22ND ACERC Conference

Provo, Utah, BYU *Feb. 26-27, 2008*

REFRACTORY-SLAG INTERACTIONS IN COAL GASIFICATION ENVIRONMENTS

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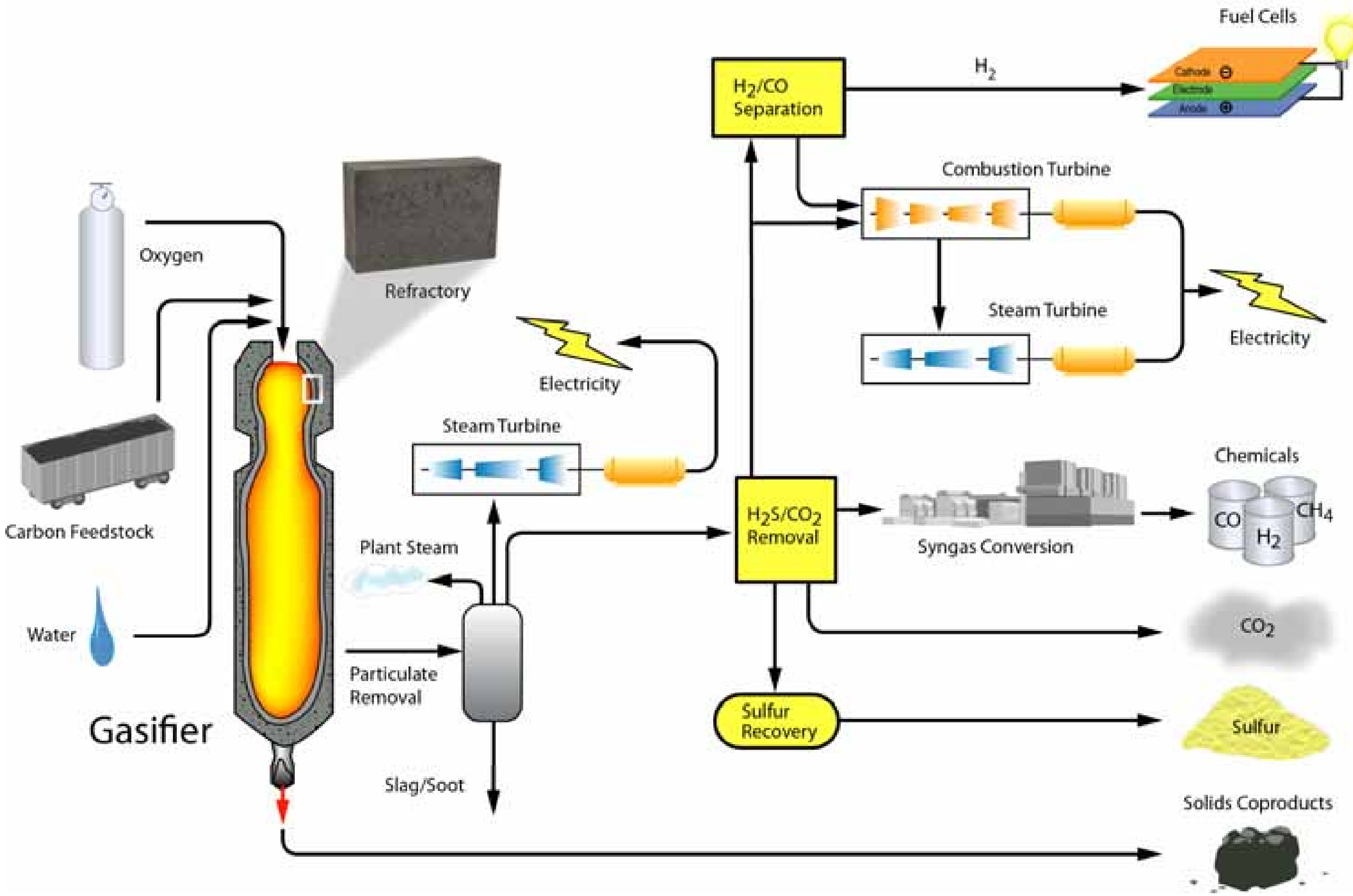
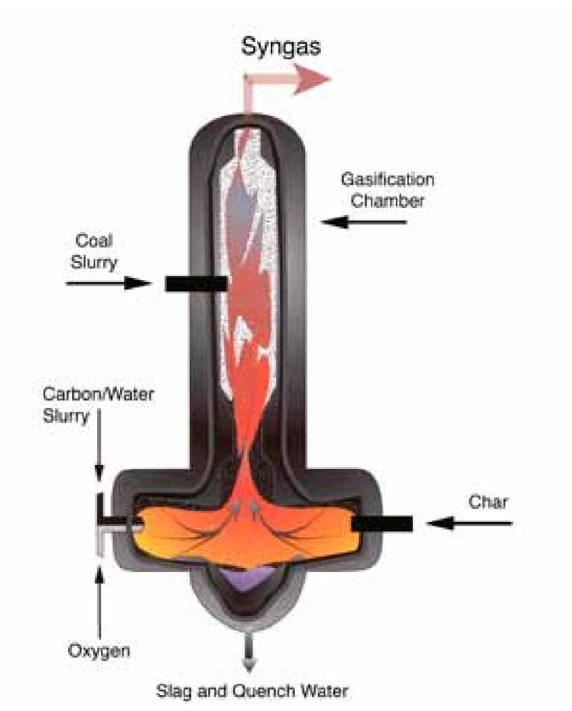
Gasification Background



Gasification Reaction

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

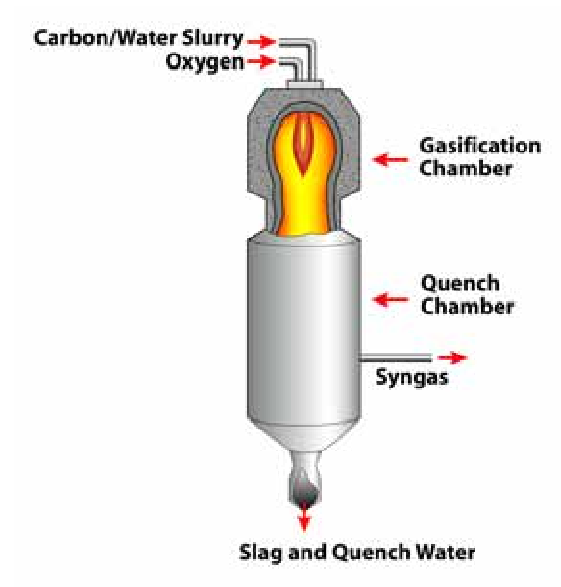
Material Challenges Inherent to Air-cooled Slagging Gasifiers



ConocoPhillips

(2 stage - syngas cooler)

- **Operating temperatures of 1325° to 1575°C**
- **Thermal cycling**
- **Reducing and oxidizing environment**
- **Corrosive slags of variable chemistry** ***(slags from minerals in carbon feedstock)***
- **Corrosive gases**
- **Pressures ≥ 400 psi**



GE Design

(1 stage - syngas cooler or water quench)

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Refractory Material Issues - Consequences

1. **Low system reliability, on-line availability**
   - gasifier down as frequently as once/month
   - possible need for "spare" gasifier

2. **Lost opportunity costs**
3. **Frequent maintenance/high costs**
4. **Need for zoning – larger "spare" material inventory**

5. **High material repair costs**
   - $1 million for refractory lining
   - long downtime for repairs
6. **Excessive safety margins**

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Gasifier Program Goals

- **Increased reliability and availability**
  - 85-95% for power generation, 90% for chemical production
  - Service life of 3 + years in power generation
- **Carbon feedstock flexibility, including biomass**

Range of Chemistry Found in Over 300 U.S. Coal Slags Due to Mineral Impurities

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

Source: W.A. Selvig and F.H. Gibson; Analysis of Ash from United States Coals; USBM Bulletin, Pub. 567; 1956, 33 pp.

Note: Petcoke slags contain V and Ni

Chemical Composition* of High Cr_2O_3 Gasifier Refractories

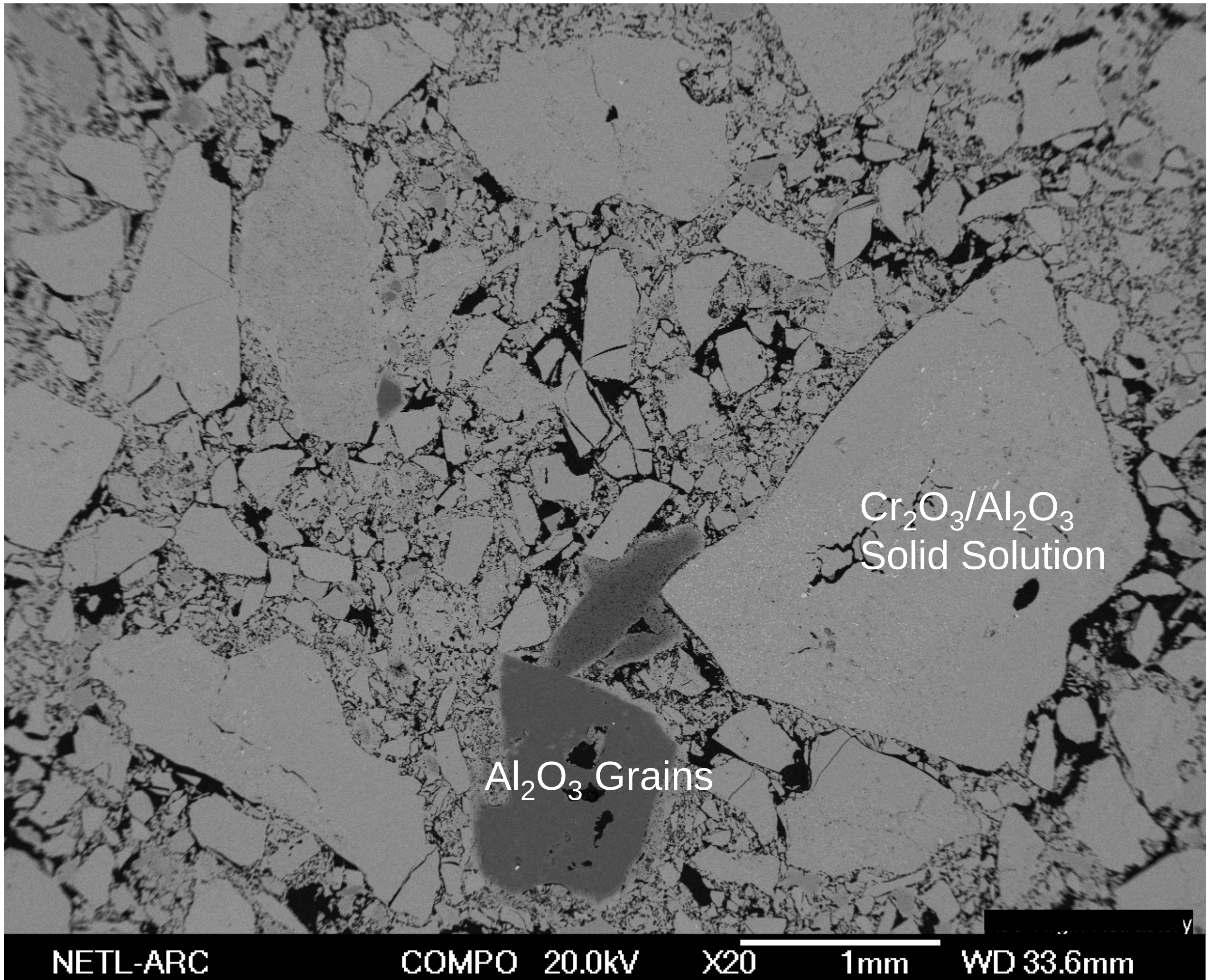
	Composition		
Chemistry	A	B	C
Cr_2O_3	89.0	87	92.0
Al_2O_3	10.2	3.0	4.7
ZrO_2	---	6.5	---
P_2O_5	---	---	3.3
Bulk Density (g/cc)	4.21	4.07	4.23
Porosity (pct)	16.7	16.5	15.0
CCS (MPa)	48.3	66.9	51.7

Conventional materials (A, B)

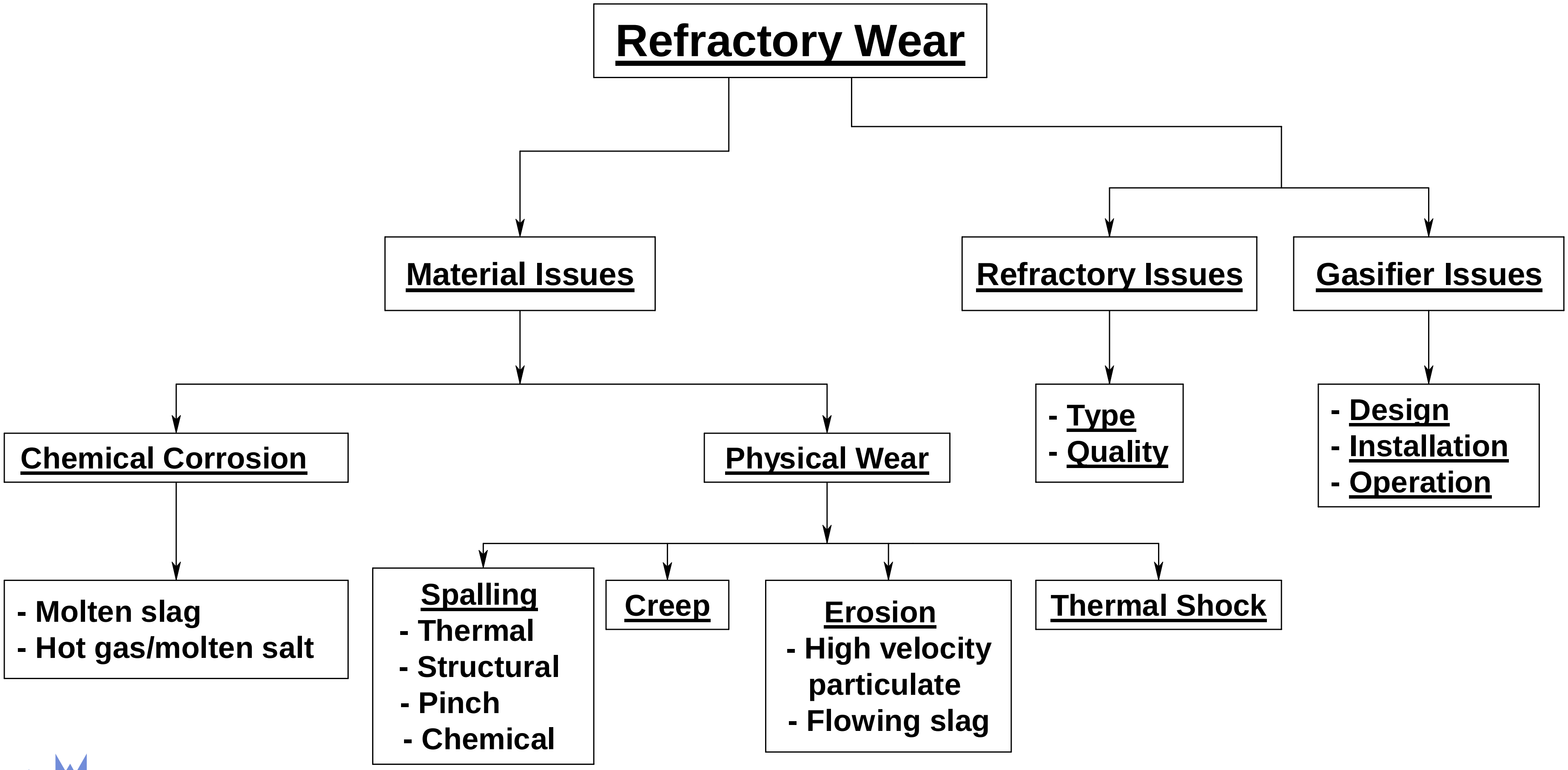
NETL developed, patented material (C)

** = Information from product data sheet*

Typical Virgin Commercial Refractory Microstructure



Cause of Refractory Wear
(High Cr_2O_3 Materials)



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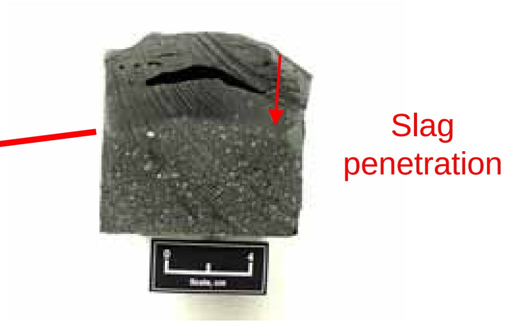
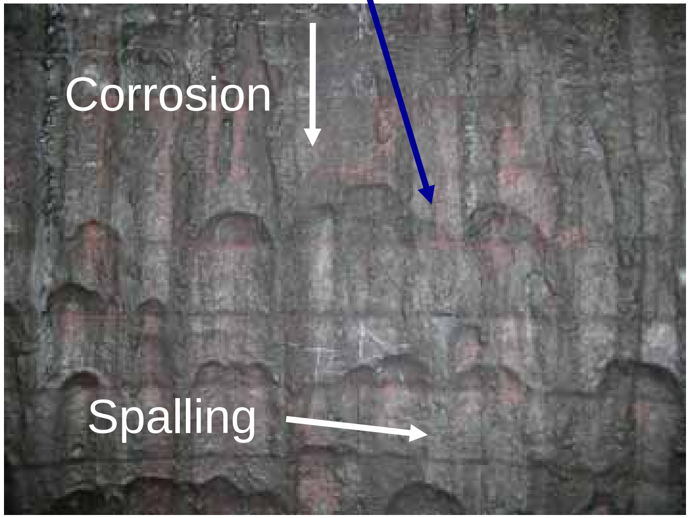
Material Challenges Inherent to Air-cooled Slagging Gasifiers





High chrome oxide liners
(60-95 pct Cr_2O_3)

- **Operating temperatures of 1325° to 1575°C**
- **Thermal cycling**
- **Reducing and oxidizing environment**
- **Corrosive slags of variable chemistry *(slags from minerals in carbon feedstock)***
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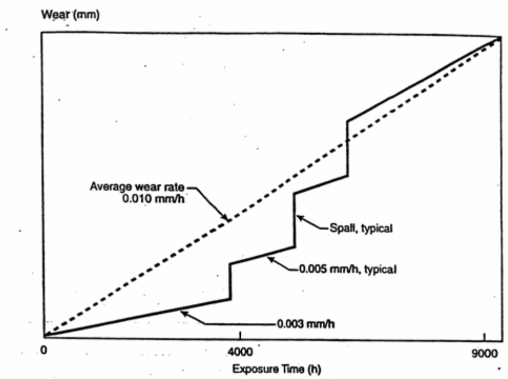
Spalling

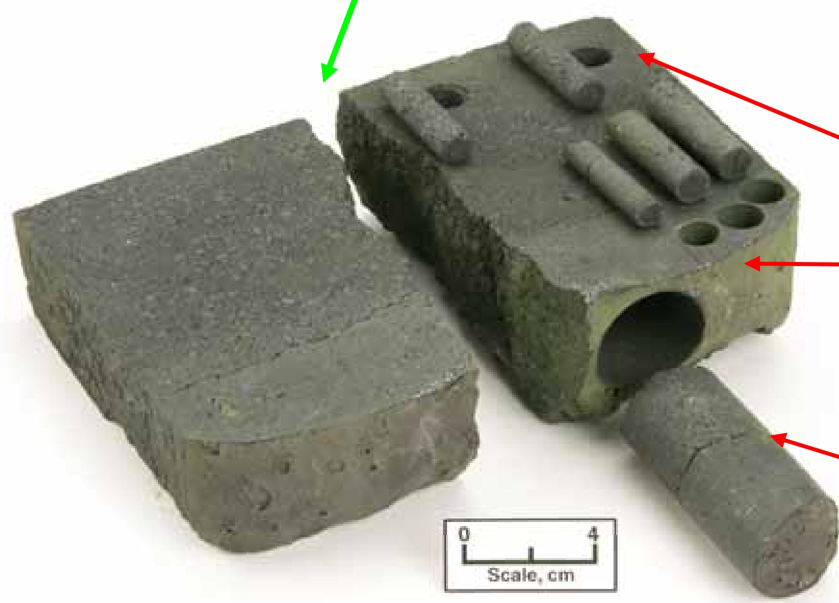


Combined Wear

W.T. Bakker, "Refractories for Present and Future Electric Power Plants," Key Engineering Materials, Trans Tech Publications, (1993), Vol. 88, pp. 41-70.

Post-Mortem Analysis

(Commercial Refractory ≈ 180 days of exposure to coal slag from 1350-1450^{o}C)



Thermal Expansion Cores

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

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

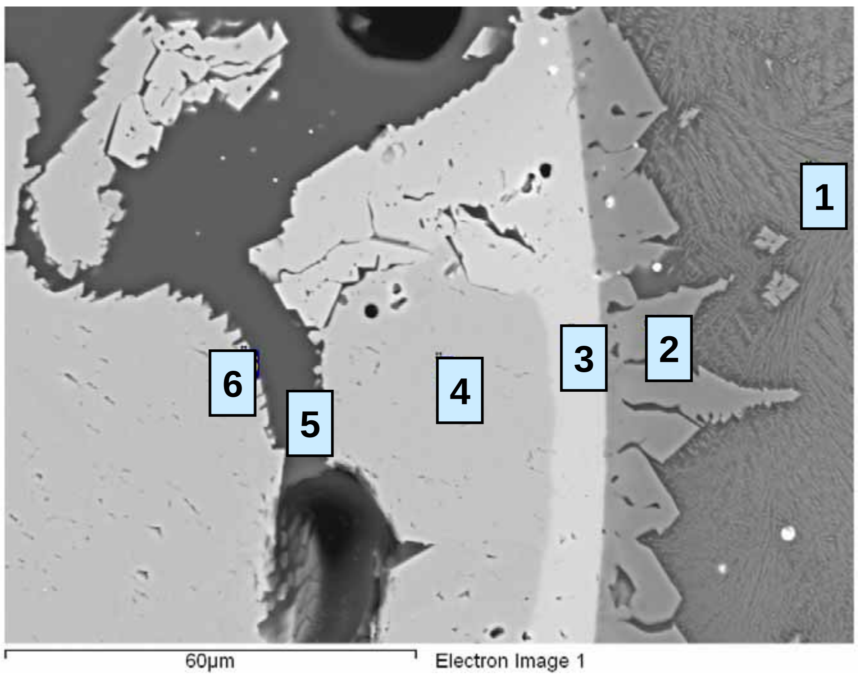
Chemical, X-Ray Crystalline Phases, Microstructure

Chemistry of High Chromia Commercial Refractory Versus Depth from Hot Face

Distance from Hot Face (mm)	Bulk Chemistry (wt pct)					X-Ray Crystalline Phases
	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**	P= Cr_2O_3 Tr=$M^*Cr_2O_4$
6.9	84.2	10.2	3.9	0.3	0.4	P= Cr_2O_3 Tr=$M^*Cr_2O_4$
11.4	83.9	10.7	3.2	0.4	0.4	P= Cr_2O_3 Tr=$M^*Cr_2O_4$
34.3	83.5	10.4	2.8	0.6	0.4	P= Cr_2O_3
43.3	83.9	9.3	2.3	**0.5**	0.2	P= Cr_2O_3
52.7	85.7	10.5	**0.9**	0.2	0.2	P= Cr_2O_3
57.2	86.1	10.5	0.2	0.0	0.2	P= Cr_2O_3
127	87.4	9.4	0.2	0.2	0.2	P= Cr_2O_3

M = (Fe, Mg, Ni, ….) solid solution

M^*Cr_2O4 = spinel



SEM Micrograph of the Slag/Refractory Interface After ≈ 85 Days of Exposure to a Coal Slag at 1400-1500^{o}C

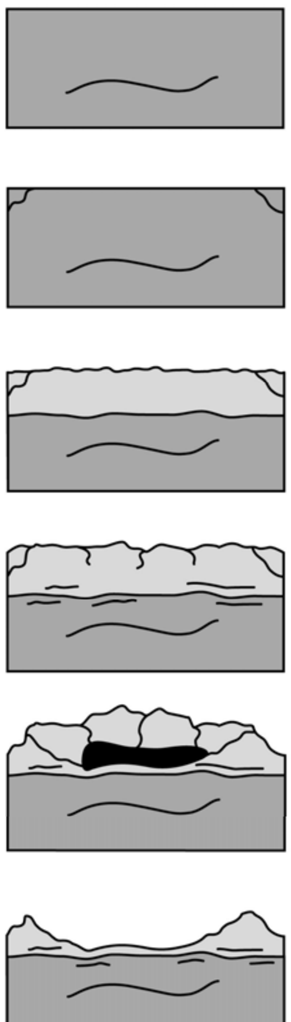
Point Chemistry

Chemistry (weight %)	Point					
	1	2	3	4	5	6
- 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

Point	Crystalline phases
1	Hercynite, Fayalite, Enstatite, Iron sulfide, Iron cordierite, Hermatite
2	Iron-alumina spinel
3	Iron-chrome spinel
4	Chromia/alumina solid solution
5	Fe depleted slag
6	Al build-up with Si

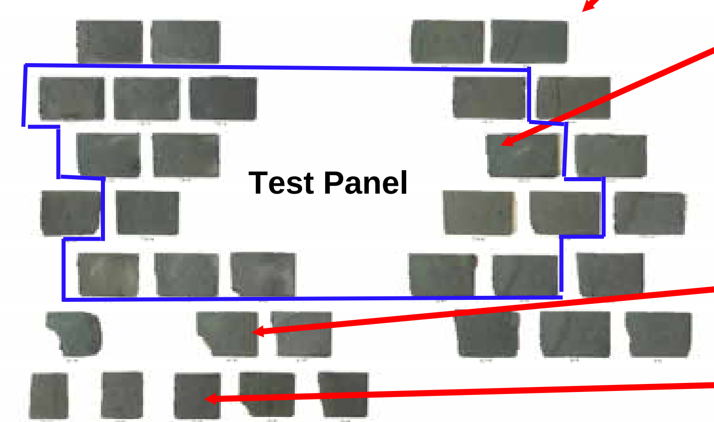
Possible Crystalline Phases

Corrosion and Spalling Wear



Stage	Sample	Description
1		***New*** • Refractory may contain internal cracks from pressing, firing.
2		***Preheat*** • Pinch spalling due to hoop stresses
3		***Infiltration, Corrosion*** • Molten slag infiltration on hot face, cracks and pores. • Surface corrosion due to slag begins
4		***Horizontal Crack Formation due to:*** • Thermal cycling • Stresss accumulation • Creep
5		***Void Formation*** • Cracks join • Internal void formation • Spalling (peeling) begins • Creep occurs on slag penetrated hot face • Hot face corrosion continues
6		***Renewed Cycle*** • Material breakoff on hot face • Steps 3-5 repeat

Internal Flaws – Improved Versus Conventional Cr_2O_3 Refractory *(sidewall test panel – 237 days)*



Cross Section of Brick in Test Panel

Conventional Refractory

Improved Phos Containing Test Refractory

Conventional Refractory

Impact of Phos on Slag Penetration, Corrosion

	Conventional	Phosphate Modified
1. No evidence of spalling in phosphate modified refractory		
2. Reduced slag penetration	25-45 mm depth	Preliminary indication, 3-5 mm depth
3. Microstructure	Higher porosity	Slag forms dense Fe/Cr spinel layer, higher viscosity slag, better thermal shock

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Conclusions

- **Slag interacts with the refractory causing wear by two means, chemical corrosion and spalling**
- **Microstructure changes occurring on the surface are primarily:**
  - a Cr_2O_3/FeO spinel that forms on the hot face refractory surface, increasing slag viscosity, slowing slag penetration
  - a high alumina layer is formed on the hot face surface. The origin of the Al_2O_3 is not clear
- **Slag infiltrates into the porous refractory, causing differences in material properties between the penetrated/non penetrated layers, leading to structural spalling.**
- **Phosphate additions to the refractory microstructure decrease spalling wear.**