

GASIFICATION SLAG AND THE MECHANISMS BY WHICH PHOSPHOROUS ADDITIONS REDUCE SLAG WEAR AND CORROSION IN HIGH Cr₂O₃ REFRACTORIES

James Bennett¹, Anna Nakano¹, Jinichiro Nakano^{1,2}, and Hugh Thomas¹

¹ US Department of Energy National Energy Technology Laboratory, 1450 Queen Ave., Albany, OR 97321 USA

²AECOM, P.O. Box 1959, Albany, OR 97321 USA

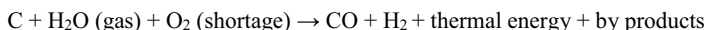
Keywords: Gasification, Refractory Wear, High Chrome Oxide

Abstract

Gasification is a high-temperature/high-pressure process that converts carbonaceous materials such as coal and/or petcoke into CO and H₂, feedstock materials used in power generation and chemical production. Gasification is considered an important technology because of its high process efficiency and the ability to capture environmental pollutants such as CO₂, SO₃ and Hg. Ash impurities in the carbon feedstock materials melt and coalesce during gasification (1325-1575°C), becoming slag that attaches to and flows down the gasifier sidewall, corroding and eroding the high Cr₂O₃ refractory liner used to protect the gasification chamber. Phosphate additions to high Cr₂O₃ refractory have been found to alter slag/refractory interactions and dramatically reduce refractory wear by the following mechanisms: a) spinel formation, b) slag chemistry changes, c) two phase liquid formation, and d) oxidation state changes. The mechanisms and how they work together to impact material wear/corrosion will be discussed.

Introduction

Gasification is a non-equilibrium process used commercially to convert high carbon materials (typically coal and/or petcoke) and water under a shortage of oxygen at high temperature and pressure into hydrogen and carbon monoxide gas (called synthesis gas or the shortened version, syngas) according to the simplified reaction:



By-products generated during gasification include hydrocarbons (primarily CH₄), minority gases (such as H₂S + CO₂), excess C as char, and ash/slag generated from minerals and organo-metallic impurities in the carbon feedstock. Air cooled entrained bed slagging gasifiers operate at temperatures between about 1325-1575°C and pressures between 2.1-6.1 MPa; consuming as much as 100 or more tons/hour of carbon feedstock. Coal and petcoke used as carbon feedstock have varying quantities of impurities depending on their sources, with coal averaging about 10 wt pct ash and petcoke about 1 wt pct. These impurities oxidize, melt, and/or coalesce to form molten slag during gasification. Slag chemistry is dependent on the carbon source, as previously described [1] and shown in Table I. When slag particles encounter the gasifier sidewall used to contain the gasification process, they typically adhere and flow down it, causing wear by

corrosion, spalling, and sometimes abrasion; as shown in Figure 1. Several types of refractory wear have been observed in gasifiers, which is shown in Figure 2. Three types are predominate; spalling, chemical dissolution, and abrasion. Abrasive wear is caused by carbon feedstock, additives, char (from carbon feedstock gasification) and/or slag particulates impacting the gasifier sidewall. It is a function of their velocity, and varies from location to location in the gasifier. Slag/refractory interactions are responsible for the two remaining types of wear - spalling and chemical dissolution of the refractory (examples shown in Figure 1). The impact of spalling and chemical dissolution wear on refractory materials is different, with a slow and predictable wear caused by chemical dissolution, and a sudden and unpredictable wear caused by structural spalling. Structural spalling is initiated by slag wetting and penetrating the high-porosity refractory, and is exacerbated by thermal cycling. The impact of refractory wear by chemical dissolution and spalling was illustrated by Bakker [2], who showed that chemical dissolution was a slow and steady wear, while spalling removed large portions of refractory at irregular intervals. A hypothetical example of these wear mechanisms is shown in Figure 3.

Table I. The average chemistry of major impurities found in Eastern U.S. coal and petcoke compiled by NETL from various sources [1]. Listings are as wt pct oxides.

Compound	Avg Coal Chemistry [1] (wt pct +/- std dev)	Avg. Petcoke Chemistry [1] (wt pct +/- std dev)
SiO ₂	43.6 +/- 16.4	14.1 +/- 8.7
Al ₂ O ₃	25.2 +/- 10.2	4.8 +/- 2.8
Fe ₂ O ₃	17.0 +/- 11.2	7.2 +/- 9.3
CaO	5.8 +/- 6.6	5.4 +/- 3.8
MgO	1.2 +/- 1.1	1.0 +/- 1.6
K ₂ O	1.4 +/- 0.7	0.5 +/- 0.4
Na ₂ O	0.9 +/- 0.6	0.8 +/- 0.8
TiO ₂	1.4 +/- 0.8	0.3 +/- 0.2
NiO	ND	8.4 +/- 3.2
V ₂ O ₅	ND	57.0 +/- 19.5

ND = Not Determined

The refractory materials used to line a gasification reaction chamber (Figure 1) can be divided into the four general classes of high chrome oxide compositions listed in Table II. Patented or proprietary additives are often made to the refractory compositions with the goal of reducing wear by limiting refractory dissolution in slag or by limiting slag penetration into the refractory.

Table II. Chemical and physical properties of the major types of refractories used in gasifiers (data from manufacturers' product data sheets)

Property	Refractory Type				
	A	B	C	D	
Chemistry (wt pct)	Cr ₂ O ₃	90.1	87.0	81.0	92.0
	Al ₂ O ₃	9.3	3.0	0.4	4.7
	ZrO ₂	NL	6.5	NL	NL
	MgO	NL	NL	17.0	NL
	P ₂ O ₅	NL	NL	NL	3.3
Porosity (pct)	14.8	16.5	12.0	15.0	

NL = Not Listed

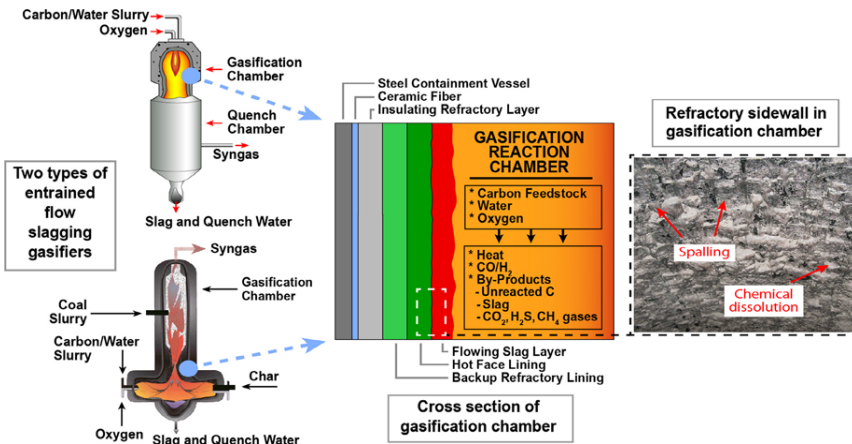


Figure 1. Two types of entrained flow slagging gasifiers with typical sidewall construction and wear patterns occurring on the refractory liner.

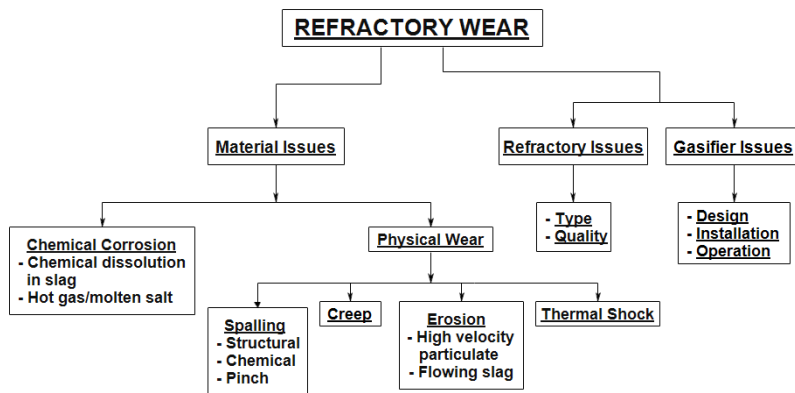


Figure 2. Types of refractory wear occurring in entrained flow slagging gasifiers.

A number of wear mechanisms have been proposed in high chrome oxide refractories to explain their superior performance over other liner materials in slagging gasifiers, with over 70 wt pct Cr_2O_3 proposed as a minimum amount necessary for adequate lining life [2]. In commercial service, it has been noted that phosphate additions to high chrome oxide refractories provide additional wear resistance, with improvements in service life of 50 pct or more observed in some commercial applications. The wear mechanisms occurring in high chrome oxide refractories with/without phosphate additions will be discussed in this paper, and include the following: a) spinel formation, b) slag chemistry changes, c) two phase liquid formation, and d) oxidation state

changes. Of those listed, spinel formation and slag chemistry changes occur in traditional refractory liners, while all four are thought to occur in materials with phosphate additions.

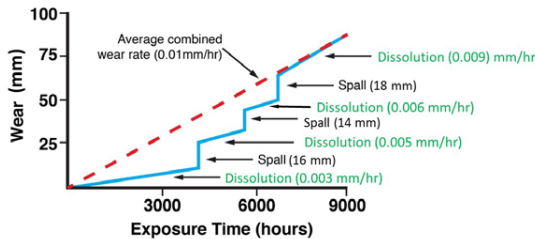


Figure 3. Hypothetical slag wear caused by spalling and dissolution of the refractory sidewall. Note spalling wear occurs as isolated incidents, while chemical dissolution occurs gradually over time [2].

Mechanisms Reducing Refractory Wear

As illustrated in Figure 2, a number of wear types are known to occur in gasifiers. The two mechanisms accounting for the greatest amount of wear, structural spalling and chemical dissolution, are shown in Figure 4. Refractory wear is influenced by the type of liner material and gasification variables including: slag composition and quantity, gasification temperature, oxygen partial pressure, carbon feedstock throughput, and gasification system cycling. The types of refractories used in gasification are listed in Table II. All are high in chrome oxide, and are based on research indicating high chrome oxide content in a refractory was necessary for sustained service life in a gasifier environment [2]. The different mechanisms thought to improve refractory performance (spinel formation, slag chemistry changes, two phase liquid formation, and oxidation state changes) are discussed individually.

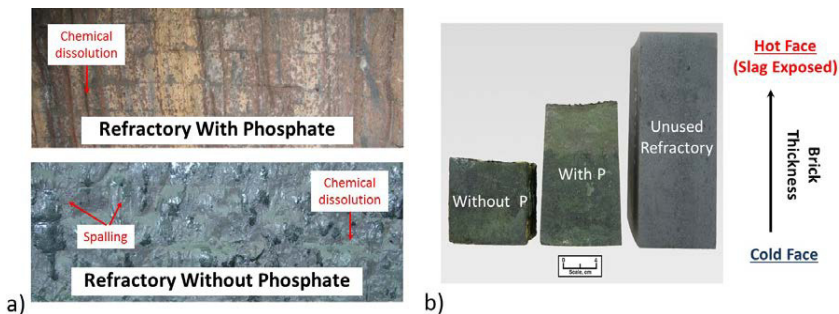


Figure 4. Spalling and chemical dissolution wear occurring in traditional refractory materials after gasifier service. a) High chrome oxide gasifier liner with/without phosphorous additions after 3 years of service, and b) side profile of refractory brick from a test panel with/without phosphorous additions after 237 days commercial service exposed to a coal slag.

a) Spinel formation

The high chrome oxide grains in gasifier refractories interact with oxides in the gasifier slag to form a complex layer structure at the refractory/slag interface, as shown in Figure 5. The $(Cr,Al)_2O_3$ refractory grain (pt 4) interacts with surface slag (pt 1) to form a solid solution zone of $(Fe,Mg)(Al,Cr)_2O_4$ as illustrated by pt 2 (composition tends toward $FeAl_2O_4$). This zone forms at the outer surface of the refractory, which is thermodynamically caused by the underlying zone of $(Fe,Mg)(Cr,Al)_2O_4$ solid solution formed at the refractory/slag interface (pt 3 – composition tends towards $FeCr_2O_4$). In general, slag oxides of Al, Fe, and/or Mg interact with $(Cr,Al)_2O_3$ grains, resulting in the two thermodynamically stable solid solution zones (pts 2 and 3) known to reduce refractory wear by chemical dissolution [3]. Note that the refractory/slag interactions alter the chemistry of slag penetrating the refractory pores, as shown in chemistry differences between pt 5 (pore slag) vs pt 1 (surface slag). It is thought that if zone 3 reaches some maximum thickness, thought to be between 20 and 50 microns, expansion differences with the underlying refractory grain and the newly created spinel result in chemical spalling, limiting the spinel layer thickness.

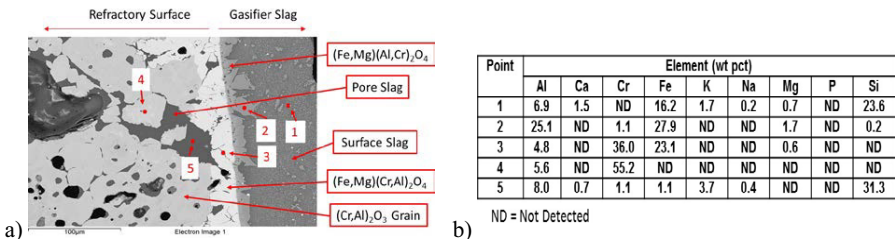


Figure 5. Surface microstructure and chemistry at the slag/refractory interface of a high chrome containing refractory with no phosphate additions determined using the SEM (in backscatter mode) and WDX. a) is the refractory/slag interface, and b) is WDX chemistry of different points indicated in image “a”). Note that oxygen and minor elements present in low quantities are not listed and that the data has not been normalized.

b) Slag chemistry changes

As noted in the “spinel formation” discussion, changes in the slag chemistry occur as it penetrates pores of the refractory and interactions occur at the slag/refractory interface. Those changes, shown in Figure 5, result from $(Cr,Al)_2O_3$ refractory grain/surface slag interactions, causing a reduction in slag Fe and an increase in Si content in pores (pt. 5). Continual interactions occur between slag iron oxide and chrome oxide in the refractory grain leading to the formation of a $(Fe,Mg)(Cr,Al)_2O_4$ solid solution (tending towards $FeCr_2O_4$). The depletion of Fe from the slag increases Si content in it. The surface and pore slag chemistry changes are illustrated in the WDX chemistry of pts 1 and 5 of Figure 5, where relative Si increased from 23.6 to 31.3 wt pct in pores vs the surface slag, while Fe decreased from 16.2 to 1.1 wt pct.

Slag chemistry changes impact slag viscosity and its ability to flow within refractory pores. Version 7.0 of FactSageTM, a thermodynamic modelling program, and the database “Melts” were used to predict slag viscosity at 1500°C for pore and surface slags for the different Fe oxidation states and the different slag chemistries listed in Figure 5. Those calculations, presented in Table III, are for slag chemistries with Fe valence states of +2 and +3. In reality, the majority of slag in

a commercial gasifier using traditions high chrome oxide refractories (i.e. non-phosphorus containing) would contain Fe in the +2 state. For the Fe in the +2 state, a theoretical viscosity of 7.6 Pa.s was predicted for the surface slag, while a value of 2570 Pa.s was predicted for the pore slag. Differences may exist in the slag viscosities if slag Fe in the +3 state is present (as Fe₂O₃), a condition that may be caused by phosphate additions to the refractory, which will be discussed later.

Table III. Viscosities at 1500°C of pore and surface slag chemistries listed in Figure 5 b as predicted by version 7.0 of FactSage™ (version 7.0, database “Melts”) if all Fe is present as FeO or as Fe₂O₃.

Slag Location	Viscosity (Pa.s) - Fe as FeO	Viscosity (Pa.s) - Fe as Fe ₂ O ₃
Surface	7.6	14
Pore	2,570	2,510

Note that the temperature going from the hot face to the cold face within a given refractory material, along with the refractory chemistry, also impact slag penetration depth. The temperature drop, depending on the thickness of the brick, can range between 20 to 5°C/cm, with thinner linings having a greater temperature drop per unit distance, but also having a higher cold face temperature than thicker linings.

c) Two phase liquid formation

Pore slag in refractories without phosphate additions exist primarily as a single liquid phase versus a complex multiphase structure that exists within refractory pores containing phosphorous additions. Figure 6 shows pore slag adjacent to a chrome oxide grain about 0.5 mm from the slag/refractory interface in a phosphorous containing high chrome oxide refractory. This sample, also shown in Figure 4 b, had 237 days of coal slag exposure in a commercial gasifier. Microstructure, chemical, and crystalline phase analysis of the sample was conducted using TEM. Note the fine size (less than 50 nm) and the wide distribution of a spherical particles rich in P, Al, Fe, Ca, and Mg in the pore slag. Only two crystalline phases were identified using electron diffraction in the spherical particles, AlPO₄ and hexagonal FeS. The presence of the spherical phases and the change in bulk pore slag chemistry caused by a reduction in Al, Fe, Ca, and Mg would cause overall pore slag viscosity to increase (thicken), further limiting its penetration into the refractory versus slag chemistry changes alone.

d) Oxidation state changes

The temperature, oxygen partial pressure, and melt chemistry in a gasification chamber impact the oxidation state of some phases. Two elements common in coal and petcoke carbon feedstock, V and Fe, are most sensitive to environmental changes, and can exist in multiple valance states depending on the gasification environment. Iron can be present as FeO, Fe₂O₃, and/or Fe₃O₄; while V can exist as VO₂, V₂O₃, V₂O₅, or other possible states. Usually the oxidation state is determined by reduction reactions in the gasification chamber, but in phosphate-containing high chrome oxide refractories, a different oxidation state can exist in the infiltrated refractory than in the gasifier. Oxygen can be released and maintained under the slag covering in the gasifier, changing (increasing) the partial pressure in refractory material at that location. The O₂ release occurs according to the following reaction: 4AlPO₄(s) ↔ 2Al₂O₃(s) + 2O₂(g) + (P₂O₃)₂(g); creating a stable higher oxygen content locally. This reaction has been

described previously [4], and is being studied to understand its impact on slag phase valance and viscosity, and on refractory wear.

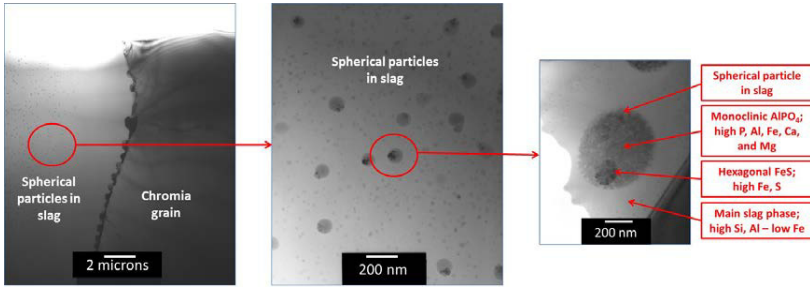


Figure 6. TEM images indicating a complex phase microstructure present in high chrome oxide pore slag with phosphate additions. The sample was exposed to slag in a commercial gasifier, and are shown in Figure 4 b. The spherical slag particles are high in Al, Fe, Ca, and Mg; while the bulk slag has become higher in Si and Al, and lower in Fe.

The impact of the multiple wear mechanisms (spinel formation, slag chemistry changes, two phase liquid formation, and oxidation state changes) is to reduce refractory wear; which have shown the greatest reductions in the high chrome oxide refractory wear when refractories contain phosphate additions (Figure 4 b). Even though sample exposures were the same for the refractories with/without phosphate additions, refractory material with phosphate additions had about 100 mm in thickness remaining on removal from the gasifier, while the refractory without phosphate additions was estimated to be about 60 mm in thickness. Slag penetration into samples shown in Fig 4 was measured by Si migration from the refractory/slag interface using SEM-WDX, and is shown in Figure 7. Phosphate additions resulted in significantly less penetration in Figure 7 b (phosphate additions) versus no phosphate additions (Figure 7 a), resulting in additional wear improvements. It is thought that two phase liquid formation and oxidation state changes caused by phosphates play a role in those additional wear improvements.

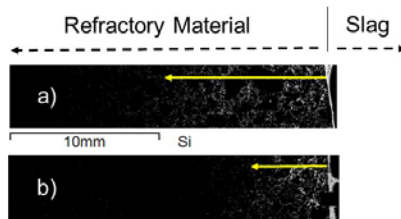


Figure 7 – Penetration of coal slag into a high chrome oxide refractory test panel of brick with/without phosphorous additions after 237 days of commercial service as measured by WDX using the SEM (samples also shown in Figure 4 b). The arrow indicates the maximum depth of Si penetration going from the exposed hot face (gasification chamber slag exposure) to the cold face on: a) refractory composition without phosphate additions, and b) refractory composition with phosphate additions.

Conclusions

Gasification is a high-temperature/high-pressure/reducing reaction converting high carbon materials such as coal and/or petcoke into CO and H₂ used in power generation and chemical production. Impurities in the carbon feedstock become ash that melt at the high temperatures of entrained bed slagging gasification (1325-1575°C), causing wear of the high chrome oxide gasifier lining protecting the gasification chamber. Refractory wear originates from many causes, with chemical dissolution and spalling being the primary ones. The following are mechanisms that reduce wear in the high chrome oxide refractories with/without phosphate additions: spinel formation, slag chemistry changes, two phase liquid formation, and oxidation state changes. A complex relationship exists between temperature, oxygen partial pressure, slag composition, and refractory composition in high chrome oxide refractories with/without phosphate additions impacting wear.

Acknowledgement

This technical effort was performed in support of the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000. This research was supported in part by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education.

References

1. J.P. Bennett et al, "Microstructure and Corrosion of Phosphate Containing Cr₂O₃ Gasifier Refractories", proceedings of Corrosion 2015, Dallas, TX, Mar. 15-19, 2015.
2. W.T. Bakker, "Refractories for Present and Future Electric Power Plants," Key Engineering Materials, Trans Tech Publications, (1993), Vol. 88, pp. 41-70.
3. J.P. Bennett and K-S. Kwong, "Failure Mechanisms in High Chrome Oxide Gasifier Refractories", Met. and Mat. Trans. A, V. 42 (2011), no. 4; p. 888-914.
4. J.P. Bennett et al, "Impact of Temperature and Oxygen Partial Pressure on Aluminum Phosphate in High Chrome Oxide Refractories," proceedings of CIMTEC 2014, Montecatini Terme, Italy, June 8-13, 2014.

DISCLAIMER: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."