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National Energy Technology Laboratory

Evaluating the Relationship between Slabbing of Cr_2O_3/MgO Refractories Used in Steelmaking and Spalling of High Chrome Oxide Refractories Used in Gasification

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Office of Fossil Energy

Outline

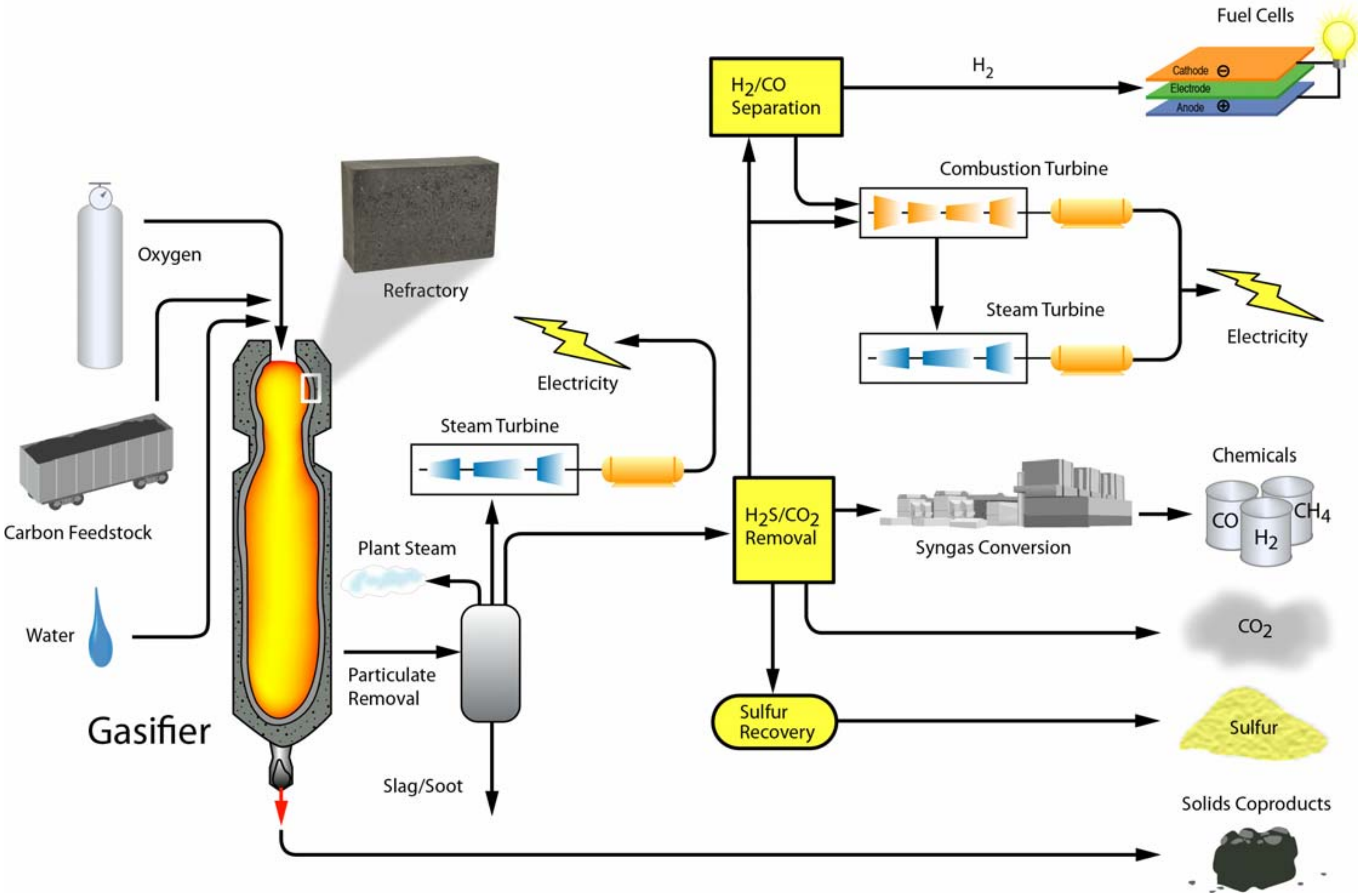
- **Acknowledgement**

  USDOE - NETL

  Advanced Gasification Technologies

  Advanced Metallurgical Processes
- **Background**
- **Issues/Consequences**
- **Post-Mortem Analysis**
- **Summary**

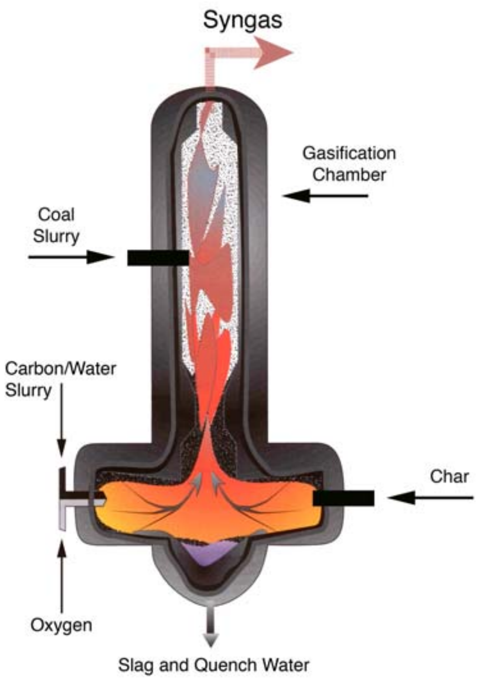
Gasification Background



Gasification Reaction

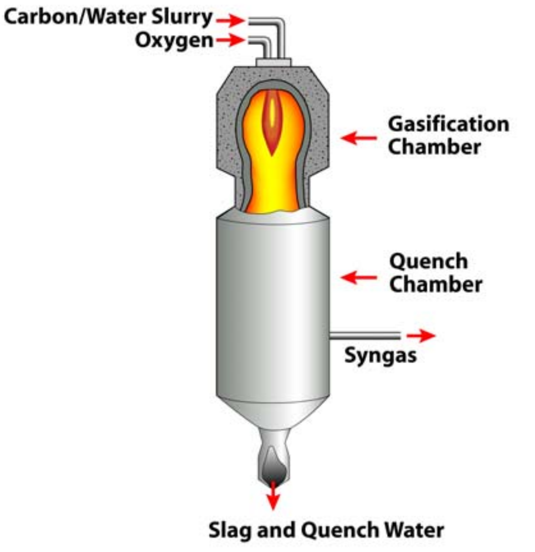
$C + H_2O$ (gas) $+ O_2 \rightarrow CO + H_2 + CO_2$ + minority gases/by-products

Material Challenges Inherent to Air-cooled Slagging Gasifiers



ConocoPhillips ***(2 stage - syngas cooler)***

- **Operating temperatures of 1325° to 1575°C.**
- **Thermal cycling.**
- **Alternating reducing and oxidizing environment.**
- **Corrosive slags of variable chemistry.**
- **Corrosive gases.**
- **Pressures ≥ 400 psi.**



GE Design ***(1 stage - syngas cooler or water quench)***

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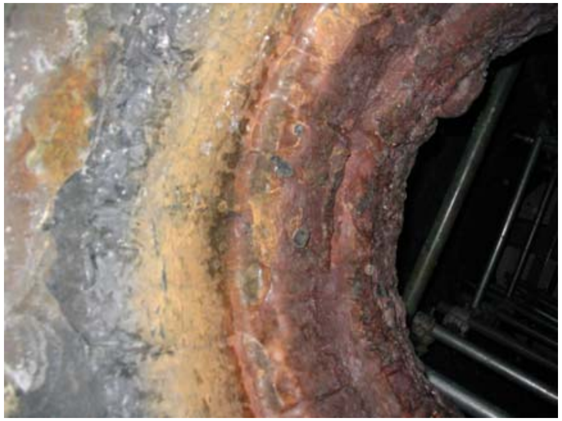
Refractory Material Issues - Consequences

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; 3-24 months**
4. **Need for zoning – larger “spare” material inventory**
5. **High material repair costs**
   - $1 million for refractory lining
6. **Excessive safety margins**



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Research Goal

Enhance gasifier reliability and economics through the development of improved refractory materials with longer service life

<u>Two major types of wear in gasifiers: *corrosion and spalling*</u>

- Research directed towards reducing/eliminating spalling wear of gasifier refractories
- Spalling wear is similar to known wear mechanisms in chromia/magnesia – magnesia/chromia steelmaking refractories (peeling, slabbing, chemical spalling)

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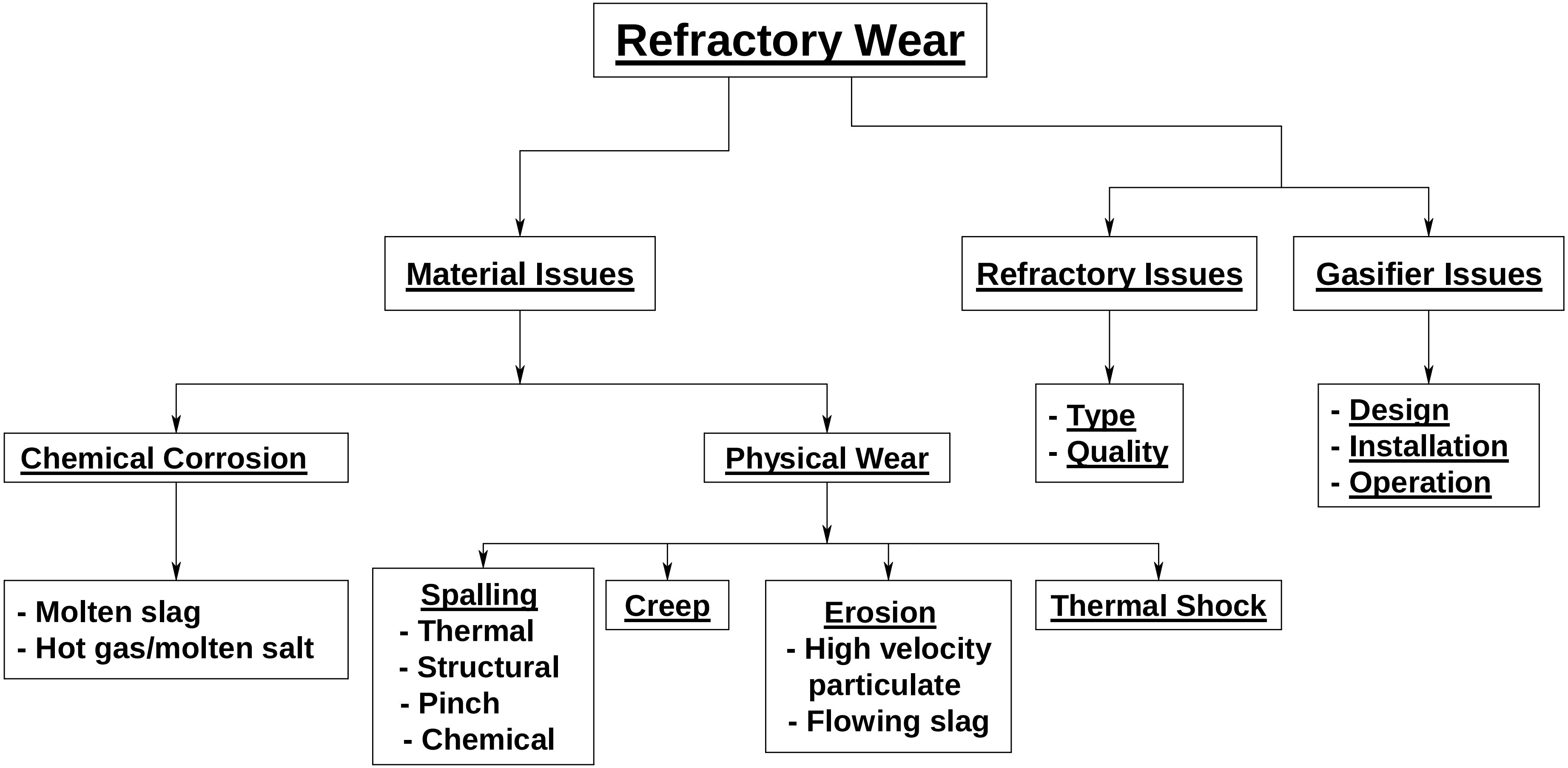
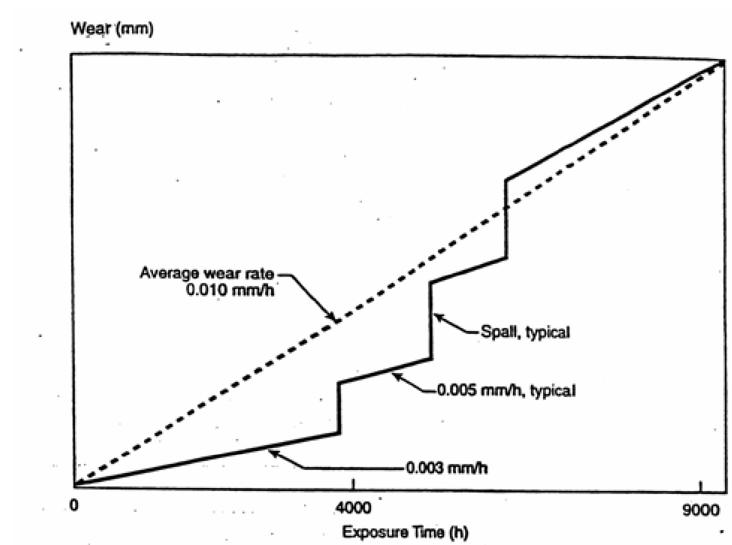
Causes of Refractory Wear in Gasfiers

(High Cr_2O_3 Materials)



Main Wear - Spalling and Chemical Corrosion



Bakker W. T. (1998) ˝Materials Guidelines for Gasification Plants˝ EPRI Report TR-110507, Palo Alto, CA.

Corrosion and Spalling

Corrosion

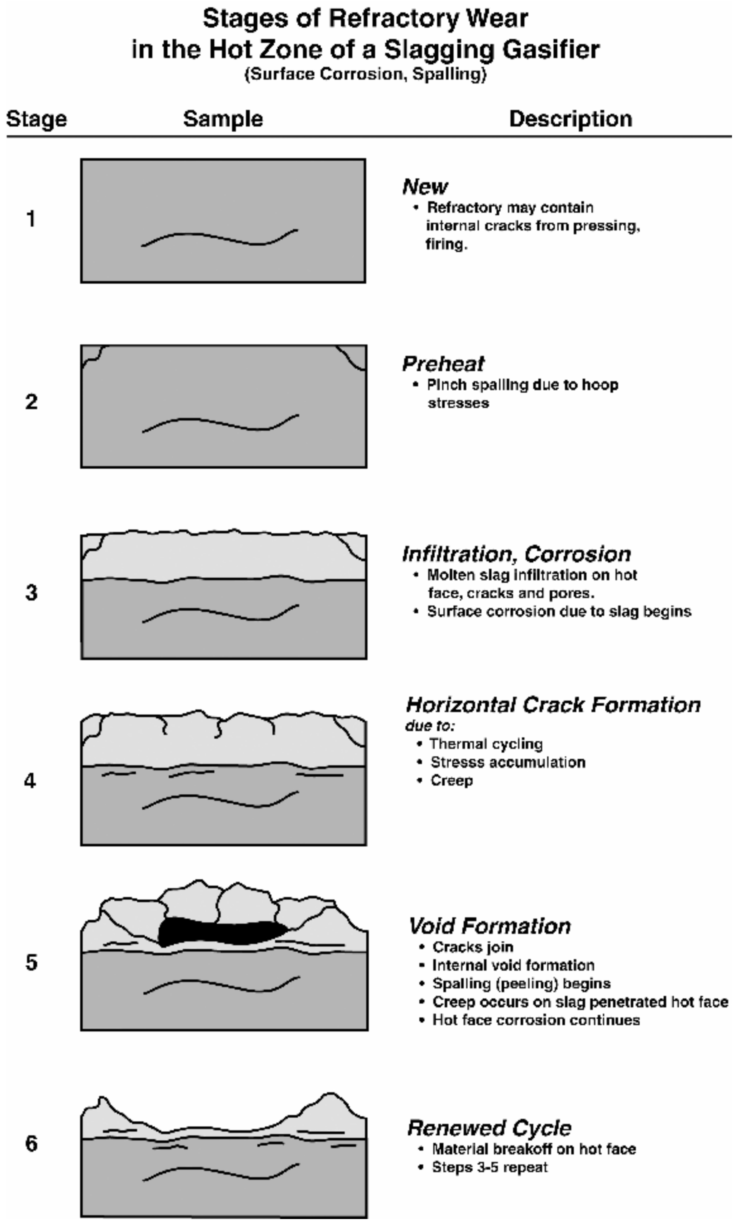
Spalling

Corrosion and Spalling

Spalling – Refractory Surface and Interior

Interior - Refractory Cross Section

Corrosion and Spalling Mechanism



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Impact of Spalling on Refractory Wear

Chemical Composition* of High Cr_2O_3 Gasifier and Steel Making Refractories

Chromia-Magnesite Steelmaking Brick

Element	Composition A	Composition B	Composition C
Cr_2O_3	90.1	87	24.8
Al_2O_3	9.3	3.0	22.3
ZrO_2	---	6.5	---
MgO	---	---	36.4
Fe_2O_3/SiO_2	---	---	3.3/4.5

Chrome Gasifier Brick

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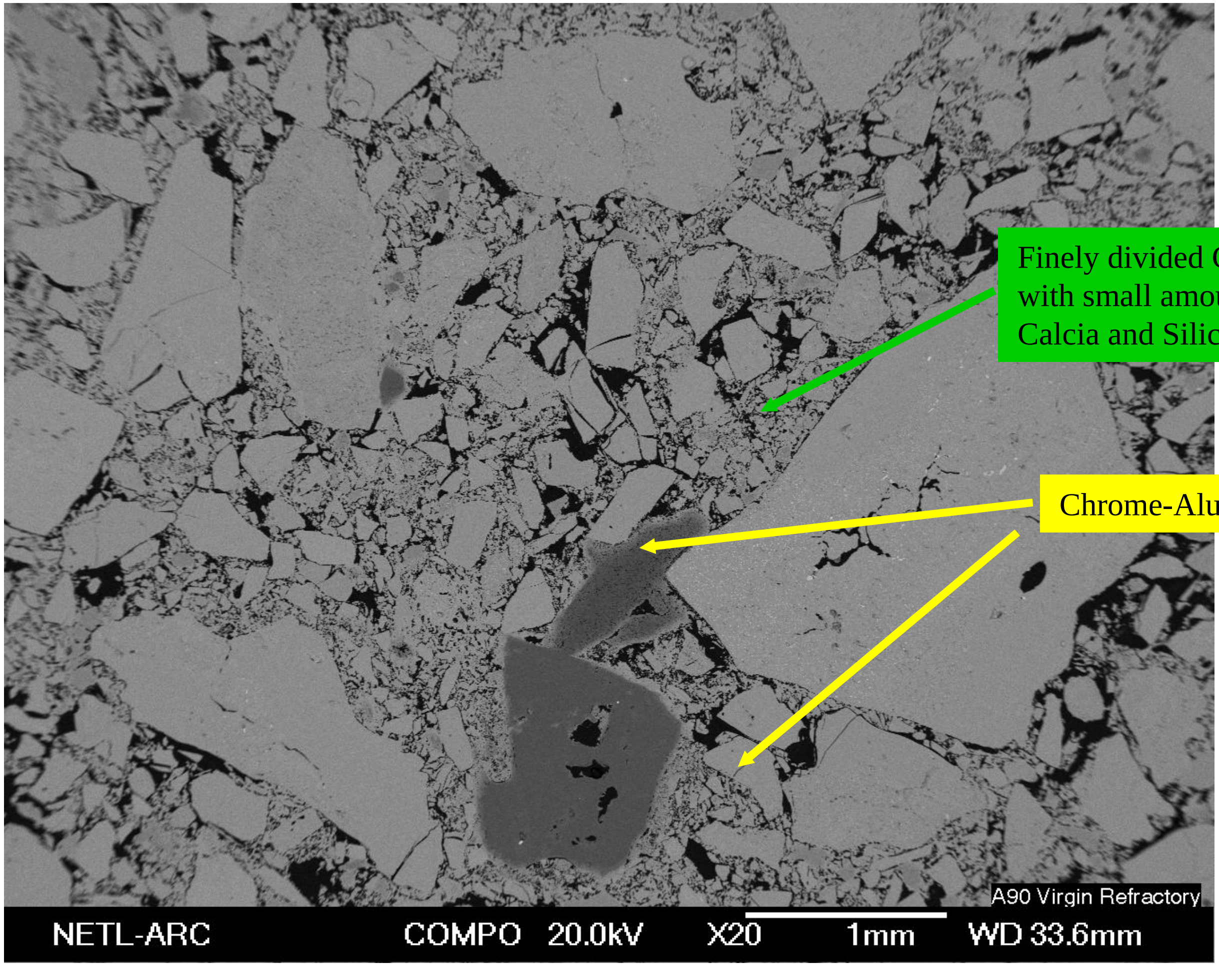
Causes of Spalling

1. **Density/porosity differences between slag infiltrated/non-infiltrated layers**
2. **Crystalline phase differences between slag infiltrated/non-infiltrated layers**
3. **Bursting expansion observed in chromia/magnesia steelmaking refractories *(reoxidation of FeO)***
4. **Reaction of alkali (Na and K) with chromia/alumina grain, resulting in the formation of disruptive sodium aluminate phases (vapor interaction)**

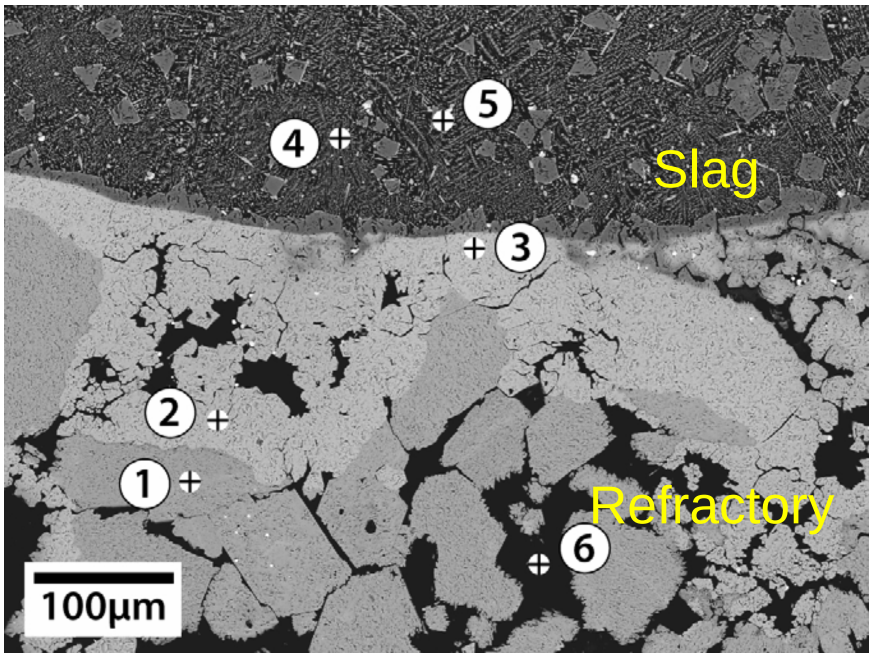
High Chrome Oxide Refractory Microstructure



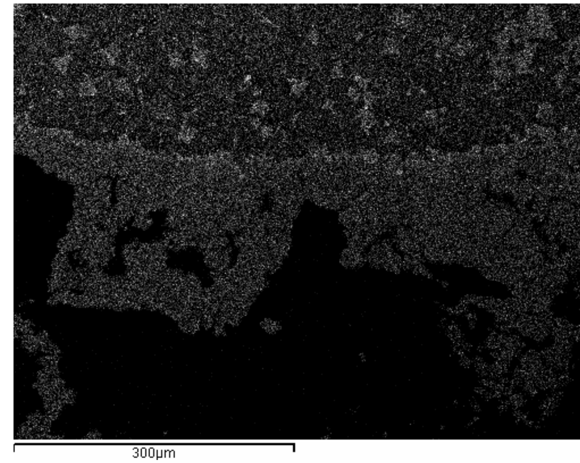
Finely divided Chrome Oxide with small amounts of Calcia and Silica

Chrome-Alumina (ss) grain

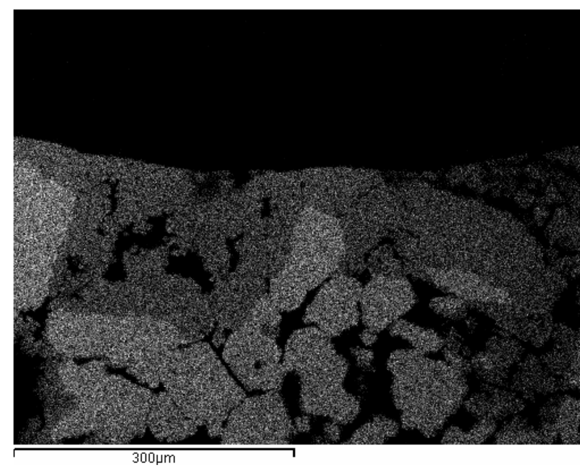
High Chrome Oxide Gasifier Refractory Infiltrated with Slag



Fe

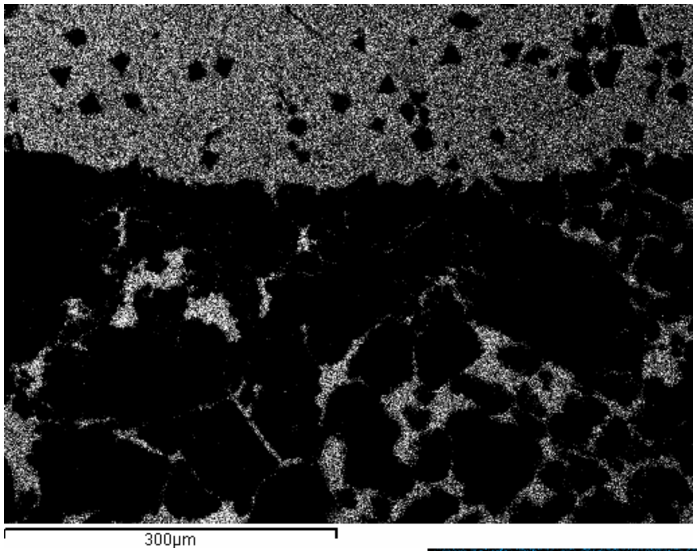


Cr

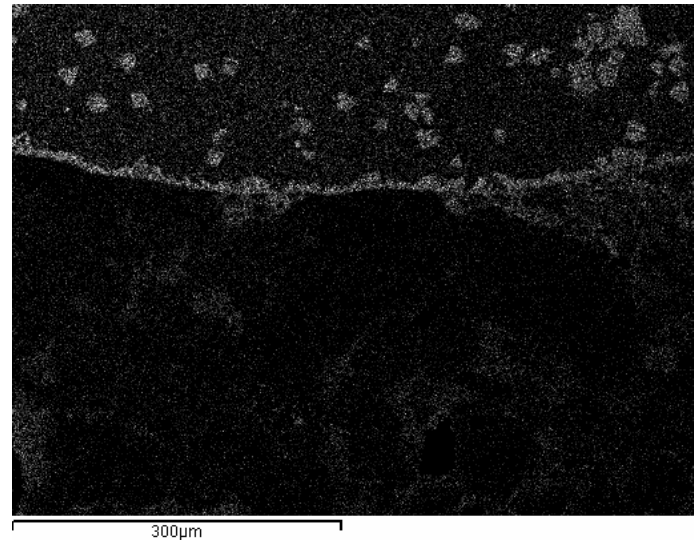


Slag diffusion, corrosion

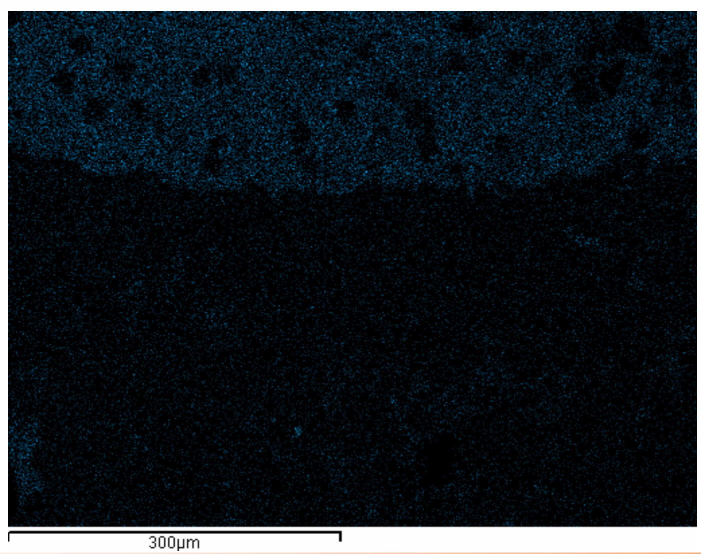
Refractory Surface Microstructure – Slag Attack
(Continued)



Si

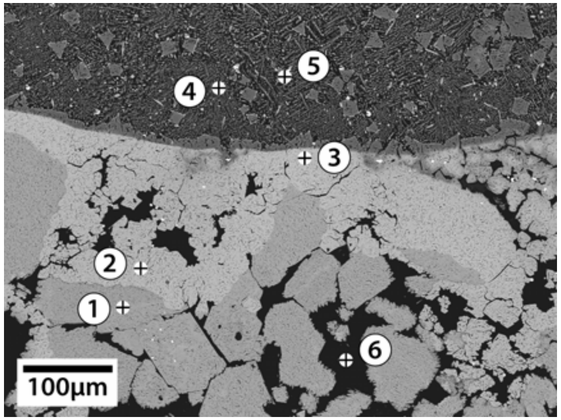


Al



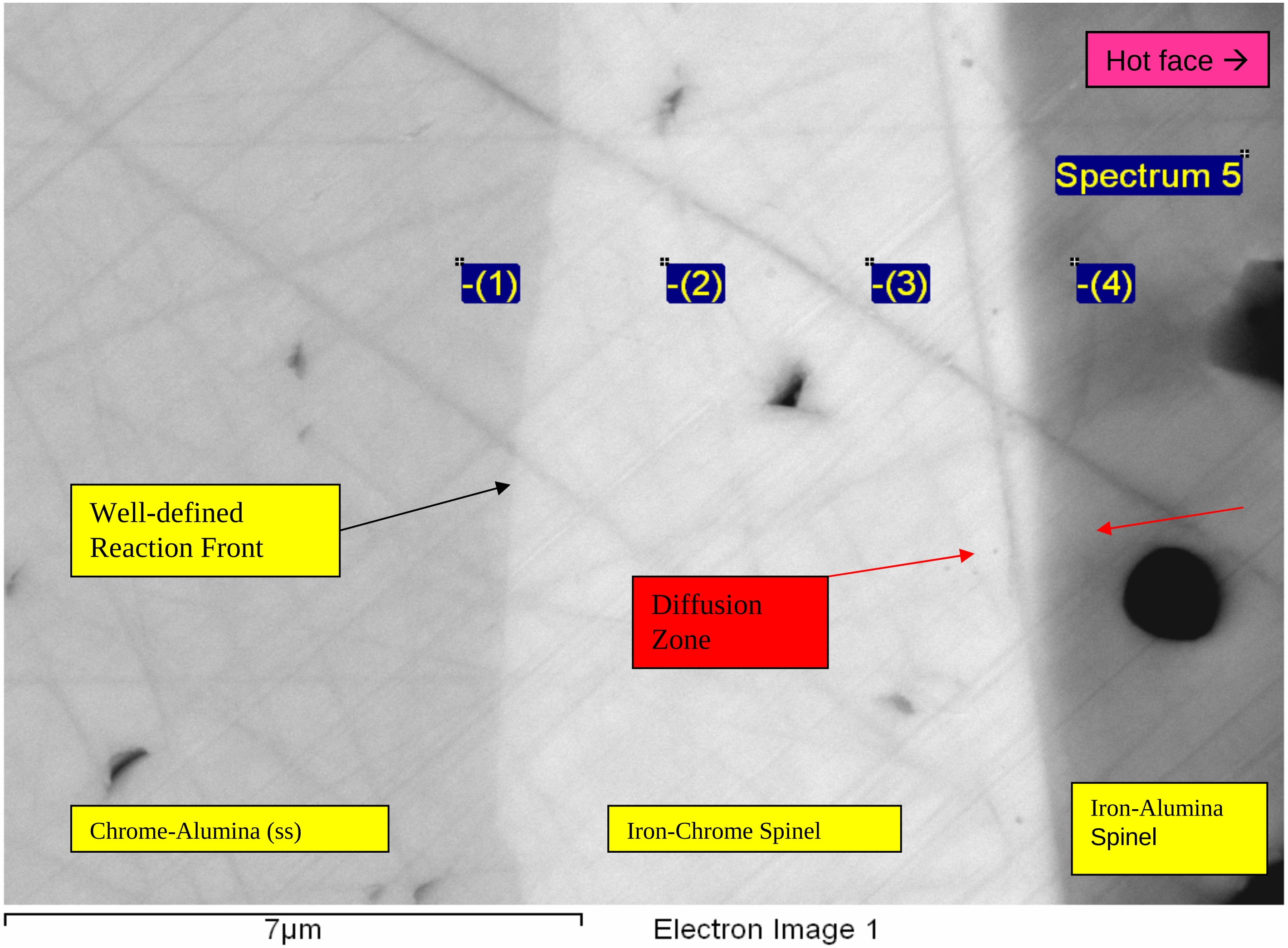
Ca

Elemental Analysis
(Refractory/Slag Interface)

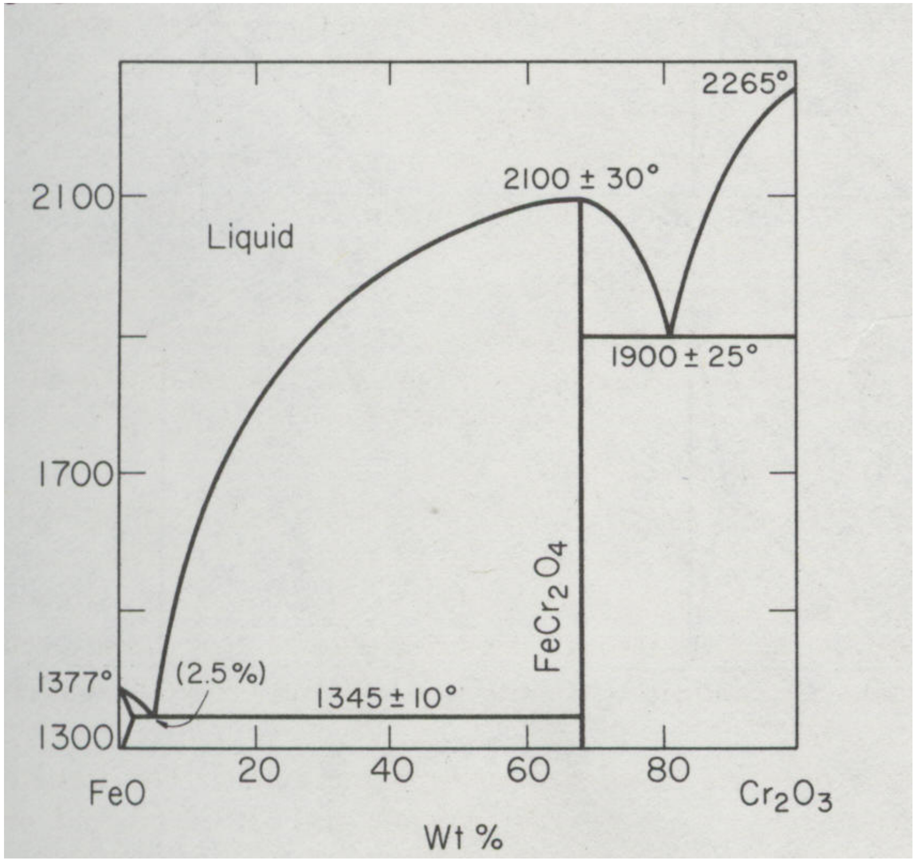


Point	Element (wt pct)				
	Cr	Al	Fe	Si	Ca
1 – int. ref. grain	63.8	5.7	-	-	-
2 – surface ref. grain ($FeCr_2O_4$)	37.8	5.6	25.2	-	-
3 – inter. ref. grain ($FeCr_2O_4$)	39.9	3.5	24.0	-	-
4 – slag	-	7.2	21.1	23.2	3.5
5 – crystallized slag ($FeAl_2O_4$)	-	27.0	31.1	-	-
6 – interior slag	1.3	8.0	1.4	32.7	1.6

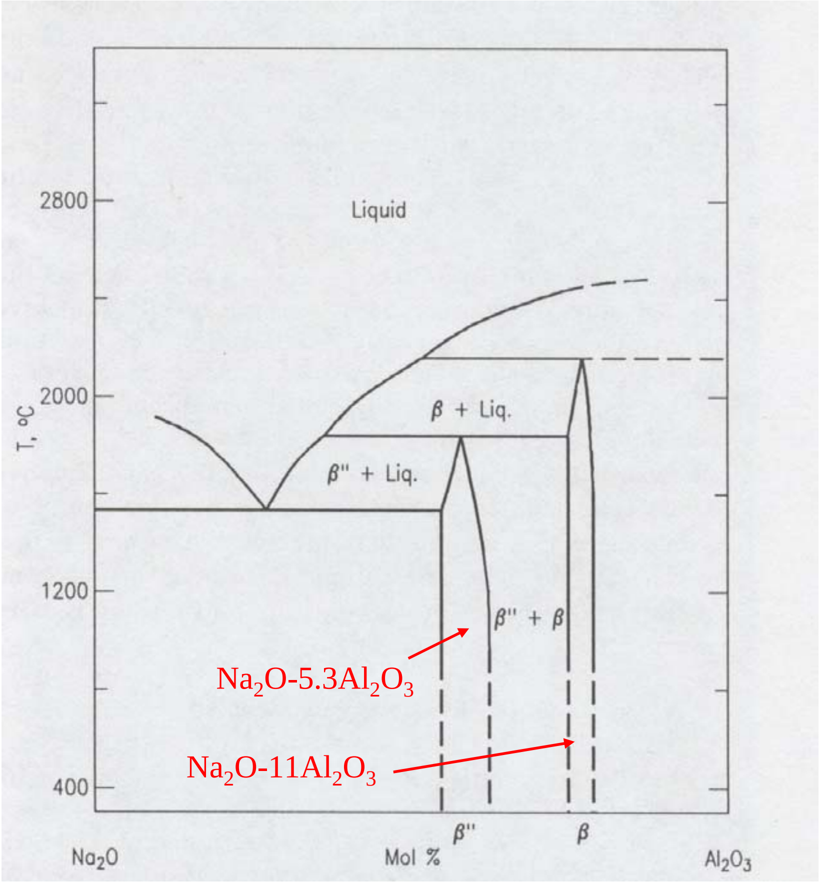
Iron – Chrome – Alumina Interactions



Known Phase Interactions



FeO – Cr_2O_3 Phase Diagram (from Phase Diagram for Ceramics 1975 Supplement, # 4187)



Na_2O – A_2O_3 Phase Diagram (from Phase Equilibria Diagrams Volume XII, # 9884)

Post-Mortem Analysis

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 of Layers

Core Analysis

(Chemical and Crystalline Phases)

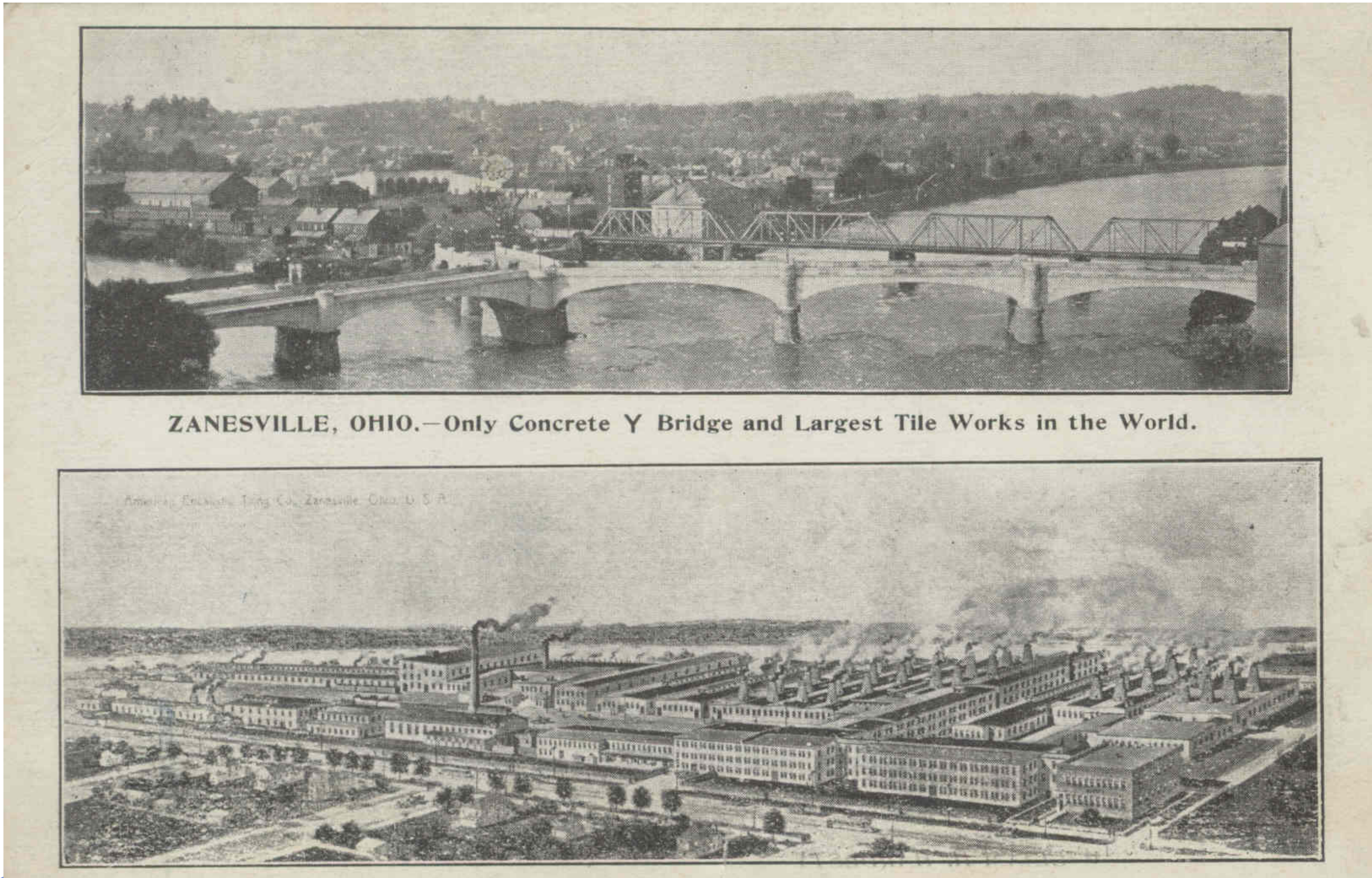
Distance from Hot Face (mm)	Bulk Chemistry (wt pct)					X-Ray Crystalline Phases
	Cr_2O_3	Al_2O_3	SiO_2	CaO	Fe	
H.F. to 2.3	80.0	10.8	5.4	0.3	1.6	P - Cr_2O_3 Tr– $FeCr_2O_4$
6.9	84.2	10.2	3.9	0.3	0.4	P - Cr_2O_3 Tr– $FeCr_2O_4$
11.4	83.9	10.7	3.2	0.4	0.4	P - Cr_2O_3 Tr– $FeCr_2O_4$
16.0	87.7	10.3	3.5	0.5	0.3	P - Cr_2O_3
20.6	83.9	10.3	3.0	0.5	0.3	Same
25.1	83.5	10.7	3.0	0.6	0.3	Same
29.7	84.3	10.4	2.7	0.6	0.3	Same
34.3	83.5	10.4	2.8	0.6	0.4	Same
38.9	82.7	10.0	1.6	0.6	0.3	Same
43.3	83.9	9.3	2.3	0.5	0.2	Same
48.0	85.4	9.6	0.6	0.1	0.2	Same
52.7	85.7	10.5	0.9	0.2	0.2	Same
57.2	86.1	10.5	0.2	0.0	0.2	Same
61.7	86.1	10.6	0.2	0.0	0.2	Same
127	87.4	9.4	0.2	0.2	0.2	Same

Summary

- Slabbing in chromia/magnesia refractories used in steelmaking and spalling in gasifier refractories are similar wear mechanisms
- Issues causing spalling/slabbing are complicated, but include:
  - Reaction between Cr_2O_3 and FeO to form $FeCr_2O_4$, increase in Al_2O_3 in Cr_2O_3, some structure swelling on surface
  - Microstructure differences between slag infiltrated/non-infiltrated areas
  - Cyclic operation of the gasifier

American Encaustic Tiling Co., 1920 – Zanesville, OH

(1st Tunnel Kiln in Used in Tile Industry, Largest Tile Producer)



Mosaic Tile Co., 1906 – Zanesville, OH
(Also Once the Largest Tile Company in the World)