FIELD TRIAL RESULTS OF NETL’s PHOSPHATE-MODIFIED HIGH CHROME OXIDE REFRACTORY MATERIAL FOR SLAGGING GASIFIERS

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Air Cooled Slagging Gasifiers Used in Gasification

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

**GE Design**
(1 stage - syngas cooler or water quench)
**Material Challenges Inherent to Air-cooled Slagging Gasifiers**

- Operating temperatures of 1325°C 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

High chrome oxide liners (60-95 pct Cr₂O₃)

Cause of Refractory Wear
(\textit{High Cr}_2\textit{O}_3 \textit{Materials})

Refractory Wear

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

Physical Wear
- Spalling
  - Thermal
  - Structural
  - Pinch
  - Chemical
- Creep
- Erosion
  - High velocity particulate
  - Flowing slag
- Thermal Shock

Refractory Issues
- Type
- Quality

Gasifier Issues
- Design
- Installation
- Operation
Typical Virgin Commercial High Cr$_2$O$_3$ Refractory Microstructure

- Cr$_2$O$_3$/Al$_2$O$_3$ Solid Solution
- Al$_2$O$_3$ Grains
Corrosive Wear of High Chrome Oxide Refractories
## Corrosion and Spalling Wear

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
</table>
| 1     | ![Image](image1.png) | **New**  
  - Refractory may contain internal cracks from pressing, firing. |
| 2     | ![Image](image2.png) | **Preheat**  
  - Pinch spalling due to hoop stresses |
| 3     | ![Image](image3.png) | **Infiltration, Corrosion**  
  - Molten slag infiltration on hot face, cracks and pores.  
  - Surface corrosion due to slag begins |
| 4     | ![Image](image4.png) | **Horizontal Crack Formation**  
  *due to:*  
  - Thermal cycling  
  - Stress accumulation  
  - Creep |
| 5     | ![Image](image5.png) | **Void Formation**  
  - Cracks join  
  - Internal void formation  
  - Spalling (peeling) begins  
  - Creep occurs on slag penetrated hot face  
  - Hot face corrosion continues |
| 6     | ![Image](image6.png) | **Renewed Cycle**  
  - Material breakoff on hot face  
  - Steps 3-5 repeat |
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
6. Excessive safety margins
Gasifier Program Goals

- Increased reliability and availability
  - 85-95% for power generation, 90% for chemical production
  - Service life of 3 + years in power generation
- Environmentally safe refractory (no Cr$^{+6}$ formation)
- Carbon feedstock flexibility, including biomass
NETL Refractory Development
(phos containing high Cr₂O₃ refractory)

NETL Developed Refractory

Commercial Refractory

Rotary Slag Testing – 1600°C
### Chemical Composition* of High Cr$_2$O$_3$ Gasifier Refractories

<table>
<thead>
<tr>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemistry</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>89.0</td>
<td>87</td>
<td>92.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>10.2</td>
<td>3.0</td>
<td>4.7</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>---</td>
<td>6.5</td>
<td>---</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>---</td>
<td>---</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>Bulk Density (g/cc)</strong></td>
<td>4.21</td>
<td>4.07</td>
<td>4.23</td>
</tr>
<tr>
<td><strong>Porosity (pct)</strong></td>
<td>16.7</td>
<td>16.5</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>CCS (MPa)</strong></td>
<td>48.3</td>
<td>66.9</td>
<td>51.7</td>
</tr>
</tbody>
</table>

*NETL /ANH developed, patented material*

*Conventional materials*

* = Information from product data sheet
# NETL Developed Cr₂O₃ Refractory Field Test Results

<table>
<thead>
<tr>
<th>Gasifier Type, Feedstock</th>
<th>Test Sample Location</th>
<th>Days Test</th>
<th>Field Trial Status</th>
<th>Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A, coal</td>
<td>Lower Cone</td>
<td>17</td>
<td>Completed</td>
<td>Run prematurely ended – inconclusive testing</td>
</tr>
<tr>
<td>Type A, coal</td>
<td>Lower Cone</td>
<td>82</td>
<td>Completed</td>
<td>Comparable or better corrosion resistance</td>
</tr>
<tr>
<td>Type A, coal</td>
<td>Sidewall</td>
<td>237</td>
<td>Completed</td>
<td>Superior spalling, comparable or better corrosion resistance</td>
</tr>
<tr>
<td>Type A, coal/petcoke</td>
<td>Slope</td>
<td>275 +</td>
<td>Underway</td>
<td>Visual only – comparable corrosion, unknown spalling</td>
</tr>
<tr>
<td>Type A, coal/petcoke</td>
<td>Throat</td>
<td>275 +</td>
<td>Underway</td>
<td>Visual only – comparable corrosion, unknown spalling</td>
</tr>
<tr>
<td>Type B, petcoke</td>
<td>Proprietary</td>
<td>300 +</td>
<td>Completed</td>
<td>Evaluation underway</td>
</tr>
</tbody>
</table>
Field Testing

Lower Cone/Throat/Slope

- NETL developed (red dots)
- Conventional (spalled)
- NETL developed (no spalling)

Sidewall

- Conventional (spalled)
Internal Flaws – Improved Versus Conventional \( \text{Cr}_2\text{O}_3 \) Refractory \((\text{sidewall test panel – 237 days})\)
**Impact of Phos on Slag Penetration, Corrosion**

1. No evidence of spalling in phosphate modified refractory

2. Reduced slag penetration
   - **Conventional**: 25-45 mm depth
   - **Phosphate Modified**: Preliminary indication, 3-5 mm depth

3. Microstructure
   - **Conventional**: Higher porosity
   - **Phosphate Modified**: Slag forms dense Fe/Cr spinel layer, higher viscosity slag, better thermal shock
NETL Developed Technology Successfully Transferred to Industry

- NETL developed a high Cr₂O₃ refractory containing phosphate additions
- Successful in field trials
- Refractory patented
- Technology licensed to Harbison and Walker Refractories Co. (May 2007)
- Product is in commercial production and use
Mixed Feedstock Issues Impacting Materials
(coal, petcoke, biomass)

• Gasification Process
  – Slag viscosity may need to be controlled through additives for proper flow
  – Possible fouling

• Refractory
  – FeO, SiO₂, alkali and alkaline earths, Cl⁻, SOₓ, and NOₓ in feedstock may cause severe slag/vapor corrosion of refractory liners
  – Mixed/variable feedstock – “new” slag chemistry can interact with refractory differently (no universal liner material)
  – Possible spent material (refractory) disposal issue – possible hazardous refractory material with +6 Cr formation (currently is not an issue)
Cr$_2$O$_3$-Free Refractory Development

- Three NETL compositions determined to have high potential for gasifier use; two targeted for commercial scale-up
- Three commercial refractory compositions selected with potential for gasifier use
- CRADA established for commercial scale-up and testing of refractory compositions; work on-going
CONCLUSIONS

- Slag interacts with the refractory causing wear by two primary means:

  1) **Structural Spalling**
  
  Slag infiltrates into the porous refractory, causing differences in material properties between the penetrated/non penetrated layers, leading to structural spalling

  2) **Chemical Corrosion**
  
  Slag interactions on the refractory surface influence corrosion (and indirectly spalling)
  - slag FeO interacts with refractory Al₂O₃ and Cr₂O₃, forming phases that impact surface corrosion behavior
  - depletion of FeO in slag on the refractory surface causes an increase in slag viscosity, slowing slag penetration into the refractory – impacting corrosion and structural spalling
CONCLUSIONS (continued)

• Field trials of the newly developed high chrome oxide refractory with phosphate additions indicated the following:
  – significant service life improvements are possible in gasifier locations where spalling was the predominant wear mechanism
  – it is unclear if changes occur in refractory service life in applications where corrosion is the predominant wear mechanism

• NETL developed refractory composition has been patented, licensed to Harbison and Walker Refractories Company, and is in commercial production
CONCLUSIONS (continued)

- Laboratory testing is underway of no-chrome oxide materials with promise as non-chrome oxide alternative refractory liners

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