Corrosion Issues In Black Liquor Gasifiers

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Colloquium on Black Liquor Combustion and Gasification
May 13-16, 2003 - Salt Lake City
Where Is Jim?

He’s either lying down on the job, wasting paper,
or waiting for the perfect photo op.
Aggressively Developing Two Gasification Processes

- **Low-temperature** - stays below the initial melting point of smelt
  - Utilizes fluidized bed design
  - Incorporates pulse heaters for better heat transfer
  - Steam reforming used for production of synfuel

- **High-temperature** - temperature reaches ~950°C - all smelt is in molten state
  - Low-pressure
    - Refractory lined vessel
    - Slight positive pressure
    - Air used for partial oxidation of organic components
  - High-pressure
    - Refractory lining or refractory coated helically coiled tube
    - Operates at about 30 atm
    - Oxygen is used for partial oxidation of organic components
Low-Temperature Technology Developed By MTCI/ThermoChem

- Steam reforming technology used
- Fluidized bed
- Black liquor and steam introduced into bottom of reformer vessel
- Heat provided through bed tubes
- Removal of sulfur as $\text{H}_2\text{S}$ adds options for pulping chemistry
Characteristics Of The Low-Temperature, Low-Pressure Black Liquor Steam Reformer/Gasifier

- Sodium carbonate particles are used for the bed material
- The bed is fluidized with steam
- The black liquor is injected into the bottom of the reformer/gasifier so that it coats the bed particles
- Heat is provided through several tube modules
- A pulsed heater provides improved heat transfer to the bed
Steam Reforming/Gasification Can Be Used With Black Liquor From Several Types Of Pulping Processes

<table>
<thead>
<tr>
<th>Pulping process</th>
<th>Pulping liquor components</th>
<th>$\text{H}_2\text{S}$ concentration in effluent gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-chem</td>
<td>NaOH</td>
<td>Minimal</td>
</tr>
<tr>
<td>Kraft</td>
<td>$\text{Na}_2\text{S} + \text{NaOH}$</td>
<td>Intermediate</td>
</tr>
<tr>
<td>Sulfite</td>
<td>$\text{SO}_2$ in Ca or Mg base</td>
<td>Significant</td>
</tr>
</tbody>
</table>

Since kraft pulping is by far the dominant process used in North America, the materials issues associated with that process will be addressed.

However, two of the initial installations of the low-temperature gasification technology are on semi-chem mills.
Environmental Compatibility Of Components Is A Concern In Low Temperature Steam Reformer/Gasifier

- Refractory lining in pulse combustion chamber
  - 1300-1500°C
  - ~5 psi amplitude 50-60 Hz pressure oscillation
  - Possible trace levels of alkali metals and H$_2$S

- Refractory lining in the reactor vessel (above and below bed level)
  - Below the bed
    - up to 621°C
    - 350 µm dia Na$_2$CO$_3$ particles moving at 0.6-0.9 m/sec (2-3 ft/sec)
  - Freeboard (above the bed)
    - < 621 °C
    - Low boiling point volatiles condensing on the refractory
Environmental Compatibility Of Components Is A Concern (continued)

- **Metallic heater tubes in the bed**
  - **On ID**
    - 50-60 Hz pressure pulses
    - Combustion gas with 4-9% O₂, low levels of H₂S, HCl; ppm of Na
  - **On OD**
    - Up to 621°C
    - Steam, H₂S, H₂, CO and Na₂CO₃ particles

- **Metallic shield tubes inside the heater tubes**
  - 1300-1550°C combustion gas (metal temperature 900-1150°C)
  - Combustion gas with 4-9% O₂, low levels of H₂S, HCl, ppm of Na
Experience Gained From Prior Demonstration Facility at New Bern Identified Critical Components

- Demonstration facility in New Bern, North Carolina
  - Kraft process
  - Nominal capacity of 96,000 pounds/day
  - Operated May 1994 – August 1995
Cracking was found on the bed tubes of the reformer/gasifier operated at the New Bern Mill.

72-tube bundle used in the New Bern steam reformer/gasifier.
Examination of cross-sectioned tubes showed cracking was intergranular.

Cracking was attributed to polythionic acid stress corrosion cracking. A stabilized stainless steel is recommended.
Continued Development at New Low Temperature Gasification Facilities Will Provide Performance Data and Assist with Material Selection

- **New** - Production facility in Trenton, Ontario
  - Semi-chem process
  - Entire black liquor production of mill
  - Mechanical start-up scheduled for June, 2003

- **New** - Production facility in Big Island, Virginia
  - Semi-chem process
  - Entire black liquor production of mill
  - Mechanical start-up scheduled for November, 2003
DOE Funding Is Supporting the Development of New Testing Facilities for Low Temperature Gasification

- **New** - Modifications of MTCI Process Development Unit
  - Long term testing of critical components
  - Testing of new materials for low temperature gasification
  - Modifications are underway

- **New** - Materials Evaluation for PulsedEnhancee Steam Reforming Gasifiers
  - Consortium composed of ORNL-LB-MTCI researchers
  - Developing and modifying materials testing facilities
  - Evaluating materials performance of specimens from DOE demonstration projects (Trenton & Big Island), MTCI-PDU and any international low temperature gasifiers available
Laboratory Studies Are Being Conducted To Identify Materials For Bed Tubes In A Sulfite Mill Reformer/Gasifier

- Microbalance tests are being conducted
- Test temperature is 675°C
- Test duration is 100 hr
- Atmosphere controlled to simulate bed environment of sulfite mill reformer/gasifier
Microbalance Results Show Super Austenitic Alloys Or Alumina Forming Alloys Will Likely Be Needed
Development of High Temperature Gasification
The High-Temperature, Low-Pressure Gasifier Is Being Commercialized at Weyerhaeuser’s New Bern Paper Mill

- Black liquor, steam and air are injected at the top of the gasifier.
- The reactor has a refractory brick lining.
- The product gas is removed just below the reactor level.
- The smelt is cooled then dissolved in water at the bottom of the vessel.
Characteristics Of The High-Temperature, Low-Pressure Black Liquor Gasifier

- A liquor injection nozzle distributes a fine spray of liquor droplets inside the vessel
- The reactor vessel has a refractory brick lining
- A stainless shell was used in the first demonstration facility
- A water-cooled metal support ring provides the transition from the reactor vessel and the quench area
- Initially, several metal rings were welded to the shell ID to provide support for the refractory bricks
Significant Materials Information Has Been Provided By High-Temperature Low-Pressure Facilities

- Test reactor in Frövifors, Sweden
  - Capacity of 75 tons dry solids/day
  - Operated in the early 1990’s

- Demonstration scale facility in New Bern, North Carolina
  - Capacity of 330 tons dry solids/day
  - Operating from December, 1996 to January, 2000
  - Shut down because of materials problems
  - Currently being rebuilt
  - Scheduled to restart around June 2003
The New Bern HTLP Gasifier Has Encountered A Number Of Serious Materials Problems

- Original mullite-based refractory lining degraded rapidly
- Metallic refractory supports suffered severe corrosion
- Water-cooled metallic support ring intended to support the refractory lining suffered extensive cracking
- The fused cast alumina replacement refractory degraded more rapidly than expected
- Cracking of the stainless steel shell was found on the ID surface
The Stainless Steel Water-Cooled Support Ring Suffered Extensive Cracking

Extensive cracking that originated on the process side of the water-cooled stainless steel support ring.
Degraded Mullite-Based Refractory Brick Was Analyzed And Laboratory Test Was Developed That Reproduced Damage

a) Brick removed from New Bern gasifier. The XRD patterns show phases present in the interior and in the degraded surface layer.

b) Sample exposed in test system. The XRD patterns show similarities in the phases present on the two samples.
The Fused Cast Alumina Refractory Had Corrosion Products Typical Of Reaction With Sodium Compounds

A piece of aluminia-based refractory that was removed from the gasifier lining and XRD pattern showing presence of reaction products.
Transgranular Cracking Was Found On Inside Surface Of Stainless Steel Reactor Shell

Analysis of the cracking showed the mechanism was chloride stress corrosion with at least one period of severe mechanical stress.
Future Developments in Black Liquor Gasification:
High-Temperature High-Pressure
Two Designs Are Being Considered For Containment In An Oxygen Blown, High-Temperature, High-Pressure Gasifier

- Designs being considered include refractory bricks and cooling screen
- Cooling screen incorporates refractory coated helical coil
- Other design uses refractory brick lining
- Uses oxygen instead of air
Characteristics Of The High-Temperature, High-Pressure Black Liquor Gasifier

- Anticipated to be replacement for entire chemical recovery boiler
- By using oxygen instead of air the gasifier can be significantly smaller
- In BLGCC mode significant improvements in energy efficiency can be made
- Thermodynamic properties under elevated pressure are not known
Experience With HTHP Gasification Is Limited But Some Materials Information Has Been Obtained

- **Pilot plant in Skoghall, Sweden**
  - Capacity of 10 tons dry solids/day
  - Operated between 1994 and 2000
  - Accumulated about 1000 hr operating on black liquor
  - Used refractory brick lining

- **Development plant in Piteå, Sweden**
  - Capacity of 20 tons dry solids/day
  - Scheduled to begin operation later this year
  - Will evaluate both containment designs
  - Refractory from the pilot plant was selected
Despite Limited Operating Time, Corrosion Products Were Found On The Skoghall Refractory Shell

XRD patterns showed that NaAlO$_2$ formed on the refractory surface.
Summary

- Black liquor gasification offers some clear advantages compared to recovery boilers
- Black liquor gasification has some significant materials problems
- For gasification to be economically justifiable, materials problems need to be resolved
- A laboratory test system has been developed that can reproduce the refractory degradation observed
- Additional laboratory testing methods are being developed to identify and test candidate materials