

COMPARISON OF REFRACTORY PERFORMANCE IN BLACK LIQUOR GASIFIERS AND A SMELT TEST SYSTEM

Roberta A. Peascoe, James R. Keiser and Camden R. Hubbard

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831, USA

J. Peter Gorog^a and Craig A. Brown^b

Weyerhaeuser Company
Tacoma^a, Washington 98477, USA
New Bern^b, North Carolina 28563, USA

Bengt H. Nilsson

Chemrec AB
Box 1033
S 65115 Karlstad, Sweden

ABSTRACT

Prior laboratory corrosion studies along with experience at the black liquor gasifier in New Bern, North Carolina, clearly demonstrate that serious material problems exist with the gasifier's refractory lining. Mullite-based and alumina-based refractories used at the New Bern facility suffered significant degradation even though they reportedly performed adequately in smaller scale systems. Oak Ridge National Laboratory's involvement in the failure analysis, and the initial exploration of suitable replacement materials, led to the realization that a simple and reliable, complementary method for refractory screening was needed. The development of a laboratory test system and its suitability for simulating the environment of black liquor gasifiers was undertaken. Identification and characterization of corrosion products were used to evaluate the test system as a rapid screening tool for refractory performance and as a predictor of refractory lifetime. Results from the test systems and plants were qualitatively similar.

INTRODUCTION

The pulp and paper industry is among the most energy and capital intensive manufacturing industries in the nation. Traditionally, the Tomlinson boiler is used to burn black liquor as a means of disposing of the organic waste and recovering the inorganic chemicals used in the kraft pulping process. However, recovery boilers have several shortcomings, including very high initial costs, relative inefficiency in producing electrical power from black liquor, and a potential for smelt-water explosions. As a more efficient, cost-effective alternative to recovery boilers, black liquor gasification is being evaluated at the bench scale and, in a few cases, at the pilot or demonstration plant level. With combined-cycle black liquor gasification, it is predicted that somewhat less steam will be generated but two to three times more electricity can be produced, giving a mill the opportunity to generate all of its own heat and power needs, as well as the potential to supply excess electricity to the grid. The gasification processes have been classified as either high temperature or low temperature depending on whether the reactor is operated, respectively,

above or below the melting point (~710°C) of the inorganic salt mixture formed during gasification. The general consensus is that, for the kraft process, high pressure high temperature (HPHT) systems will be highly efficient.

The first black liquor gasifier was a Swedish demonstration plant, Frövi, that processed 80 tons of dry solids/day between 1991-1996 built by Kvaerner Chemrec. A HPHT pilot plant black liquor gasifier at Skoghall, Sweden, also built by Kvaerner Chemrec, previously operated at 950°C and cycled daily between black liquor gasification under reducing conditions to LPG-burning under oxidizing (stand by) conditions. During the daily conversion between black liquor gasification and stand by mode there was a temperature drop to 800°C. The total time spent under black liquor gasification conditions was about 1000h, or less than two months, over the operating lifetime. During that time, refractory loss of 15 to 40mm was observed.

Weyerhaeuser and Kvaerner Chemrec built the first commercial scale high temperature black liquor gasifier at the Weyerhaeuser Company's paper mill in New Bern, NC. The gasifier is constructed with a cylindrical stainless steel shell lined with refractory bricks. During operation, the gasifier's atmosphere is a highly reactive, reducing environment with high sodium carbonate and sodium sulfide contents. The unit operates at an estimated temperature of 950°C. Due to the harsh environment, numerous materials issues have surfaced at this facility.

The experiences at the New Bern and Skoghall gasifiers clearly demonstrate that serious material problems exist with the refractory lining. ORNL's involvement in the failure analysis and initial exploration of suitable replacement materials led to the realization that a simple and reliable complementary method for screening materials needed to be developed. The importance of this task is demonstrated by the observation that the initial test methods used to evaluate refractory materials in smelt environments did not accurately predict the performance experienced in the New Bern gasifier. This study suggests that a smelt immersion furnace can mimic refractory exposure in black liquor gasifiers, and addresses the problem of predicting degradation and material loss from the refractory lining.

EXPERIMENTAL

The aim of this paper is to analyze and compare the degradation products observed in refractory linings exposed in the New Bern and Skoghall gasifiers and to evaluate samples immersed in molten smelt. Samples of Gouda LP60AAP, a dense mullite refractory brick, and Jargal-M brick, a mixed - and -alumina brick, were obtained after exposure in Weyerhaeuser's New Bern LPHT black liquor gasifier. Exposed samples of Jargal-M were also obtained from the HTHP Kvaerner Chemrec Pilot Plant at Skoghall. The gasifier-exposed samples are compared to laboratory test samples after immersion in molten smelt.

Exposure System

To simulate the environment of a black liquor gasifier, a furnace was constructed to suspend a test sample in molten smelt. The vertical tube furnace has three zones and is capable of temperatures up to 1300°C. A thermocouple control maintains the molten smelt at approximately 1000°C throughout the immersion test. Argon gas is 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 the system was continuously purged and air tight. A complete description of the test furnace and operating conditions will be reported in a separate paper.

To mimic the gasifier environment as well as possible, the smelt was supplied from the recovery boiler at Weyerhaeuser's Pulp and Paper mill in New Bern, NC. X-ray patterns of solidified smelt reveal the presence of crystalline phases of sodium sulfide, sodium sulfate, and sodium carbonate. The furnace system was ramped for about 18 hours to approximately 1000°C before the sample (~110 x 26 x 13mm) was lowered into the smelt for either a 50 or a 100 hour exposure. The sample was raised and cooled for 24 hours before examination. Photographs and measurements of exposed portion of the sample were taken and averaged both before and after immersion in molten smelt to check for dimensional changes and expansion. Since the total bar was not fully immersed, changes in length were not used in expansion calculations.

Sample Preparation and Characterization

Samples exposed in a gasifier or in the immersion laboratory test were evaluated using optical examination and X-ray diffraction. Extreme care was taken in preparing the individual test specimens because of their highly hygroscopic behavior and solubility of some of the degradation products. Changes in dehydrated NaAlO₂, a hygroscopic compound found in some gasifier samples, are not observed in samples exposed to ambient conditions for an hour but do show marked changes after an 8-hour exposure. Due to this, the mullite samples from the New Bern gasifier were ground for X-ray analyses in an inert atmosphere glove box. The data collection was carried out on a Scintag PAD V powder diffractometer with Cu K radiation ($\lambda = 1.5406 \text{ \AA}$) with the sample at ambient conditions. Relatively rapid data collection strategies were employed (~30 min. per specimen). No detectable changes were found in the powder patterns due to this limited exposure.

Parts of the α -alumina samples from the New Bern and Skoghall units along with immersion test samples were sliced using glycerin lubricant/coolant, mounted in epoxy resin for micrographic analysis, dried in a heating oven, covered with parafilm and stored in a dessicator prior to examination. X-ray patterns of epoxy-mounted samples were obtained. The remaining uncut portion of the gasifier samples, along with the cut immersion test samples, were stored in a dessicator prior to being ground rapidly (less than 10 minutes) under ambient conditions and then sealed in protective sample holders so that longer x-ray scans (1.5h) could be undertaken. Using protective sample

holders, no changes in diffraction patterns for samples x-rayed immediately and again 2 days later were observed. Additional characterization using optical microscopy and electron microprobe was undertaken as necessary.

RESULTS

As Received Mullite Refractory

Bricks of a mullite (Al₆Si₂O₁₃)-based refractory was supplied by N.V. Gouda Vuurvast. The bricks contained a minor amount of a cristobalite (SiO₂) / opal (SiO₂ x H₂O) like phase in both the gasifier and laboratory samples and a minor component of andalusite (Al₂SiO₅) in the gasifier bricks but not in the laboratory test bricks. The variation in the amount of andalusite can result from the manufacturing process. The macroscopic appearance of the material is very coarse with up to several millimeters (maximum measured 5mm) thickness of mullite crystals bonded with a fine crystalline phase. According to the suppliers data sheet, the average chemical composition of the material is 58 wt.% Al₂O₃, 37 wt% SiO₂, 0.9wt% Fe₂O₃ and minor amounts of P₂O₅ in the bonding phase. The apparent porosity was given as 9%; the maximum service temperature was specified as 1650°C.

Exposed Mullite Samples from New Bern Gasifier

Examination of the mullite lining from the New Bern black liquor gasifier showed considerable degradation and evidence of

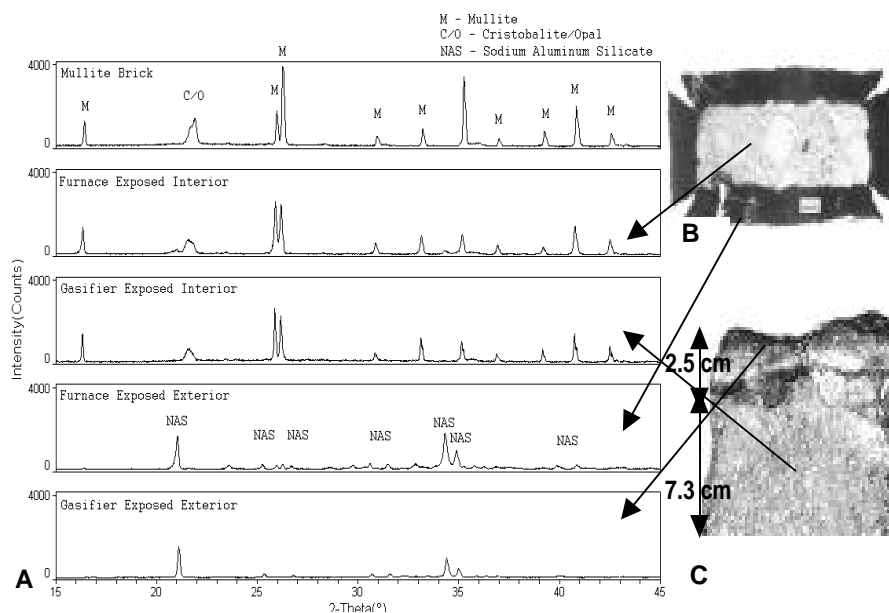


Figure 1. A)/(left) XRD patterns of mullite brick as received, laboratory furnace exposed interior, gasifier exposed interior, laboratory furnace exposed exterior and gasifier exposed exterior. The relative relationship to sampling area in exposed material removed from the furnace test system (B) and from the New Bern gasifier (C) are indicated by arrows.

B)/(top right) Micrograph of a cross section of mullite after exposure to molten smelt in the laboratory test furnace shows a gap formation between the expanded surface layers and the intersection with the unaltered core.

C)/(bottom right) Photograph of mullite brick #1 after exposure in the New Bern gasifier with the 2.5cm surface/reaction zones and the 7.3cm intermediate/bulk zones marked.

chemical and or thermal spalling. The hot surface of the refractory lining exhibited a color change and bubble formation of approximately 1-3cm thick. While more prevalent near the dome of the gasifier, bubbles occurred over the entire surface of the lining. Two bricks, 23cm deep on installation, were obtained from the New Bern gasifier and divided into sections. Brick one (figure 1C), roughly 10.2cm deep after exposure, was sampled in four areas: the surface, a blue reaction zone (2.5cm), an intermediate reaction zone and an interior bulk sample. Brick two, roughly 5.7cm deep after exposure, was sampled at three areas: the surface, the reaction zone (0.5cm) and an interior bulk sample. X-ray examination of a bulk sample taken from the interior of each brick showed no change in chemical composition in the mullite or the cristobalite/opal phase from that of the unreacted brick, but the andalusite phase was absent from both of these samples.

In brick one (figure 1C), the surface had a minor amount of mullite present along with nosean ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$) and sodium aluminum silicate ($\text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4$). The reaction zones contained mullite and cristobalite/opal phases that increased in abundance with depth. Nosean was present in the outer reaction zone while the sodium aluminum silicate was present in both reaction zones and a trace amount was seen in the bulk sample. In brick two the surface layer contained sodium aluminum silicate and a minor amount of sodium silicate hydrate ($\text{Na}_2\text{SiO}_3 \cdot 8\text{H}_2\text{O}$), while in the reaction layer the major phase was sodium aluminum silicate with a minor amount of sodium carbonate sulfate ($\text{Na}_6\text{CO}_3(\text{SO}_4)_2$) present. Neither mullite nor the cristobalite/opal phases were apparent in the diffraction patterns of the reaction zone or surface samples.

Mullite Samples Exposed in Furnace Test System

After immersion in smelt at 1000°C for 50 hours, the sample had expanded uniformly from an average width and depth of 25.44mm x 12.73mm to 29.0mm x 18.6mm, respectively. Due to this expansion, there were open cracks running along the length of the bar. Upon cross sectioning the bar, the cracks were revealed as gaps between the expanded surface layers that extend through the reacted exterior layer and end at the interface with the core of visually unaltered material. The reacted layer had a constant depth that was roughly twice as thick for the 100h sample as for the 50h sample indicating a time dependence for chemical reactions and refractory expansion. The outer layer and the inner core were separated, ground and x-rayed. The inner core consisted of mullite and the cristobalite/opal phase, while the outer layer was predominately sodium aluminum silicate along with a minor amount of mullite and a number of unidentified minor peaks that are probably a mixture of sodium aluminum/silicon sulfides, sulfates and carbonates.

As Received Fused-Cast α - / β -Alumina

A fused-cast mixed α - / β -alumina refractory, having a bulk density of 3.17 g/cm³, and chemical composition of 95% Al_2O_3 , 4% Na_2O , 0.5% SiO_2 and 0.5% other, was supplied by Corhart Refractories. This refractory is designed primarily for use in glass melters. The high density, impermeability and volume stability also make it suitable for a number of non-glass applications including liners for chemical process equipment, electrolytic cells and as hot face linings for kilns.

Exposed α - / β -Alumina from New Bern Gasifier

Examination of the α - / β -alumina lining's hot face surface inside the New Bern black-liquor gasifier, showed degradation and some spalling. The hot surface of the refractory lining exhibited a color change from light blue or green to the white interior. The spalls and bowed surfaces of reacted material were approximately 2.5cm in depth. Samples of surface spalls and the interior of the brick were collected at the time of lining removal and stored in a dry environment until ground in air and placed immediately in air-sensitive sample holders for 1.5 hr x-ray scans. In the spall samples, NaAlO_2 was found along with α - and β -alumina while only α - and β -aluminas were identified in the interior of the α - / β -alumina bricks. These bricks, after removal from the gasifier, developed a powdery white layer on the outer surface over a two month period when stored in a dry warehouse. X-ray analysis showed the mineral trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) was the major phase present with $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})$ and $\text{Na}_2\text{Al}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ as minor phases.

Exposed α - / β -Alumina from Skoghall Gasifier

Three bricks from the top rows, 1, 2 and 4, of the α - / β -alumina refractory lining were removed by Kvaerner Chemrec from the Skoghall Pilot Plant and shipped to ORNL in Sept. 2000. Refractory loss of the lining was more significant in the center near row 4 (20-40mm) than at the top, rows 1 and 2, of the barrel (15-30mm). These bricks were sliced using oil so that two 2.5cm x 2.5cm cores approximately 5cm to 6.5cm in length, from the hot to the cold face, were removed from the center of each brick. One core sample from each brick was sealed in epoxy, sliced and mounted for micrographic analysis and x-ray examination. X-ray examination of the epoxy mounted samples showed that a NaAlO_2 phase plus the original α - and β -aluminas were present in all samples. To better identify the phase composition within the brick, sections of a second core sample taken from the center of the gasifier barrel was ground in air and placed immediately in air-sensitive sample holders for 1.5 hr x-ray scans. Starting from the hot face, the sample was divided into four sections. The first section was a green colored surface layer approximately 3mm thick. The next three sections were each approximately 2cm thick and varied in color from light purple to tan to white. The green surface consisted primarily of NaAlO_2 with a minor amount of gibbsite, $\text{Al}(\text{OH})_3$. In the next layer (light purple), NaAlO_2 plus α - and β -alumina were present while in the tan layer only a minor amount of NaAlO_2 was detected, with the major phases being α - and β -alumina. The only crystalline phases present in the interior were α - and β -alumina.

α - / β -Alumina Samples Exposed in Laboratory Test System

Examination of the α - / β -alumina samples after immersion in molten smelt at 1000° C for 100 hours indicated only a surface change of white to black. The sample expanded slightly from an average width and depth of 24.98mm x 12.02mm to 25.11mm x 12.13mm for an average expansion of 0.7%. When the bar was cross sectioned, the alteration in color was seen to remain throughout the sample but the only crystalline material present in the x-ray patterns was α - and β -alumina. White crystallites of the mineral trona formed on the outer surface of the remaining samples after storage in a dessicator, indicating Na^+ ion penetration during immersion.

DISCUSSION

Samples of mullite refractory and the α -alumina refractory exposed in the molten smelt test furnace exhibited the same overall reaction products and chemical alterations observed in gasifier exposures. However, it was difficult to obtain a surface sample from laboratory exposure that was comparable to surface samples obtained from a gasifier lining due to the minimal volume of the surface layer of the laboratory test samples available from which enough material for XRD examination could be obtained. While all surface samples were not identical, the correlation between overall reaction of the gasifier refractories and the laboratory test samples is quite good.

Laboratory test samples of the mullite refractory showed a marked volumetric expansion with an accompanying loss of structural integrity exhibited by the formation of gaps at the corners in the laboratory samples. In these unconstrained samples there is room for surface expansion, but the cylindrical surface of the gasifier's lining did not allow for refractory expansion. Furthermore, for the mullite refractory, eutectics exists at 915°C, 760°C and 732°C for nepheline (a $\text{NaAlSi}_3\text{O}_8$ solid solution) with either Carnegieite/ Na_2SiO_3 , or $\text{Na}_2\text{SiO}_3/\text{Na}_2\text{Si}_2\text{O}_5$, or $\text{Na}_2\text{Si}_2\text{O}_5/\text{albite}$, respectively. Which occurs depends on SiO_2 and Na_2O concentrations[1]. Thus in operating black liquor gasifiers and the laboratory test system, a liquid phase can develop within the mullite refractory as Na_2O concentration increases. As a result, surface expansion coupled with the loss of structural integrity led to the spalling of the mullite lining.

For the α -alumina samples, both the smelt penetration and its subsequent reaction with α -alumina to form a succession of compounds caused significant volume changes and could account for the changes in the refractory observed in the New Bern gasifier. The formation of trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) on the surface of the laboratory test samples and New Bern samples indicates that molten smelt had penetrated into these samples and the overall 0.7% expansion in the laboratory test sample was due to smelt penetration. Since Thery and Briancon found that α -alumina and Na_2CO_3 slowly reacted to form NaAlO_2 at 800°C[2], it is likely that given more time laboratory test samples would expand further as α -alumina reacted with molten smelt to form NaAlO_2 . α -alumina, however, would most likely expand with either the addition of Na_2O or the displacement of Al^{3+} to form Na-rich β - or γ -alumina. Both β - and γ -alumina are solid solutions with Na^+ "conduction planes" between spinel blocks [3]. In α -alumina structures, additional Na^+ ions are accommodated by the introduction of O^{2-} ions that create new tetrahedral sites into which Al^{3+} ions from the spinel block transfer. In β -alumina structures, additional Na^+ ions are compensated by displacing Al^{3+} , forming vacancies in the spinel block. Longer immersion tests should confirm these reactions.

As described by Carniglia and Barna[4], spalling or slabbing is a classic phenomenon associated with the freezing of a penetrating and aggressive liquid. The liquid forms a moving penetration front that parallels the hot face until it approaches a depth where the liquid finally freezes. Debonding of crystals by dissolution follows this penetration in time, and as a thermally activated process slows with increasing depth and decreasing

temperature, a weakened zone forms that is less deep than the penetration zone. A common view is that a change in volume subjects the refractory to a shear strain parallel to the surface.

The expansion process and subsequent spalling or slabbing differed between the mullite and α -alumina linings. When the mullite refractory expanded along the hot face and liquid phases formed, it lost structural integrity and spalled. On the other hand, the α -alumina lining did not lose its structural integrity to the same extent, so expansion was accommodated partly through spalling and partly through a significant radial expansion of the gasifier's lining.

CONCLUSIONS

The results from laboratory testing were qualitatively similar to those from plant exposures. Thus, it can be concluded that immersion testing in molten smelt mimicked the refractory performance in the gasifiers and can be used to predict refractory performance. This indicates that by using the laboratory test furnace, refractory material can be checked prior to installation for susceptibility to smelt penetration and chemical alterations that cause expansion and/or alter structural stability. This makes available the capability to reliably and rapidly screen a number of refractory materials prior to installation and could greatly reduce development costs and increase lining reliability.

ACKNOWLEDGEMENTS

We would like to thank Christina Hoffmann for work done on the characterization of gasifier samples. We are indebted to Corhart Refractories and N. V. Gouda Vuurvast for supplying samples of the refractory materials used in the New Bern gasifier. Partial funding and valuable assistance was furnished by the Weyerhaeuser Company. The contribution of materials by Weyerhaeuser and Chemrec is gratefully acknowledged. Previous refractory screening tests were carried out at the Swedish Ceramic Institute, and the Shoghall gasifier lining provider was SEPR, France. Many thanks for the pilot plant hospitality to Stora Enso, Skoghall. Research sponsored in part by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Forest Products Industries of the Future, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

REFERENCES

- [1] E. F. Osborn and A. Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems", Plate 4, published by the American Ceramic Society and the E. Orton, Jr., Ceramic Foundation, 1960: from FIG. 501. System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$; Phases Diagrams for Ceramists, compiled at the National Institute for Standard and Technology, Gaithersburg, MD.
- [2] J. Thery and D. Briancon, *Hautes Temp. Refract.* 1, 221-7 (1964).
- [3] A. R. West, *Solid State Chemistry and Its Applications*, 468-471, John Wiley & Sons Ltd., New York, NY, (1987).
- [4] S. C. Carniglia and G. L. Barna, *Handbook of Industrial Refractories Technology; Principles, Types, Properties and Applications*, 226-228, Noyes Publications William Andrew Publishing, LLC, Park Ridge, NY, (1992).