Containment Materials Issues in High-Temperature Black Liquor Gasification

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Our Study Of Containment Materials For High-Temperature Gasification Has Concentrated On The New Bern Gasifier

- Construction of the New Bern high-temperature gasifier began in November, 1995
- This gasifier had its first production run in December, 1996
- Several refractory repairs or replacements were made in 1997 and 1998
- In early 1999, the lining was replaced with a fusion cast alumina refractory
- In December, 1999, cracking was discovered in the stainless steel gasifier vessel, and the gasifier was taken out of service
- The rebuilt gasifier resumed operation in late June, 2003, with a different fusion cast alumina refractory
- In October, 2004, a fusion cast magnesia-alumina spinel refractory lining was installed
The High-Temperature Gasifier Subjects The Structural Materials To Very Hostile Environments

- The hot-face refractory is exposed to molten smelt at temperatures of 950-1000°C

- The back-up refractory is exposed to somewhat lower temperatures (800-900°C) and to smelt components that are transported through cracks and joints in the hot-face refractory

- The temperature gradients and the volume increase resulting from reaction with smelt components produce highly compressive stresses on the surface of the hot-face refractory

- Expansion of the refractory lining can create large tensile stresses in the metallic shell
## Containment Materials Used In The New Bern HT Gasifier

<table>
<thead>
<tr>
<th>Time period</th>
<th>Reactor shell</th>
<th>Back-up refractory lining</th>
<th>Hot-face refractory lining</th>
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</thead>
<tbody>
<tr>
<td>Dec 1996 – Early 1999</td>
<td>316L stainless steel</td>
<td>Super duty refractory brick</td>
<td>60% Al₂O₃, SiO₂ brick</td>
</tr>
<tr>
<td>Early 1999 – Dec 1999</td>
<td>316L stainless steel</td>
<td>Fusion cast β Al₂O₃</td>
<td>Fusion cast α/β Al₂O₃ – manufacturer A</td>
</tr>
<tr>
<td>Jan 2000 – June 2003</td>
<td>Gasifier out of service</td>
<td></td>
<td></td>
</tr>
<tr>
<td>June 2003 – Sept 2004</td>
<td>Carbon steel</td>
<td>High-alumina bonded brick</td>
<td>Fusion cast α/β Al₂O₃ – manufacturer B</td>
</tr>
<tr>
<td>Oct 2004 – present</td>
<td>Carbon steel</td>
<td>Bonded mullite – based refractory</td>
<td>Fusion cast MgO-Al₂O₃ spinel</td>
</tr>
</tbody>
</table>
ORNL Examined Two Mullite Bricks Removed From The Original Lining Of The New Bern Gasifier

After about ten months of operation, less than half the brick remained at time of removal. Samples taken from the bulk, reaction zone and surface regions of both bricks were analyzed using XRD and microscopic techniques, and compounds were identified that were a result of reaction of the smelt with the refractory.
ORNL’s Smelt Immersion Test Facility Simulates Exposure Of Materials To Molten Smelt In The New Bern Gasifier

Exposures are typically conducted at 900 or 1000°C for 50 or 100 hours
Immersion Tests Are Able To Reproduce The Degradation Seen In Refractories Exposed In High-Temperature Gasifiers

- Alumina-silica (mullite) based samples exposed in the New Bern gasifier and in the immersion test system have reaction products such as nosean \((\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4)\) and nepheline \((\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)\) on their surfaces.

- Fusion cast alumina refractories exposed in the gasifier and the test system show an increase in the sodium content near the surface with a surface layer enriched in \(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3\), sodium aluminate \((\text{NaAlO}_2)\)
Increasing the amount of \( \text{Na}_2\text{O} \) in \( \text{Al}_2\text{O}_3 \) results in phase changes and volume increases, so it is not unreasonable to expect significant stresses to develop and some degradation to occur.
Samples Of New Bern’s Fusion Cast $\alpha/\beta\ \text{Al}_2\text{O}_3$ Replacement Lining Contained The NaAlO$_2$ Reaction Product
NaAlO$_2$ was found on the surface and in the reaction zones of fusion cast alumina samples from the Skoghall High-Pressure Black Liquor Gasifier.
Core-Drilled Samples Of The Fusion Cast Alumina Linings Provided Information About Extent Of Reaction With Smelt

- Working Lining: $\alpha/\beta$ alumina
- Backup Lining: $\beta$ alumina

- $\text{NaAlO}_2$ found on hot face
- Increased Na content found at back of the working lining and front of backup lining
- No $\text{NaAlO}_2$ detected in backup lining

Diagram: Cumulative Phase (%)

- $\alpha\text{-Al}_2\text{O}_3$
- $\beta\text{-Al}_2\text{O}_3$
- $\text{NaAlO}_2$

Distance From Hot Face (mm)

1 inch
Reaction Of Alumina Refractory With Sodium Compounds Caused Dimensional And Microstructural Changes

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume Expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>-</td>
</tr>
<tr>
<td>β-Al₂O₃</td>
<td>31</td>
</tr>
<tr>
<td>β'-Al₂O₃</td>
<td>32</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>133</td>
</tr>
</tbody>
</table>
The New Bern Gasifier Was Out Of Service For More Than Two Years. When A Decision Was Made To Rebuild The Gasifier, A Number Of Design And Material Changes Were Made

New Refractory/Shell System Design

- Hemispherical Dome
- Carbon steel refractory containment which is not susceptible to Cl⁻ SCC
- Crushable metal foam used between refractory and carbon steel shell
- Fusion-cast alumina working lining (from different supplier) over high alumina backup lining
- Expansion allowance for growth of refractory based on data collected after one year of operation
- Test bricks of alternate materials were also installed
Laboratory Testing And Evaluation Of Previously Exposed Materials Guided Selection Of Alternate Refractories

- Molten salt immersion test facility allowed immersion of refractory samples in molten salt at 1000°C
- Light microscopy, scanning electron microscopy and electron microprobe were used to characterize the extent of reaction between refractories and salt
- Studies of refractories exposed previously in operating gasifiers and exposed in the immersion test facility provided guidance on selection of the refractory lining material
- Refractory studies also identified alternate materials to be exposed as test bricks in the lining of the rebuilt gasifier
In February 2004, the gasifier was shut down for quench system repairs and refractory examination.

- Pieces of refractory brick were being recovered on a regular basis from the trap on the quench tank.

- Visual inspection of the lining showed considerable damage of the refractory lining in some areas, while other areas appeared to be relatively unaffected.

- Core-drilling was used to collect samples from eight different bricks in the lining including samples from test bricks of three alternate refractories.

- Examination also showed severe thinning in some sections of the cooled support ring.
Cross-Sections Of The Core-Drilled Samples Removed In January 2004 Showed Cracking And Discoloration

Microprobe examinations showed extensive sodium penetration in the alumina samples.
In September 2004, a Fusion-Cast Spinel Lining was installed and 40 strain gauges were mounted on the vessel shell.

- Strain gauges are installed on five levels of the gasifier vessel.
- Strain gauges replace some previously installed by Weyerhaeuser at different locations.
- Two strain gauges and a thermocouple are located in four positions around the circumference on each of the five levels.
During the first 7+ months of operation, strain on the shell increased at a fairly low rate.
Strain Showed A Perturbation After The Lining Was Partially Quenched In Water; Hoop Resumed Linear Increase
An Explanation Was Needed For The Increasing Strain Of The Shell

- The fusion cast spinel refractory did not appear to be undergoing extensive reaction or volume change.

- Inspections of the foam lining showed it was being crushed by the refractory.

- These observations led to a question about the integrity of the back-up lining.

- In order to assess the condition of the back-up lining, a core-drilled sample was taken by drilling through the hot-face lining into the back-up lining.
Only a portion of the back-up lining was collected, but this sample showed extensive degradation on the hotter side. The sample was visibly degraded, and X-ray diffraction studies showed extensive reaction with components of the smelt suggesting the back-up lining likely made a significant contribution to the strain on the gasifier shell.
The Observed Degradation Of The Back-up Lining Led To A Concentrated Effort To Find Alternate Refractories

- At the urging of project participants, a number of high mullite content materials were tested.
- Results of tests conducted previously were reviewed, and vendors were sought for some of the promising materials.
- A company specializing in calcia-alumina refractories for the aluminum industry was found, and special compositions more suitable for smelt resistance were formulated and tested.
- Samples of magnesia-rich refractories from several manufacturers were obtained and tested.
The Suggested Mullite Refractories Reacted Extensively, And In Some Cases, Completely, With Molten Smelt
Formulations Of The Calcia-Alumina Refractories Showed Very Good Resistance To Molten Smelt at 900°C

A sample of an alkaline aluminate is shown in the badly reacted metal holder. This refractory will be installed during the next lining replacement.
Two Magnesia-Rich Refractories Have Demonstrated Good Resistance To Molten Smelt At 900°C

Magnesia-rich refractories after 100 h in molten smelt at 900°C

Further studies are planned
Summary

- Degradation of the refractory linings has been attributed to reaction of the refractories with sodium compounds in the smelt and particularly with Na₂O.

- Experience and laboratory studies have shown that a fusion-cast magnesia-alumina spinel refractory has very good resistance to molten smelt at 1000°C.

- Degradation of the back-up refractory lining appears to be a significant contributor to the stresses on the gasifier shell, but studies have found two refractory types with better resistance to molten smelt at 900°C.

- The refractory lining to be installed in October will employ the recommended materials – fusion cast magnesia-alumina spinel for the “hot-face” lining and calcia-alumina refractory for the “back-up” lining.