Improved Materials For High-Temperature Black Liquor Gasification

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This Project Builds On A Previous Project

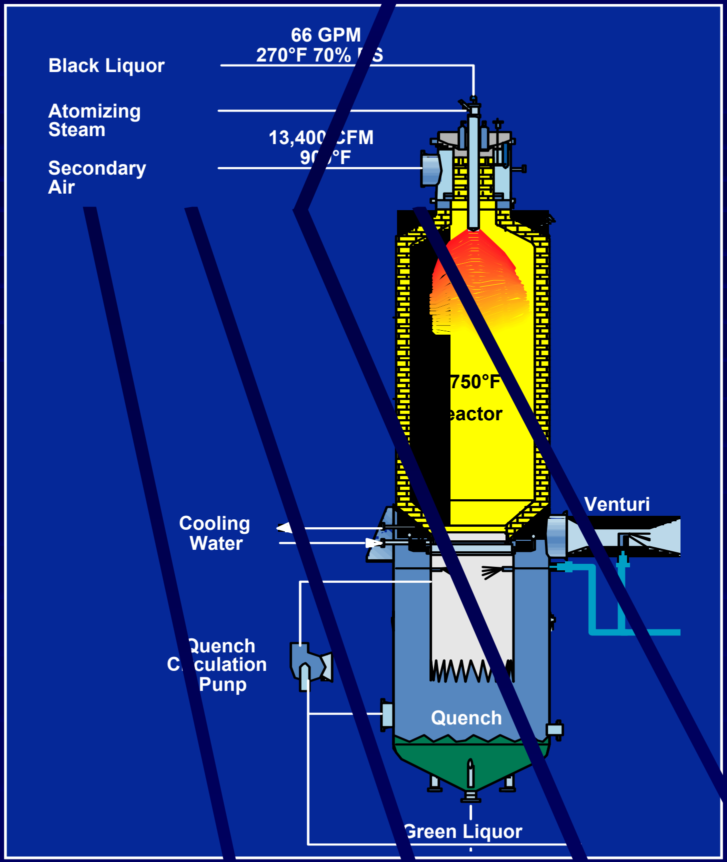
- The previous project addressed refractory structural materials for high-temperature black liquor gasifiers
- As part of the previous project several test systems were built
  - Smelt immersion test system
  - Rotary refractory test furnace
- Exposed refractory samples from several high-temperature gasifiers were examined
- Project was completed September 30, 2003

Improved Materials For High-Temperature Black Liquor Gasification

Goals. Develop better refractories and other structural components for use under current and future gasification conditions

Challenge: The gasifier's refractory lining and liquor spray nozzle of the gasifier historically have had unacceptably short lifetimes. More degradation-resistant materials are needed

Benefits: Implementation of combined cycle black liquor gasification is projected to offer up to $6.5 billion in cumulative energy cost savings and a significant reduction in gaseous emissions. In addition, up to 156 billion kWh of distributed energy could be produced



FY05 Activities: Examine exposed refractories; continue laboratory tests of refractories, conduct tests of potential liquor nozzle materials, refine models of gasifiers and liquor nozzles

Participants. Weyerhaeuser Company, Chemrec AB, Monofrax Refractories, ANH Refractories, Corhart Refractories, Process Simulations Limited, Simulent, Inc,. University of Missouri-Rolla

Improved Materials For High-Temperature Black Liquor Gasification

Barrier-Pathway Approach

Barriers

- Degradation of gasifier's refractory lining by reaction with molten alkali salts
- Degradation by wear/corrosion of black liquor nozzles

Pathways

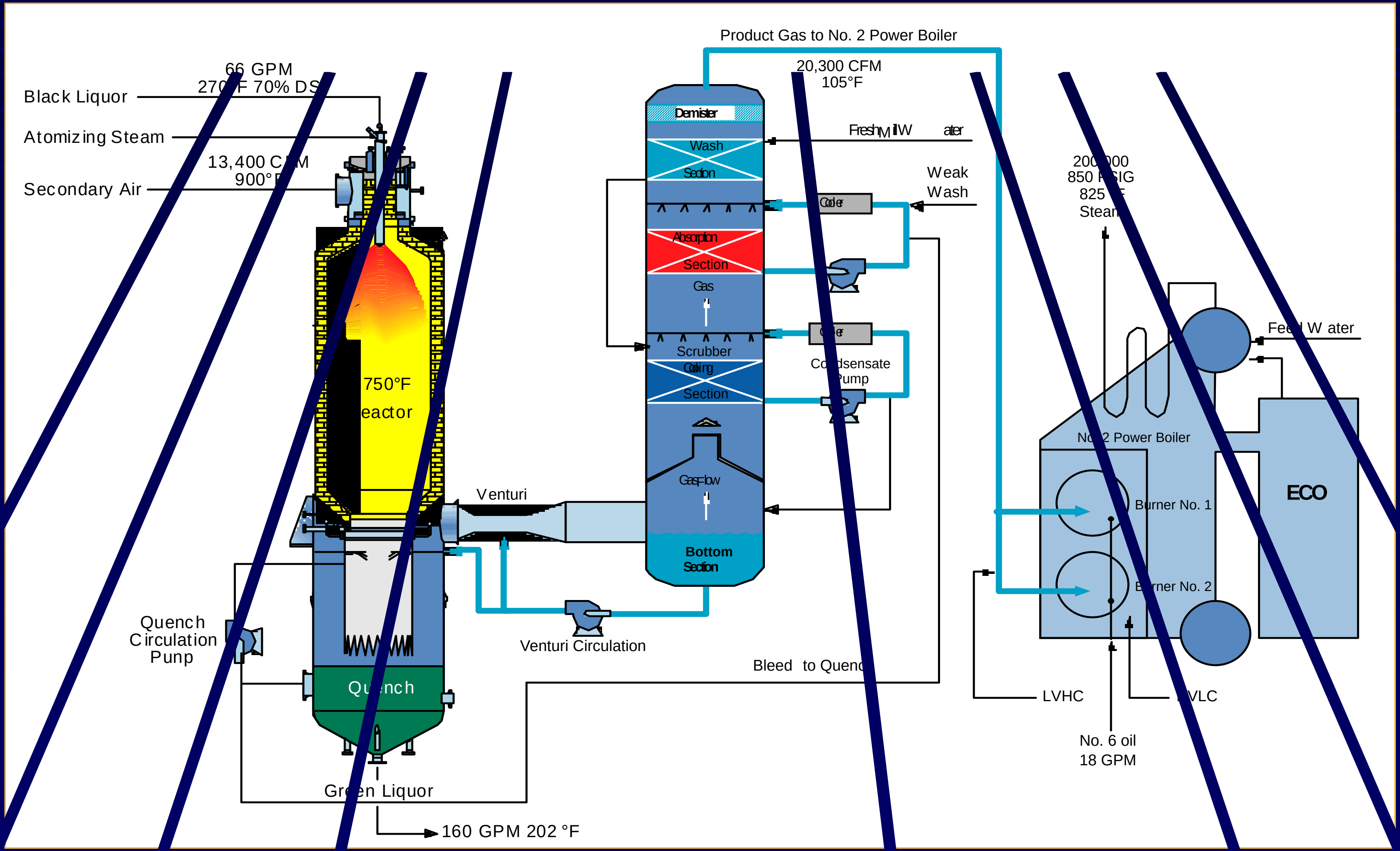
- Characterize environment through modeling of gasifier vessel and nozzle
- Evaluation refractories exposed in high-temperature gasifiers
- Conduct laboratory tests of refractories
- Evaluate wear-resistant materials for spray nozzles

Critical Metrics

- Refractory lifetime is increased by at least a factor of two
- New materials allow nozzle lifetime to be increased from a few months to at least twelve months
- 50% capacity increase

Switch to combined cycle black liquor gasification could result in reduction of emissions and more efficient power production

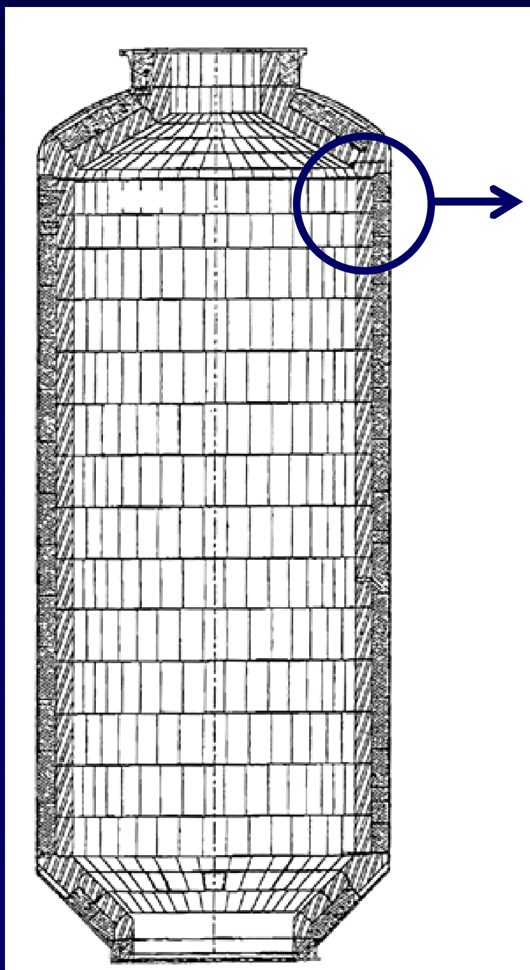
Main Components Of Gasifier Installed At New Bern



History Of Commercial Black Liquor Gasifier Constructed At Mill In New Bern, NC

❖ Project Release	June 29, 1995
❖ Start Construction	November 1995
❖ First Product Run	December 1996
❖ Taken out of Service (Shell Failure)	December 1999
❖ Final Decision to Rebuild gasifier	April 2002
❖ Restart Gasifier	June 27, 2003

Original Fused Cast Alumina Lining Replaced The 60% Alumina Brick That Degraded Rapidly

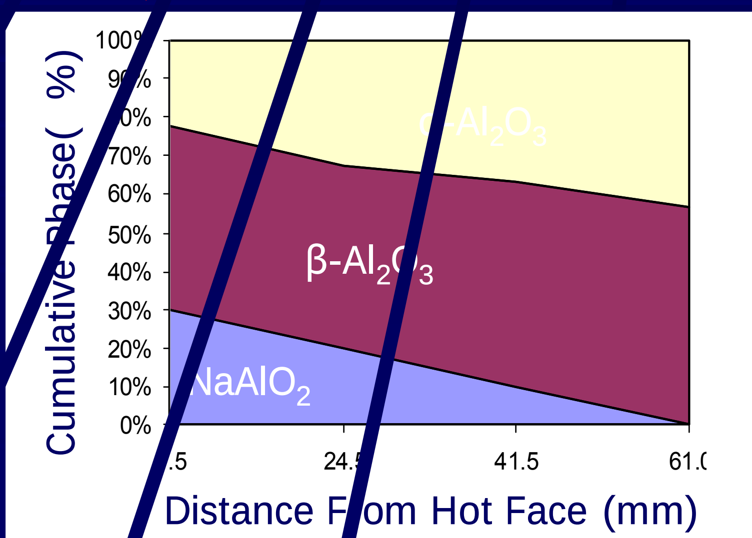


- ⇒ 150mm (~6”) $\alpha+\beta$ fused cast alumina
  - ⇒ 1/64” mica sheet
    - ⇒ 150mm (~6”) β fused cast alumina
      - ⇒ 2x1/64” mica sheet
        - ⇒ 3/8” fiber blanket
          - ⇒ 1/8” insulating board
            - ⇒ 3/8” 316L Stainless Steel

Core Samples Of The Fused Cast Alumina Lining Were Removed For Inspection

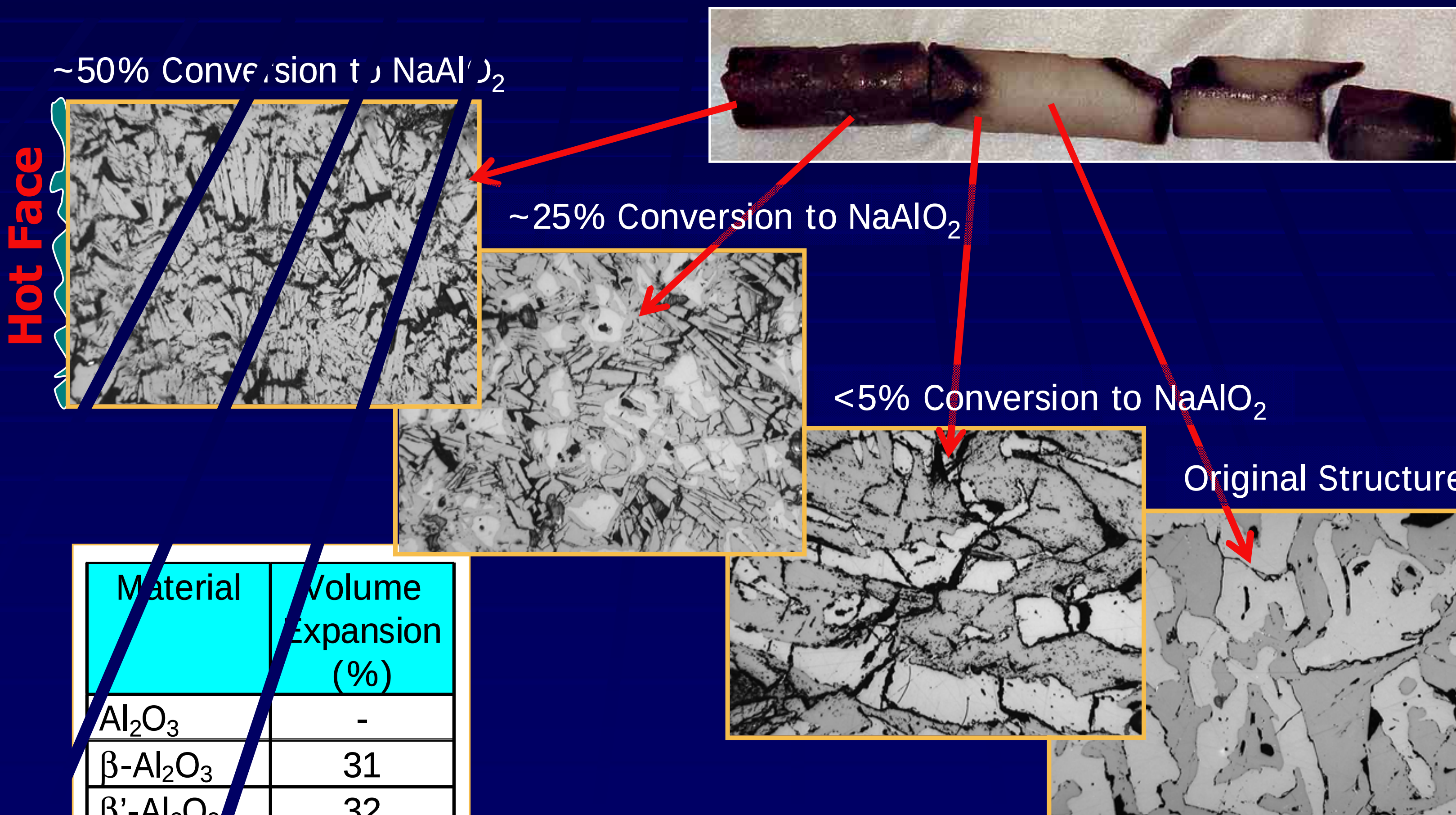
Working Lining: Jargal M

Backup Lining: Jargal H



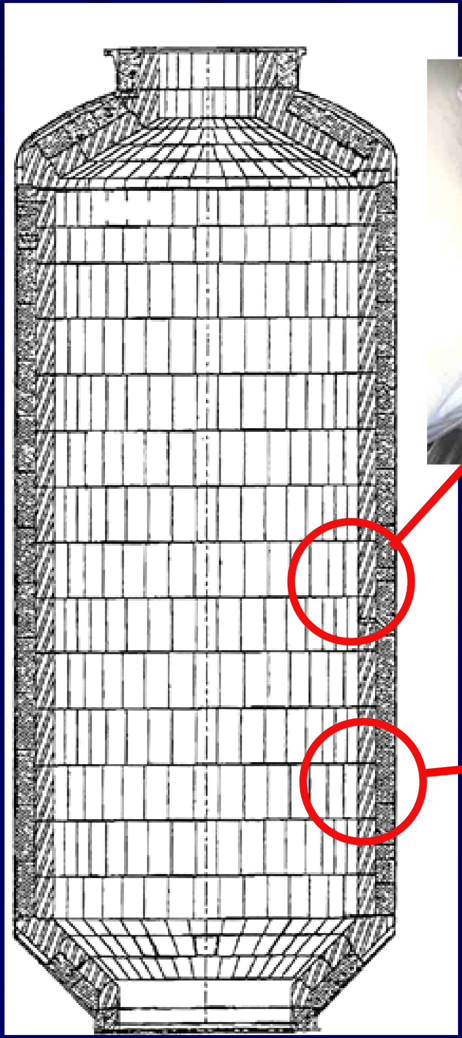
- $NaAlO_2$ found on hot face
- Increased Na content found at back of the working lining and front of backup lining
- No $NaAlO_2$ detected in backup lining

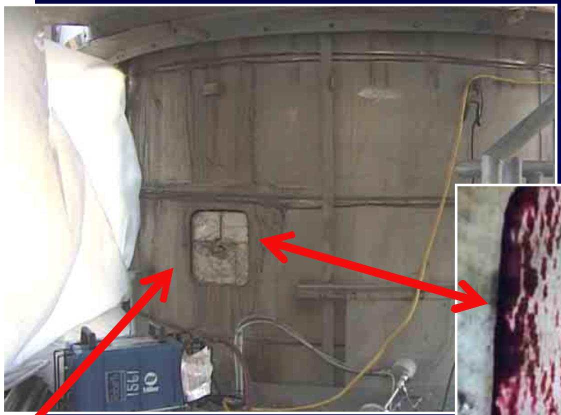
Observed Microstructural Changes Resulted From Reaction With Sodium



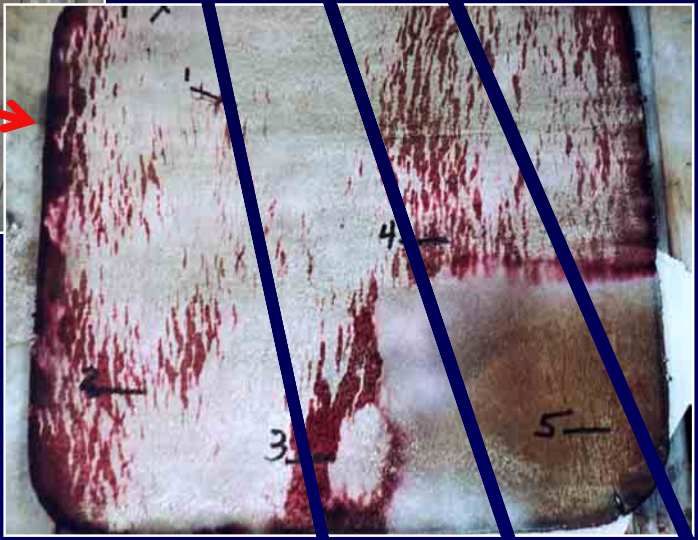
Material	Volume Expansion (%)
Al_2O_3	-
β-Al_2O_3	31
β'-Al_2O_3	32
$NaAlO_2$	133

When A Crack Was Found In The Gasifier Shell Several Sections Were Removed and Inspected





Dye penetrant tests showed many cracks in the vertical direction

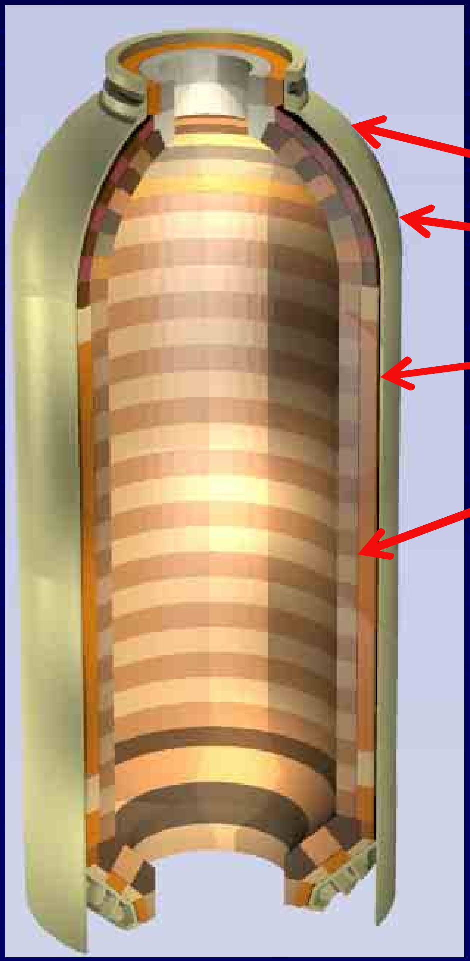


Through-wall crack on the shell was first indication seen by mill personnel

Root Causes of Failure Were Identified

- Mill water used during installation likely contained chlorides which contaminated materials adjacent to the shell
- Water condensed on the inside of the shell during start ups and shut downs and dissolved the chlorides
- Cycling of the unit concentrated the chlorides on the shell surface
- The chemical expansion of the refractory lining caused high tensile hoop stress in the shell
- The presence of tensile stress and aqueous solution of chlorides caused Stress Corrosion Cracking (SCC) in the 316L shell
- Tensile stress introduced during operation caused some of the cracks to grow through the shell
- Above mechanism repeatedly occurred until the pressure vessel failed

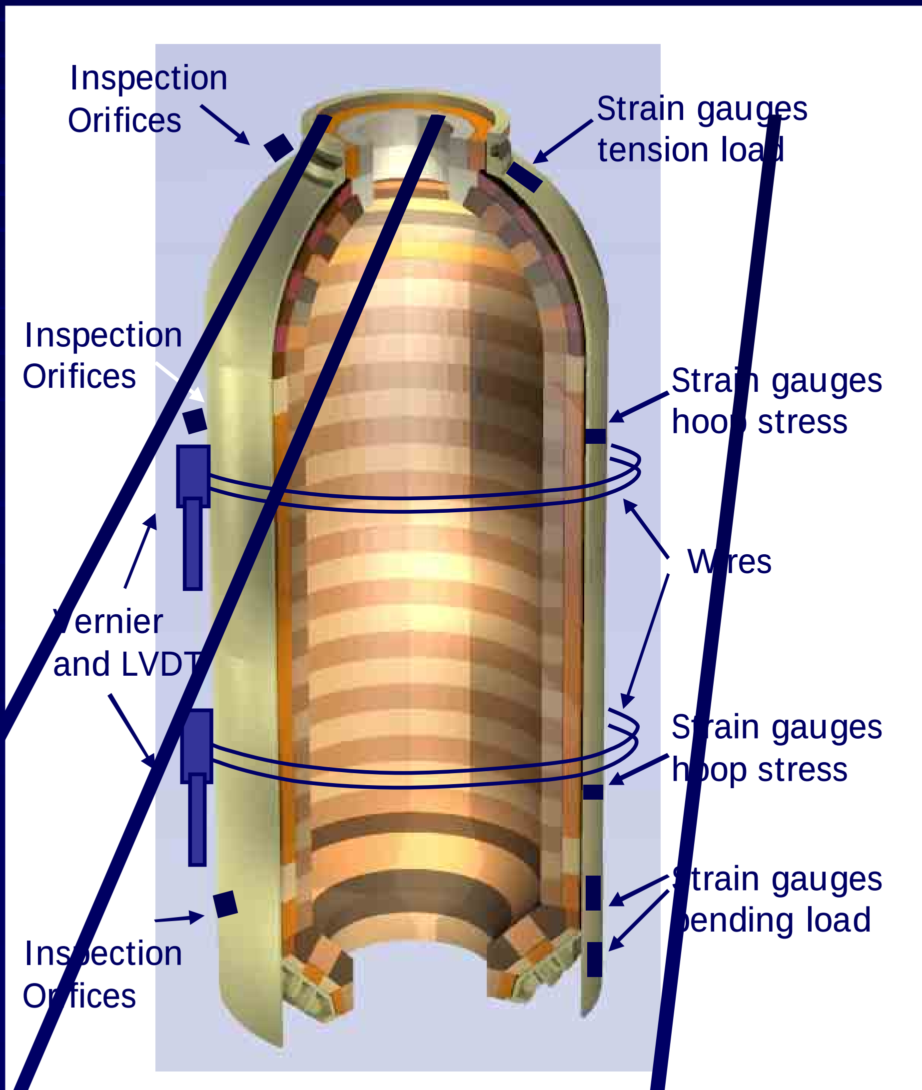
New Bern Gasifier Restoration Project



New Refractory/Shell System Design

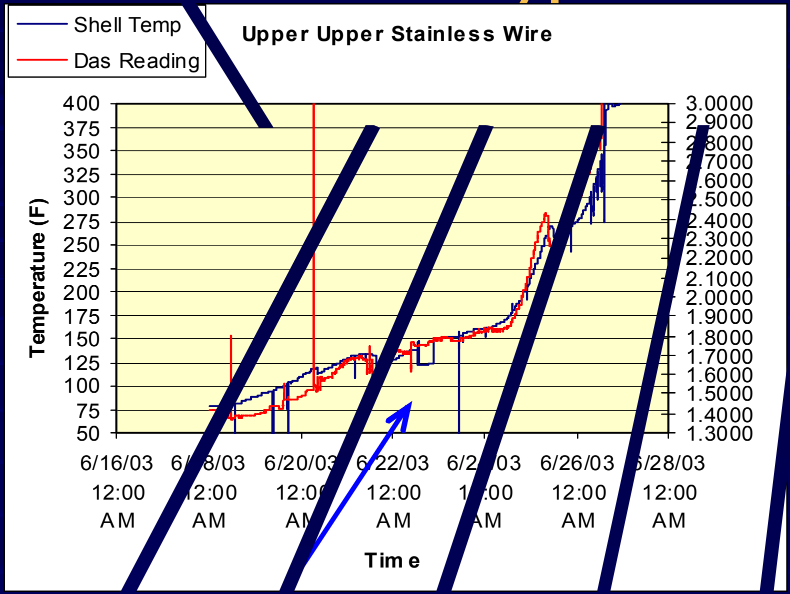
- Hemispherical Dome
- Carbon steel refractory containment which is not susceptible to Cl-SCC
- Crushable metal foam used between refractory and shell
- Fused cast alumina working lining over high alumina backup lining
- Expansion allowance for growth of refractory based on data collected after one year of operation

Strain Monitoring System Assesses Shell Deformation



- Strain gauges mounted at two elevations on the barrel, in the bottom cone and at the top of the dome
- Wires with Vernier scales and LVDTs mounted on two elevations on the barrel
- Inspection orifices (with plugs) on the barrel and dome

Typical LVDT Data Analysis

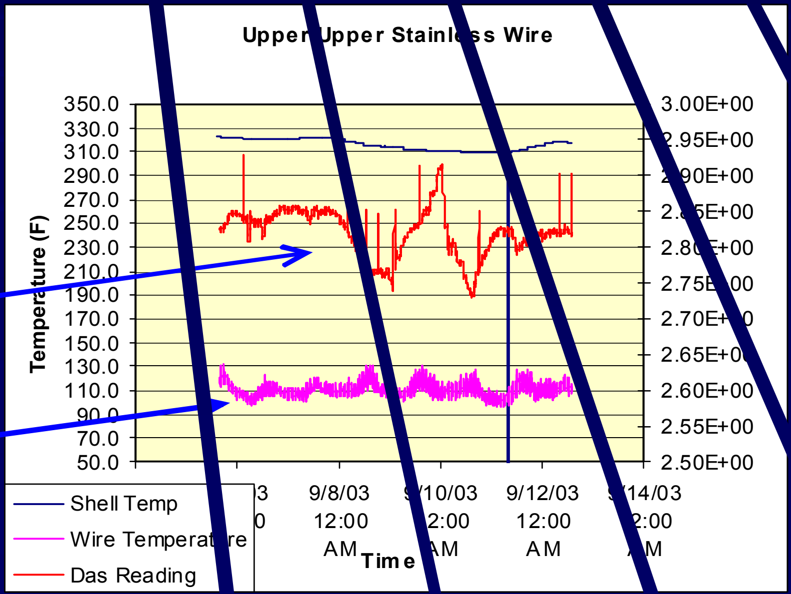


- Foam expansion is computed from shell stress
- Shell stress is determined from LVDT data after corrections have to be applied for:
  - Thermal expansion of wire
  - Thermal expansion of shell

LVDT data tracked well with shell temperature at startup

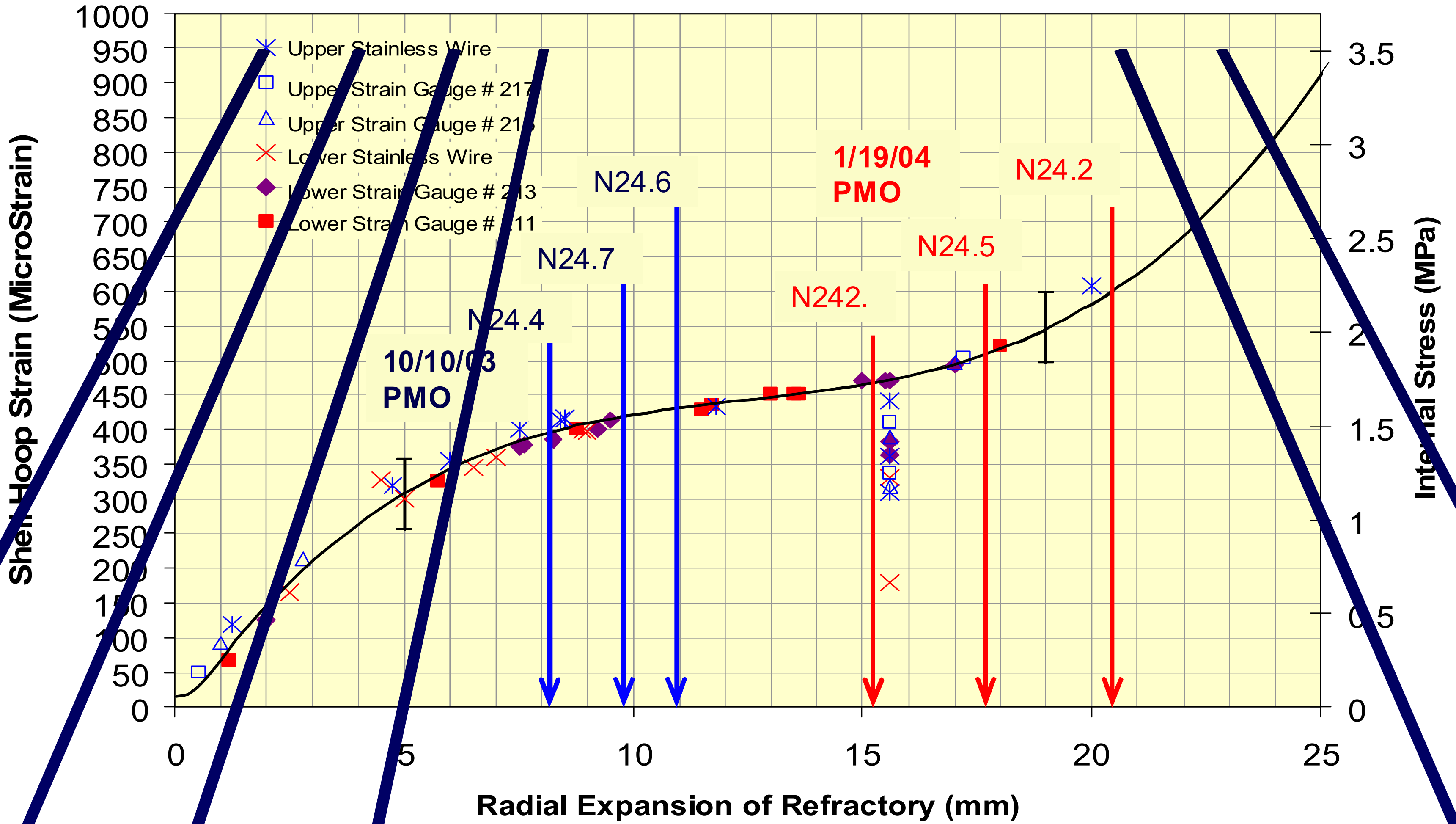
Effect of shell loading can be seen

Day time - night time temperature variations



Radial Refractory Expansion

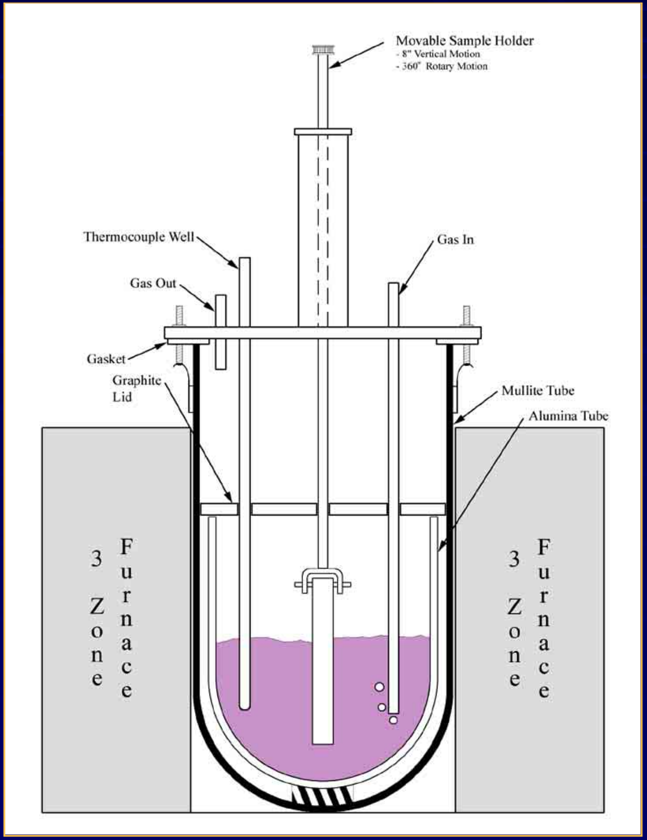
(Data from start-up to Mid April-04)



Progress To Date

- This project builds on a recently completed project on gasifier materials
- Exposures of test refractories in molten smelt have continued
- Four refractories exposed in the New Bern gasifier have been examined
- Based on analysis results, a refractory recommendation has been made
- A system has been built for testing wear-resistant nozzle materials
- Subcontracts have been placed for gasifier and nozzle modeling

A Laboratory Test Facility Permits Exposure Of Refractory And Metallic Samples To Molten Salts



Many Types Of Refractories Have Been Tested

- Commercially available refractories
- Experimental or developmental refractories from commercial supplies
- Experimental refractories produced by subcontractors
- Experimental refractories developed in our laboratory
- Commercial refractories with commercial and experimental coatings

Based on results of immersion tests, three test refractories were recommended for exposure in the rebuilt gasifier

The New Bern Gasifier Was Inspected In Mid-January After 6½ Months Of Operation

Ref actory lining near bottom of barrel portion of gasifier vessel. Note red l nes indica ting apparent cracks on most blocks except for two in the second row (uppe r right).

Core-Drilled Samples Were Collected From The Primary Refractory And Three Test Materials

Core drilling was done with kerosene instead of water as the lubricant/coolant to avoid dissolving water-soluble corrosion products.

Cross-Sections Of The Core-Drilled Samples Revealed Significant Differences

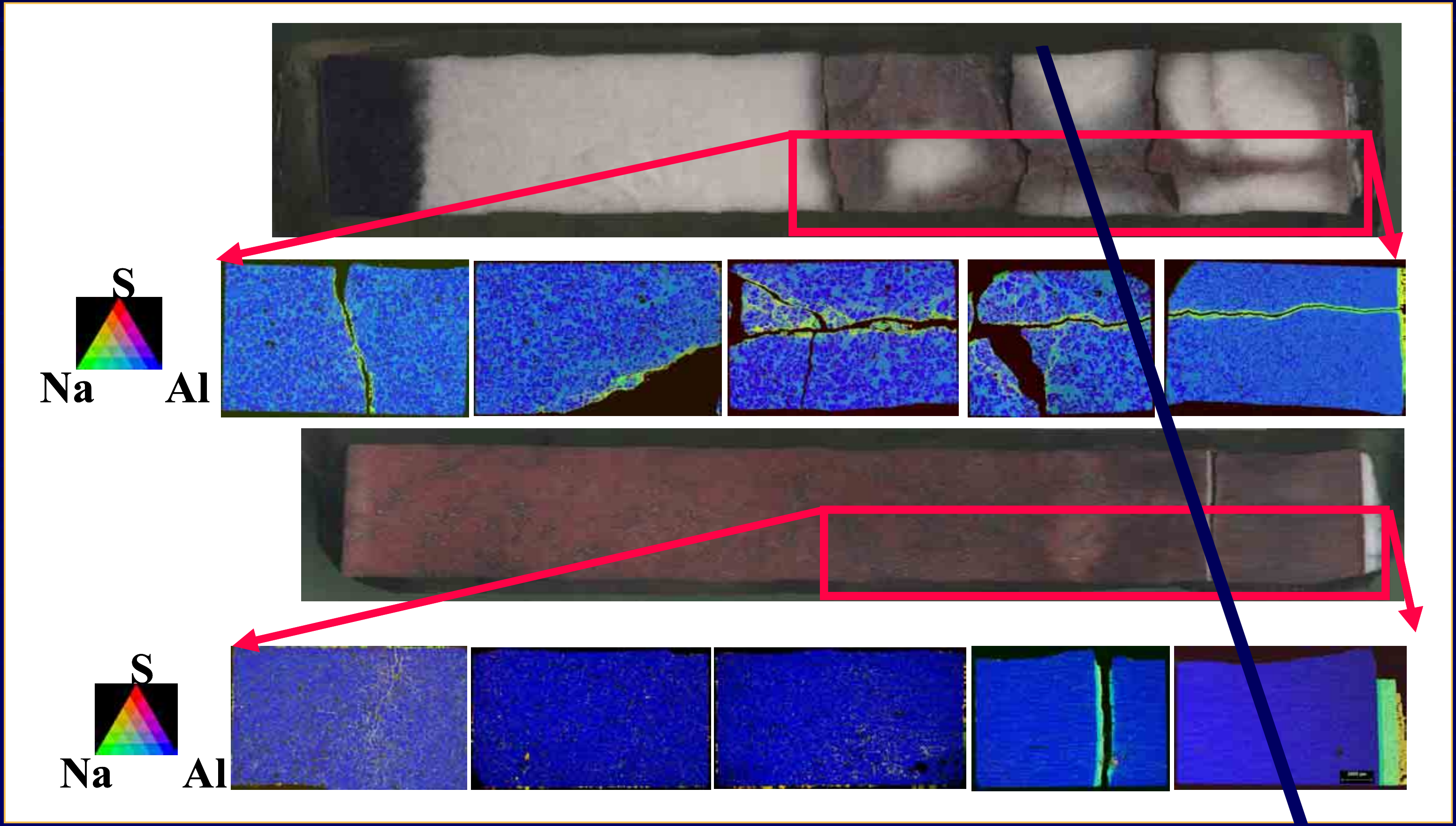
Fusion-cast alumina refractory

Fusion-cast magnesia-alumina refractory

Alternate fusion cast alumina refractory

Bonded magnesia-alumina refractory (outlined at left)

The Electron Microprobe Provided Elemental Maps Of The Core-Drilled Refractory Samples



Overlaid elemental maps of sodium, sulfur and aluminum for the fusion α/β refractory (upper) and a fusion-cast magnesia-alumina spinel (lower).

Conclusions From Examination Of Core-Drilled Refractory Samples

- The fusion-cast α/β-alumina showed less spalling than any refractory previously used for the vessel lining
- Cracking was evident through about the first half of the fusion-cast α/β-alumina bricks that were examined
- The fusion-cast magnesia-alumina spinel showed less cracking and penetration of sodium than the fusion-cast α/β-alumina
- The alternate fusion-cast α/β-alumina and the bonded magnesia-alumina bricks reacted more extensively

Current Black Liquor Injection Nozzle Mixes Steam And Liquor But Exit End Of Holes In Nozzle Suffer Significant Wastage

Cross section of black liquor nozzle

Delivery end of nozzle showing wastage

The New Nozzle Allows Insertion Of Wear-Resistant Test Materials

Inserts of various wear-resistant ceramic and metallic materials are being fabricated and will be tested in this system

Modeling Studies Of Gasifier Components Are Planned

- A subcontract has been placed with Simulent Incorporated for modeling of the black liquor nozzle
- A subcontract has been placed with Process Simulations Limited for CFD modeling of fluid flow in the gasifier
- Both subcontracts are receiving matching funds from the Canadian government
- Thermochemical modeling will be conducted at ORNL to study interactions between the refractories and the gasifier environment

Future Plans

- Smelt immersion testing of various refractories will continue
  - Primary candidates – address orientation effects & microstructural effects
  - Surface-treated refractories
  - Other alternate materials
- Refractory scheduled to be removed from the gasifier in September will be analyzed
  - Primary lining
  - Three test materials
- Tests of wear-resistant nozzle materials will be conducted
- Modeling of gasifier components will be continued

Commercialization Plans

- Close cooperation is continuing with the designer/developer of the high-temperature gasification process used in the New Bern gasifier
- Refractory materials identified in the ORNL-led studies are likely to be used in the scaled-up system being built in Piteå, Sweden
- A patent application has been submitted for a coating process that provides increased lifetime of refractory bricks in molten alkali salts
- A patent application has been drafted for use of the fusion-cast magnesia-alumina spinel in black liquor gasifiers