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Industrial Materials for the Future

Final Technical Report

Improved Materials for High-Temperature Black Liquor Gasification

June 2006

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Disclaimer

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Abbreviations and Acronyms

CCBLG	combined cycle black liquor gasification
DOE	U.S. Department of Energy
EDS	energy dispersive spectroscopy
FEM	finite element modeling
IMF	Industrial Materials for the Future (DOE)
IOF	Industries of the Future
ITP	Industrial Technologies Program (DOE)
LVDT	linear variable displacement transducer
MPLUS	Metals Processing Laboratory User Facility
OIT	Office of Industrial Technologies (DOE)
ORNL	Oak Ridge National Laboratory
PSL	Process Simulations Ltd.
R&D	research and development
SEM	scanning electron microscopy
tds/d	tons of dry solids per day
UMR	University of Missouri–Rolla
XRD	X-ray diffraction

1. Executive Summary

1.1 Research and Development

This project has successfully accomplished its goals and in some areas exceeded them. This success has been accomplished by addressing three main objectives: (1) identification of a refractory material with the corrosion resistance and mechanical integrity to endure at least one year and preferably at least two; (2) development of materials for black liquor injection nozzles and sensor/thermocouple protection tubes to permit operation for the required time period; and (3) identification of the fluid flow and temperature characteristics needed to understand the environments in which refractory materials and injection nozzles must function.

Over 100 corrosion studies have been carried out on experimental and commercial refractory materials utilizing an immersion test system constructed at Oak Ridge National Laboratory (ORNL) to simulate the black liquor gasifier environment. Such testing has provided a screening tool for candidate materials to be used as the lining in the Weyerhaeuser New Bern gasifier. Materials passing the ORNL immersion test have been found to demonstrate similar success in the actual service environment of the New Bern gasifier.

Based on data and recommendations from the laboratory immersion tests (corrosion studies for 100 h at 1000°C), an alternative fusion-cast alumina lining material was installed in the New Bern gasifier that was found to last nearly one year. These data and recommendations as well as installed test panels in the New Bern gasifier led next to the installation of a fusion-cast magnesia alumina lining in the New Bern gasifier; this material has lasted for over 18 months of service and has the potential for lasting over two years.

Work was carried out to identify chrome-free mortar systems that would not react with the molten smelt environment. Several new mortar systems have been identified which are expected to provide one- to two-year lifetimes—i.e., a time equivalent to that of the lining bricks. In addition, several new candidate backup lining material systems have been identified based on the results of laboratory immersion testing at 900°C, and an alternative refractory material based on alkali-aluminate was developed in collaboration with a small domestic refractory producer. This material is scheduled to be installed in the New Bern gasifier in mid- to late 2006.

A modified liquor nozzle was designed and constructed to test a number of materials that should be more resistant to erosion and corrosion than the material currently used. Inserts made of three erosion-resistant metallic materials were fabricated, along with inserts made of three ceramic materials. The assembled system was sent to the New Bern mill for installation in the gasifier in 2005. Following operation of the gasifier using the modified nozzle, inserts will be removed and analyzed for degradation by erosion and/or corrosion. Although no materials have been directly identified for sensor/thermocouple protection tubes, several of the refractory material systems identified for lining material applications may be applicable for use in this capacity.

Modeling studies were conducted with the ultimate goal of better characterizing the fluid flow in the liquor spray nozzle and to characterize the temperature and composition of the material in contact with the refractory lining of the gasifier. Results of the Simulent studies suggest the droplet distribution in the spray does not match what was used in previous models, and the Process Simulations Ltd. (PSL) modeling suggests the temperature distribution is higher at the bottom of the gasifier than previously thought. Modeling results also suggest that the refractory temperature in the gasifier can be reduced by changing the liquor spray and that because of the strong swirl, a separation zone could be formed at the corner of the conical wall where it meets the vertical barrel wall, and some the liquor droplets could be suspended in this zone. The accumulation of droplets in this area could cause instabilities in the performance and also in corrosion of the refractory.

1.2 Technology Transfer

Intellectual property has been generated as a result of this significant research effort, and great progress has been made in advancing the art of black liquor gasification. New refractory materials have been developed, and in the case of the fusion-cast magnesia-alumina spinel, an old material has been resurrected for a new application. One U.S. patent has been applied for, and another patent application is being prepared regarding the application of refractory lining systems for gasification and other high-temperature, high-alkali environments.

1.3 Commercialization

During the entire duration of this project, the researchers at ORNL worked with the corporate research staff and New Bern Mill staff of Weyerhaeuser. In addition, the research team worked closely with refractory producers and suppliers. As a result of this project, Monofrax has begun supplying a material for the hot-face lining of the gasifier that was produced in the past for other applications, but was currently no longer in production. Also, ORNL and Westmoreland Advanced Materials have collaborated to develop a new refractory material based on alkali-aluminate for use in the backup lining of the gasifier. In addition, other refractory manufacturers have developed new materials or found currently existing materials that may be applicable in the future for black liquor gasification and other high-temperature, high-alkali environments.

1.4 Recommendations

- It would be useful to analyze the nozzle insert materials that were installed at the New Bern mill in 2005.
- Efforts should be made to determine whether optimization of newly identified and newly developed backup lining materials is possible.
- Additional work should be performed to analyze samples of the current lining material after two years of exposure.
- It would be beneficial to continue the monitoring of strains on the gasifier shell and to repair any malfunctioning sensors.
- Periodic sampling and analysis of the new lining materials installed in late 2006 during service could provide feedback on the performance of these new materials.

2. Introduction

The predominant paper-making process in North American mills is the kraft process, in which an aqueous solution of sodium hydroxide and sodium sulfide is used to effect the fiber separation. The Tomlinson boiler is an essential component of a kraft mill, as it generates the steam necessary for operating the mill and allows the mill to recycle the pulping chemicals. By recycling the pulping chemicals, the mill avoids the expense of replacing them and also avoids the damage to the environment that would occur in discarding the spent chemicals. The Tomlinson boiler, generally referred to as a black liquor recovery boiler, processes the concentrated waste stream containing the spent pulping chemicals while burning the unused organic components of the wood. Burning the organic components produces enough steam to satisfy the mill's requirements while also generating more than half the electrical power required for operation of the mill.

Despite reducing the costs for chemicals and providing environmental advantages, these boilers are relatively inefficient with respect to steam and power production, and they emit relatively high levels of pollutants. In addition, the recovery boiler is the most expensive component of a kraft mill and can pose serious safety issues if the cooling water in the tubes that form the vessel walls comes in contact with the mixture of molten salts, generally referred to as smelt, that accumulates on the floor of the boiler.

Alternatives to recovery boilers have been investigated by paper companies, recovery boiler manufacturers, and other organizations. A paper by Whitty and Baxter provides a good summary of the many approaches that have been pursued.[1] Black liquor gasification is one of the most widely studied alternatives. Thorough economic studies conducted by Larson and associates have shown that combined cycle black liquor gasification (CCBLG) has the potential for more efficient recovery of the energy content of the black liquor.[2,3] In addition to more efficient energy recovery, black liquor gasification has a potential to reduce emissions, lessen or eliminate the molten smelt-water explosion issue, and provide a favorable rate of return on the incremental investment.

As described by Whitty and Baxter,[1] two of the gasification processes have been developed to a greater extent, and these processes are being utilized in three North American mills. Two mills, one in Virginia and one in Ontario, that operate on the semi-chem pulping process have installed, and are operating with, gasifiers that utilize the low-temperature gasification process developed by Manufacturing and Technology Conversion International, Inc., of Baltimore, Maryland.[4] A third mill has a gasifier operating on the high-temperature process developed by Chemrec AB of Stockholm, Sweden.[5] In this process, the temperature is maintained around 950°C, well above the melting point of the salt. As a result of the higher-temperature operation, gasification occurs at a much faster rate, but a molten smelt phase is formed and must be contained.

As discussed by Larson et al., both of these gasification processes have some favorable aspects.[2,3] However, both have issues with containment materials—primarily metallic materials in the case of the lower-temperature process, and both refractory and metallic materials for the higher-temperature process. This project addressed improved materials for the high-temperature gasifier and showed significant advances regarding the containment materials for the gasification vessel.

3. Background

In order to produce pulp and paper economically by the kraft process, there must be 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 heat recovered from the boiler has been utilized in the form of steam for operation of the mill, as well as for generation of electricity. The ability of recovery boilers to perform the required tasks has contributed to making the kraft pulping process the dominant papermaking process. However, recovery boilers have shortcomings, including higher-than-desired emission levels, relative inefficiency in producing electrical power from the black liquor, and the possibility of smelt-water explosions. As an alternative to recovery boilers, black liquor gasification is being evaluated in a number of pilot and demonstration scale facilities.

In the high-temperature gasification process, black liquor is atomized using steam. These steam droplets are mixed with air or oxygen and then partially combusted at about 950°C to provide the heat necessary for the chemical reduction of the sodium sulfate. The products are a combustible gas and droplets of molten salts, which are primarily sodium carbonate and sodium sulfide. Some of these molten droplets hit the reactor vessel's refractory lining and flow down the wall to the outlet of the reactor.

The high-temperature gasification process can be operated near atmospheric pressure or at significantly elevated pressure. To fully achieve the anticipated benefits of CCBLG, the higher-pressure process would need to be employed. A near-atmospheric-pressure commercial-sized gasifier was installed at the Frövifors mill in Sweden in 1991. This unit was sized at 75 metric tons of dry solids per day (tds/d) and reportedly operated at a high level of performance.[1,6] There is also some experience from a pilot-scale (10 tds/d) high-pressure unit that was operated in Sweden. The gasifier primarily used with this project, at the Weyerhaeuser mill in New Bern, North Carolina, is rated at 330 tds/d and employs a near-atmospheric pressure environment. In addition, a high-pressure system has been constructed at the Energy Technology Center in Piteå, Sweden, with initial shake-down testing begun in 2005.

The operating experience with black liquor gasifiers in North America is very limited. A low-temperature, pulse-heated black liquor steam reformer/gasifier was developed in 1994 by MTCI/ThermoChem, Inc., and was operated at the Weyerhaeuser mill in New Bern, North Carolina. In 1996 a high-temperature, low-pressure unit developed by Kvaerner/Chemrec (now Chemrec AB) was installed at the same New Bern mill. 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. Because of materials-related problems, this reactor was taken out of service in December 1999. ORNL staff members participated in the analysis of the failed components and contributed information that was used by Weyerhaeuser when the decision was made to rebuild the gasifier. The rebuilt gasifier resumed operation in late June 2003.

A schematic of the New Bern gasifier is shown in Fig. 3.1. In this system, black liquor, steam, and air are injected into the top of the cylindrically shaped, refractory-lined vessel. The liquor and steam are injected through a specially designed spray nozzle while, simultaneously, preheated air is injected through a windbox with angled vanes that impart a swirl pattern to the air flow. The amount of air injected is substoichiometric such that only sufficient combustion occurs to maintain the operating temperature and provide the energy necessary for reduction of sodium sulfate. When the black liquor is injected into the reactor vessel, the water in the liquor is volatilized, the organic components are degraded by oxidation or pyrolysis, and the sodium sulfate is reduced, primarily to sodium sulfide and hydrogen sulfide. The molten alkali salts contact the internal surfaces of the gasifier. The top of the gasifier vessel is a refractory-lined, dome structure, while the bottom of the vessel is a refractory-lined cone that serves to direct the gaseous and liquid products into the quench area.

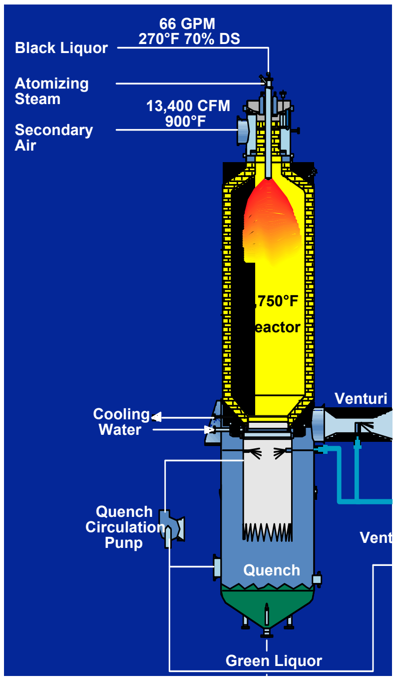


Fig. 3.1. Schematic of New Bern high-temperature low-pressure gasifier.

The bottom of the cylindrical vessel consists of a cone arrangement that significantly reduces the effective cross section of the vessel and directs the flow of the product gas and molten salts downward through the quench sprayers. The inorganic salts drop into the green liquor tank, where they dissolve in the aqueous solution in the bottom of the vessel, while the product gas is removed from the vessel through a side port. In a CCBLG, this product gas would be cleaned and routed to a gas turbine where it would serve as fuel. The environment inside the gasifier vessel is around 950°C and consists of gases, including several corrosive species, and molten alkali salts. This environment is so hostile that no commercially available alloy has been found that can survive for any extended period. Consequently, a refractory lining has been employed for the top dome, the cylindrical barrel and the lower cone. It has been found, however, that most refractories have a limited lifetime in this environment. The current design utilizes a two-component lining with a more corrosion-resistant refractory as the inner lining and an outer lining that has less corrosion resistance but better thermal insulating properties.

A few metallic components, such as injector nozzles, thermowells, and refractory support rings, have to be used in the reaction vessel, but lifetimes have been limited. The nozzle used to inject liquor and steam is subjected to erosion and corrosion, and a number of materials and designs have been tried. The cooling effect from the liquor and steam that flow through the nozzle have helped to prolong the life of this component, but lifetimes are still limited. Both metallic and refractory materials have been tried for the thermowells that contain the thermocouples used to measure the temperature inside the reaction vessel. No material has been found that survives more than several months. Initially, metallic support rings were welded to the gasifier shell at several levels to support the refractory lining. Although made of N12160, a cobalt-containing, corrosion-resistant alloy, these rings corroded badly in a fairly short time, and the vessel design had to be modified to eliminate these metallic components.

The transition from the refractory lining to the quench section is made with the cooled support ring. This metallic ring is internally cooled with circulating water but, like the nozzle, has been found to suffer from significant corrosion. The outer containment of the vessel is a metallic shell that is protected from excessively high temperature by the refractory lining on the inside and by forced flow of ambient air over the outer surface.

In the gasifier's original construction, type 316L stainless steel was used for the vessel shell, and a bonded alumino-silicate refractory was selected for the innermost, high-temperature lining. This refractory was selected by the original provider of the 1996 gasifier (Chemrec), reportedly on the basis of testing conducted in Sweden. The gasifier was first fired in mid-December 1996 and during the early periods of operation was subjected to undesirably frequent thermal cycles, which are thought to have accelerated the degradation of the refractory. Pieces of refractory were collected in the trap at the bottom of the green liquor quench tank at an unexpectedly high rate, and inspection of the lining after a fairly short period of operation showed significant degradation of the innermost refractory lining. Operation with this initial lining continued for over a year, and refractory samples were removed for characterization on several occasions.

Around the first of December 1997, inspection of the gasifier lining showed significant degradation of the refractory in the upper third of the gasifier. This portion of the lining was replaced with spare material that was stocked in New Bern, and samples of this refractory were removed from the gasifier for examination to identify the reaction products and to determine the reaction mechanisms. As a result of the extensive damage that was observed in a relatively short time, studies were initiated in Sweden to identify a more suitable refractory.

At ORNL, unexposed and exposed refractory samples from the original gasifier lining were examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron microprobe analytical techniques. Crystalline phases were identified that were present in concentrations of at least a few percent along with amorphous phases and/or phases that were present in relatively small concentrations. These phases included mullite ($Al_6Si_2O_{13}$), cristobalite (SiO_2), opal (SiO_2xH_2O), and andalusite [$Al_2(SiO_4)O$] present in the unexposed brick, and reaction products such as nosean ($Na_8Al_6Si_6O_{24}SO_4$) and a Carnegieite-like-phase sodium aluminum silicate ($Na_2O{\bullet}Al_2O_3{\bullet}SiO_2$). From the refractory analyses and the observations of the refractory in the gasifier, it was apparent that this refractory lacked adequate corrosion resistance for the application. Therefore, studies were performed to identify a more suitable material.

In early 1999, a new refractory lining was prepared for installation based on data and recommendations from the laboratory testing. The new refractory was a fusion-cast α/β-alumina material produced in North America, with insulating brick composed of fusion-cast β-alumina (produced by the same U.S. refractory company) installed behind the inner lining. Following a shutdown of the reactor, nine core-drilled samples of the gasifier lining were collected, along with pieces of refractory that appeared as "bubbles" protruding from the surface of the refractory bricks.

The bubble pieces and most of the core-drilled samples were examined. In addition to samples of the primary lining and the backing brick, a few bricks of an equivalent material from an alternate manufacturer had been exposed in the gasifier, and samples of these materials were also included in the analyses. Analysis techniques included the same methods as used on the original lining: XRD, SEM, and microprobe analysis.

The phase diagram for the $NaAlO_2$ and Al_2O_3 system, as shown in Fig. 3.2, indicates a series of phases with an increasing Na:Al ratio from right to left across the phase diagram. The β-alumina phase has a ratio of 1:11; while the β-like alumina phase has a ratio around 1:6 and $NaAlO_2$ has a ratio of 1:1. Additionally, theoretical calculations predict that a significant volume increase occurs with the increase in the amount of sodium in the alumina-rich phase.

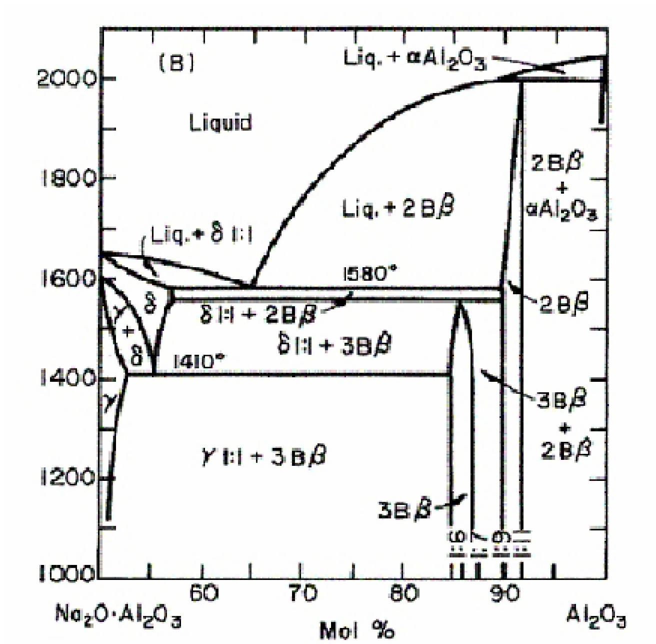


Fig. 3.2. Phase diagram for $NaAlO_2$ – Al_2O_3 system.

Examination of the exposed refractory samples showed that some of these additional phases were present—in particular, the β-like alumina and $NaAlO_2$.[7] The β-alumina refractories from both manufacturers contained these two reaction products, which probably formed as a result of penetration by and subsequently reaction with the sodium salts. The mixed alumina refractories both showed formation of the β-like alumina phase, but the mixed alumina refractory from the second manufacturer did not show evidence of $NaAlO_2$ formation, while the material from the manufacturer of the gasifier lining did have the phase present. Other observations of significance were that sodium, sulfur, and silicon moved through the refractory primarily along grain boundaries, while potassium appeared to be much more mobile and able to move through the grains with relative ease. Furthermore, reaction products (β-like alumina and $NaAlO_2$) are highly hygroscopic and are likely to form a hydrate under the conditions present in the gasifier while it is cooling.[7]

Operation of the New Bern gasifier was continued until it was again shut down for replacement of significant amounts of the fusion-cast alumina refractory. During this replacement a through-wall crack was discovered in the barrel of the gasifier vessel shell; this crack was found to originate on the inner surface of the shell. Consequently, several sections were cut from the shell for examination. It was determined, based on the crack characteristics, the operating temperature, the stress state, and the chemical environment, that the cracking was most likely due to chloride stress corrosion or a result of chloride introduced into the gasifier system and the resulting stress from the expansion of the refractory that occurred when the refractory reacted with the alkali salts. Because the gasifier shell was considered a pressure vessel, the presence of the through-wall crack made further operation in violation of the pressure vessel code. Consequently, the decision was made to discontinue operation of the gasifier.

Two other projects relevant to the gasifier materials issues have also been conducted at ORNL. The first, primarily addressing the testing and development of refractory structural materials, came to a conclusion at the end of the 2003 fiscal year. The second project was directed to development of high-chromium-content alloys for use in black liquor gasifiers and recovery boilers. Alloys developed in this project have been exposed in a recovery boiler and in the New Bern high-temperature gasifier, but funding for this effort was reduced during FY 2003 and terminated at the end of FY 2003, a year earlier than the schedule in the original project.

3.1 Statement of Objectives

The objectives of the current project were to (1) identify a refractory material with the corrosion resistance and mechanical integrity to last at least one year and preferably at least two years in the black liquor gasifier environment, (2) develop materials for black liquor injection nozzles and sensor/thermocouple protection tubes to permit operation of these components for economically and technically feasible time periods, and (3) identify the fluid flow and temperature characteristics of the gasifier in order to understand the environments encountered by the refractory materials and injection nozzles.

The industrial viability of the high-temperature, atmospheric-pressure gasification technology employed at Weyerhaeuser's New Bern 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.

3.2 Project Tasks

The main objectives of this project were successfully accomplished by performing the following tasks:

Task I: Corrosion Studies of Candidate Refractories for Use as Lining Materials

Corrosion studies of various possible refractories were performed utilizing an immersion test system constructed at ORNL. To simulate the environment of a black liquor gasifier, a test sample was suspended in molten smelt at approximately 1000°C while argon gas was bubbled continuously through the smelt to ensure uniform temperature and smelt composition. To mimic the gasifier environment as much as possible, the smelt used was supplied from the recovery boiler at Weyerhaeuser's pulp and paper mill in New Bern. Exposure times were generally either 50 or 100 h. Following testing, photographs and measurements of exposed portions of the sample were taken and averaged both before and after immersion in the molten smelt to check for dimensional changes and expansion. Nearly all samples were evaluated using optical microscopy and XRD, with selected samples also being examined using electron microprobe.

Task II: Replacement of Lining with Alternative Fusion-Cast Alumina Material

The gasifier at New Bern was rebuilt with a carbon steel shell in order to eliminate some of the potential stress corrosion mechanisms that are operative with stainless steel and with a fusion cast α/β-alumina from the alternate manufacturer used for the innermost lining. Test pieces of three promising refractory materials from the previous corrosion studies were also installed as part of the new gasifier lining. In an effort to provide some resistance to expansion of the refractory, compressible metal foam was installed between the outermost refractory and the carbon steel gasifier shell. Prior to installation, the metal foam was tested to determine its crushing strength at the temperature and in the environment expected for gasifier operation.

Problems with the quench spray system led to an unplanned shutdown of the gasifier. At this time, eight core-drilled samples were collected from the refractory lining at selected locations to include the three refractory test pieces, as well as several samples of the primary refractory lining. XRD, SEM, and microprobe examination were performed on two of these samples: the fusion-cast α/β-alumina refractory that was the primary refractory lining material and the fusion-cast magnesia-alumina spinel that was one of the three test materials selected from the corrosion testing.

Task III: Installation and Evaluation of a Strain Monitoring System

In order to protect the pressure vessel from damage by expansion of the lining, a strain monitoring system consisting of a number of strain gauges, inspection orifices, and hoop wires [with Vernier scales and linear variable displacement transducers (LVDTs)] was designed and installed by Weyerhaeuser. The purpose of this system was to monitor the stresses and strains in the vessel and from these measurements to estimate the expansion behavior of the refractory lining. The axial and radial strain on the pressure vessel was monitored at four elevations, with the circumferential expansion of the barrel also being measured as a backup. Temperatures at various locations on the vessel were also measured, allowing the thermal expansion component of the strain to be calculated and accounted for. A finite-element model of the vessel was also developed at ORNL to use in conjunction with these strain measurements. By adjusting refractory load in the model, the actual measured strain values could be reproduced. In this way it was possible to calculate the refractory expansion and loads necessary to produce the measured strains and thereby the actual stresses in the reactor vessel cone.

Task IV: Replacement of Lining with Fusion-Cast Magnesia-Alumina Material

Strain gauge measurements showed that expansion of the refractory and crushing of the metallic foam led to significant loading on the gasifier's carbon steel shell and expansion and cracking; chemical reaction was also seen on core-drilled samples. These measurements and observations led to the decision to replace the lining and foam. On the basis of test results from laboratory studies and exposure in the gasifier, it was decided that a new refractory lining composed of fusion-cast magnesia-alumina spinel would be installed in September 2004.

Refractory core-drill samples were taken during a gasifier shutdown in mid-March 2005. Examination of these samples showed that a few of the bricks had more internal porosity than previously examined samples; however, the refractory material itself did not show evidence of reaction with the molten smelt except for a thin layer on the surface. In late May 2005, the mill suffered a short, unplanned power outage, resulting in a portion of the hot refractory lining being water-quenched to near room temperature. Core-drilled samples from the quenched lining brick were examined and subjected to compression testing. Microstructural examination of the refractory samples did not reveal any evidence that the refractory was damaged by the water quench, and compression testing indicated that the refractory had not been significantly degraded by the water quench.

To date (after 18 months of operation), the fusion-cast magnesia-alumina spinel lining has been found to be performing well. During subsequent shutdowns of the gasifier for other reasons, the refractory lining has been examined and found to be holding up well with minimal loss of material due to spalling and negligible observable expansion of the refractory lining.

Task V: Installation and Evaluation of Updated Strain Monitoring System

In order to monitor any expansion of the new refractory in a precise fashion, an array of 40 strain gauges and 20 thermocouples was installed on the gasifier shell. The strain gauges were mounted so that axial and circumferential strains can be measured at four positions around the vessel and at five different levels. A thermocouple was also located at each strain gauge pair location.

Task VI: Evaluation of Refractory Mortar System

Testing was carried out to identify chromium-free mortar materials for the New Bern gasifier. Samples of Monofrax L were bonded together in a “sandwich” configuration using the various mortars and were subjected to smelt immersion testing. Alternative alumina-based, spinel-based, silica-bonded alumino-silicate, and proprietary commercial mortar compositions were tested through immersion testing, and the results were compared with baseline results obtained using the current chrome-containing mortar material.

Additional testing of the mortar materials was performed using a “tuning fork” configuration where a slot was cut in the base of a Monofrax L refractory piece and mortar material was used to fill the slot. This arrangement provided a compressive force on two sides which acted against expansion of the refractory. The mortar was free to expand in the other two directions, similar to what would occur on the free mortar surface in the vessel. Samples were prepared using the current chrome-containing mortar, the high-alumina-based and silicon-bonded alumino-silicate mortars tested previously, and experimental mortar compositions provided by the University of Missouri–Rolla and a small refractory manufacturer.

ORNL was also asked to evaluate the mechanical strength of refractory mortar compositions for use in the New Bern gasifier. The two mortar compositions analyzed were the air-set, high-temperature alumina-chrome mortar currently being used in the vessel and a high-purity, 95% high-alumina, phosphate-bonded mortar which was a candidate replacement for the current chrome-containing mortar. Samples were tested in compression to evaluate the effects of loads applied by expansion of vessel refractory lining. Mechanical testing was performed at room temperature in simple compression.

Task VII: Modeling

Modeling studies were conducted with the ultimate goal of better characterizing the fluid flow in the liquor spray nozzle and of characterizing the temperature and composition of the material in contact with the refractory lining of the gasifier. Work was conducted at Process Simulations Ltd. (PSL), with the objective of improving the model of the New Bern gasifier initially developed by PSL for Weyerhaeuser. Researchers at Simulent, Inc., conducted work to model the black liquor spray nozzle.

Task VIII: Evaluation of Backup Lining Material

Following evaluation of the replacement of the fusion-cast alumina lining with the fusion-cast magnesium-aluminum spinel refractory lining and evaluation of the refractory mortar testing, it was decided that the strain seen on the vessel shell must be due to expansion of the refractory mortar or the backup lining. Analysis of a backup lining core sample, performed using optical microscopy and XRD, revealed that the backup lining material (an alumino-silicate brick material) was highly degraded by smelt penetration/reaction.

Alternative refractory materials composed of mullite, MgO, and alkali-aluminate were evaluated as candidates to replace the alumino-silicate backup lining material. Immersion testing was performed at 900°C. As part of this work, an alternative refractory material based on alkali-aluminate was developed in collaboration with a small domestic refractory producer.

Task IX: Evaluation of Liquor Nozzle Configuration

A modified liquor nozzle was designed and constructed to test a number of materials that should be more resistant to erosion and corrosion than the material currently used. Inserts made of three erosion-resistant metallic materials were fabricated as well as inserts made of three ceramic materials. The assembled system was sent to the New Bern mill for installation in the gasifier. Following operation of the gasifier using the modified nozzle, inserts will be removed and analyzed for wear by erosion and corrosion.

Task X: Replacement of Lining with Suggested Material Improvements

Based on the findings from the evaluation of refractory mortar materials and evaluation of backup lining materials, several modifications to the current lining system have been suggested. These modifications should be implemented during the next full relining of the gasifier vessel, which is scheduled for the fall of 2006.

Task XI: Writing of Reports

Annual technical reports and a final report (this document) were written to document the results of this program.

4. Results and Discussion

4.1 Corrosion Studies of Candidate Refractories for Use as Lining Materials

Over the extent of the project, corrosion studies of various refractories were performed. Candidate refractory materials were screened utilizing an immersion test system constructed at ORNL. To simulate the environment of a black liquor gasifier, a test sample was suspended in molten smelt. A three-zone vertical tube furnace capable of temperatures up to 1200°C was used to heat the smelt and sample to test temperatures. A control thermocouple maintained the molten smelt at approximately 1000°C throughout the immersion test while argon gas was bubbled continuously through the molten smelt to ensure uniform temperature and smelt composition. Outlet gas was monitored to collect the water from the system and to ensure that the system was continuously purged and air-tight. A schematic of the immersion test system is shown in Fig. 4.1.

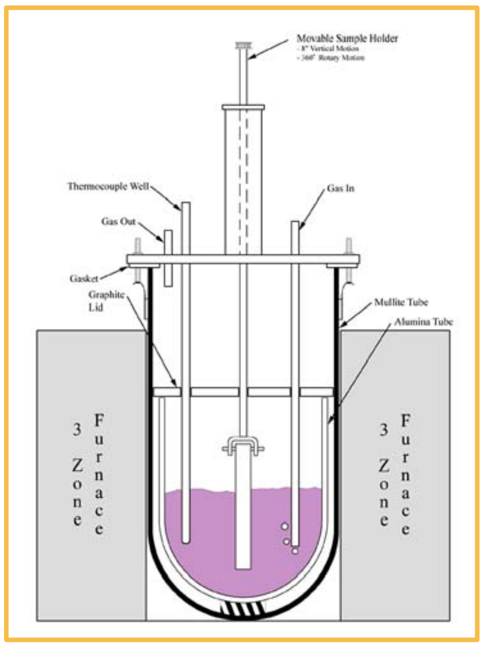


Fig. 4.1. Schematic of ORNL immersion test system.

To mimic the gasifier environment as much as possible, the smelt used was supplied from the recovery boiler at Weyerhaeuser's pulp and paper mill in New Bern. X-ray patterns of the solidified smelt revealed the presence of crystalline phases of sodium sulfide, sodium sulfate, and sodium carbonate. The furnace system was ramped over a period of ≈18 h to testing temperature (900 or 1000°C) before the test sample (~110 × 26 ×13 mm) was lowered into the smelt. Exposure times were generally either 50 or 100 h. Following testing, the test sample was raised out of the smelt and cooled for ≈24 h before examination. Photographs and measurements of exposed portions of the sample were taken and averaged both before and after immersion in the molten smelt to check for dimensional changes and expansion. Since the bar was not fully immersed, changes in length were not used in expansion calculations.

Following immersion testing, samples were generally evaluated using optical microscopy and XRD. Extreme care was taken in preparing the individual test specimens due to their highly hygroscopic behavior and the solubility of some of the degradation products.

Testing was performed on samples from numerous refractory suppliers, including both commercially available and experimental materials. Test materials included mullites, alumino-silicate bricks, fusion cast aluminas, alumina-based and chrome-containing mortars, phosphate-bonded mortars, coated samples provided under an MPLUS-funded project, bonded spinels, different fusion cast magnesia-alumina spinels with magnesia content ranging from 2.5 to about 60%, high-MgO castable and brick materials, spinel castables, and alkali-aluminate materials.

4.2 Replacement of Lining with Alternative Fusion-Cast Alumina Material

In April 2002 it was decided to rebuild the New Bern gasifier. The rebuilt gasifier was designed with a carbon steel shell in order to eliminate some of the potential stress corrosion mechanisms that are operative with stainless steel. The fusion-cast α/β-alumina from the alternate manufacturer was selected as the material for the innermost lining, and test pieces of three promising refractory materials from the previous corrosion studies were installed as part of the new gasifier lining. In an effort to provide some resistance to expansion of the refractory, compressible metal foam was installed between the outermost refractory and the carbon steel gasifier shell. Prior to installation, testing of the metal foam was conducted to determine its crushing strength at temperature and in the environment expected for gasifier operation. This rebuilt gasifier began operation in late June 2003.

In mid-January 2004 the gasifier was taken off-line to evaluate and modify the quench spray system. At this time, eight core-drilled samples were collected from the refractory lining at selected locations. These locations included the three refractory test pieces as well as several samples of the primary refractory lining. In order to minimize the possible effects of water and moist air, kerosene was used as the lubricant/coolant for the core drilling, the samples were sealed in evacuated bags as soon after collection as possible, and, once transported to the laboratory, they were embedded in epoxy. Four of the core-drilled samples are shown in Fig. 4.2, and longitudinal cross-sections of the four samples are shown in Fig. 4.3. Based on the visual examination of these samples, it was decided that the more thorough XRD, SEM, and microprobe examination would concentrate on two of these samples: the fusion-cast α/β-alumina refractory that was the primary refractory lining material and the fusion-cast magnesia-alumina spinel that was one of the three test materials selected from the corrosion testing.

Visual examination of the fusion-cast α/β-alumina sample showed darkened areas, particularly along the cracks. On all of these samples (as well as the fusion-cast α/β-alumina samples from the alternate supplier), the material around the cracks was black or dark gray, and the shade of gray got lighter with distance from the cracks. The fusion-cast spinel was a deep red, but there were significant light-colored deposits on the fracture surface that appeared to be similar to deposits on the hot-side surface. These deposits are thought to be residual smelt.

Microstructural studies by optical microscopy of the fusion-cast α/β-alumina and the fusion-cast magnesia-alumina spinel samples showed that there was little change in the microstructure of the exposed as compared with the unexposed samples. Grain size and morphology were relatively unaffected, and signs of smelt penetration into areas in the grain (away from the cracks) were not seen, as supported by the XRD data. The only noticeable change seen in the micrographs is a possible increase in porosity as a result of exposure. It is not clear, though, if this is due to exposure or due to block-to-block or location-to-location variations inherent in fusion-cast materials.

Fig. 4.2. Images of core-drilled specimens. *From top to bottom:* primary fusion-cast alumina lining material, fusion-cast magnesia-alumina spinel test block, alternative fusion-cast alumina test block, and bonded magnesia-alumina spinel test block (outlined on left).

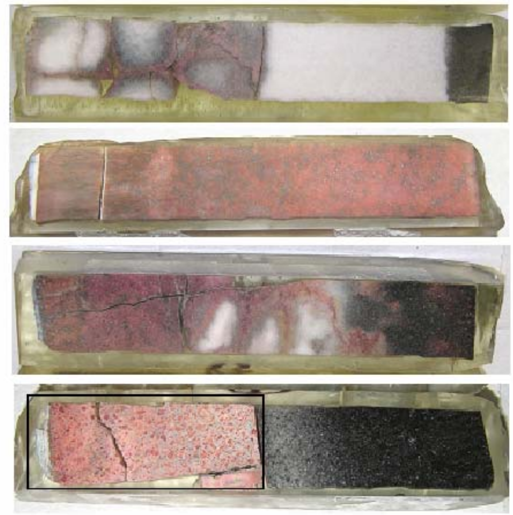


Fig. 4.3. Cross-sections of core-drilled specimens shown in Fig. 4.2. *From top to bottom:* primary fusion-cast alumina lining material, fusion-cast magnesia-alumina spinel test block, alternative fusion-cast alumina test block, and bonded magnesia-alumina spinel test block (outlined on left).

X-ray diffraction studies showed formation of sodium aluminate along the cracks in both samples, but the indications are that the amount and depth of this reaction product was much greater in the fusion-cast alumina sample. The concentration of reaction products could not be easily quantified with XRD, but semi-quantitative estimates suggested the amount decreased with distance from the cracks and was proportional to the darkening of the alumina in the fusion-cast alumina samples. The presence of sodium aluminate in the interior of the refractories could only be explained by penetration of sodium compounds during operation of the gasifier with accompanying reaction with the alumina matrix.

Electron microprobe studies provided elemental maps of the samples that gave a better indication of the extent of penetration of smelt components, particularly in the situation where the reaction product was not crystalline and consequently not detectable by XRD. Fig. 4.4 shows overlays of the sodium, sulfur, and aluminum maps for the fusion-cast α/β-alumina and the fusion-cast magnesia-alumina spinel samples. Along the cracks in both samples the green and yellow colors are apparent, indicating the presence of sodium (green) and a sodium-sulfur compound (yellow) in the refractory. These colors are also present on the hot-side surface of both samples. The varying shades of blue in the fusion-cast alumina sample indicate the presence of sodium in the alumina; by contrast, there is very little variation in the spinel. Some sodium should be present in the alumina sample, since it contains a mixture of α- and β-alumina, but the green and yellow suggest that additional sodium has been transported into the sample.

Considering all the examination results, it appears that there is greater penetration of sodium into the fusion-cast alumina sample than into the fusion-cast spinel sample. This would be in agreement with the extent of cracking observed, since the phase transformations associated with reaction of sodium with alumina and the spinel cause significant volume increases.

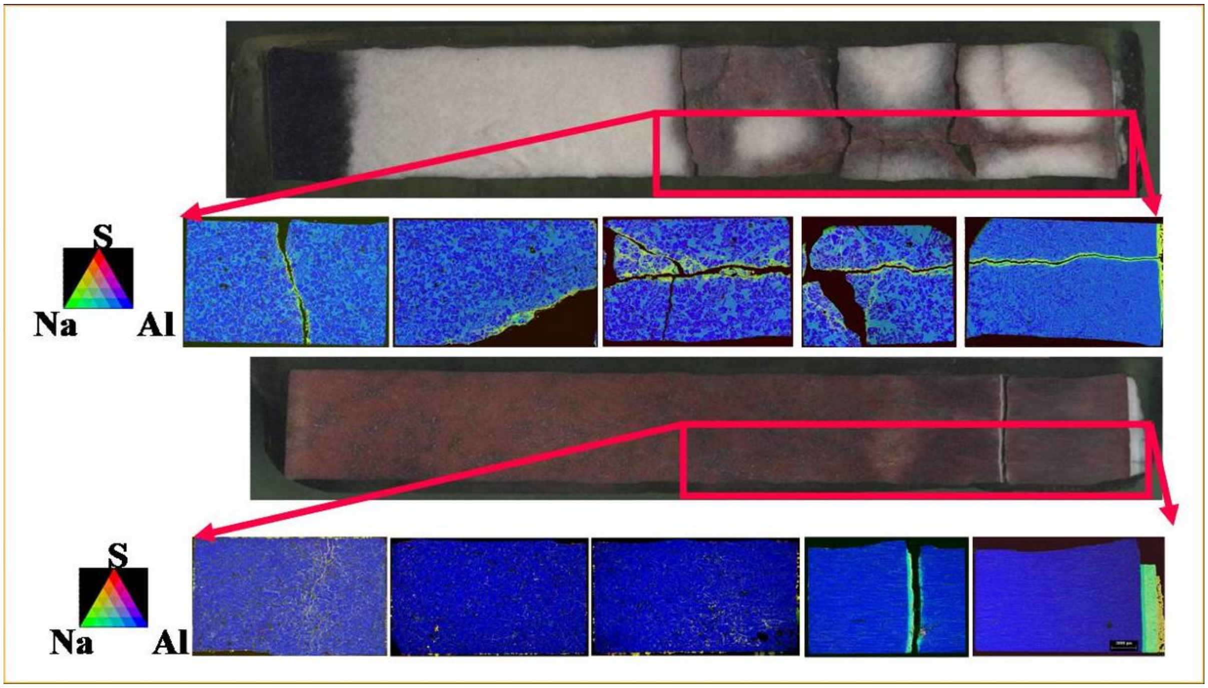


Fig. 4.4. Overlaid elemental maps of sodium, sulfur, and aluminum for fusion-cast α/β-alumina refractory (*top*) and fusion-cast magnesia-alumina spinel refractory (*bottom*).

4.3 Installation and Evaluation of a Strain Monitoring System

In order to protect the pressure vessel from damage by the lining expansion, a strain monitoring system was designed and installed by Weyerhaeuser. The purpose of this system was to monitor the stresses and strains in the vessel and from these to estimate the expansion behavior of the refractory lining. The strain monitoring system, shown in Fig. 4.5, consisted of a number of strain gauges, inspection orifices, and hoop wires (with Vernier scales and LVDTs) installed on the pressure vessel. Strain gauges measured the axial and radial strain on the pressure vessel at four elevations: at the top of the dome, at the upper and lower sections of the barrel, and at the bottom where the cone was attached to the barrel. As a backup measure, the circumferential expansion of the barrel was also measured by looping hoop wires around the barrel section at the upper and lower elevations. The wires rode on low-friction ball bearings to minimize errors due to hysteresis. The ends of the wires were attached to Vernier scales so that small changes in the diameter of the pressure vessel could be measured. LVDT transducers were used to transmit the readings to a computer. Temperatures at various locations on the vessel were also measured, allowing the thermal expansion component of the strain to be calculated and accounted for.

The stress-strain relationship of the metal foam (between the refractory lining and the shell) at the operating temperature was obtained by conventional Instron measurements. The circumferential strain values measured on the shell were then converted to equivalent radial stress on the metal foam, since the shell properties are known. The foam compression was then computed using the stress-strain curve for the foam and the radial stress. Assuming that the metal foam does not deteriorate in the gasifier environment, shell stresses as well as refractory expansion can be computed. This approach was found to work reasonably well. Good agreement was also obtained against actual displacement of the refractory bricks as measured through inspection orifices during planned maintenance outages.

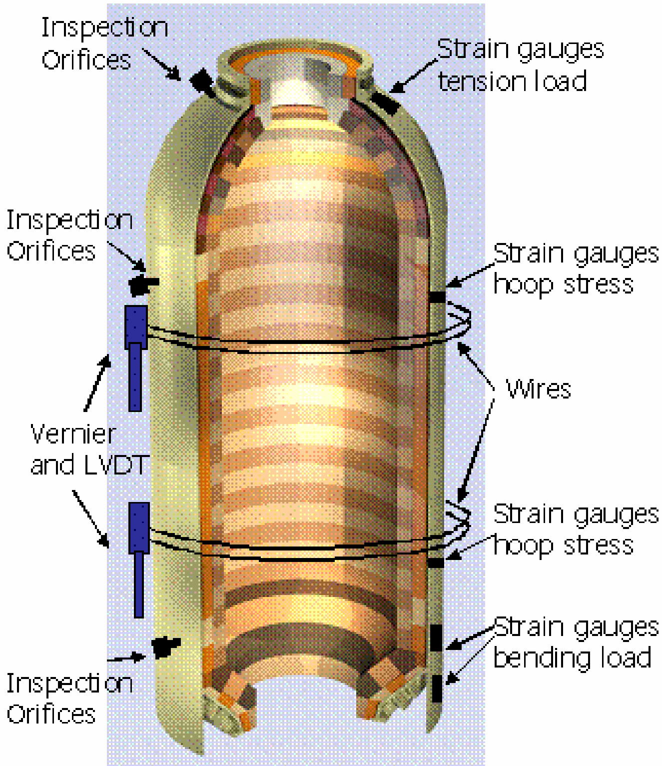


Fig. 4.5. Locations of gauges for vessel strain monitoring system.

Vertical expansion was monitored by strain gauges located on the vessel dome and on the vessel wall adjacent to the intersection of the internal refractory support cone. A finite element model of the vessel was developed to use in conjunction with these strain measurements. By adjusting refractory load in the model, the actual measured strain values could be reproduced. In this way it was possible to calculate the refractory expansion and loads necessary to produce the measured strains and thus the actual stresses in the reactor vessel cone.

The results of the radial expansion, shown in Fig. 4.6, indicated that during the first six months of operation the lining expanded at a slightly faster rate than during the last six months of operation. There was less brick spalling reported during the first six months, which may have been responsible for a higher rate of expansion. The lower rate of spalling may have been due to less stress on the lining during the initial phases of foam compression. As the unit operated and the metal foam was compressed, it densified, and the stress required to compress it increased. This seems to have reduced the rate of expansion and increased the rate of refractory spalling reported by the mill. The refractory lining expanded not only along the radial direction but also along the vertical direction. The lining pressed against the dome of the vessel, and a reaction force was imposed on the cone at the bottom. This reaction force was very large, on the order of thousands of tons, due to the large projected area of the dome. This large force deformed the shell in the vicinity of the cone attachment. These deformations were measured by the strain gauges near the cone attachment. Fig. 4.7 shows an example of the initial and deformed shapes of the reactor vessel and cone as computed by finite element modeling (FEM) analysis using the expansion data. The FEM model results showed that the peak stress occurred at the inner surface of the barrel at the location of the cone attachment weld. The deflections at the center of the cone were small enough to be acceptable.

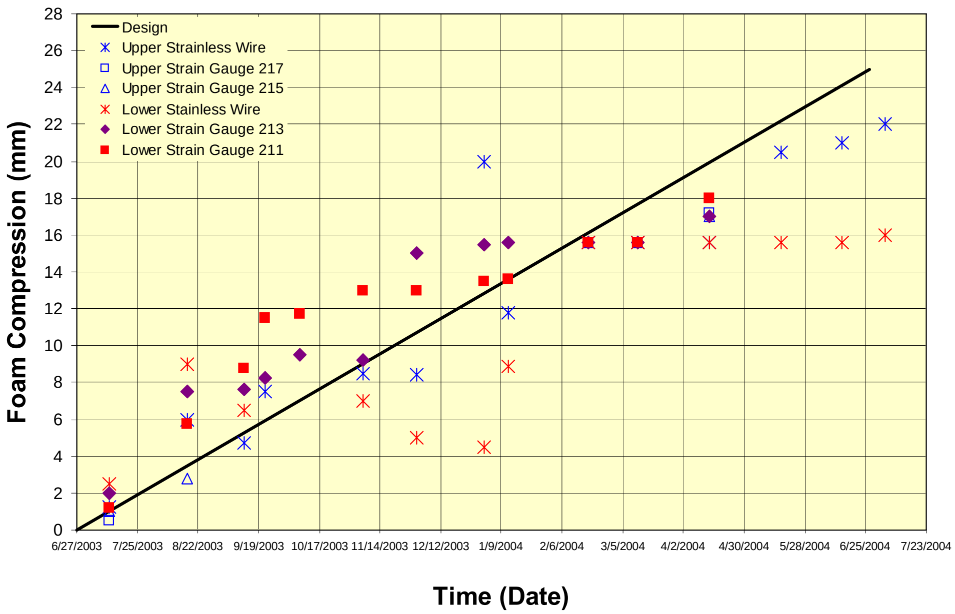


Fig. 4.6. Strain monitoring results calculated using strain monitoring system.

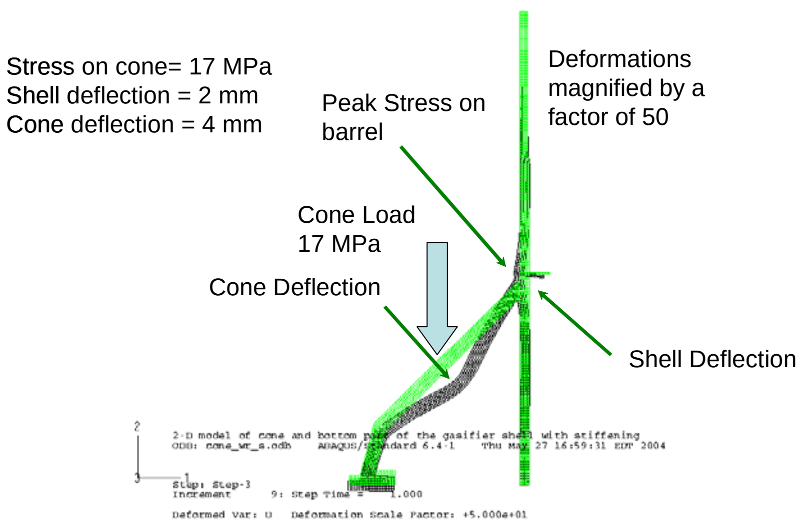


Fig. 4.7. Example of FEM prediction for the deflection in the vessel barrel and cone based on analysis of the expansion data.

4.4 Replacement of Lining with Fusion-Cast Magnesia-Alumina Material

The strain gauge measurements showed that expansion of the refractory had crushed the foam and was exerting significant loading on the gasifier's carbon steel shell. Although the innermost surface of the refractory lining did not show degradation as extensive as seen with previous linings, the amount of expansion and the cracking and reaction seen on the core-drilled samples led to the decision to replace the lining and foam.

On the basis of test results from laboratory studies and exposure in the gasifier, it was decided that the new refractory lining to be installed would be composed of fusion-cast magnesia-alumina spinel. The appropriate materials were purchased, and the installation was completed near the end of September 2004. At the time of this installation, new compressible metal foam was also installed.

The gasifier was again taken off-line in the spring of 2005 to evaluate and modify the cooled support ring and the water spray quenching system. At this time, the opportunity was taken to examine the refractory lining. Six core-drilled samples of the magnesia-alumina refractory were collected and examined at ORNL. Examination of these samples showed that a few of the bricks had more internal porosity than previously examined samples, but the refractory material itself did not show evidence of reaction with the molten smelt except for a thin layer on the surface. An example of a core-drilled sample is shown in Fig. 4.8.

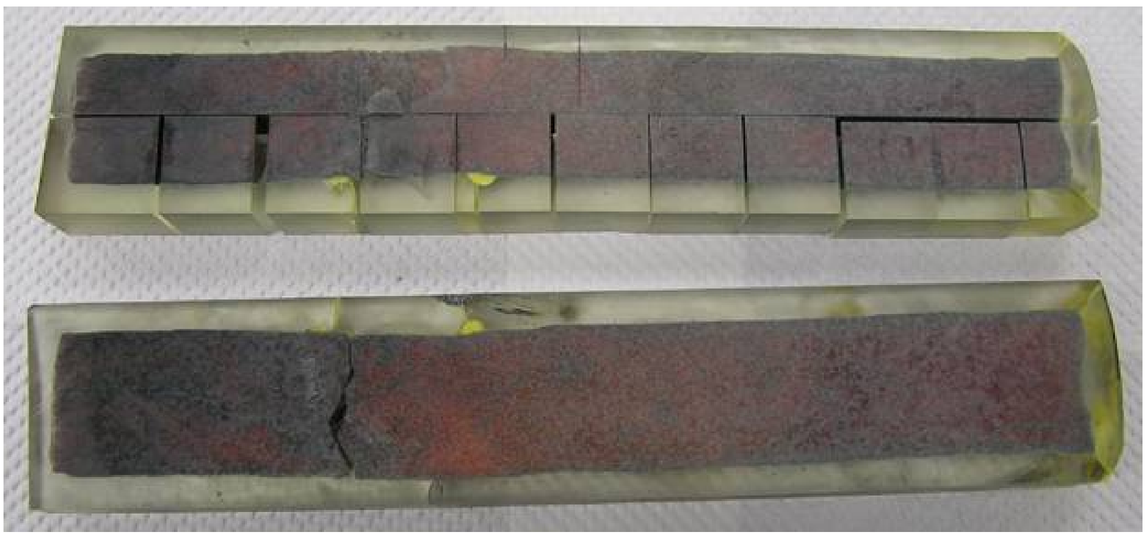


Fig. 4.8. Cross-sections of core-drilled specimens from fusion-cast magnesia-alumina spinel lining. The top specimen is sectioned for analysis; the bottom specimen is as-drilled showing crack.

In May 2005, the mill suffered a short, unplanned power outage. When power was restored and operation was reestablished, a drain valve in the gasifier failed to open, and the water level in the gasifier rose high enough to cover many rows of the refractory lining. This resulted in a portion of the hot refractory lining being water-quenched to near room temperature. Because there was concern that this caused significant damage to the lining, an unanticipated ORNL effort was undertaken to try to assess the extent of damage to the refractory. The damage was particularly severe on the refractory in the lower cone, which was the only portion of the refractory lining that was not made from the magnesia-alumina spinel. Consequently, two core-drilled samples were removed for examination at ORNL in order to determine if immersion in water had caused any damage to the spinel refractory. The samples were examined with the usual analytical tools, and room-temperature compression tests were conducted. Microstructural examination of the refractory samples did not reveal any evidence that the refractory was damaged by the water quench. Compression tests were run on samples of the water-quenched refractory and on samples of unexposed and previously exposed spinel refractory. Results indicated the refractory had not been significantly degraded by the water quench.

To date, the fusion-cast magnesia-alumina spinel lining has been found to be performing well. During subsequent shutdowns of the gasifier for other reasons, the refractory lining has been examined and found to be holding up well with minimal loss of material due to spalling and negligible observable expansion of the refractory lining.

4.5 Installation and Evaluation of Updated Strain Monitoring System

In order to monitor any expansion of the new refractory in a precise fashion, 40 strain gauges and 20 thermocouples were installed on the gasifier shell. The strain gauges were mounted so that axial and circumferential strains can be measured at 20 locations (4 positions around the vessel at 5 different levels). A thermocouple was also located at each strain gauge pair location. Two of the monitored levels were on the metal shell near the bottom of the barrel portion of the refractory in order to measure any deflection of the cone. Locations of the strain gauges and thermocouples are shown in Fig. 4.9.

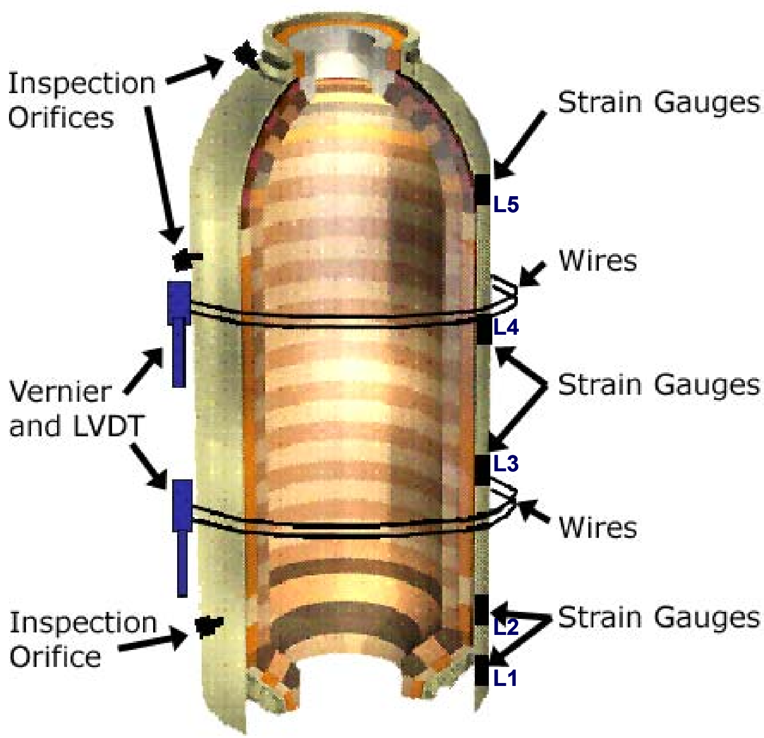


Fig. 4.9. New locations of strain gauges and thermocouples for vessel strain monitoring system.

After the first six months of operation, these strain gauges showed less evidence of refractory expansion than seen with the previous refractory lining. After about eight months of operation, the deformation remained significantly less than it was during the first operating period that began in June 2003. However, after the water quenching incident near the end of May, the rate of deformation increased significantly. After a few months of this higher rate of loading, the load appears to have remained nearly constant for the remainder of the period being studied. Data from the strain monitoring system is shown in Fig. 4.10.

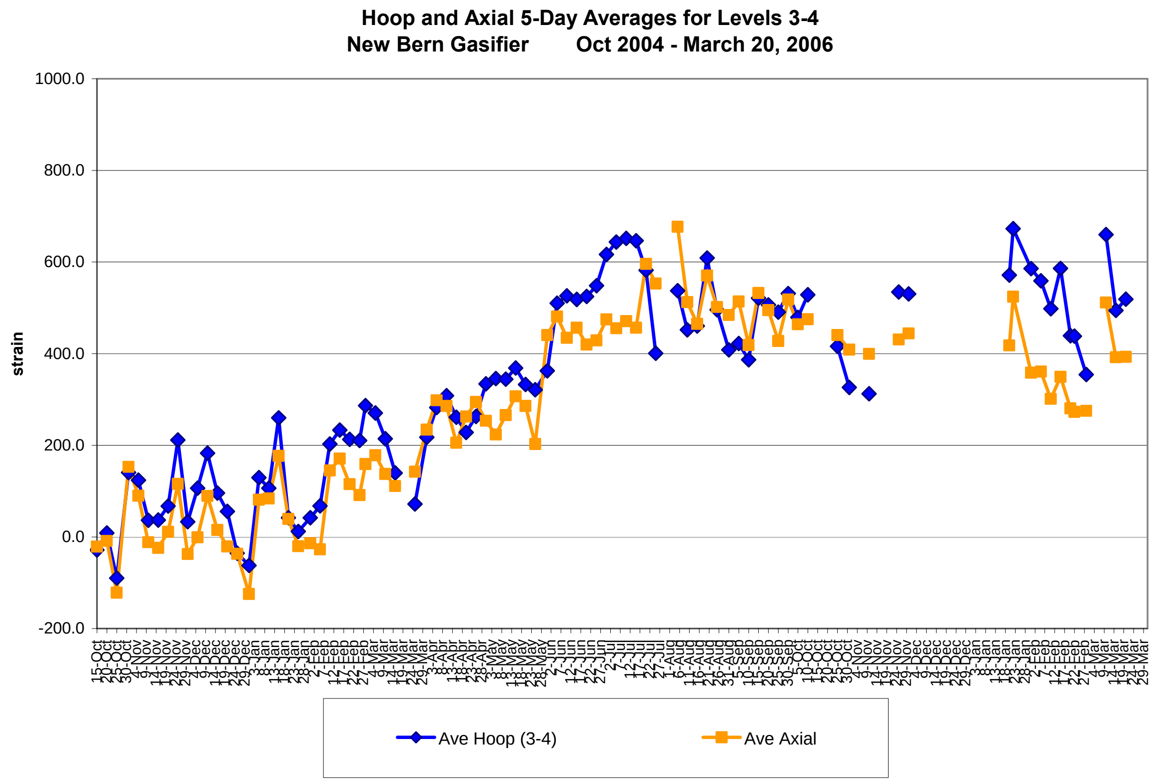


Fig. 4.10. Strain monitoring results obtained using updated strain monitoring system.

4.6 Evaluation of Refractory Mortar System

Testing was carried out in an effort to identify alternative mortar materials for the New Bern gasifier. In order to study the corrosion resistance of various current and potential mortar materials, samples of Monofrax L were bonded together with the various mortars in a “sandwich” configuration as shown in Fig. 4.11. These samples were then subject to the smelt immersion testing using the system described above. Alternative alumina-based, spinel based, silica bonded alumino-silicate, and proprietary commercial mortar compositions were tested through immersion testing and results were compared to base-line results obtained using the current alumina-chrome mortar material.

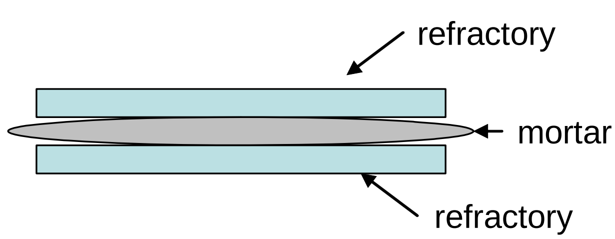
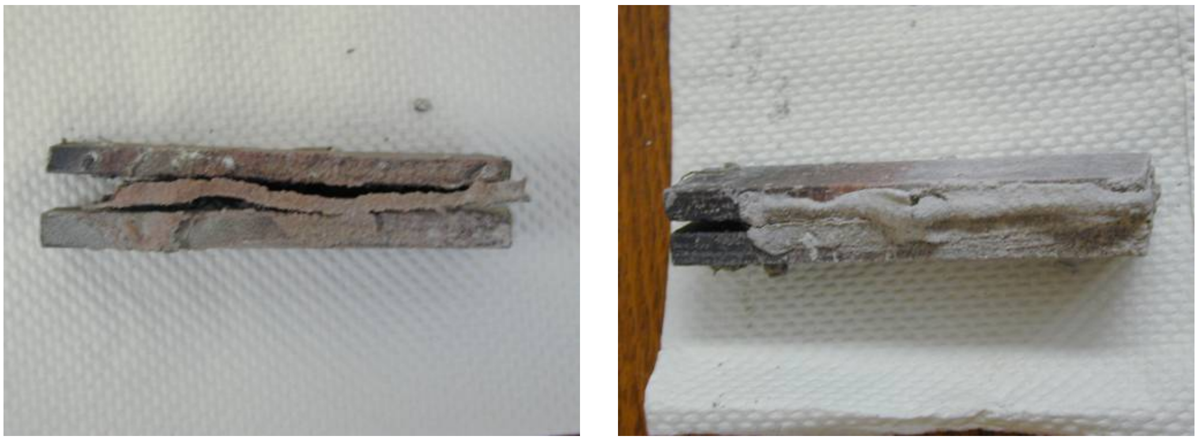


Fig. 4.11. Initial refractory/mortar sample configuration (“sandwich” configuration).

Initial immersion testing showed that the mortar materials all expanded during exposure, resulting in separation of the refractory brick pieces. This is thought to have occurred because no compressive forces were acting on the samples as would be present in the actual refractory installation. Examples of test samples after immersion testing are shown in Fig. 4.12. From the results of this testing it was concluded that the high-alumina mortar performed best, followed by the silicon bonded mortar. The alumina-chrome mortar actually performed the worst in this test because of a large amount of expansion in the mortar.



(a) Current alumina-chrome mortar **(b) Alternative high-alumina mortar**

Fig. 4.12. Refractory/mortar samples in "sandwich" configuration after immersion testing.

Additional testing of the mortar materials was performed using a "tuning fork" configuration where a slot was cut in the base of a Monofrax L refractory piece and mortar material was used to fill the slot. This arrangement, shown in Fig. 4.13, provided a compressive force on two sides which acted against expansion of the refractory. The mortar was free to expand in the other two directions, similar to what would occur on the free mortar surface in the vessel.

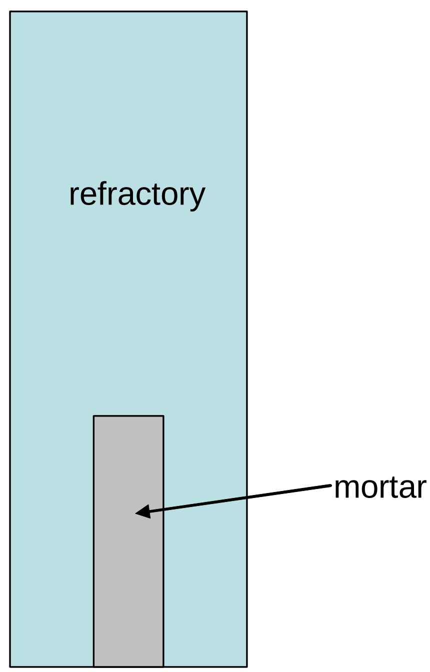


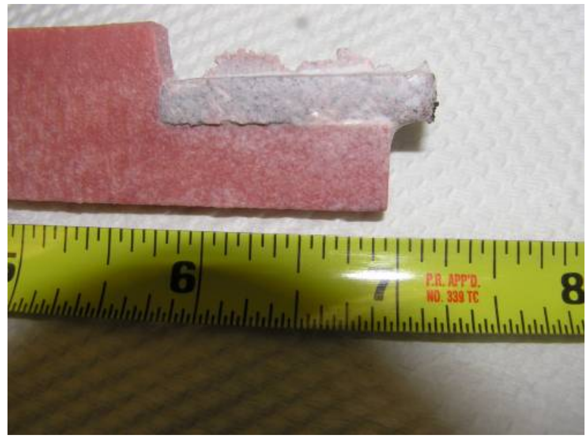
Fig. 4.13. Alternative refractory/mortar sample configuration ("tuning fork" configuration).

Samples were prepared using the current alumina-chrome mortar, the high-alumina-based and silicon-bonded alumino-silicate mortars tested previously, and experimental mortar compositions provided by the University of Missouri—Rolla (UMR) and a small refractory manufacturer. Examples of test samples after immersion testing are shown in Fig. 4.14.

The high-alumina mortar performed well in regard to corrosion, but showed considerable expansion. The silicon-bonded mortar system did not survive the immersion test. The alumina-chrome mortar was found to perform better in this test, but still showed considerable expansion. The UMR experimental mortar, which was composed of a phosphate-bonded system specifically designed for use with fusion-cast magnesium-aluminum spinel brick, performed extremely well. The experimental mortar system provided by the small refractory manufacturer based on some of their castable compositions also was found to show good corrosion resistance in the molten smelt, with only a small amount of expansion.

ORNL also evaluated the mechanical strength of refractory mortar compositions for use in the New Bern gasifier. The two mortar compositions analyzed were an air-set high-temperature alumina-chrome mortar and a high-purity, 95% high-alumina, phosphate-bonded mortar. Samples were tested

(a) Current alumina-chrome mortar



(b) Alternative high-alumina mortar

(c) Silica-bonded alumino-silicate mortar

(d) UMR experimental mortar

Fig. 4.14. Refractory/mortar samples in "tuning fork" configuration after immersion testing.

in compression to evaluate the effects of loads applied by expansion of the vessel refractory lining. Mechanical testing was performed at room temperature with simple compression. Compression of the mortar samples occurred in two stages for all samples tested. The mortar sample initially began to break down (to individual and agglomerated particles) upon application of the load, but the mortar material was held together between the two push rods by the compressive force. Some material was squeezed out between the two pushrods, but for the most part the sample remained in one piece. The mortar material then was consolidated by the subsequent compressive forces, much like a simple press consolidating powder. This resulted in most of the sample being able to carry the compressive loads applied during testing without apparent failure.

Upon completion of the test, the sample was unloaded and removed from the test setup. It was found that the mortar samples were friable upon handling; the areas not consolidated by the pressure of the push rods were easily broke off by handling. Areas consolidated by the push rods during testing initially held their shape but were easily broken apart by hand. Samples before and after testing are shown in Fig. 4.15. Characteristic plots of compressive stress vs strain for each material are shown in Fig. 4.16.

(a) Alumina-chrome mortar

(b) High-alumina mortar

Fig. 4.15. Refractory mortar samples before (right) and after (left) testing.

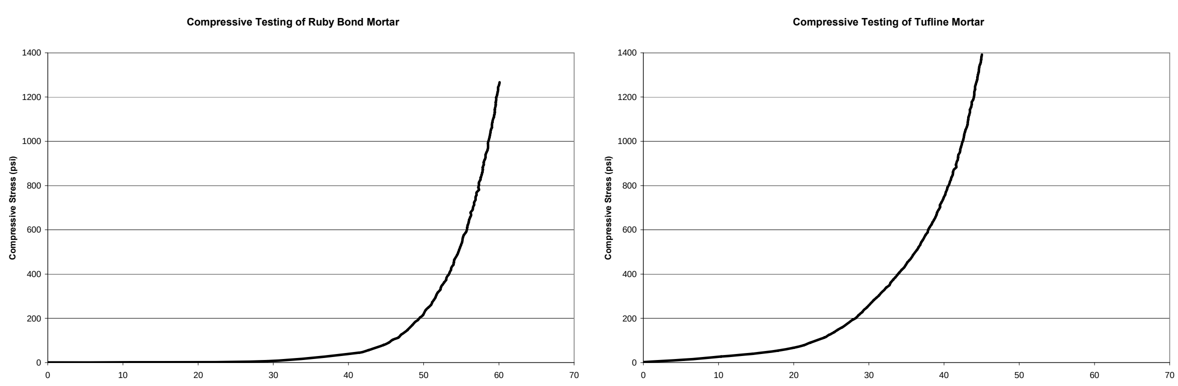


Fig. 4.16. Characteristic plots of compressive stress vs. strain for refractory mortar materials.

4.7 Modeling Task

Modeling studies were conducted with the ultimate goal of better characterizing the fluid flow in the liquor spray nozzle and characterizing the temperature and composition of the material in contact with the refractory lining of the gasifier. Work was conducted at Process Simulations Ltd. (PSL) with the objective of improving the model of the New Bern gasifier initially developed by PSL for Weyerhaeuser. Researchers at Simulent, Inc., conducted work to model the black liquor spray nozzle. Results of the Simulent studies suggest that the droplet distribution in the spray does not match what was used in previous models, and the PSL modeling suggests that the temperature distribution is higher at the bottom of the gasifier than previously thought. The model of the projected trajectory of liquor droplets is shown in Fig. 4.17.

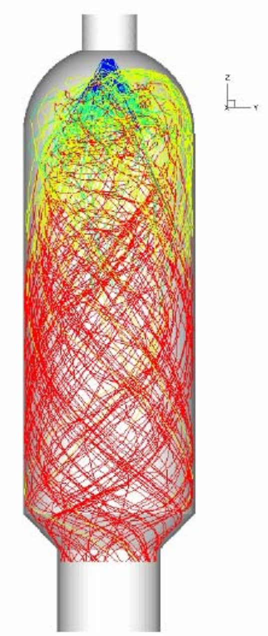


Fig. 4.17. Predicted liquor droplet trajectories in gasifier.

For testing, a uniform liquor spray was assumed, with 200-μm-diameter droplets, and a uniform injection velocity for all liquor droplets. Use of the uniform liquor spray distribution and the real liquor spray distribution predicted in other modeling studies results in the refractory temperature shown in Fig. 4.18. The predicted maximum refractory temperature is 1134°C in the case of real liquor spray and 1070°C in the case of uniform spray. Therefore, these modeling results suggest that the refractory temperature in the gasifier is higher than originally assumed and may be able to be reduced by changing the liquor spray.

The New Bern gasifier utilizes a conical bottom design to reduce the reactor cross section from a larger diameter to a smaller diameter. Modeling showed that because of the strong swirl created by this decrease in diameter, a separation zone could be formed at the corner of the conical wall where it meets the vertical barrel wall, and some the liquor droplets could be suspended in this zone. The accumulation of droplets in this area could cause instabilities in the performance and also lead to corrosion of the refractory.

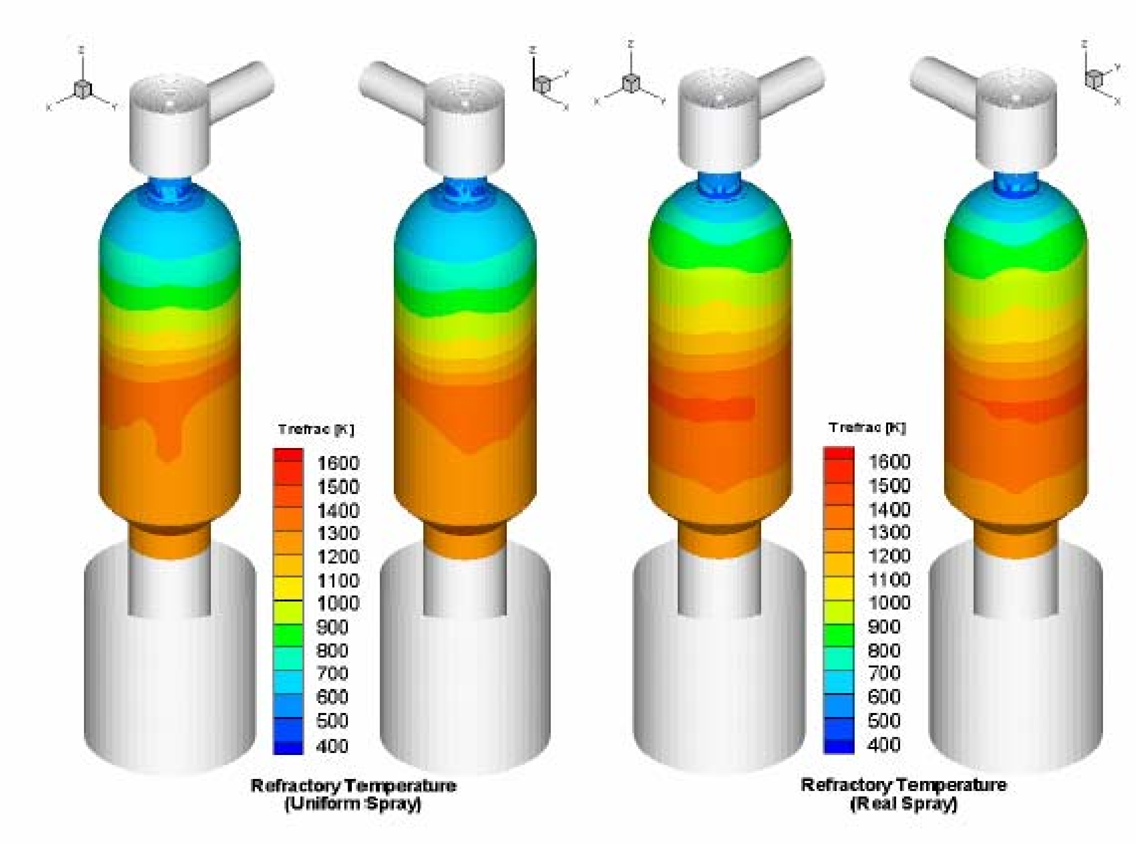


Fig. 4.18. Predicted refractory temperature with different liquor spray.

4.8 Evaluation of Backup Lining Material

Following evaluation of the replacement of the fusion-cast alumina lining with the fusion-cast magnesium-aluminum spinel refractory lining and evaluation of the refractory mortar testing, it was decided that the strain seen on the vessel shell must be due to expansion of the refractory mortar or the backup lining. A core sample was taken of the vessel backup lining, as shown in Fig. 4.19. This core revealed that the backup lining (an alumino-silicate brick material) was highly degraded by smelt penetration/reaction. Penetration/reaction was severe enough at the refractory hot face that the first 2–5 cm of the brick crumbled upon removal. Additionally, discoloration due to reaction of the brick with alkali from the smelt was evident for an additional ≈5 cm.

Analysis of this core by XRD found that the mullite (alumina-silica) phase was either partially or totally replaced by a sodium aluminum silicate phase in samples. Consequently, one-half of the core was sectioned and examined more thoroughly. Microprobe maps indicated that sodium and sulfur had penetrated into the darkened sections that extended through nearly half the core-drilled section. X-ray analysis indicated that the presence of cristobalite and mullite declined as a function of the distance to the Monofrax L brick while the presence of the sodium aluminum silicate phase increased. The rate of decline in cristobalite was more pronounced than for mullite, suggesting that cristobalite reacted first.

The presence of reaction products in the backup brick indicated that the Monofrax L layer was not protecting the backup brick from chemical/thermal exposure and that, thus, the mechanical loading of the carbon steel vessel might be occurring—probably in large part—because of the reaction and

Fig. 4.19. Backup lining core sample removed from New Bern gasifier showing crumbled hot face and discoloration due to smelt penetration/reaction.

consequent expansion of the backup lining. This is probably due to the higher thermal conductivity of the fusion-cast magnesium-aluminum spinel, as compared to the original bonded and alumina lining materials; the consequence would be that the hot face of the backup lining was at a higher temperature than in the original arrangement. As a result of this observation, additional corrosion tests were performed in an effort to identify a better material for the backup lining, one capable of operating in a molten smelt environment at temperatures as high as 900°C.

Alternative refractory materials composed of mullite, MgO, and alkali-aluminate were evaluated as replacements for the current (alumino-silicate) backup lining material. Immersion testing was performed at 900°C using the system described previously. Immersion testing of various mullite materials resulted in complete destruction of the refractory samples due to exposure with the molten smelt. Several commercially available refractory castable materials with high MgO content (greater that 70%) showed promise as candidate backup lining materials. These materials showed minor expansion and retention of sharp corners after 100 h of exposure in the smelt immersion test system, as shown in Fig. 4.20.

In tests conducted several years ago, samples of an ORNL-fabricated alkali-aluminate refractory performed very well in the laboratory testing. At the time no manufacturer could be found who had a commercially available refractory of approximately that composition. Recently, a company was identified that makes bonded refractories in the composition range of interest. An alternative refractory material based on alkali-aluminate was developed in collaboration with this small domestic refractory producer. This material was found to be highly resistant to molten smelt penetration and showed minimal expansion and retention of sharp corners after 100 h of exposure in the smelt immersion testing, as shown in Fig. 4.21.

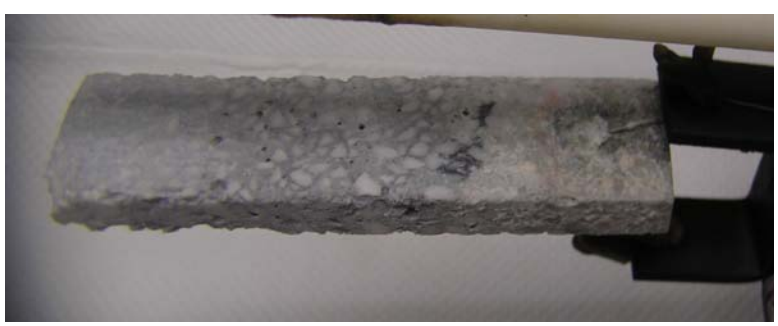


Fig. 4.20. Candidate high-MgO alternative backup lining material after smelt immersion testing.

Fig. 4.21. ORNL-developed alkali-aluminate backup lining material after smelt immersion testing. Note the extent of degradation of the metallic holder held in proximity of the molten smelt.

4.9 Evaluation of Liquor Nozzle Configuration

A modified liquor nozzle was designed and constructed to test a number of materials that should be more resistant to erosion and corrosion than the material currently used. Inserts made of three erosion-resistant metallic materials as well as inserts made of three ceramic materials were fabricated. The modified nozzle and examples of inserts are shown in Fig. 4.22. The assembled system was sent to the New Bern mill for installation in the gasifier in 2005. Following operation of the gasifier using the modified nozzle, inserts will be removed and analyzed for wear by erosion-corrosion.

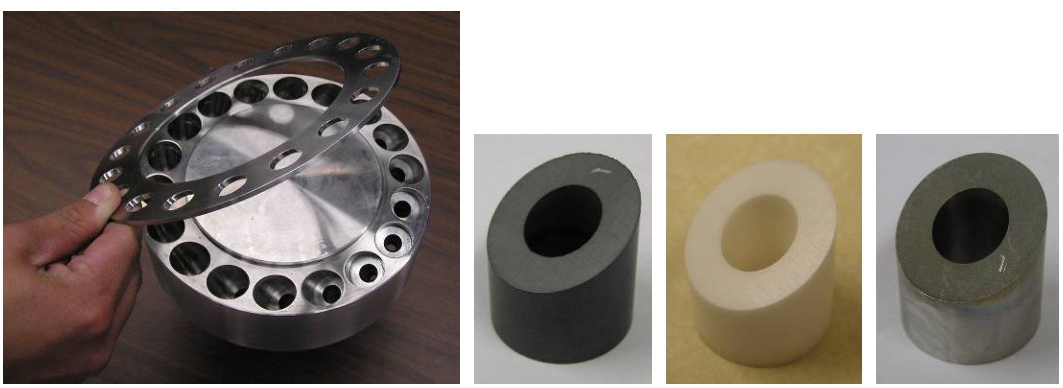


Fig. 4.22. Modified liquor nozzle and examples of silicon carbide, zirconia, and alloy 605 inserts.

4.10 Replacement of Lining with Suggested Material Improvements

Based on the findings from the evaluation of refractory mortar materials and evaluation of backup lining materials, several modifications to the current lining system have been suggested. These modifications are scheduled to be implemented during the next full relining of the gasifier vessel.

In regard to the refractory mortar, it was found that expansion of the current chrome-alumina mortar, when subjected to black liquor smelt, is probably contributing to the strains seen on the vessel shell.

In addition, the high-alumina mortar that was originally proposed as a replacement for the chrome-alumina mortar, in an effort to remove chrome from the lining materials, also showed a large amount of expansion when subjected to molten smelt. A UMR experimental mortar, composed of a phosphate-bonded system specifically designed for use with fusion-cast magnesium-aluminum spinel, was found to perform well in the molten smelt environment. Therefore, the recommendation regarding the use of mortar materials is to remove as much mortar as possible from the vessel refractory lining. This could be accomplished by providing only "butter" joints on the hot-face lining using the UMR phosphate-bonded mortar system. It may be possible to remove mortar joints on the backup lining completely, with mortar used only in select locations to make up for imperfections in the backup lining brick or dimensional tolerances.

It was found that either a high-MgO or an alkali-aluminate based material could be used for the backup lining. The high-MgO materials are currently commercially available. The alkali-aluminate-based material should be commercially available by mid-2006.

No alternative material with a structure and chemical composition similar to that of the fusion-cast magnesium-aluminum spinel brick currently being used for the hot-face lining is commercially available. Other materials used for this application have been found to exhibit inferior service lives, as previously discussed. Further, over 100 laboratory immersion corrosion tests have been performed on both commercial and experimental refractory materials, with none to date found to perform as well as the material currently being used for the hot-face lining.

5. Accomplishments

5.1 Technical Accomplishments

This project has successfully accomplished, and in some areas exceeded, its goals. The accomplishments of the project are the following:

- Identification of a refractory material with the corrosion resistance and mechanical integrity to last at least one year and preferably at least two years
  - Over 100 corrosion studies have been carried out on experimental and commercial refractory materials utilizing an immersion test system constructed at ORNL to simulate the black liquor gasifier environment. Such testing has provided a screening tool for candidate materials to be used as lining materials in Weyerhaeuser's New Bern, North Carolina, gasifier. Materials passing the ORNL immersion test have been found to exhibit similar success in the actual service environment of the New Bern gasifier.
  - Based on data and recommendations from the laboratory immersion test corrosion studies, an alternative fusion-cast alumina lining material was installed in the New Bern gasifier that was found to last nearly one year.
  - Based on data and recommendations from the laboratory immersion test corrosion studies and installed test panels in the New Bern gasifier, a *fusion-cast magnesia-alumina lining material* was installed in the New Bern gasifier. This material has lasted for over 18 months of service and has the potential of lasting for more than two years. A patent has been filed on the application of this material in high-temperature, high-alkali environments.
  - Work was carried out to identify alternative mortar systems which would not react with the molten smelt environment. Several new chromium-free mortar systems have been identified and are expected to provide 1- to 2-year lifetimes—lifetimes that are equivalent to those of the lining bricks.
  - Several new candidate backup lining material systems have been identified based on laboratory immersion testing results. Also, an *alternative refractory material based on alkali-aluminate* was developed in collaboration with a small domestic refractory producer. This material is scheduled to be installed in the New Bern gasifier in mid- to late 2006. A patent on the application of this material in high-temperature, high-alkali environments will be filed after a successful industrial trial.

- Development of materials for black liquor injection nozzles and sensor/thermocouple protection tubes to permit operation for the required time period
  - A modified liquor nozzle was designed and constructed to test a number of materials that should be more resistant to erosion and corrosion than the material currently used. Inserts made of three erosion-resistant metallic materials as well as of three ceramic materials were fabricated.
  - The assembled system was sent to the New Bern mill for installation in the gasifer in 2005. Following operation of the gasifier using the modified nozzle, these materials should be removed and analyzed for wear by erosion/corrosion.
  - Although no materials have been directly identified for sensor/thermocouple protection tubes, several of the refractory material systems identified for lining material applications may be applicable for use in this capacity.

- Identification of fluid flow and temperature characteristics that will enable an understanding of the environments encountered by refractory materials and injection nozzles
  - Modeling studies were conducted with the ultimate goal of better characterizing the fluid flow in the liquor spray nozzle and of characterizing the temperature and composition of the material in contact with the refractory lining of the gasifier. Work was conducted at Process Simulations Ltd. (PSL) with the objective of improving the model of the New Bern gasifier initially developed by PSL for Weyerhaeuser. Researchers at Simulent, Inc., conducted work to model the black liquor spray nozzle.
  - The results of the Simulent studies suggest that the droplet distribution in the spray does not match what was used in previous models, and the PSL modeling suggests that the temperature distribution is higher at the bottom of the gasifier than previously thought.
  - Modeling results suggest that the refractory temperature in the gasifier can be reduced by changing the liquor spray.
  - Modeling showed that because of the strong swirl, a separation zone could be formed at the corner of the conical wall where it meets the vertical barrel wall, and some the liquor droplets could be suspended in this zone. The accumulation of droplets in this area could cause instabilities in the performance and also lead to corrosion of the refractory.

5.2 Technology Transfer

Intellectual property has been generated as a result of this significant research effort, and great progress has been made in advancing the art of black liquor gasification. New refractory materials have been developed, and in the case of the fusion-cast magnesia-alumina spinel, a previous material has been identified and tested for a new application. One U.S. patent has been applied for, and another patent application regarding the application of refractory lining systems for gasification and other high-temperature/high-alkali environments is being prepared.

The goal of this project, funded under the DOE ITP, was to develop technology applicable to the commercialization of black liquor gasification technology. Many of the materials identified and developed through this project will also be cross-cutting in nature, as they will be applicable to any high-temperature/high-alkali environment.

Throughout this project, the researchers at ORNL worked closely with Weyerhaeuser corporate research staff and the staff of Weyerhaeuser's New Bern Mill. In addition, the research team worked closely with refractory producers and suppliers. As a result, Monofrax has begun supplying a material for the hot-face lining of the gasifier that had been produced in the past for other applications but was currently no longer in production. Also, ORNL and Westmoreland Advanced Materials have collaborated to develop a new refractory material based on alkali-aluminate for use in the backup lining of the gasifier. In addition, other refractory manufacturers have developed new materials or found currently existing materials that may be applicable in the future for black liquor gasification and other high-temperature/high-alkali environments.

5.3 Publications and Patents

The research undertaken in this project has contributed to the refereed literature, with numerous publications appearing in technical journals and conference proceedings. Below is a list of the publications and patents that have come from this project. In addition, numerous presentations have been made at corrosion, pulp and paper, refractory, and energy-related meetings, including TAPPI, NACE, Unified International Technical Conference on Refractories (UNITECR), and International Energy Agency (IEA) meetings.

5.3.1 Publications

Roberta A. Peascoe, James R. Keiser, James G. Hemrick, Michael P. Brady, Pavlo Sachenko, Camden R. Hubbard, Ron D. Ott, and Craig A. Blue, "Materials Issues in High Temperature Black Liquor Gasification," paper presented at 2003 TAPPI Fall Technical Conference, Chicago, Oct. 26–29, 2003.

James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, Peter F. Tortorelli, and Bruce A. Pint, "Performance of Materials in Black Liquor Gasification Environments," Paper 04251, Corrosion 2004, New Orleans, March 28–April 1, 2004.

James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, and Michael P. Brady, "Selection and Development of Refractory Structural Materials for Black Liquor Gasification," paper presented at 2004 TAPPI Paper Summit, Atlanta, May 3–5, 2004.

James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, and Bruce A. Pint, "Materials Issues in Black Liquor Gasification Systems," Proceedings of the 11th International Symposium on Corrosion in the Pulp and Paper Industry, Charleston, SC, June 7–11, 2004.

J. G. Hemrick, J. R. Keiser, R. A. Peascoe, C. R. Hubbard, and E. Lara-Curzio, "Gasification Containment Materials Related Research at Oak Ridge National Laboratory," *Refractories Applications and News*, Nov./Dec. 2004.

James R. Keiser, Roberta A. Peascoe, James G. Hemrick, Camden R. Hubbard, Gorti B. Sarma, J. Peter Gorog, and Zia Abdullah, "Materials Performance in High-Temperature Black Liquor Gasification," Paper No 05314, Corrosion/2005, Houston, April 3–7, 2005 (published by NACE International and distributed as individual papers and in the proceedings of Corrosion/2005).

James G. Hemrick, James R. Keiser, Roberta A. Peascoe, Camden R. Hubbard, and Edgar Lara-Curzio "Refractory Testing and Evaluation at Oak Ridge National Laboratory for Black Liquor Gasifier Applications," Proceedings of UNITECR' 05, Orlando, FL, November 8–11, 2005.

Bruce A. Pint and James R. Keiser, "Materials Selection for High Temperature Heat Exchangers" Paper 06469, Corrosion/2006, San Diego, March 12–16, 2006 (published by NACE International and distributed as individual papers and in the proceedings of Corrosion/2006).

5.3.2 Patents

Roberta A. Peascoe-Meisner, James R. Keiser, James G. Hemrick, Camden R. Hubbard, J. Peter Gorog, and Amul Gupta, "$MgAl_2O_4$ Spinel Refractory as Containment Liner For High-Temperature Alkali Salt Containing Environments," patent filed September 2005.

Kenneth McGowan, James Keiser, James Hemrick, Roberta Peascoe-Meisner, Peter Gorog, "Calcium (Hexa) Aluminate Refractory Linings and/or Chemical Barriers for High Temperature and High Alkali/Alkaline Environments," being prepared for filing.

6. Conclusions

The laboratory immersion test system built and operated at ORNL was found to successfully screen samples from numerous refractory suppliers, including both commercially available and experimental materials. This system was found to provide an accurate prediction of how these materials would perform in the actual gasifier environment. Test materials included mullites, alumino-silicate bricks, fusion-cast aluminas, alumina-based and chrome-containing mortars, phosphate-bonded mortars, coated samples provided under an MPLUS-funded project, bonded spinels, different fusion-cast magnesia-alumina spinels with magnesia content ranging from 2.5% to about 60%, high-MgO castable and brick materials, spinel castables, and alkali-aluminate materials.

This testing identified several candidate material systems that perform well in the New Bern gasifier. Fusion-cast aluminas were found to survive for nearly one year, and magnesia-alumina spinels have operated successfully for 18 months and are expected to survive for two years. Alkali-aluminates and high-MgO-content materials have also been identified for backup lining applications.

No other material with a similar structure and chemical composition to that of the fusion-cast magnesium-aluminum spinel brick currently being used for the hot-face lining is commercially available. Other materials used for this application have been found to have inferior service lives, as previously discussed. Further, over 100 laboratory immersion tests have been performed on other materials (both commercial and experimental), but none to date has performed as well as the material currently being used for the hot-face lining.

Operating experience accumulated with the high-temperature gasifier at New Bern, North Carolina, has confirmed that the molten alkali salts degrade many types of refractories. Fusion-cast alumina materials were shown to provide a great improvement in lifetime over materials used previously. Further improvement was realized with fusion-cast magnesia-alumina spinel refractory, which appears to be the most resistant to degradation found to date, exhibiting over a year of service life and expected to be capable of over two years of service life.

Regarding the use of refractory mortar, it was found that expansion of the current chrome-alumina mortar when subjected to black liquor smelt is likely contributing to the strains seen on the vessel shell. Additionally, the candidate high-alumina mortar that was originally proposed as a replacement for the current chrome-alumina mortar also showed a large amount of expansion when subjected to molten smelt. A UMR experimental mortar, composed of a phosphate bonded system specifically designed for use with fusion-cast magnesium-aluminum spinel, was found to perform well in the molten smelt environment.

Strain gauges installed on the gasifier vessel shell provided valuable information about the expansion of the refractory, and a new set of strain gauges and thermocouples has been installed in order to monitor the loading caused by the currently installed spinel refractory. These results provide information for a direct comparison of the expansion of the two refractories. Measurements to date suggest that the fusion-cast magnesia-alumina spinel is expanding less than the fusion-cast α/β-alumina used previously.

A modified liquor nozzle was designed and constructed to test a number of materials that should be more resistant to erosion and corrosion than the material currently used. Inserts made of three erosion-resistant metallic materials were fabricated, along with inserts made of three ceramic materials. The assembled system was sent to the New Bern mill for installation in the gasifer in 2005.

Following operation of the gasifier using the modified nozzle, inserts should be removed and analyzed for wear by erosion/corrosion. Although no materials have been directly identified for sensor/thermocouple protection tubes, several of the refractory material systems identified for lining material applications may be applicable for use in this capacity.

Results of the modeling studies suggest that the temperature distribution is higher at the bottom of the gasifier than previously thought. Therefore, it may be possible to reduce the refractory temperature in the gasifier by changing the liquor spray. Also, modeling showed that because of the strong swirl, a separation zone could be formed at the corner of the conical wall where it meets the vertical barrel wall, and some the liquor droplets could be suspended in this zone. The accumulation of droplets in this area could cause instabilities in the performance and also in corrosion of the refractory.

7. Recommendations

This research project has successfully accomplished, and in some areas exceeded, its goals. This has been accomplished by addressing three main objectives: (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 black liquor injection nozzles and sensor/thermocouple protection tubes to permit operation for the required time period; and (3) identification of fluid flow and temperature characteristics that will enable an understanding of the environments encountered by refractory materials and injection nozzles.

It is recommended that the following additional efforts be carried out.

- It would be useful to analyze the nozzle insert materials installed at the New Bern mill in 2005 to gain further knowledge about wear due to erosion and corrosion when subjected to black liquor. As a follow-up to this test it may be necessary to identify additional materials or consider new nozzle designs based on materials that were found to perform well in this testing.
- It may be possible to further optimize the alternative back-up materials identified and developed through this project.
- It is recommended that additional work be performed to analyze samples of the current lining material after two years of exposure. The fusion-cast magnesium-aluminum hot-face lining material appears to be performing well to date, but analysis of the lining upon removal after two years of service would be beneficial in evaluating the true performance of this material.
- The monitoring of the expansion of the new refractory utilizing the array of 40 strain gauges and 20 thermocouples on the gasifier shell has yielded a great deal of valuable information. It would be beneficial to continue the monitoring of strains in this fashion and to repair any malfunctioning sensors.
- The entire refractory lining of the gasifier at New Bern is scheduled to be replaced in late 2006 based on the recommendations generated from this project. Periodic sampling and analysis of the new lining materials during service could provide feedback on the performance of these new materials.

8. References

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