the primary cause of refractory failure. Impurities typically compose less than one pct of petcoke, and can be 10 pct or more of coal. The carbon feedstock is ground to about 100 microns or less in particle size, after which it is injected with water and oxygen under high pressure into the gasifier. The air cooled slagging gasifier designs shown in figures 1a and b can process over 1400 tons/day of a carbon feedstock, producing large quantities of slag from the mineral impurities (up to 100 tons or more tons per day). This waste product must exit through the base of the gasifier as a liquid or it will clog the exit port, causing operations to cease. The molten slag generated by ash is a corrosive liquid that interacts with the refractory lining; producing new mineral phases, causing chemical dissolution of the refractory material, and penetrating the porous refractory lining; all contributing to premature refractory lining failure.

Table 1: Chemical composition and physical properties of high chrome oxide refractories commonly used in air cooled slagging gasifiers

Property	Brick Type	
	A	B
Cr_2O_3	90.3	87.3
Al_2O_3	7.0	2.5
ZrO_2	0.01	5.2
Bulk Density (gms/cc)	4.21	4.07
Porosity (pct)	16.7	16.5
CCS (MPa)	48.3	66.9

*Data from manufacturer's technical data sheet

In general, the operational temperature of gasification in an air cooled slagging gasifier is dependent on the ash chemistry and its viscosity. Ideal operation is in a narrow temperature range that allows the slag to exit the gasifier as a fluid and not build up in the base exit port, yet at a temperature low enough to minimize chemical interactions with the refractory liner. An average chemistry of approximately 300 US[6] coal samples from across the US are listed in table 2, and data from a limited number of petcoke slags[7-9] are listed in table 3. With interest growing in mixed feedstock of coal, petcoke, and/or biomass; understanding and controlling slag chemistry is important for optimal gasifier operation. From table 2, it is evident that coal contains varying but high percentages of oxide materials of Si, Al, Ca and Fe; and from table 3, that petcoke contain these oxides in addition to high levels of Ni and V oxides. Although not listed, biomass can vary extensively in ash percentage and chemistry depending on the source; but is typically high in silica, alkali, and alkaline earths.

Table 2: Range of chemistry found in over 300 U.S. coal slags due to mineral impurities [6].

Material	Weight Percent			
	Max.	Min.	Avg.	Std. dev.
SiO_2	68.5	7.1	43.6	16.4
Al_2O_3	38.6	4.1	25.2	10.2
Fe_2O_3	69.7	2.1	17.0	11.2
CaO	45.1	0.5	5.8	6.6
MgO	8.0	0.1	1.2	1.1
K_2O	3.5	0.2	1.4	0.7
Na_2O	6.5	0.3	0.9	0.6
TiO_2	3.7	0.4	1.4	0.8

Gasifier operators have identified refractory service life as the most important barrier to widespread commercialization of gasification technology[10]. 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 5-21 days for lining repair. Gasifier users desire an 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 desired. Failure to meet these goals has impacted the utilization of gasification technology.

In this study, post-mortem examination of high chrome oxide refractory brick removed from service in air cooled slagging gasifiers using coal as a feedstock will be discussed, with emphasis on slag/refractory interactions that lead to hot face refractory failure.

Table 3: Range of chemistry found in select petcoke slags due to impurities [7-9]

Material	Weight Percent			
	Max.	Min.	Avg.	Std. dev.
SiO_2	18.9	3.1	14.1	8.7
Al_2O_3	9.4	0.5	4.8	2.8
Fe_2O_3	31.6	1.2	7.2	9.3
CaO	11.9	2.0	5.4	3.8
MgO	5.1	0.3	1.0	1.6
K_2O	0.7	0.3	0.5	0.4
Na_2O	2.3	0.1	0.8	0.8
TiO_2	0.6	0.2	0.3	0.2
NiO	11.4	2.9	8.4	3.2
V_2O_5	79.4	30.2	57.0	19.5

POST-MORTEM ANALYSIS OF SPENT HIGH CHROME OXIDE REFRACTORIES

BULK STRUCTURE

Refractory wear in slagging gasifiers is caused by a number of factors, as shown in figure 3. Slag corrosion and spalling are the primary wear mechanisms, but operational issues; such as the frequency of gasifier cycling, gasification temperature, heating and cooling rates, and ash chemistry and quantity; interact to influence the rate of refractory wear. Spalling causes the most disruptive and least predictable wear to a gasifier operation.

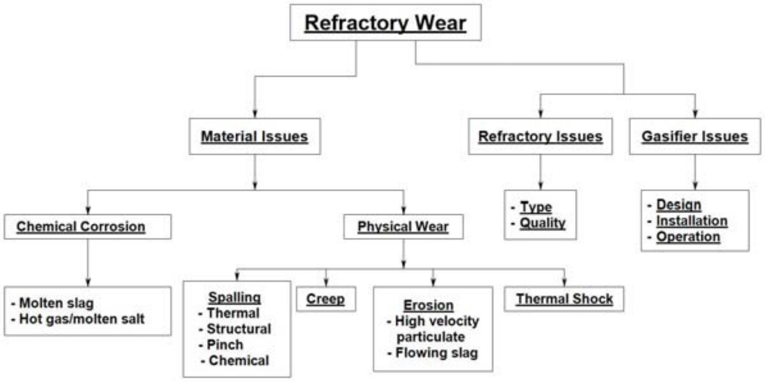


Figure 3 – Causes of wear in a refractory material when used in a air cooled slagging gasifier.

The impact of spalling on refractory wear in a gasifier is shown in figure 4a, where different stages of spalling on the slope/throat intersection in a gasifier are shown. The high Cr_2O_3 samples shown had over 2,000 hours of service at temperatures in the range of 1400-1500^{o}C. Note the rough surface appearance of the sidewall refractories, with different thicknesses on the refractory surfaces. Figure 4b shows a cross section of a refractory take from a gasifier sidewall, where similar rough surface effects were noted. The cause of spalling is noted by an arrow, which points to a large crack spanning the brick cross-section parallel to the hot face. Cracks form beneath the surface of the refractory in the slag infiltrated area, and link together. The surface pieces can separate from the refractory during use because of poor intergrain bonding. The thickness of spalled refractory material can range from the 2-5 to 30 mm.

a. b.

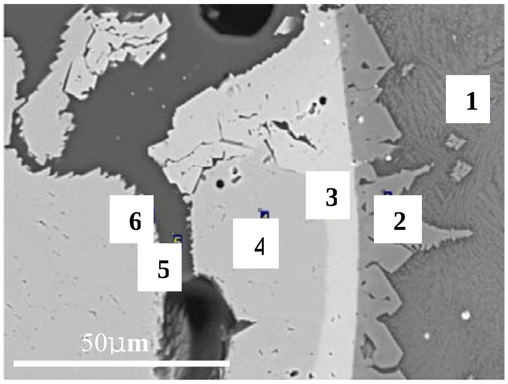
Figure 4 – High chrome oxide refractory with over 2000 hrs of service from 1300-1500^{o}C. a) Surface wear is caused by corrosion and spalling. Note the cobbled appearance, which is due to spalling. b) Cross section of a high chrome oxide refractory showing spalling as it occurs. (arrow points to spalling crack, dashed line to maximum depth of slag infiltration.)

Spalling rapidly removes protective refractory material from the gasifier interior, shortening the lining's service life and leading to premature shutdown of the gasifier for repair. It is a process that repeats itself throughout a gasifier's service. Spalling can originate from many different causes, as is shown in figure 3. In the air cooled slagging gasifiers studied, structural spalling is one of the most disruptive forms of spalling. It is caused by slag penetration into the porous microstructure (≈16 pct) of the weakly bonded high chrome oxide refractory material. During service, slag can penetrate to depths of 35 mm or more below the hot face (see figure 4b), with depth of penetration limited by compositional changes occurring in the slag that increase slag viscosity, and by the temperature drop in the refractory from the hot face to the cold face. The removal of spalled material from the surface of a refractory causes the highly irregular hot face visible on the refractory hot face shown in figure 4a.

MICROSTRUCTURE ANALYSIS

A SEM backscatter image of the slag/refractory interface in a 90 wt pct chrome oxide/10 wt pct alumina refractory after approximately 2000 hrs of exposure to a coal gasifier slag from 1400-1500^{o}C is shown in figure 5a, along with the chemistry and crystalline phases (or possible phases) at points 1-6 (figure 5b). Slag is located at the far right of the image in figure 5a (area around point 1), and has infiltrated the pores of the refractory (through point 5). The slag away from the refractory surface can form any of a number of crystalline components on cool down, with some types indicated in figure 5b. As the slag infiltrates pores, a decrease in Fe and an increase in Si are noted (point 1 versus 5).

A crystalline phase is identified on the surface of the refractory at point 2 (at the slag/refractory interface), which is high in Al and Fe (hercynite - $FeAl_2O_4$). It is not clear if this layer crystallizes from the slag on cool down or if it exists at gasification temperature; and what is the source of aluminum in the layer. Point 3, on the surface of the refractory grain, is in a diffusion zone, with high levels of Fe and Cr, and is lower in Al versus the starting chromia/alumina solid solution (point 4). FeO from the slag interacts with Cr_2O_3 at the surface of the refractory to form an iron-chrome spinel of fixed composition ($FeCr_2O_4$). The relationship between areas in points 2 and 3 impacts surface wear. Indications are that the Al in the chromia/alumina refractory grain diffuses towards the grain surface when in contact with slag, interacting with slag Fe to form a specific compound ($FeAl_2O_4$). The flow of slag over the refractory surface provides a constant source of FeO for this interaction. If this mechanism occurs, the rate of Al, Fe, and Cr diffusion and compound formation in the surface layers impact layer thickness and refractory wear. It appears when the iron oxide/chromia spinel layer formed at point 3 becomes thicker than about 5-10 mm, it begins to experience chemical spalling, which may accelerate the breakup of the refractory surface into the slag (observed in the thicker areas of figure 5a), versus if chemical dissolution was the only factor in surface corrosion. The cause of chemical spalling may be volume changes associated with the formation of new spinel phases. Iron content is lower in the slag that has penetrated the refractory grain (point 5 versus point 1) because it has interacted with the refractory grain surface to form spinel as it penetrates the refractory, changing slag chemistry, which causes an increase in slag viscosity (due to higher Si and lower Fe content), and causes a decrease in the ability of the slag to chemically interact with the refractory grain (see point 6 chemistry).



a)

Zone Property	Zones					
	1	2	3	4	5	6
Chemistry (Wt %) - Al	6.9	27.3	1.7	2.8	7.5	5.7
- Si	23.9	0.2	0.1	0.1	40.2	3.8
- Fe	20.8	31.7	23.6	0.2	1.5	0.5
- Ca	1.5	-	-	-	0.5	-
- Cr	0.1	1.5	42.7	62.1	1.5	53.0
Possible Crystalline Phases	Fayalite, Others*	Hercynite	Fe/Cr Spinel	Cr/Al Solid Solution	Fe depleted slag	High Cr, minor Al and Si

*Others can include Hercanite, Iron Sulfide, Iron Cordierite, or other crystalline phases

b)

Figure 5 – Microstructural analysis of a high chrome oxide refractory sample taken from an air cooled slagging gasifier after approximately 2000 hrs of exposure to a coal slag at about 1400-1500°C. a) SEM micrograph (backscatter) image of the slag/refractory interface. b) WEDX chemical analysis of points in figure 5a.

CONCLUSIONS

Wear of high chromia/alumina refractories used to line air cooled slagging gasifiers is predominantly caused by chemical dissolution of the refractory and by spalling, although other factors impact wear. Two types of spalling commonly occur; 1) structural spalling of the refractory surface caused by deep (20-35 mm) slag penetration in the porous refractory, and 2) chemical spalling on the refractory grain surface caused by FeO interaction with chromia in the chromia/alumina solid solution of the refractory grain. Aluminium appears to diffuse from the chromia/alumina refractory grain, forming a diffusion layer of $FeAl_2O_4$ on the grain surface. A second source of Al may be from the slag. Iron oxide in the slag is depleted through interactions with the refractory, increasing slag viscosity as it penetrates within the refractory, and decreasing the ability of slag to interact chemically with the refractory grain.

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