Refractory Materials for Slagging Gasifiers

Cynthia A. Powell
James P. Bennett, Kyei-Sing Kwong, Arthur V. Petty, Rick Krabbe, and Hugh Thomas
Office of Research & Development
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 1325° to 1575° C.
• Frequent thermal cycling.
• Reducing and oxidizing environments.
• Corrosive slags of variable chemistry.
• Corrosive gases.
• Pressures ≥ 400 psi.
Causes for Refractory Failure

**Refractory Wear**

**Material Issues**
- Chemical Corrosion
  - Molten slag
  - Hot gas/molten salt

**Physical Wear**
- Spalling
  - Thermal
  - Structural
  - Pinch
  - Chemical
- Creep

**Refractory Issues**
- Erosion
  - High velocity particulate
  - Flowing slag
- Thermal Shock
  - Type
  - Quality

**Gasifier Issues**
- Design
- Installation
- Operation
Causes for Refractory Failure: Chemical Corrosion

Refractory dissolution in the dynamic slag environment is inevitable, but in Cr$_2$O$_3$ 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$_2$O$_3$ Refractory Developed and Patented by the NETL

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

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

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$_2$O$_3$ Refractories?

- Industry desire for fuel flexibility leads to questions regarding the suitability of Cr$_2$O$_3$ refractories in ash/slag environments that are high in alkalis and alkaline earths.
- The use of Cr$_2$O$_3$ refractories limits opportunities to employ repair techniques adopted by other industries that could extend refractory life and increase gasifier availability.
- High Cr$_2$O$_3$ refractories are difficult to produce and expensive as a result. In addition, domestic suppliers are dwindling.
Research Goal: Viable Non-Cr$_2$O$_3$ Alternatives

• Same materials performance issues are likely in non-chrome 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$_2$O$_3$ Alternatives

Thermodynamics suggests that few materials will match Cr$_2$O$_3$ performance with regard to chemical stability, but that refractories in the ZrO$_2$ and Al$_2$O$_3$ + 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$_2$O$_3$ Alternatives

Slag Composition:
- 46.9 SiO$_2$
- 27.1 Al$_2$O$_3$
- 18.3 FeO
- 6.2 CaO
- 1.5 K$_2$O

$P_{O2} = 10^{-7}$

Molten Slag (g)

Performance “Sweet Spot”
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$_2$O$_3$ 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

**Gasifier Issues**
- TC Placement *(location in gasifier)*
- TC Installation *(hole size, depth)*
- Mechanical *(shear, slag binding)*
- Operation *(temp, throughput, etc.)*

**Thermocouple Assembly**
- Design issues
- Fabrication defects*

**Chemical Corrosion**
- Slag*
- Vapor*
- Metallic iron*

* = Possible refractory related issue
Thermocouple Failure during Gasifier Operation

Initial Installation

During Gasification

Flowing Slag
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$_2$O$_3$ refractory has been developed, patented, and the technology licensed to industry.

• Laboratory proof-of-concept continues on several non Cr$_2$O$_3$ 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!