ADMINISTRATIVE INFORMATION

1. **Project Name:** Improved Materials for High-Temperature Black Liquor Gasification

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4. **Project Partners:**
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5. **Date Project Initiated:** October 1, 2003

6. **Expected Completion Date:** June 30, 2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** The industrial viability of the high-temperature, atmospheric-pressure gasification technology employed at Weyerhaeuser’s New Bern, North Carolina mill depends primarily on 1) optimum integrity of structural components including refractories and other materials, and 2) increasing the throughput capacity of processing black liquor by approximately 50%. The goal of this project is to develop improved corrosion resistant refractories and other structural components for use under current and future increased throughput gasification conditions.

8. **Technical Barrier(s) Being Addressed:** The economic production of pulp and paper by the kraft process requires efficient recovery of chemicals and energy from the black liquor produced in the pulping process. Traditionally, the Tomlinson boiler has been used to burn black liquor as a means of disposing of the organic components and recovering the inorganic chemicals used in pulping. The ability of recovery boilers to perform the required tasks has contributed to the kraft pulping process becoming the dominant papermaking process. However, recovery boilers have shortcomings including higher than desired emission levels and relative inefficiency in producing electrical power from the black liquor. Black liquor gasification offers an alternative to recovery boilers. However, the operating experience with black liquor gasifiers in North America is very limited. A high-temperature, low-pressure gasifier developed by Kvaerner/Chemrec (now Chemrec AB) was installed at the New Bern mill in 1996. This gasifier uses a refractory-lined entrained flow reactor in which black liquor is gasified by exposure, under reducing conditions, to air. The reactor operates at 950°C which is well above the melting temperature of the inorganic salts. The corrosive/abrasive nature of the black liquor degrades the liquid injection nozzle, and the salts cause premature failure of the refractory lining and other components. Successful implementation of this technology requires that structural materials be identified with significantly improved lifetimes.
9. **Project Pathway:** For this technology to reach the level where it will be commercially accepted, a number of materials issues need to be resolved including 1) identification of a refractory material with the corrosion resistance and mechanical integrity to last at least one year and preferably at least two years, 2) development of materials for improved black liquor injection nozzles, and 3) identification of the fluid flow and temperature characteristics in order to understand the environments encountered by the refractory materials and injection nozzles.

10. **Critical Metrics:** Success of the program will be measured by achieving several goals –
- Identification of a refractory lining material that has a lifetime of at least one year and preferably two years,
- Identification of a wear resistant material that significantly reduces the erosion/corrosion of the liquor nozzles,
- Identification of back-up (lower temperature) refractory lining that has a lifetime at least equal to that of the higher temperature (hot-face) refractory lining, and
- Characterization of the fluid flow and temperature characteristics in the gasifier vessel and the liquor nozzles to allow a 50% increase in the black liquor throughput without increasing degradation of the structural components of the gasifier.

**PROJECT PLANS AND PROGRESS**

11. **Past Accomplishments:** The refractory studies conducted in this project have led to the identification of a “hot-face” refractory lining that has better resistance to corrosion by molten smelt than any other refractory utilized in the New Bern gasifier. This refractory, the fusion-cast magnesia-alumina spinel marketed as Monofrax L, has survived for over 20 months in the New Bern gasifier, and it was also selected for use in the high-pressure, oxygen-blown gasifier that has recently begun operation in Piteå, Sweden. The refractory initially used in the New Bern gasifier had a lifetime of around 6 months. The first fusion-cast refractory installed in the gasifier had a lifetime of about a year while the current lining, which was identified and recommended by ORNL during the early stages of this project, is now expected to survive for about two years.

As part of this project, laboratory examinations have been conducted on a number of samples removed from the New Bern gasifier. In February, 2004, eight core-drilled samples were removed for examination, and these samples confirmed the superior corrosion resistance of Monofrax L that had been demonstrated in laboratory studies. Additional core-drilled samples were collected during 2005, including cores immediately after the gasifier was accidentally flooded with water and later in the year to document the condition of the back-up lining. These examinations confirmed the integrity of the Monofrax L despite the quenching in water, and they established that the back-up lining was reacting with smelt to the extent that stress on the gasifier shell was likely due to expansion of the back-up refractory rather than the hot-face Monofrax L lining.

As noted previously, ORNL was responsible for installing strain gauges and thermocouples at 20 locations on the gasifier shell, and ORNL staff members have been collecting and analyzing this data since the installation. Results of the strain measurements are collected and analyzed at ORNL and communicated to the appropriate Weyerhaeuser personnel on a regular basis. These results have demonstrated the loading on the shell has continued to increase as a function of time.

Two studies addressed issues with the nozzle used to spray the black liquor into the gasifier. Modeling studies conducted by Simulent, Inc. to characterize the fluid flow from the nozzle were brought to a conclusion. A modified nozzle was built and installed in the gasifier to permit testing the corrosion/erosion behavior of a number of materials that could be used in the nozzle. The nozzle
modeling results were supplied to Process Simulations Limited for inclusion in their CFD model of the gasifier. These studies provided temperatures and fluid compositions for better understanding of the gasifier environments.

12. **Future Plans:** Funding for this project was essentially expended by the end of the second quarter FY2006; only a small amount of unspent funds remained in the accounts of the ORNL staff members collecting and analyzing the strain data. Once those funds are used, all project work will stop. The refractory materials recommended by ORNL for the hot-face and back-up refractory linings and the mortar have been accepted by the Weyerhaeuser New Bern staff, and those materials have been ordered for the replacement lining to be installed in Fall, 2007. By using the refractory materials and mortar recommended by ORNL, it is expected the lining may be able to operate for as much as three years.

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<tr>
<th>Date</th>
<th>Milestone/Deliverable</th>
<th>Partner Activities</th>
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<tbody>
<tr>
<td>March, 2006</td>
<td>Complete testing of back-up lining materials</td>
<td>Partners – Provide samples of refractory materials modified to optimize corrosion resistance</td>
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<tr>
<td>March, 2006</td>
<td>Recommend material for back-up lining</td>
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<tr>
<td>March, 2006</td>
<td>Provide timely reports (probably monthly) of the strain of the gasifier shell</td>
<td>Partner – Provide power and telephone line for remote access to on-site ORNL computer collecting strain and temperature data</td>
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13. **Project Changes:** Because of the observation made in July 2005 that the back-up refractory lining was degrading to a much greater extent than expected, the laboratory studies of refractory behavior were directed toward finding less expensive materials with improved resistance to smelt corrosion at 900°C.

14. **Commercialization Potential, Plans, and Activities:** The ORNL studies on refractory materials have led to three patent disclosures one of which was submitted in collaboration with Weyerhaeuser and the refractory manufacturer while another was done in collaboration with the refractory manufacturer. A decision was made not to pursue the third.

The New Bern black liquor gasifier is a commercial facility, and as such, the refractory technology developed as part of this project should be considered to have been implemented industrially. Furthermore, the technology developed through this project should have significant impact on the selection of the refractory structural materials as well as the design of the vessel and the liquor nozzles for any future installation.

15. **Patents, Publications, Presentations:**

   **Patents**
   - “MgAl$_2$O$_4$ Spinel Refractory Containment Liner for High-Temperature Alkali-Containing Environments”
   - “Calcium (Hexa)Aluminate Refractory Linings and/or Chemical Barriers for High Temperature and High Alkali/Alkaline Environments”

   **Publications**

Presentations
• Presentations were made by James Keiser at the International Energy Agency Annex XV meetings on Black Liquor and Biomass Gasification that were held August 22-24, 2005, in Piteå, Sweden, and February 20-22, 2006, in Washington, North Carolina.