ADMINISTRATIVE INFORMATION

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

2. **Lead Organization:** Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6156

3. **Principal Investigator:** James R. Keiser, 865-574-4453 / 865-241-0215 / keiserjr@ornl.gov

4. **Project Partners:** Weyerhaeuser Company, J. Peter Gorog, peter.gorog@weyerhaeuser.com, 253-924-6514
Vesuvius Monofrax Refractories, Amul Gupta, Amul_Gupta@vesuvius.com, 716-483-3326
SEPR Refractories, Michael Nelson, Nelson.m@insightbb.com, 812-282-1682
Harbison-Walker (ANH) Refractories, Michael Wallen, mike.wallen@hwr.com, 412-375-6897

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

6. **Expected Completion Date:** March 31, 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. These salts caused premature failure of the refractory lining and very severe degradation of the liquid injection nozzle 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, 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 increased degradation of the structural components of the gasifier.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:** This project was preceded by other projects that included analysis of many exposed refractory samples removed from gasifiers. These other projects included exposure of a significant number of refractory samples in the ORNL smelt immersion test systems. These analyses and laboratory tests provided guidance on the selection of the structural materials used in rebuilding the gasifier for the June, 2003 restart. The current project has built on the accumulated knowledge with the goal of enabling further improvements in the selection of materials for the gasifier.

    As part of the current project, in February, 2004, eight refractory samples were removed from the gasifier by core-drilling into selected bricks. These samples were subsequently examined extensively at ORNL in order to determine the extent to which each of the materials reacted with the gasifier environment, and in particular, the molten sodium compounds. These thorough examinations showed that the fusion-cast magnesia-alumina spinel provided by Vesuvius-Monofrax Refractories showed less interaction than any previously tested commercially-available material.

    During this fiscal year, 100 hour, 1000°C smelt immersion tests were conducted on a large number of samples. Many of the tests were conducted to better characterize various magnesia-alumina spinel refractories and to quantify the behavior of the surface of the refractories when the columnar grain structure developed during solidification. Results of these immersion tests and the analysis of the core-drilled samples provided the basis for Weyerhaeuser's decision to install this refractory in the barrel and dome of the gasifier when the refractory was replaced in September, 2004. During the September refractory installation, new strain gauges and thermocouples were installed on the gasifier shell as part of the ORNL task to characterize the behavior of the refractory and its effect on the shell. Results of the strain measurements are collected and analyzed at ORNL and communicated to the appropriate personnel on a regular basis.

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

12. **Future Plans:** For the remained of FY2005, work will continue in a number of areas. Laboratory testing of candidate refractory materials will continue, and any material that shows corrosion

resistance equal to or better than the currently used magnesia-alumina spinel will be recommended for exposure as test pieces in the gasifier. The laboratory testing will also continue on mortars that could be alternatives to the currently used material. Again, any material identified in the laboratory testing will be recommended to Weyerhaeuser for testing in the gasifier.

Monitoring of the strain and temperature of the gasifier shell will be continued as part of the effort to evaluate the performance of the refractory lining. Data collected will be analyzed then reported to Weyerhaeuser mill personnel.

Refractory samples were removed in February, 2005, and examination of those samples will continue. In addition, it is anticipated that the gasifier will be opened for inspection in October, 2005, and ORNL staff will participate in the inspection as well as the possible collection of additional refractory samples if it is deemed to be appropriate.

Studies to identify materials with greater erosion/corrosion resistance will continue in the effort to find alternate materials for the black liquor nozzle. Carefully selected test materials will be exposed in the gasifier and evaluated at ORNL. Modeling of the liquor nozzle will continue in an effort to find small modifications in the nozzle that would better distribute the liquor in the gasifier. Input from the nozzle modeling will be incorporated in the gasifier vessel modeling to better understand the fluid distribution and the temperatures in the gasifier. Changes that would lead to a more uniform temperature distribution in the gasifier could prolong the life of the refractory lining.

FY2006 funding for this project will be reduced to about half the level of funding in FY2004 and FY2005. Consequently, the modeling work will be significantly reduced or eliminated, and testing of alternate refractories will, likewise, be reduced or stopped. Testing of alternate mortars could be continued if significantly better materials have not been identified. Inspection of gasifier components (refractory lining, liquor nozzle and other metallic components) will be continued while strain monitoring and reporting on deformation of the gasifier shell will also continue.

Date	Milestone/Deliverable	Partner Activities
Sept., 2005	Recommend alternate mortars for installation during October, 2005 gasifier inspection	
Dec., 2005	Complete analysis of refractory samples removed from gasifier in September, 2005	
April, 2006	Complete analysis of refractory samples removed from gasifier in February, 2006	
April, 2006	Continue strain and temperature data collection and analysis with reporting of results to Weyerhaeuser on no less than a monthly basis	
March 2005	Provide PSL with black liquor spray characteristics for a single nozzle – update as new calculations are made	Simulent Inc. - Modeling of black liquor nozzle to determine spray characteristics including droplet size and distribution
March 2005	As new calculations are made, report results to other researchers and Weyerhaeuser staff for consideration in operational and design decisions	PSL – Modeling of fluid flow in gasifier and incorporation of Simulent data to better describe the introduction of black liquor into the gasifier

13. **Project Changes:** During the operating period of June, 2003 to September, 2004, deformation of the gasifier shell was monitored by Weyerhaeuser personnel using strain gauges and a series of wires. When Weyerhaeuser determined they did not have the resources to update the strain gauge system and continue the monitoring, ORNL assumed responsibility for the effort. This information was critical in order to make a quantitative comparison of the performance of the previous Monofrax M lining with the newly installed (Monofrax L) spinel lining. ORNL personnel installed strain gauges and thermocouples at 20 locations on the gasifier shell and installed the instrumentation for data collection. Subsequently, ORNL staff members have been collecting and analyzing the strain data, and reports are provided to Weyerhaeuser mill personnel and research staff on a regular basis.

14. **Commercialization Potential, Plans, and Activities:** The ORNL studies on refractory materials have led to two patent disclosures one of which was submitted in collaboration with Weyerhaeuser and the refractory manufacturer. When black liquor gasification technology advances to industrial implementation, the technology developed through this project should have significant impact on the selection of structural materials as well as the design of the vessel and the liquor nozzles.

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

Patent Disclosure

$MgAl_2O_4$ Spinel Refractory Containment Liner for High-Temperature Alkali-Containing Environments

Publications

"Performance Of Materials In Black Liquor Gasification Environments", James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, Peter F. Tortorelli and Bruce A. Pint, Paper 04251, NACE International Corrosion/2004, March 28-April 1, 2004, New Orleans, Louisiana.

"Selection And Development Of Refractory Structural Materials For Black Liquor Gasification", James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, Michael P. Brady and J. Peter Gorog, TAPPI Paper Summit, May 3-5, 2004, Atlanta, Georgia.

"Materials Issues in Black Liquor Gasification Systems", James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard Bruce A. Pint, J. Peter Gorog, Ravi R. Chandran and Peggy Y. Hou, 11th International Symposium on Corrosion in the Pulp and Paper Industry, June 6-10, 2004, Charleston, South Carolina.

"Materials Performance in High-Temperature Black-Liquor Gasification", James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, Gorti B. Sarma, J. Peter Gorog and Zia Abdullah, Paper 05314, NACE International Corrosion/2005, April 3-7, 2005, Houston.

Presentations –

"Performance of Materials in Black Liquor Gasification Environments", James R. Keiser, NACE International Corrosion/2004, March 29, 2004, New Orleans.

"Selection And Development Of Refractory Structural Materials For Black Liquor Gasification", James R. Keiser, TAPPI Paper Summit, May 5, 2004, Atlanta, Georgia.

"Materials Issues in Black Liquor Gasification Systems", James R. Keiser, 11th International Symposium on Corrosion in the Pulp and Paper Industry, June 6-10, 2004, Charleston, South Carolina.

"Materials Performance in Black Liquor Gasification Systems", James R. Keiser, ASM Materials Solutions Conference, October 19, 2004, Columbus, Ohio.

Individual presentations were made by Jerry Yuan, Nasser Ashgriz, Peter Gorog and James Keiser at the International Energy Agency Annex XV meetings on Black Liquor and Biomass Gasification that were held August 30-September 1, 2004 in Turku, Finland, and February 14-16, 2005 in Lynchburg, Virginia.