

**Preliminary Report on
REFRACTORY-SLAG INTERACTIONS
in a GASIFICATION SYSTEM**

J. Rowers, K.Collins, J.Bennett, K.Kwong
U.S. Department of Energy
Albany Research Center
Albany, OR, USA

Abstract:

Gasifier systems for power generation are being developed to utilize a variety of fuels at temperatures up to 1600°C. One system being considered by the US Department of Energy is an entrained bed slagging gasifier. Because of concerns over refractory-slag interactions, the effects were studied of different coal slags (from commercial gasifiers and from laboratory constructed artificial slags) on high chrome-alumina refractories. Materials were exposed to simulated gasification atmospheres using a modified cup-like test. Refractory-slag interactions are reported for slag penetration and refractory corrosion, crystalline phase change, and microstructure alterations. Results are then compared to refractory bricks that have been removed from a gasifier chamber after 15,000 hours of operation. This study showed that the reaction of refractories with slags in commercial plants could be duplicated in the laboratory using cup-like tests, and by the effects of gasifier slags could be understood by studying the effects of the different slag components and artificial slags.

Introduction:

Currently, refractory liners in demonstration COAL - GASIFIER power generation facilities have a usable life of approximately 10,000 - 20,000 hours. Because of the high cost of refractory bricks and for the need of extensive shutdown time to change refractory liners (often more than two weeks), extending the time between refractory repair or exchange to [50,000 - 100,000 hours] would be beneficial.

This study was designed to develop an understanding of long-term operating effects on the refractories in commercial gasifiers by studying results from short-term laboratory tests. By understanding the causes that currently limit refractory life, it may be possible to extend the life (i) by improving in refractory materials or fabrication, (ii) by additives to the fuel supply, (iii) by altering operating conditions, and/or (iv) by changing combustion chamber design. The immediate goal of this study is to understand the coal slag-refractory interaction which previous study has indicated may account for over 60% of refractory loss (1). A summary of findings from previous gasifier refractory-slag interaction studies is presented in the APPENDIX.

CUP-LIKE TESTS were developed in which slags (individual slag components, combinations of slag components, artificial gasifier slag, and gasifier slags) were added to holes drilled in commercial gasifier refractories. These combinations were subjected to conditions simulating those in a reducing gasifier. Results from these laboratory tests were compared to Aspent@ refractories (i.e., refractories that have been removed from gasifiers after more than 10,000 hours of operation).

Current laboratory testing using cup-like tests has limitations and advantages. Cup-like test limitations include: (i) test duration (laboratory tests generally run fewer than 100 hours, less than 1% of current commercial operation time, which eliminates characterizing long-term effects such as creep), (ii) static tests (the refractory-slag interface is not continuously being exposed to a new supply of slag, thus erosion effects can not be determined), (iii) isothermal tests (the entire refractory sample is held at a uniform temperature so there is no thermal gradient across the refractory and such effects as thermal expansion can not be studied), and (iv) the scale of the test is limited (therefore such phenomena as compression and hoop stress levels associated with a larger commercial facility can not be duplicated). Cup-like testing does, however, have advantages: (i) economics of laboratory-scale testing, (ii) ease of sample handling, (iii) ability to change operating conditions without affecting plant operation, and (iv) ability to run multiple samples under identical conditions.

In the first phase of the study, cup-like and gasifier refractories were compared to validate the use of short-term cup-like tests, to determine what modifications might be necessary, and to discover what shortcomings of laboratory testing may exist.

Experimentation:

Commercial high chrome/alumina refractories were characterized for chemical components, composition, (**TABLE I**), and microstructure. Slags obtained from two commercial coal-gasifier facilities (TECO Polk County, FL and WABASH, ID) were characterized for chemistry (**TABLE II**), size distribution, and microstructure (**FIGURE I**). After the gasifier slags were characterized and chemical compositions of the gasifier slags were compared to the coal slurry feed stock, samples of artificial slag were made (**TABLE III**).

Cup-like tests were conducted using a commercial grade, 85% dense, high chrome-alumina coal gasifier refractory (AUREX - 75). Samples were sectioned from the as-received refractory blocks and holes (approximately 10mm in diameter and 10mm deep) were drilled into the sections. The holes were filled with artificial slags and slags from gasifiers. Based upon results from a previous study (**1**) a single set of furnace conditions was used. Samples were heated for 24 hours at 1550°C in a closed tube furnace and through which a 50-50 argon-carbon monoxide gas mixture flowed that had previously been bubbled through water. (For a more complete description of the cup-like tests see reference 1).

Characterization of the slag-refractory interaction included: (i) examining macroscopic surface to evaluate the refractory degeneration (**FIGURE II**), (ii) machining off part of the interaction surface to determine possible chemical interaction and refractory phase change, (iii) measuring the depth of slag penetration, (iv) determining slag chemistry to monitor possible dissolving away of the refractory (**TABLE IV**), and (v) examining the refractory microscopically to determine the extent of refractory morphology change.

Samples of spent refractories were also characterized. Refractory bricks were sectioned and examined. Microscopic and chemical analyses were obtained from the slag-refractory interface and from sectioned samples taken at selected depths within the refractory (**TABLE IV**).

Data and Analysis:

The slag chemistry changed little from that of the coal chemistry, except for the carbon concentration. The major difference between the slurry chemistry and the fines (the suspended particles that were carried out of the gasifier with the gasifier gases) was the nitrogen and sulfur concentrations. This difference is due to the nitrogen in the coal feed or slurry most likely being the part of the solid organic coal which was turned into nitrous gases during gasification and iron sulfide (pyrite) which was changed to iron oxide. Size distribution of the bottom slag shows two distinct concentrations: approximately 2mm and approximately 0.3mm. Microscopic examination showed the particles from the two distributions to have distinct morphologies. The larger particles appear to be fragmented liquid droplets. The smaller particles appear to be partially sintered fine-grained particles typical of the fine particles (Figure I).

The refractory used for the cup-like tests (AUREX-70) was composed of sintered, solid solution (Cr, Al)₂O₃ particles.

Slags chosen for the cup-like tests were: bottom slags obtained from commercial gasifiers, an artificial slag composed of mixtures of elemental powders of oxides with a composition similar to the gasifier bottom slag, and additions of individual and combinations of elemental slag components.

After firing, macroscopic examination of cup-like test slag-refractory surfaces showed that the commercial gasifiers and artificial slag behaved similarly. The majority of the slag melted and completely infiltrated into the refractory (**FIGURE III**). Surface characteristics varied considerably with different slag compositions. SEM microscopic examination of the refractory cross-sections showed the effects of the varying components on the interior of the refractories (**FIGURE IV**). Silica (SiO₂) penetrated the refractory, in excess of 5mm within 24 hours; however, there was no noticeable slag-refractory reaction. In contrast, calcia (CaO) diffused into and also reacted with the refractory, especially dissolving the finer refractory particles, producing a sponge-like refractory microstructure. Ferrous oxide (FeO) had very limited penetration but strongly reacted with the surface of the refractory producing a phase change from a sesquioxide, (Cr₂O₃), to a spinel, (Cr,Fe)₃O₄, and a dense, solid interface.

Examination of the spent refractory has just begun (**FIGURE V**). Preliminary evidence shows similar slag-refractory reactions between the spent refractory and the cup-like tests. One difference was the presence of a thin layer (approximately 1-3mm thick) of slag on the spent refractory surface. The upper 20 - 30 mm appeared to have a denser morphology which, after chemical analysis of the different profile sections, was attributed to slag penetration. Also present was a crack running the length of the refractory at about 30 to 40 mm from the hot-face. There were no slag deposits inside the crack. Investigation is underway into crack formation to find if it is related to slag-refractory interaction or to long term stress. The crack did not cause the refractory to split. Chemical profile analysis (from wet-chemistry and X-ray fluorescence) of the spent refractory showed the silica and to some extent the calcia concentration to drop off in two stages: one slightly above the crack and the other approximately 10 mm below. In contrast, the iron concentration was limited to the top 10 mm and formed a spinel, (Mg, Fe)(Cr, Al)₂O₄.

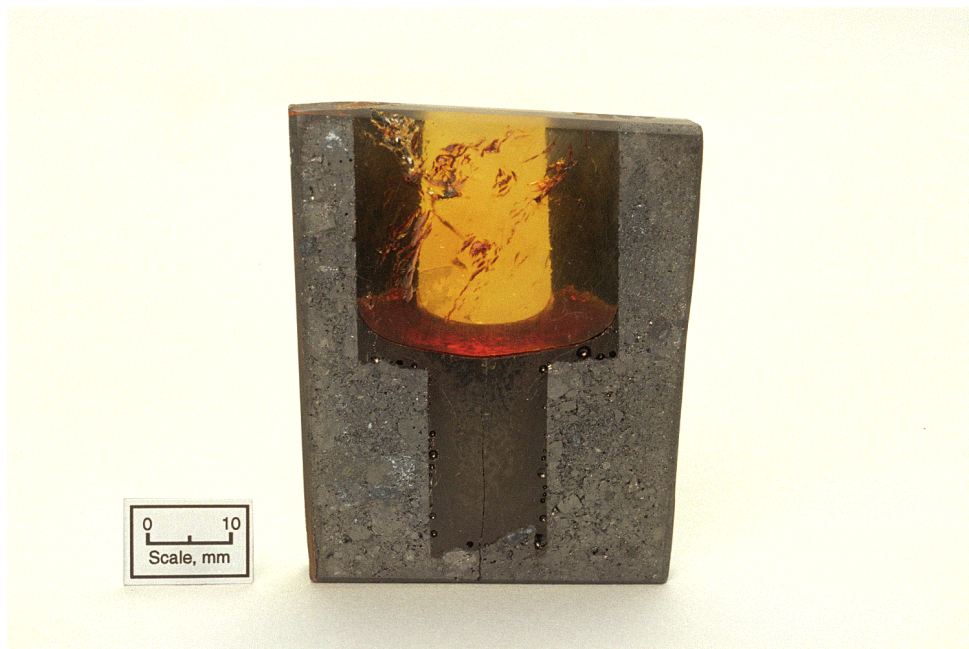
Summary:

The goal of this study was to validate that short-term laboratory tests, such as cup-like tests, could produce slag-refractory interactions similar to those produced in commercial slagging coal gasifiers. Understanding the slag-refractory interactions and the role of the slag components may provide an economical means of controlling refractory-slag erosion/corrosion and extend refractory lifetime. The use of gasifier slags and mixtures of slag oxides did allow the effects of oxides on gasifier refractories to be studied and to determine if the oxide-refractory interactions were accumulative or synergistic or if one slag component would overwhelm the effects of others.

Preliminary analysis of the spent refractory showed that the results from the cup-like tests are very similar to the slag-refractory interactions observed in commercial gasifier processes. The reactions of the gasifier slags with the refractory liner can be simulated by artificial slags and understood by studying the effects of the various slag components.

Future Program Objectives and Goals:

Current studies are underway to overcome the current cup-like test limitations and to broaden the understanding of slag-refractory interactions especially for co-fired systems, (i) to build larger cup-like test capabilities in which sufficient slag is used to simulate continuous slag-refractory interactions, (ii) to use a larger supply of slag that will run continuously over the refractory surface to evaluate slag erosion, (ii) to simulate thermal gradients across the refractory, and (iv) to duplicate numerous thermal cycles (gasifier start-ups and shut-downs). However, to date no means has been determined that can simulate the effects of long term creep and stress on slag saturated refractories.



REFERENCES:

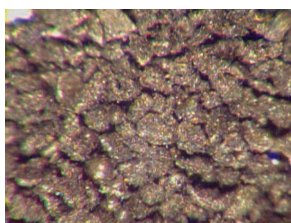
- 1 J.Rawers, J.Kwong, and J.Bennett, Materials at High Temperature, vol.16, no.4, pp.219, 1999
- 2 W.Bakker, S.Greenberg, M.Trondt, and U.Gerhardus, Ceramic Bulletin, vo..63, no.7, pp.871, 1984
- 3 W.Bakker, S.Darling, and W.Coons, Ceramics Bulletin, vol.62, no.12, pp.1359, 1983
- 4 M.Buroni, G.DelPiero, L.Pellegrini, and S.Serenelli, Coal Sci. Tech., vol.11, pp.571, 1987
- 5 S.Greembure, P.Poeppel, etc., Argonne National Lab. Report ANL/Fe-83-31 Sept. 1988

FIGURE I GASIFIER SLAG PARTICLE MICROSTRUCTURE

Bottom sieve size -10 +14



Bottom sieve size -48 +100



Fines sieve size -100 +200

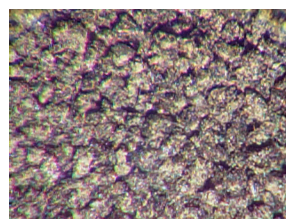
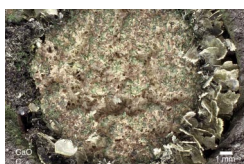


FIGURE II SLAG - REFRACTORY SURFACE FEATURES OF CUP-LIKE TEST

As-received



CaO + C



CaO + SiO₂ + FeO + C



Bottom Slag



FIGURE III SLAG INFILTRATION / PENETRATION CROSS-SECTION

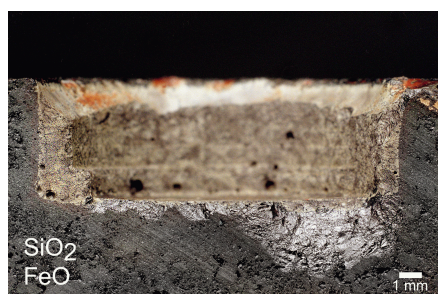


FIGURE IV: SEM CROSS-SECTION PENETRATION AND CHEMISTRY:

RED slag-refractory chemistry at interface region, phase $(\text{Cr,Fe})_3\text{O}_4$
BLUE refractory interior chemistry as - received composition, phase Cr_2O_3
GREEN slag chemistry that had penetrated into refractory

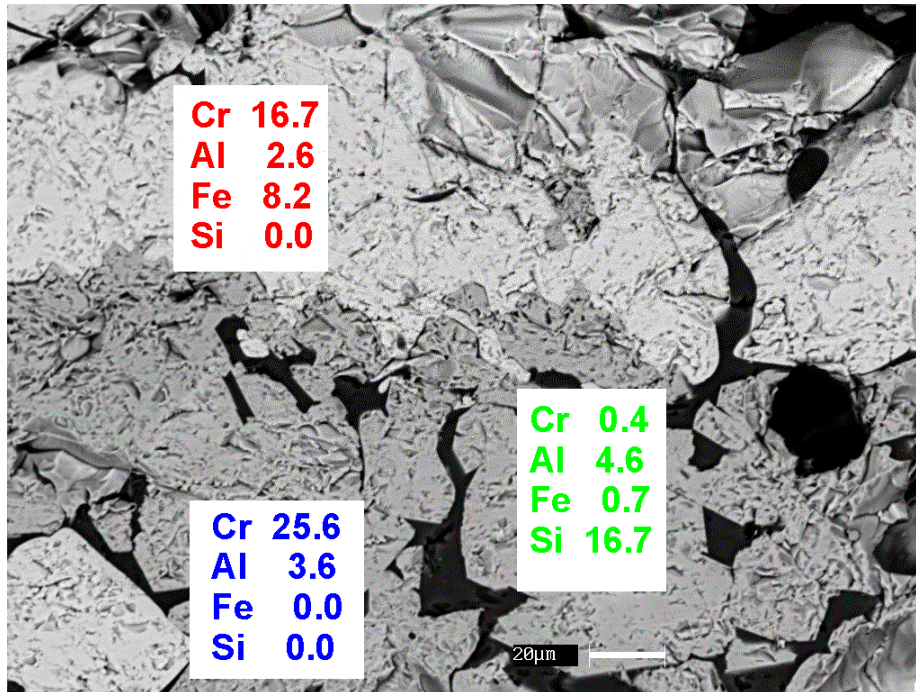
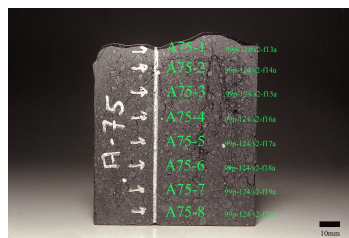


FIGURE V: SPENT REFRACTORY ANALYSIS

ASpent@ refractory



Cross-Section



Slag- Refractory Interface

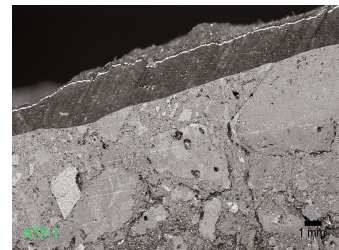


TABLE I: Refractory Chemistry, wt%

	Cr	Al	Ca	Mg	Si	Fe
A-90	63.9	3.6	0.12	0.10	0.09	0.03
A-75	54.7	9.8	0.19	0.28	0.12	0.08
A-40	27.6	28.2	0.22	-.-	0.05	0.04

TABLE II: Carbon - Corrected ATOMIC-% SLAG CHEMISTRY

Chemistry	Slurry	Fines	Bottom			
	grab	grab	grab	grab	-6 +8	-200 +325
Si	18.8	17.3	20.8	19.6	18.8	16.9
Al	7.2	6.8	7.7	7.2	6.5	7.4
Fe	7.2	6.6	7.2	7.1	6.6	9.6
Ca	2.0	1.8	2.7	2.4	2.6	2.3
Na	3.7	1.1	1.2	0.9	1.1	1.0
S	4.7	3.6	1.0	0.9	0.3	3.0
N	10.6	0.8	0.8	1.0	0.3	1.2
Cr	0.004	0.005	0.010	0.011	0.012	0.005
C	80.0	53.1	33.1	40.1	0.5	25.5

TABLE III_SLAG COMPOSITIONS

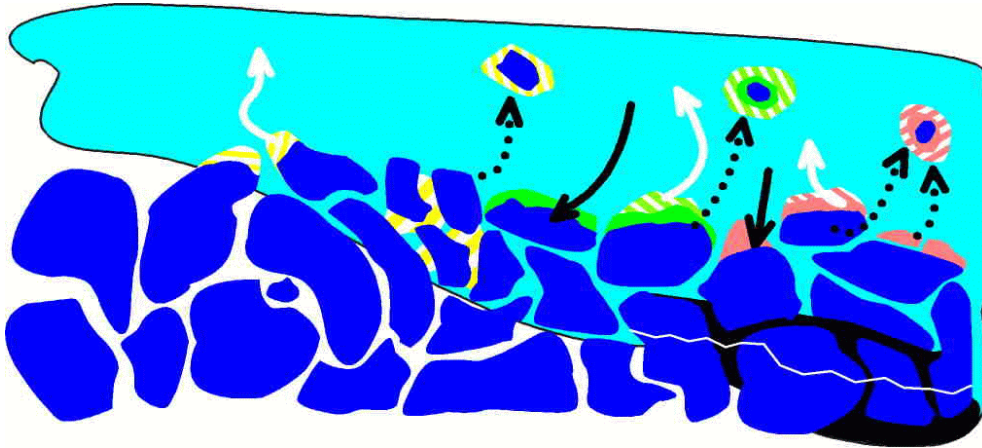
Artificial composition, wt%			
SiO ₂	CaO	FeO	X
100			
50	50		
33	33		C
33	33	33	
25	25	25	C
25	25	25	Na₂O
25	25	25	VO₂
33	33		FeS
Gasifier Slags, wt%			
Artificial Ill. no. 6	52SiO ₂ , 20Fe ₂ O ₃ , 20Al ₂ O ₃ , 7CaO, 1MgO -0C		
Ill. no. 6	53SiO ₂ , 18Fe ₂ O ₃ , 19Al ₂ O ₃ , 7CaO, 1MgO -0C		
Wabash	46SiO ₂ , 18Fe ₂ O ₃ , 19Al ₂ O ₃ , 5CaO, 2MgO - (3C)		
Polk	38SiO ₂ , 23Fe ₂ O ₃ , 13Al ₂ O ₃ , 4CaO, 1MgO - (23C)		

TABLE V: Slag - Refractory Interactions: cup like test, A-70 refractory, 1550 °C, 24 hours, environment: Ar-CO/H₂O

Artificial composition, wt%				Surface	Penetration, mm	X-ray data	Sample Depth	Slag Chemistry, atomic % (SEM-EDX)						
SiO ₂	CaO	FeO	X		Si - Ca - Fe -X/Mg	major, minor		Cr	Al	O	Si	Ca	Fe	BX--
100					>5 - 0 - 0 - 0	(Cr,Al) ₂ O ₃	Top > -5mm	0.1 0.6	0.1 0.3	66.9 64.7	32.7 32.7	0.03 0.10	0.03 0.10	
50	50				>5 - >5 - 0 - -2	(Cr,Al) ₂ O ₃	Top > -5mm	0.4 0.4	4.4 0.8	69.7 68.3	12.5 31.3	12.9 0.0		
33	33		C		>5 - >5 - 0 - >5	(Cr,Al) ₂ O ₃	Top > -5mm							C
33	33	33			>5 - >5 - 0 - -2	(Cr ₂ -CrAl)O ₃ ⁺ (FeCr) ₃ O ₄	Top > -5mm	0.5 2.1	8.2 9.3	59.9 63.1	15.4 15.9	15.5 8.9	0.6 0.1	
25	25	25	C		>5 - >5 - 1 - -1	(Cr ₂ -CrAl)O ₃ ⁺ (FeCr) ₃ O ₄	Top > -5mm	0.3 0.4	3.5 5.3	67.7 67.8	12.7 11.9	13.7 14.2	1.0 0.1	C .11 C .11
25	25	25	Na ₂ O	≤ 0.2mm	3 - 2 - 2 - 0	(Cr ₂ -CrAl)O ₃ ⁺ (FeCr) ₃ O ₄ Ca ₂ Al ₂ SiO ₇	Top > -5mm	0.3 0.4	5.1 7.0	65.7 69.2	11.7 8.2	12.4 15.5	0.5 0.0	Na=4.2 Na=1.3
25	25	25	VO ₂	≤ 0.2mm	5 - 5 - 1 - 1	(Cr ₂ -CrAl)O ₃ ⁺ (FeCr) ₃ O ₄	Top	0.8	6.6	70.8	11.5	10.2	0.2	V =0.1
33	33		FeS		4 - 4 - 4 - 4(S)	(Cr ₂ -CrAl)O ₃ ⁺ (FeCr) ₃ O ₄	Top > -5mm							S
Gasifier Slags, wt%								Cr	Al	O	Si	Ca	Fe	Mg
Artificial Ill. no. 6 52SiO ₂ , 20Fe ₂ O ₃ , 20Al ₂ O ₃ , 7CaO, 1MgO -0C				≤ 0.2mm	>5 - >5 - 1 - 0	(Cr,Al) ₂ O ₃ , (FeCr) ₃ O ₄ amorphous matrix	Top > -5mm	0.6 1.4 0.0	4.9 5.2 8.7	69.7 69.3 63.	13.9 13.7 21.4	9.4 9.2 5.0	0.3 0.0 5.6	0.5 0.6 0.0
Ill. no. 6 53SiO ₂ , 18Fe ₂ O ₃ , 19Al ₂ O ₃ , 7CaO, 1MgO -0C				≤ 0.2mm	>5 - >5 - 0 - 0	(Cr,Al) ₂ O ₃ , (FeCr) ₃ O ₄ Ca ₂ Al ₂ SiO ₇ , Fe ₂ O ₃	Top > -5mm	0.3 1.6 0.0	4.9 5.5 8.4	68.0 67.0 63.0	19.7 14.5 22.7	4.1 10.0 5.0	0.6 0.2 4.8	0.2 0.8 0.0
Polk 38SiO ₂ , 23Fe ₂ O ₃ , 13Al ₂ O ₃ , 4CaO, 1MgO - (23C)				≤ 0.1mm	>5 - >5 - 0 - 0	(Cr,Al) ₂ O ₃ , Al ₂ O ₃ , Fe(metal)	Top > -5mm	0.4 4.3 0.0 0.0	4.7 4.5 2.6 7.9	68.9 68.8 21.5 63.0	19.4 18.7 7.2 20.7	3.2 2.3 1.3 3.8	0.5 0.0 2.0 5.7	1.3 1.3 -- 0.0
Gasifier Chamber Refractory					Si - Ca - Fe - K			Cr	Al	O	Si	Ca	Fe	Mg
spent refractory (A-70) slag-refractory interface-inside slag-refractory interface-top						(Cr,Al) ₂ O ₃ (Cr,Al) ₂ O ₃ (Cr,Al) ₂ O ₃ , (Cr,Fe) ₃ O ₄	-50mm -10mm Top	27.4 25.7 18.6	4.9 4.8 2.8	70.2 70.0 66.0	0.0 0.0 0.0	0.03 0.02 0.04	0.1 0.2 11.1	0.1 0.1 0.1
slag Polk large grain slag-refractory interface-top slag-refractory interface-inside				≤ 0.1mm	18 - 8 - <1 - 9	Amorphous Amorphous, (Cr,Fe) ₃ O ₄ Amorphous Amorphous Amorphous Amorphous	SLAG Top -3 mm -7 mm -11 mm -17 mm		3.5 4.1 4.5 4.6 5.4 7.2	67.0 67.3 65.0 69.4 68.7 68.5	18.0 22.8 19.0 16.0 16.3 17.3	2.0 2.1 2.4 2.6 4.9 5.3	7.6 0.9 1.0 0.5 0.1 0.2	1.1 0.5 0.3 0.6 2.0 3.2

APPENDIX

Gasifier Refractory Erosion



SLAG ACTION

INTERFACE REACTIONS
CHANGE COMPOSITIONS
NEW PHASE FORMED
THERMAL / MECHANICAL

REFRACTORY REACTION

DISSOLVE REFRACTORY
DISSOLVE PARTICLE BONDING
STRESS INDUCE FRACTURE



From previous studies (2, 3, 4, 5), degradation of the refractory with coal slag can be summarized using one or more of the following processes:

- (1) refractory dissolution:
 $\text{Cr}_2\text{O}_3,(\text{solid}) \text{ B} > \text{Cr}_2\text{O}_3,(\text{liquid})$
- (2) refractory particle debonding:
dissolving of particle bonds and particles infusing into slag
- (3) slag - refractory elemental replacement:
 $\text{Cr}_2\text{O}_3 + \text{MO}_x \text{ B} > (\text{M}, \text{Cr})_2\text{O}_3, (\text{solid or liquid})$
- (4) slag - refractory reaction producing new phases:
 $\text{Cr}_2\text{O}_3 + \text{MO}_x \text{ B} > (\text{M}, \text{Cr})_x\text{O}_y, (\text{solid or liquid})$
- (5) slag - refractory physical mismatch:
variation in properties causing stress and fragmentation
- (6) slag penetration into refractory pores:
slag penetrates into 14-17% porosity
- (7) slag wear-abrasion-erosion:
slag velocity est. 4-20 m/hour and viscosity less than 20 poise
- (8) stress (and thermal cycle) loadings:
resulting in fragmentation and spallation

