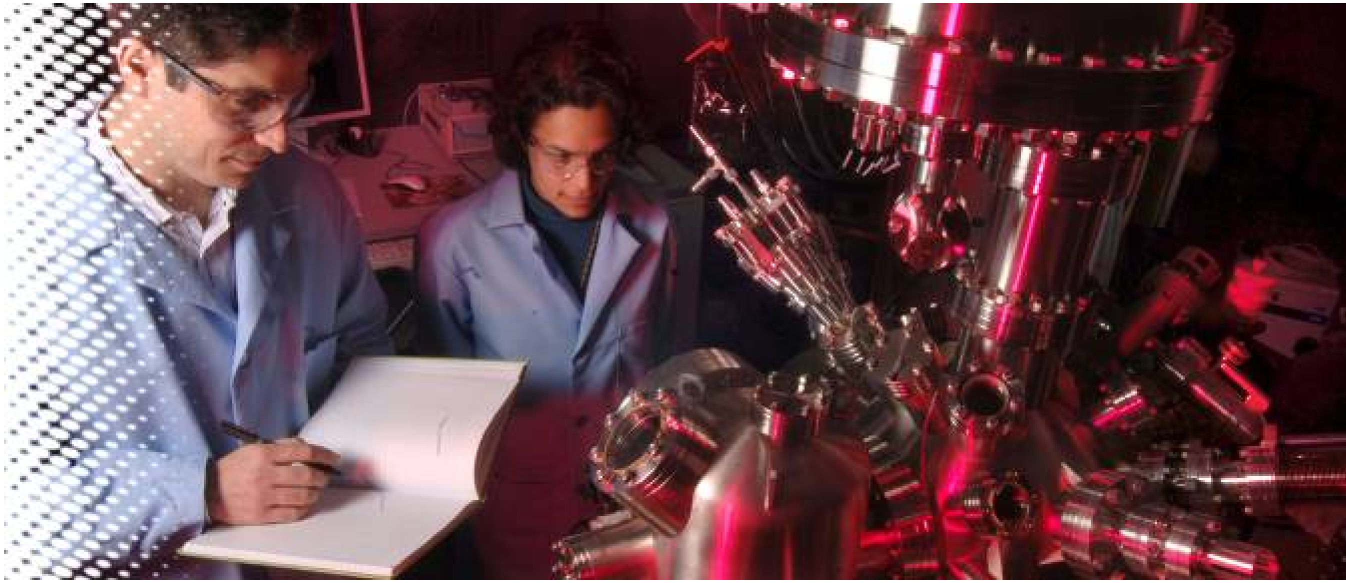
NATIONAL ENERGY TECHNOLOGY LABORATORY



Refractory Materials for Slagging Gasifiers

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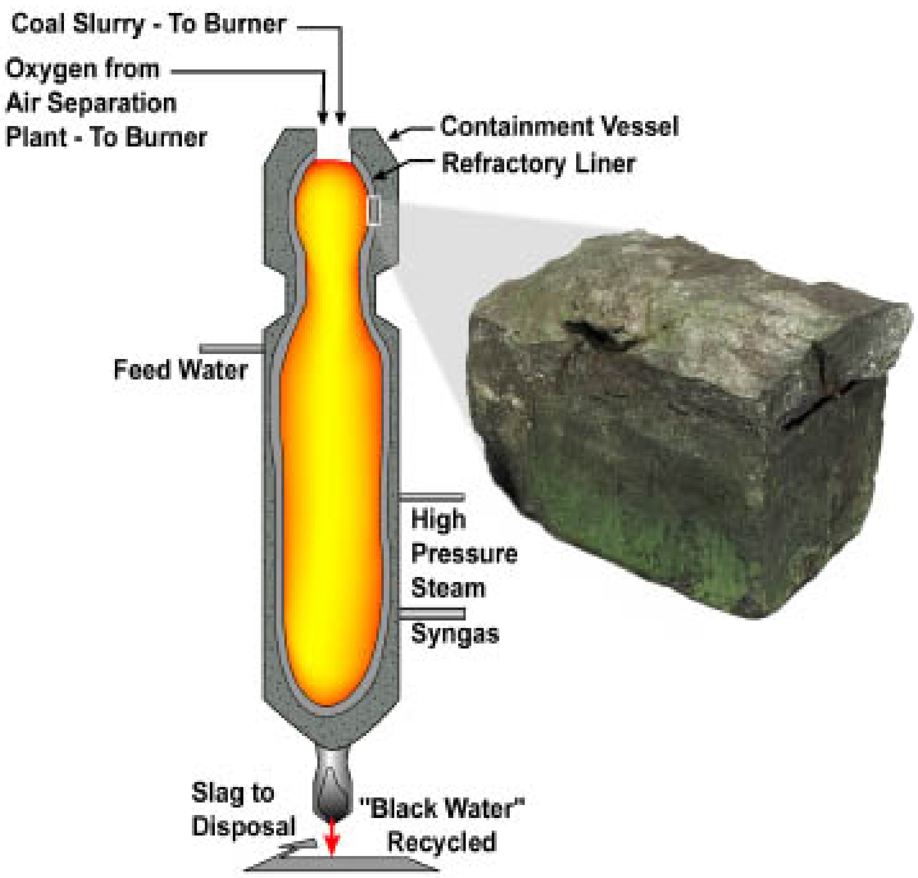
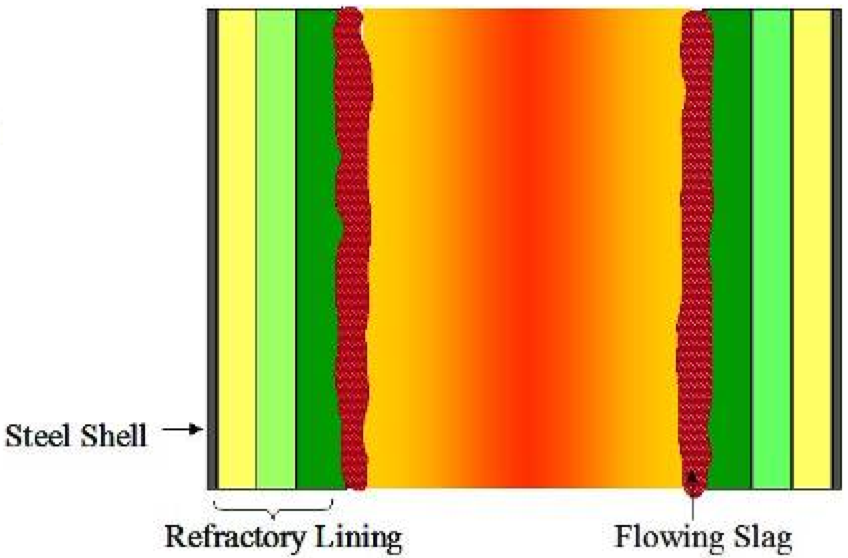
Project Objectives

- **Improved Refractories that lead to increased gasifier reliability, availability, and economics**
  – 85-95% for power generation, 90% for chemical production
  – Service life of 3 + years in power generation
- **Carbon feedstock flexibility**
- **Refractories that are environmentally friendly**
- **Reliable temperature measurement for the duration of a gasifier campaign**

Reliability and Availability of the Gasifier Island Depends on Materials Performance



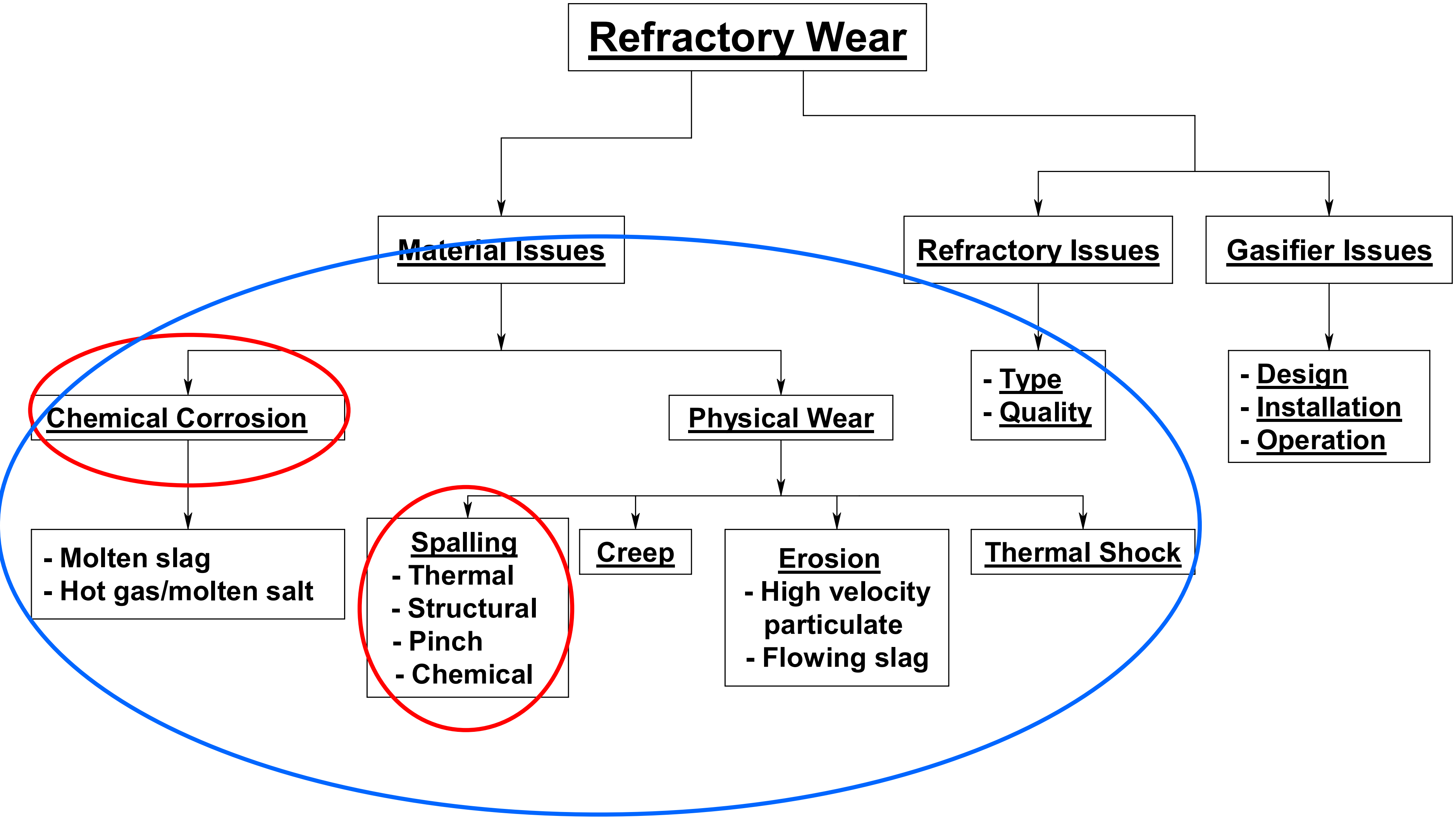


Refractory replacement cycle can be as frequently as every 90 days

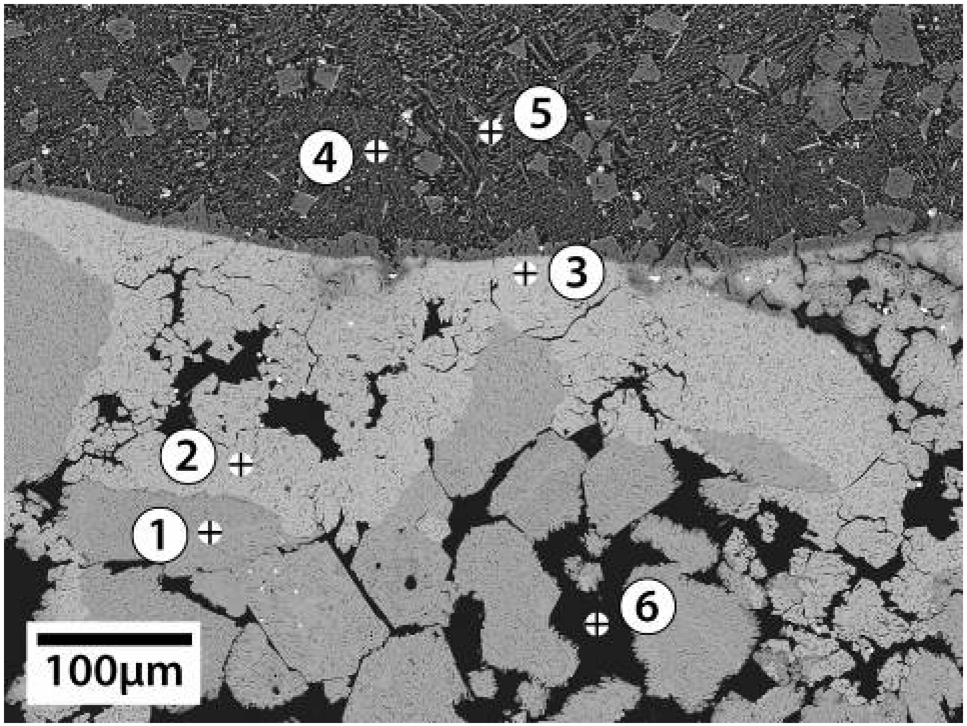
Materials Challenges Associated with Slagging Gasifiers

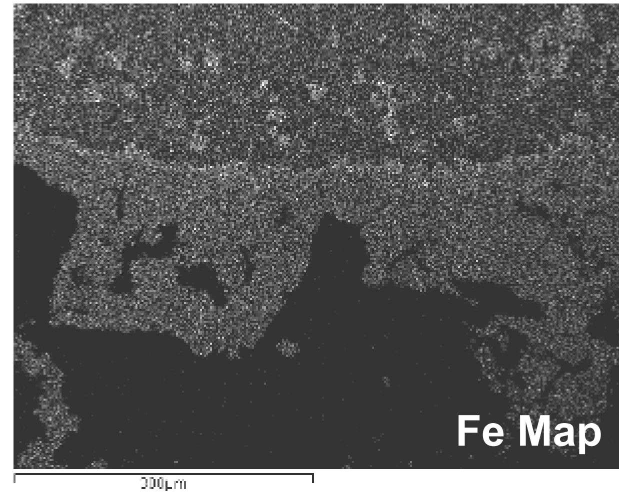
- Process temperatures of 1325º to 1575º C.
- Frequent thermal cycling.
- Reducing and oxidizing environments.
- Corrosive slags of variable chemistry.
- Corrosive gases.
- Pressures ≥ 400 psi.

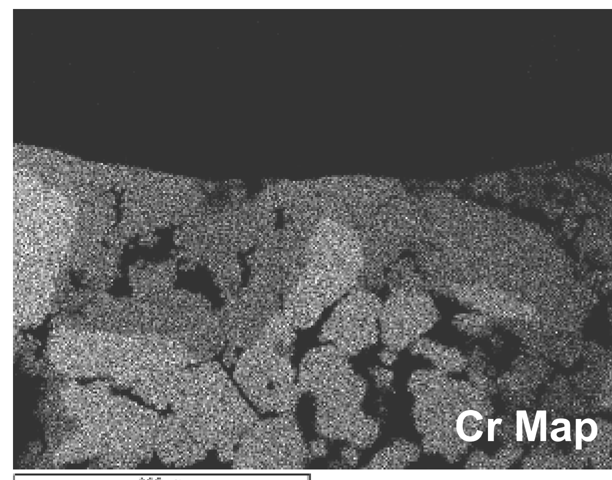
Causes for Refractory Failure



Causes for Refractory Failure: Chemical Corrosion

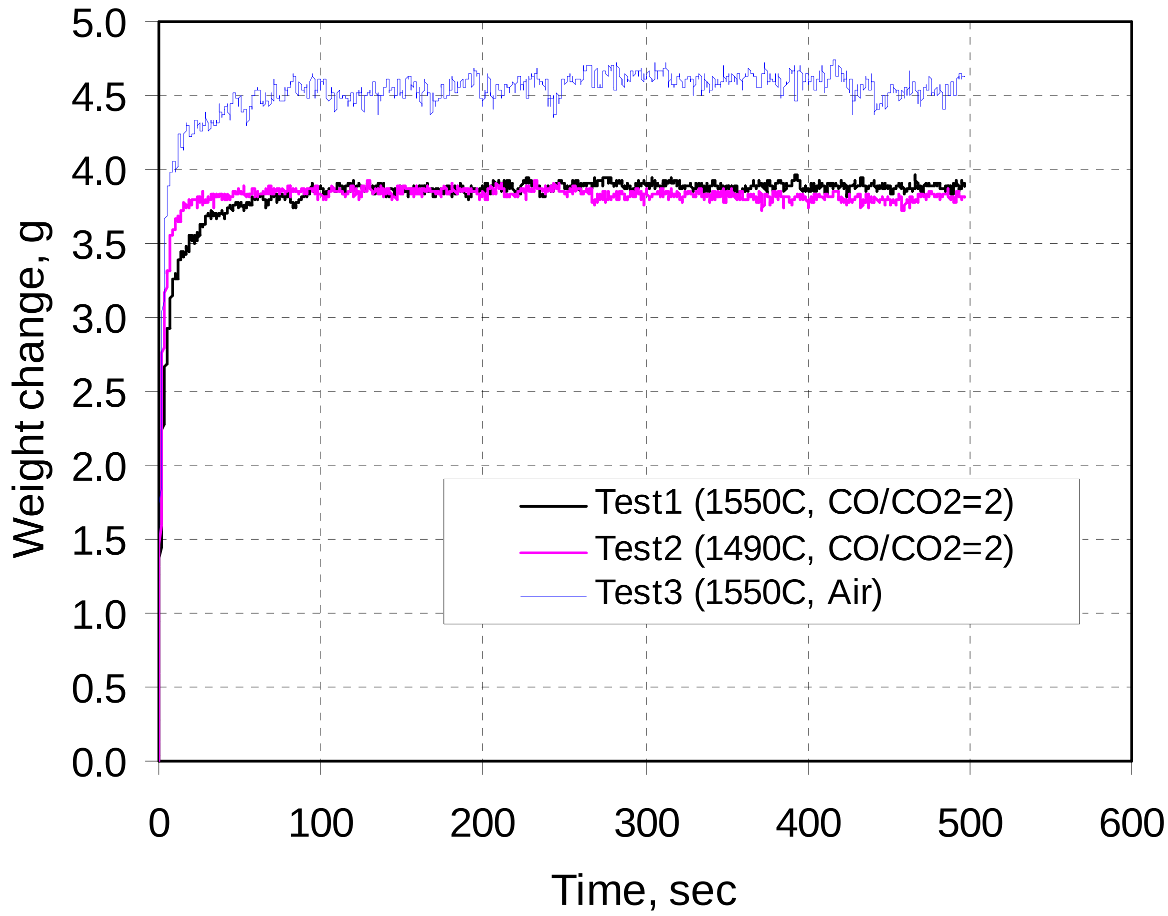






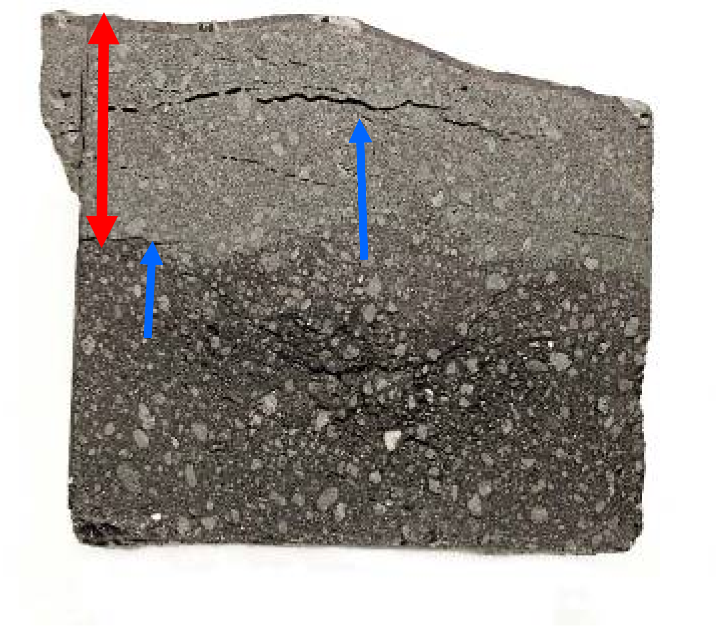
Refractory dissolution in the dynamic slag environment is inevitable, but in Cr_2O_3 refractories, it is a relatively slow process.

Causes for Refractory Failure: Slag Penetration



Slag rapidly penetrates the refractory microstructure, setting the stage for spalling …

Causes for Refractory Failure: Spalling



Spalling results in significant material loss, and much shorter refractory life when compared to chemical corrosion.

Refractory Solution: Phosphate Modified Cr_2O_3 Refractory Developed and Patented by the NETL

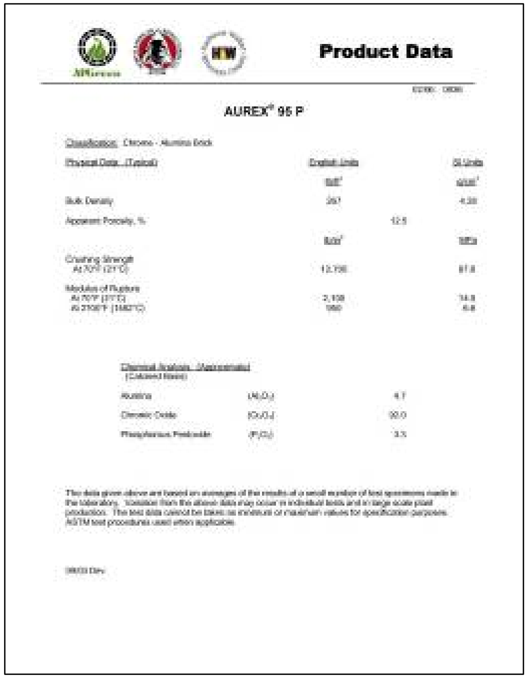
- Decrease slag penetration.
- Eliminate spalling.
- Maintain chemical corrosion resistance.

NETL Refractory

Previous Commercial “Best”

U.S. Patent 6,815,386 “Use of Phosphates to Reduce Slag Penetration in Cr2O3-Based Refractories.” Licensed by NETL in May, 2007, to Harbison-Walker Refractories Company

Refractory Solution: Aurex® 95P



Product Data

AUREX® 95 P

Classification: Chrome - Alumina Brick

Physical Data (Typical)	English Units		SI Units
	lb/ft^3		g/cm^3
Bulk Density	287		[illegible]
Apparent Porosity, %		12.5	
	lb/in^2		MPa
Crushing Strength At 70°F (21°C)	12,700		87.6
Modulus of Rupture At 70°F (21°C)	2,150		14.8
At 2700°F (1482°C)	990		6.8

Chemical Analysis (Approximate) (Calcined Basis)

Alumina	(Al_2O_3)	4.7
Chromic Oxide	(Cr_2O_3)	92.0
Phosphorous Pentoxide	(P_2O_5)	3.3

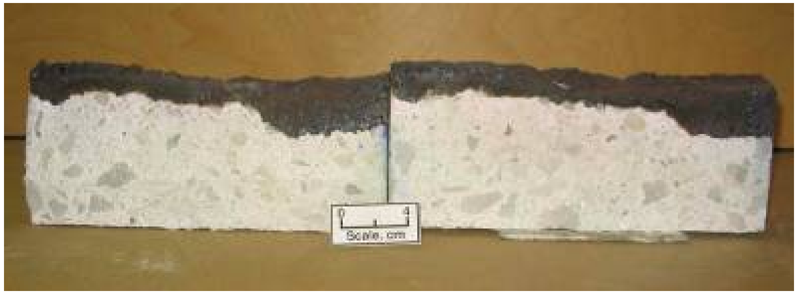
Field tests in commercial gasifiers with coal and/or petroleum coke feedstocks confirm elimination of spalling as a primary wear mechanism in Aurex® 95P and continued high resistance to chemical dissolution.

Why Push Beyond Cr_2O_3 Refractories?

- Industry desire for fuel flexibility leads to questions regarding the suitability of Cr_2O_3 refractories in ash/slag environments that are high in alkalis and alkaline earths.
- The use of Cr_2O_3 refractories limits opportunities to employ repair techniques adopted by other industries that could extend refractory life and increase gasifier availability.
- High Cr_2O_3 refractories are difficult to produce and expensive as a result. In addition, domestic suppliers are dwindling.

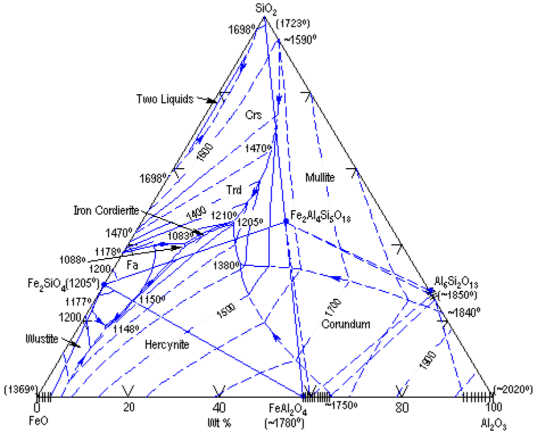
Research Goal: Viable Non-Cr_2O_3 Alternatives

- **Same materials performance issues are likely in non-chome systems – refractory loss expected to be dominated by dissolution and/or reaction with the slag.**
- **Approach is to identify materials systems that are relatively stable in the gasifier environment and then to manipulate microstructure and microchemistry to optimize performance.**
- **Laboratory proof of concept is followed by scale-up with industrial partners.**

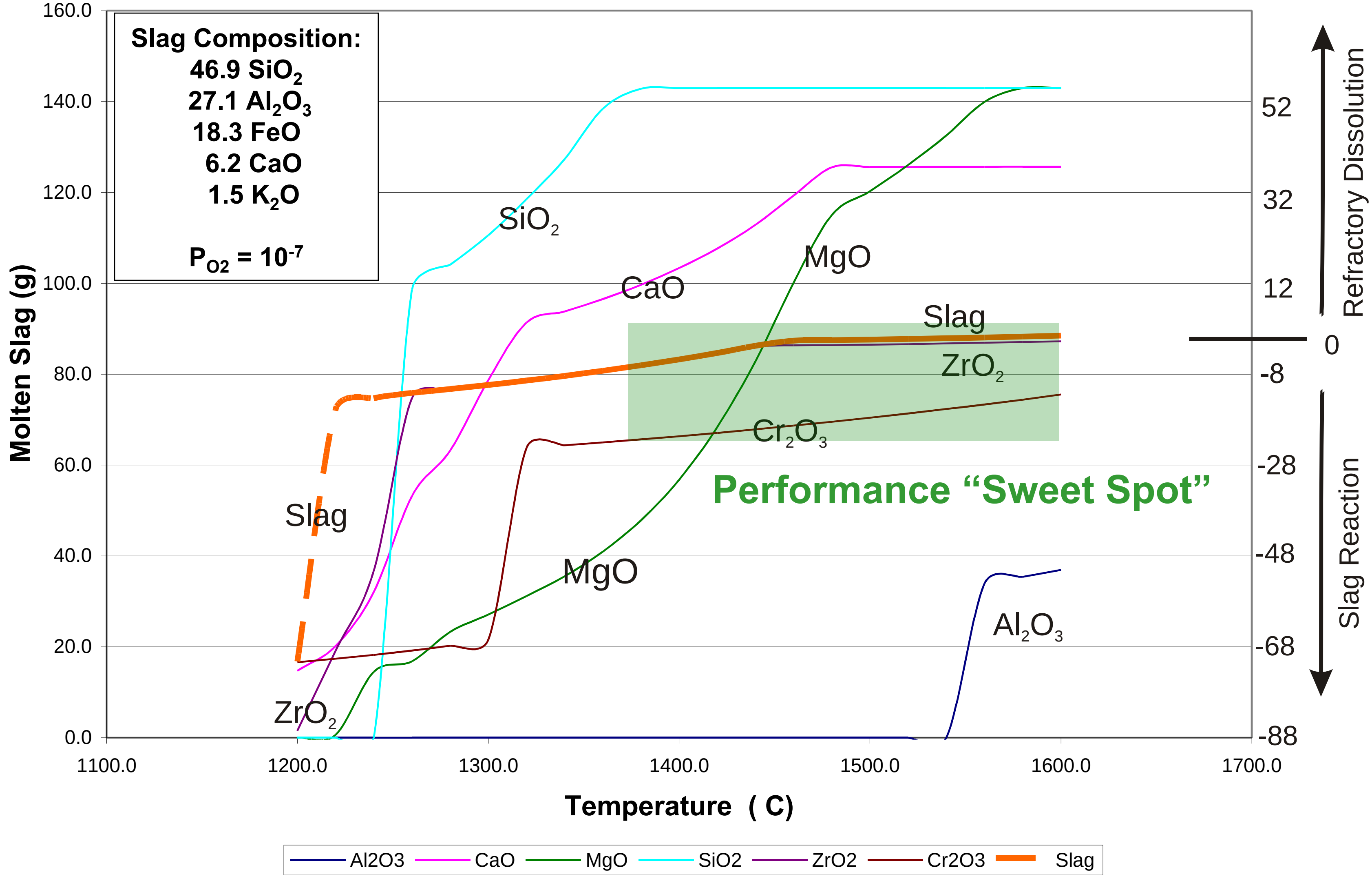


Possible Non-Cr_2O_3 Alternatives

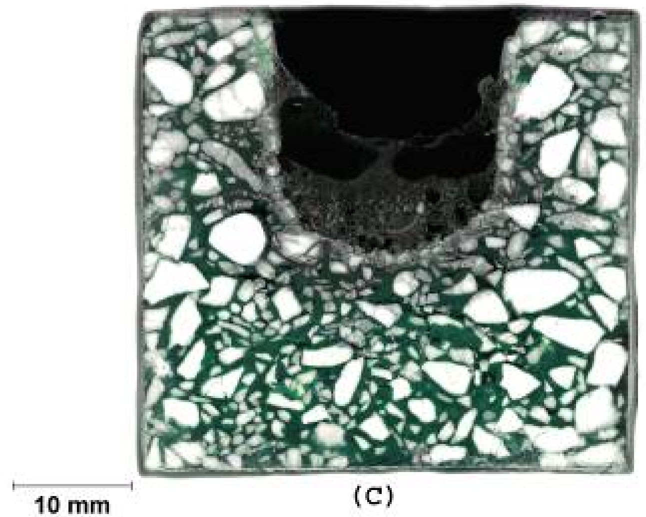
Thermodynamics suggests that few materials will match Cr_2O_3 performance with regard to chemical stability, but that refractories in the ZrO_2 and Al_2O_3 + MgO systems have potential, depending on ash chemistries. Practical experience also suggests several microstructural and microchemical manipulations that could enhance refractory performance.



The Search for Non-Cr_2O_3 Alternatives



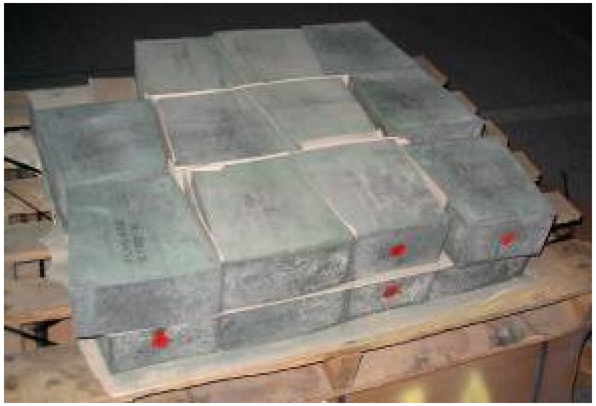
Laboratory Proof of Concept



Static laboratory exposure tests confirm or deny thermodynamic predictions, and the impact of macrostructure/microstructure design on refractory stability.

Next Steps: Scale-up with Industrial Partners

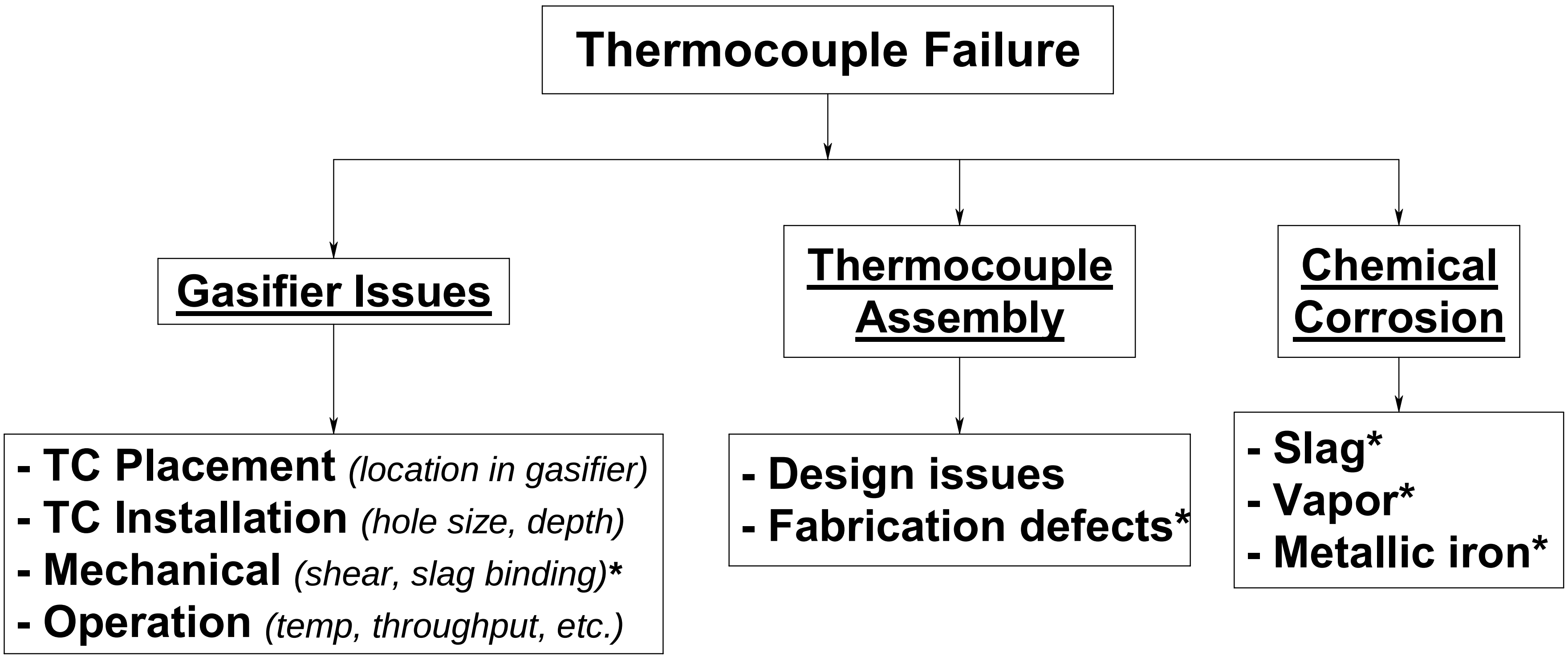
- Promising new materials have been selected based on laboratory tests, and have been scaled up, in collaboration with several commercial partners, for dynamic laboratory testing.
- Dynamic laboratory tests are underway, with initial results confirming several potential non-Cr_2O_3 alternatives.



Temperature Sensors for Effective Gasifier Operation

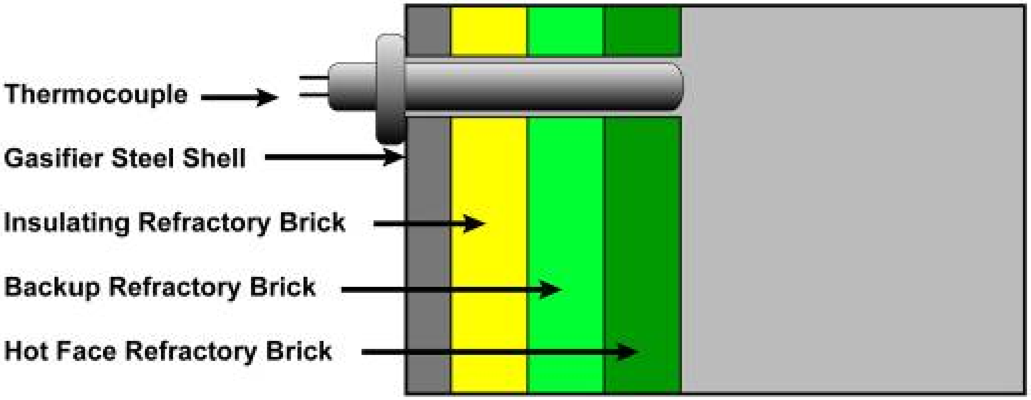
- Thermocouples are currently the most-commonly used method of process temperature measurement.
- Thermocouples rarely last an entire gasifier campaign, and can fail early in the start-up process. Replacement requires gasifier shutdown.
- Effective temperature control will impact system reliability, availability, and economics.
- Strategies that can extend thermocouple life are the goal of this project.

Factors Impacting Thermocouple Failure

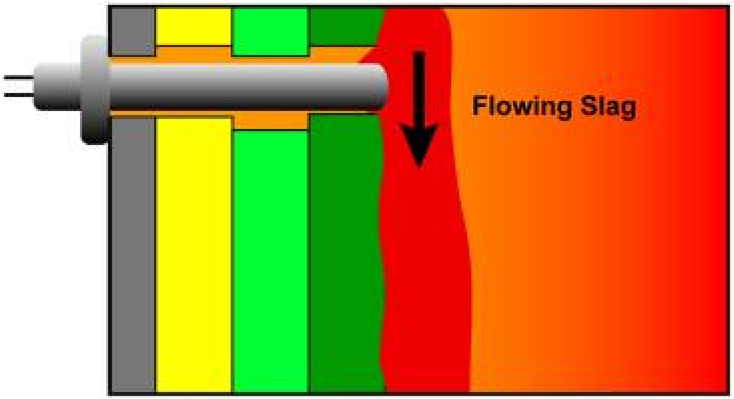


* = Possible refractory related issue

Thermocouple Failure during Gasifier Operation



Initial Installation



During Gasification

Improved Sensor Reliability through Better Engineered Protection Materials

NETL-recommended fabrication procedure to reduce processing flaws, combined with NETL-developed filler material to reduce slag penetration and attack

Improved Sensor Reliability through Engineered Protection Materials

An improved refractory thermocouple well block could also provide better thermocouple protection in the gasifier environment.

Improved Sensor Reliability through a Better Understanding of Sensor Failure

Tracking system implemented to document causes and frequencies of thermocouple failure.

Current Project Status

- An improved performance high Cr_2O_3 refractory has been developed, patented, and the technology licensed to industry.
- Laboratory proof-of-concept continues on several non Cr_2O_3 refractory materials that show promise for gasifier applications where fuel flexibility is desirable.
- Understanding of thermocouple failure in gasifiers continues to evolve, with remediation strategies being developed in collaboration with gasifier users.

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Thank You!