Title: Refractory for Black Liquor Gasifiers

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ABSTRACT

The University of Missouri-Rolla will identify materials that will permit the safe, reliable and economical operation of combined cycle gasifiers by the pulp and paper industry. The primary emphasis of this project will be to resolve the material problems encountered during the operation of low-pressure high-temperature (LPHT) and low-pressure low-temperature (LPLT) gasifiers while simultaneously understanding the materials barriers to the successful demonstration of high-pressure high-temperature (HPHT) black liquor gasifiers. This study will define the chemical, thermal and physical conditions in current and proposed gasifier designs and then modify existing materials and develop new materials to successfully meet the formidable material challenges.

Resolving the material challenges of black liquor gasification combined cycle technology will provide energy, environmental, and economic benefits that include higher thermal efficiencies, up to three times greater electrical output per unit of fuel, and lower emissions. In the near term, adoption of this technology will allow the pulp and paper industry greater capital effectiveness and flexibility, as gasifiers are added to increase mill capacity. In the long term, combined-cycle gasification will lessen the industry's environmental impact while increasing its potential for energy production, allowing the production of all the mill's heat and power needs along with surplus electricity being returned to the grid. An added benefit will be the potential elimination of the possibility of smelt-water explosions, which constitute an important safety concern wherever conventional Tomlinson recovery boilers are operated.

Developing cost-effective materials with improved performance in gasifier environments may be the best answer to the material challenges presented by black liquor gasification. Refractory materials may be selected/developed that either react with the gasifier environment to form protective surfaces in-situ; are functionally-graded to give the best combination of thermal, mechanical, and physical properties and chemical stability; or are relatively inexpensive, reliable repair materials. Material development will be divided into 2 tasks:

Task 1, Development and property determinations of improved and existing refractory systems for black liquor containment. Refractory systems of interest include magnesium aluminate and barium aluminate for binder materials, both dry and hydratable, and materials with high alumina contents, 85-95 wt%, aluminum oxide, 5.0-15.0 wt%, and BaO, SrO, CaO, ZrO_2 and SiC.

Task 2, Finite element analysis of heat flow and thermal stress/strain in the refractory lining and steel shell of existing and proposed vessel designs. Stress and strain due to thermal and chemical expansion has been observed to be detrimental to the lifespan of existing black liquor gasifiers. The thermal and chemical strain as well as corrosion rates must be accounted for in order to predict the lifetime of the gasifier containment materials.

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INTRODUCTION

The Tomlinson recovery boiler is the conventional technology for recovering cooking chemicals and energy from black liquor. As a potential replacement for the Tomlinson recovery boiler, black liquor gasification (BLG) technology has garnered much interest over the last two decades in the papermaking industry. The BLG technology has higher energy efficiency and generates far more power with overall lower cost than conventional technology. It improves safety by reducing the risk associated with smelt-water explosions. It reduces the wastewater discharges and harmful emissions into the environment. BLG systems recover sodium and sulfur as separate streams that can be blended to produce a wide range of pulping liquor compositions [Stigsson (1998)]. As a technique that is still under development, it has problems including refractory failure during operation due to a combined effect of chemical reaction and thermomechanical stress [Brown and Hunter (1998), Dickinson, Verrill and Kitto (1998)]. The objective of this study is to investigate the failure behavior of refractory lining under chemical and thermomechanical loading by using an analytical model.

High temperature black liquor gasifiers are generally cylindrical in shape as shown in Figure 1. The height ranges from 1.5 m to 25 m and diameter ranges from 0.5 m to 5 m. In the gasifier reactor vessels, there are usually 2-6 coaxial layers of component lining [Taber (2003)]. Refractory lining is used to protect the exterior metallic part of the gasifier vessel. A dense refractory material layer is designed to be exposed to the highest temperature environment. The second “safety” layer is usually made of a similar material. Subsequent layers are used to provide insulation and allow for expansion. The steel shell is used to provide reaction space and confinement. The gasifier generally operates at temperature ranging from 950 to 1000 ^{o}C.

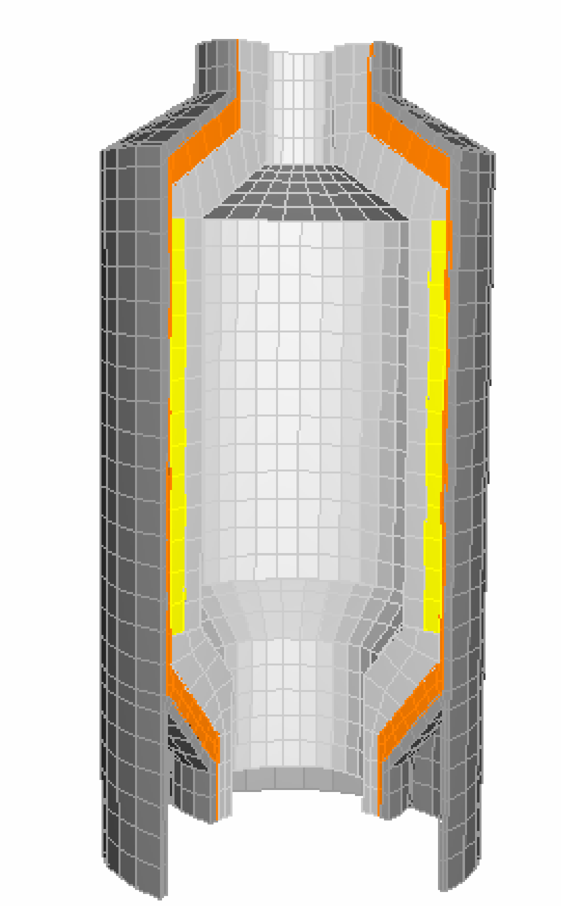

Figure 1 Schematic construction of a typical high temperature gasifier

The commercial high temperature black liquor gasifier was developed by Kvaerner Chemrec. A pilot plant first started running in 1994 at a pulp mill near Karlstad, Sweden [Larson, Consonni and Katofsky (2003)]. The first commercial size Chemrec system (75-100 tons of dry solids/day) was built at the AssiDomän mill in Frövifors in 1991. This air blown gasifier has performed well and been proven to be easy to operate and maintain. The first commercial Chemrec system in North America started operation in 1996 at Weyerhaeuser's New Bern, SC, USA [Brown and Hunter (1998)]. It was an atmospheric, air-blown, entrained bed gasifier operating between 950-1000 ^{o}C with a capacity of 350 ton black liquor solids per day. However, this system was shutdown in January 2000 due to failure of the stainless steel shell [Brown and Landalv (2001)].

Black liquor gasification converts the organic components into combustible fuel gas and leaves inorganic components as smelt to generate high-quality green liquor for regenerating pulping chemicals [Kelleher and Kohl (1986)]. The combustible gas contains carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), water vapor (H_2O) and hydrogen sulfide (H_2S). The smelt drops are mainly sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S). Some of the smelt drops form a thin layer of smelt flowing along the reactor wall.

The current refractory materials for the BLG reactor vessel lining are not deemed adequate. The combination of high temperature and alkalinity produces an aggressive environment for the reactor lining. Chemrec has used several refractory materials in the pilot units and the commercial atmospheric units. The refractories last from 1 to 18 months, with a replacement cost of up to 1 million dollars and several weeks of downtime. Severe refractory thinning occurred and several bricks were found lost from the upper part of the gasifier vessel during operation. The refractory lining is subjected to the penetration of sodium and subsequent reactions with alkali-rich molten smelt, such that the refractory undergoes significant volume change and strength degradation. Several refractory samples have been studied after immersion in molten smelt by Peascoe, Keiser, Hubbard, Brady and Gorog (2001). The results of their study are summarized below. For mullite based refractories, molten smelt first attacks mullite and forms sodium aluminum silicates. This reaction is accompanied by a volume change. A significant surface expansion occurs during immersion testing in smelt. Furthermore, a liquid phase can develop in the mullite refractory as Na_2O concentration increases. Surface expansion coupled with the loss of structural integrity lead to the spalling of the lining. $MgAl_2O_4$ spinel based refractories react with the smelt to form $NaAlO_2$ and MgO, with an associated expansion of 2.1% to 13%. For α/β-alumina refractories, expansion was accommodated partly through spalling and a significant radial expansion of the gasifier's lining. The alumina refractories show the least corrosion, the chemical expansion of alumina samples is from 0 to 0.7%. Due to this reason, fused cast alumina which is expansive and sensitive to thermal shock is being used in the most recent commercial high temperature black liquor gasifier at New Burn, SC, USA, [Brown, Leary, Gorog and Abdullah (2004)].

Computer simulation of existing materials will accelerate the development of these new materials. Compared to experimental characterization, computer simulation is much faster and more economical. Finite element modeling of damage evolution in refractory linings exposed to high temperature and aggressive chemical environment was presented.

EXECUTIVE SUMMARY

Black liquor gasification is a high potential technology for production of energy which allows substitution for other sources of energy. This process uses a waste of the pulp and paper industry as black liquor to produce synthetic gas and steam for production of electricity; therefore development of this technology not only recovers the waste of the paper industry but also decreases dependency on fossil fuel.

Today one of the main obstacles in the development of this technology is the development of refractory materials for protective lining of the gasifier. So far the materials used for this application have been based on alumino-silicate refractories but, thermodynamics and experience shows that these materials are not sufficiently resistant to black liquor under the harsh working conditions of Black liquor gasifiers. Consequently development of cost-effective materials with improved performance in gasifier environments to answer the material challenges presented by black liquor gasification (HTHP, HTLP) is the objective of this project. Refractories provided by in-kind sponsors were tested by cup testing, density/porosity determinations, chemical analysis and microscopy. The best performing materials in the cup testing were fused cast materials.

Computer simulation of existing materials will accelerate materials research in developing these new materials, and it is less costly and time consuming. Finite element modeling was conducted in this study.

EXPERIMENTAL

Cup testing has been used for the preliminary determinations of smelt refractory reactions for Task 1.3. Cup test processing was performed at UMR. Cups were prepared from monolithic materials according to the manufacturers directions as a 9” long by 4.5” wide by 3” deep sample with 2 of 1.5” diameter by 1.5” deep holes formed during casting. Brick samples were cut from a 9 inch straight into 2 of 4.5 inch by 4.5 inch by 2.5 inch specimens. A diamond core drill cored a 1.5” diameter by 1.5” deep core. The core was removed with a chisel.

The removed cores were used to determine density by ASTM C-830-00 and sectioned for chemical analysis by ICP and microscopy. The cups are processed by drying at 110°C for 24 hours. The cup was charged with 50 grams of raw black liquor smelt. Heated at 1°C/minute to 1000 °C, held 240 hours at 1000°C and cooled at 1°C/minute to 25 °C, in an argon flooded furnace.

Additional tests are being performed as described in earlier reports and ASTM standards for Task 1.4 – Submit for Industrial Trial. In addition, all components replaced in industry are being modeled by the finite element method to predict failure mode, stresses and eventually lifetime.

RESULTS AND DISCUSSION

Project is progressing according to plan as shown in Table 1. Task 1.3 is currently complete, additional materials will be tested under this task if requested by manufacturers or end-users. Task 1.4 is in the beginning stages. Materials are being tested and modeled for the pulse combustors at Big Island. Currently a spinel lining is being used in New Bern, although there is no strong connection between the selection of the spinel lining and this project. Mortar testing might be performed for Weyerhaeuser as part of this project for New Bern to be used with the spinel lining.

Table 1 Gantt Chart

Task Name	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
1.0 Refractory Determination												
1.1 Perform Thermodynamic Modeling												
1.1.1 Compile Material Data Table												
1.1.2 Compile Reactions												
1.1.3 Compile Gibb's Free Energies												
1.1.4 Compile Phase Diagrams												
1.2 Measure Properties												
1.3 Conduct Simulative Corrosion												
1.4 Submit for Industrial Trial												
2.0 Model Development												
3.0 Project Management												
3.1 Task 1.1 Report					12/31◊							
3.2 Task 1.2 Report							6/30◊					
3.3 Task 1.3 Report										3/31◊		
3.4 Task 1.4 Report												9/30◊
3.5 Task 2.0 Report												9/30◊
3.6 Task 3.0 Report												9/30◊
3.7 Quarterly Reports			7/31◊	10/31◊	1/31◊	4/30◊	7/31◊	10/31◊	1/31◊	4/30◊	7/31◊	9/30◊
3.8 Continuation Report			7/31◊				7/31◊					9/30◊

Task 1.3

Table 1 shows the data for the cups tested to date.

Table 2 Performance and data for tested refractories

Sample Number	Al2O3 %	SiO2 %	ZrO2 %	MgO %	CaO %	Fe2O3 %	Na2O %	TiO2 %	P2O5 %	impurities %	Density (g/cc)	Theoretical Density (g/cc)	% Theoretical Density	Performance
5	93.29		5.07							1.64	3.43	4.06	84.37	Good
10	72.29	26.24								1.47	2.56	3.47	73.85	Good
16	59.46	34.06				1.51		2.33		2.64	2.46	3.35	73.35	Good
18	80.14	16.45			1.27					2.14	2.91	3.64	80.04	Good
20	97.23	1.17								1.6		3.94		Good
21	95.3	0.25		2.34						2.11	3.60	3.95	91.24	Good
25	78.2	18.1		0.1	0.1	1.4		1.9		0.2	2.69	3.17	85.02	Good
26	84	7.5		8	0.2	0.1				0.2	3.02	3.55	85.09	Good
27	0.7	0.5		96.5	1.1	0.7				0.5	2.98	3.52	84.59	Good
4	95.61		2.67							1.71	3.07	4.01	76.60	Small Cracks
8	88.72	0.8	7.76							2.72	3.29	4.10	80.19	Small Cracks
9	89.62	0.82	7.97							1.58	3.39	4.10	82.79	Small Cracks
11	89.43	0.78	7.78							2.01	3.33	4.10	81.24	Small Cracks
12	80.21	17.31								2.48	2.54	3.64	69.75	Small Cracks
13	89.74	0.81	8.11							1.34	3.24	4.10	78.99	Small Cracks
15	2.52	36.74	57.84							2.9	3.78	4.42	85.62	Small Cracks
17	95.95	0.21			0.89					2.95	3.00	3.94	76.23	Small Cracks
19	89.37	0.17		2.35			2.32		4.47	1.3	2.79	3.84	72.75	Small Cracks
24	87.1	11.36								1.54	2.82	3.69	76.41	Small Cracks
1	79.3	18.75								1.95	2.64	3.61	73.20	Failed
2	84.84	1.17	12.27							1.72	3.31	4.15	79.85	Failed
3	73.7	24.18								2.72	2.42	3.53	68.67	Failed
6	74.74	14.72	8.91							1.63	2.91	3.86	75.40	Failed
7	73.81	9.51	15.18							1.5	3.05	4.08	74.79	Failed
14	80.34	17.48								2.18	2.52	3.63	69.54	Failed

Sample number: 27

Type: Magnesia Brick

Chemistry: MgO: 96.5/98.5; CaO: Max. 1.1; Fe2O3: Max. 0.7; Al2O3: Max. 0.7; SiO2: Max. 0.5.

Density: 2.98 g/cc

Porosity: 15.4 %

Notes:

Sample 27 performed very well in the cup tests.

No reaction interface is visible on the surface of this sample. The RL and CL images illustrate the microstructure of a MgO brick (>96 % MgO) subjected to black liquor (Na_2SO_4 + Na_2CO_3) corrosion test at 1000^oC for 240 hours. Samples are taken from “left”, “right” and “bottom” sides of the test cup to determine smelt penetration and degree of refractory alteration in all three dimensions. Microstructures are identical or similar in all side and smelt penetration and the degree of alteration were indistinguishable in polished samples.

Most important feature observed was the intense delineation of grain boundaries of sintered MgO clinkers due to smelt vapor penetration. The matrix (not well polished) does not appear to be smelt but rather fine MgO bond but may contain smelt component. An XRD run has been performed to confirm this. Although, no direct intense reaction is observed between smelt and MgO, the silicate impurities in the matrix and in grain boundaries would react readily resulting in refractory deterioration or mechanical disintegration.

Pre-Test Microstructure

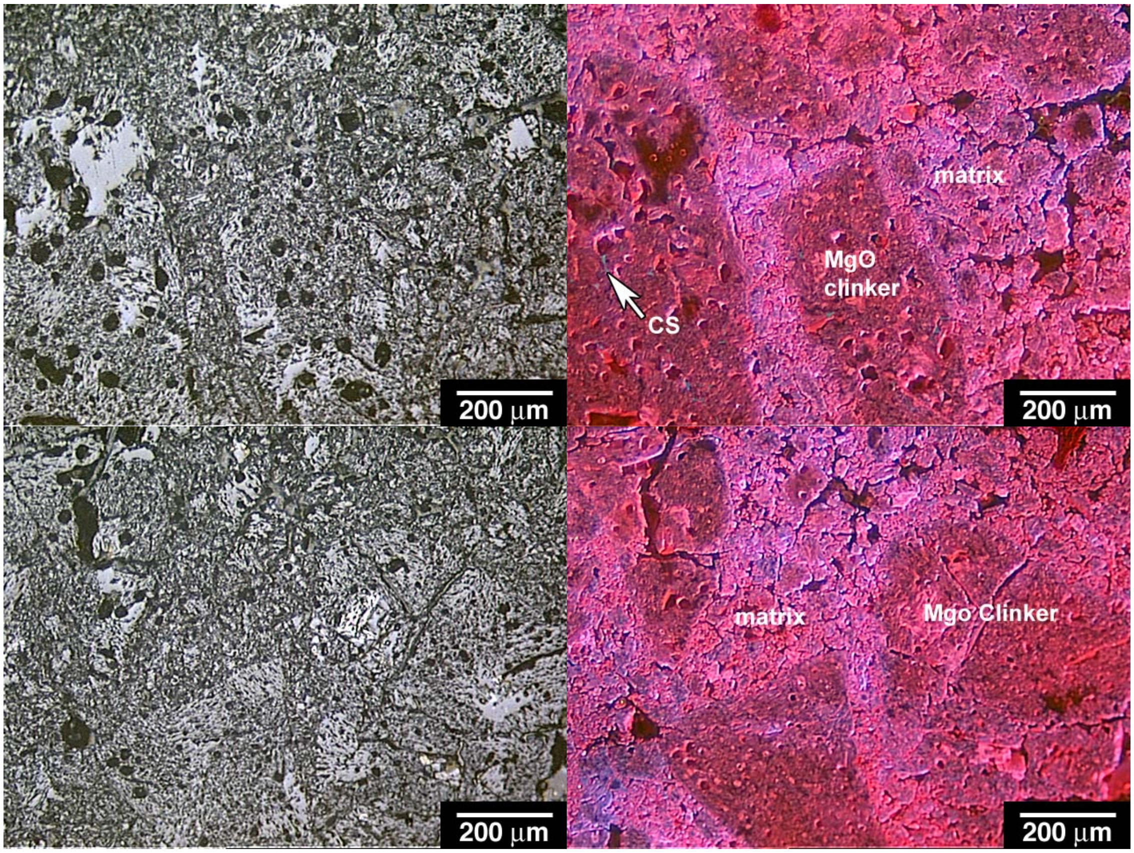

Figure 2 RL and CL pair of micrographs taken from an unused sample 27.

The unused brick is made from silicate bonded MgO (>96 % MgO). The silicate bond in MgO clinker is calcium silicate (CS) bond. Forsterite (Mg_2SiO_4) and monticellite ($CaMgSiO_4$) are not recognized under RL/CL microscopy. Calcium silicate bond makes the brick more refractory, CaO/SiO_2 ratio is larger than 1. As shown in RL/CL micrographs of tested samples, strong grain boundary delineation is observed in MgO clinker suggesting reaction between silicate bond and black liquor, although no intense reaction or reaction product is observed between black liquor and MgO brick. We suggest that before MgO brick is recommended for BLG, an in-situ test must be performed.

Post-Test Microstructure

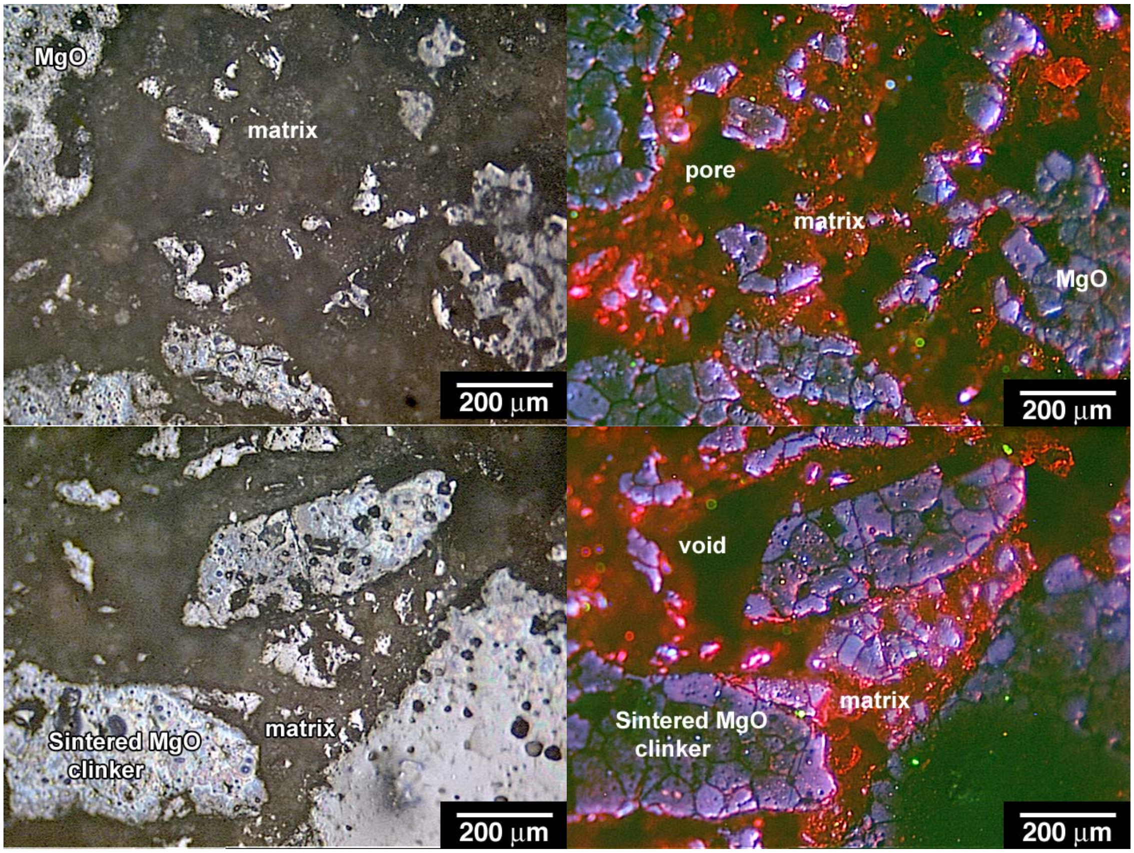

Figure 3 RL and CL microstructure of sample 27 subjected to black liquor cup test. These samples are made from the "Left" side of the test cup.

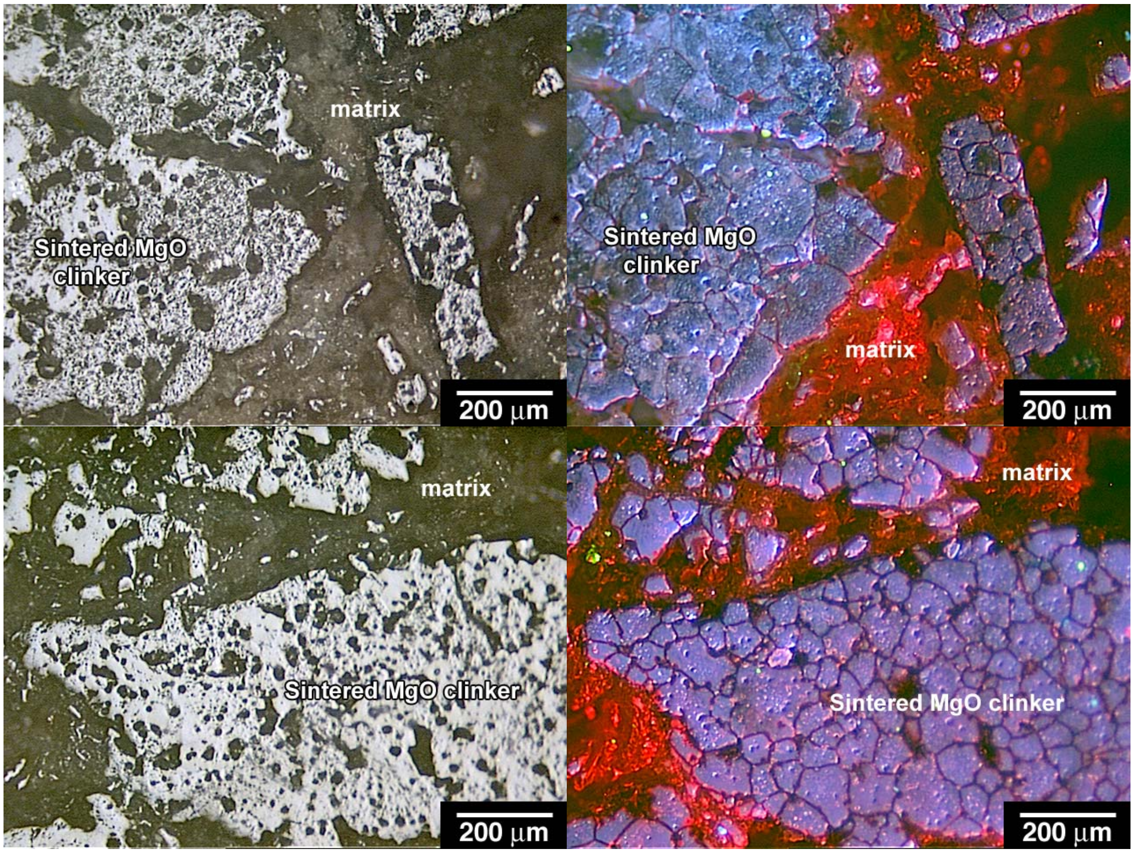

Figure 4 RL and CL microstructure of sample 27 subjected to black liquor cup test. This sample is made from the "Right" side of the test cup.

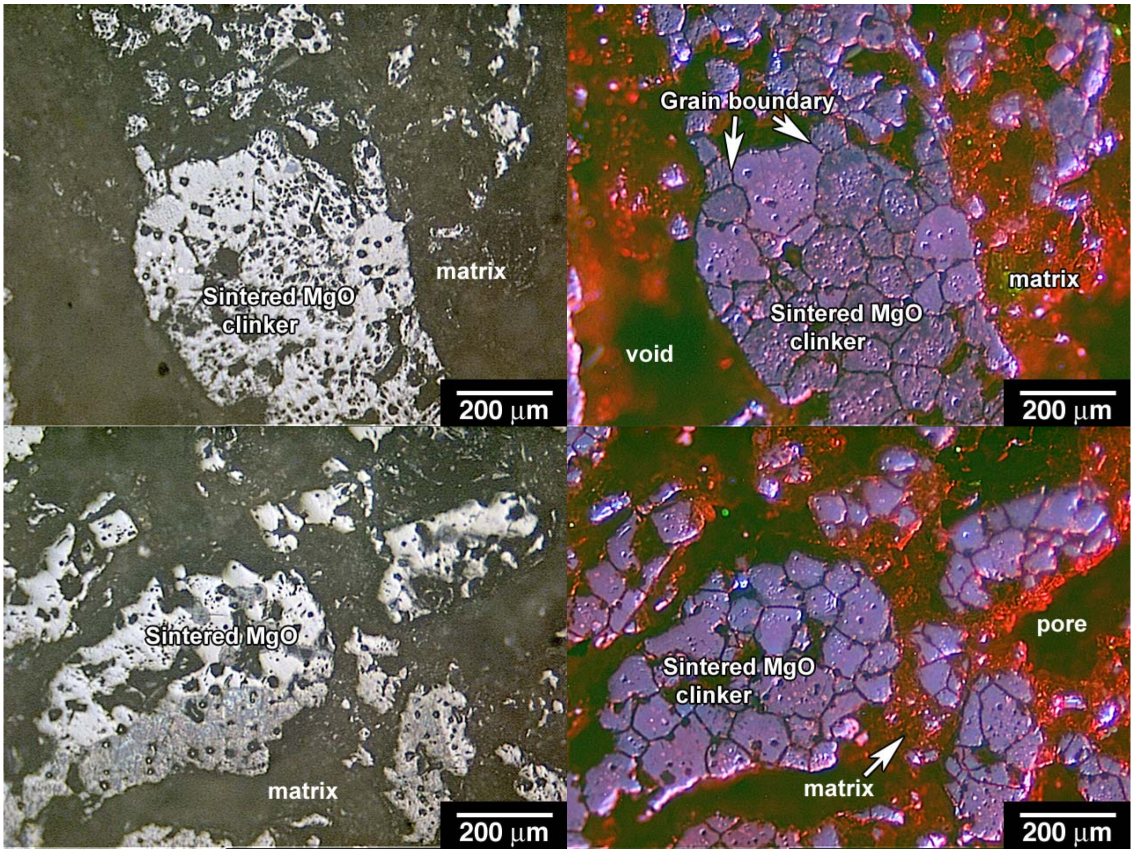

Figure 5 RL and CL microstructures of sample 27 subjected to black liquor cup test. Sample is taken from the "Bottom" side of the test cup.

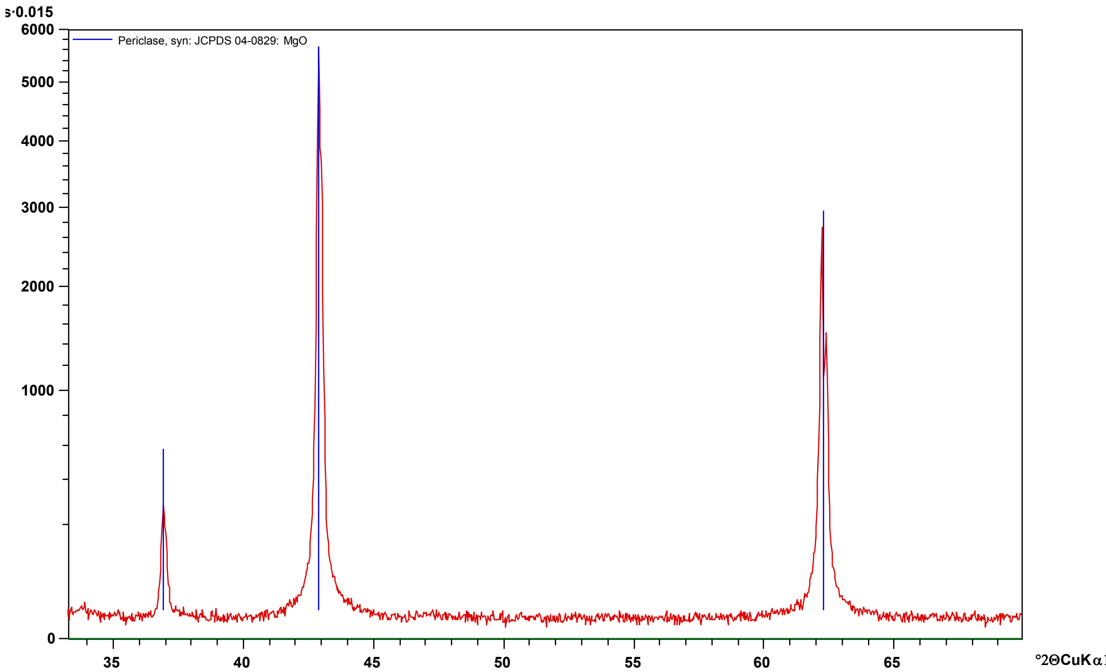

Figure 6 XRD pattern of sample 27 subjected to black liquor cup test, showing diffraction lines of only Periclase (MgO). The black liquor has a very poor crystallinity and strong MgO diffraction lines obscure the Na-carbonate and sulfate diffraction lines.

Cup Sample

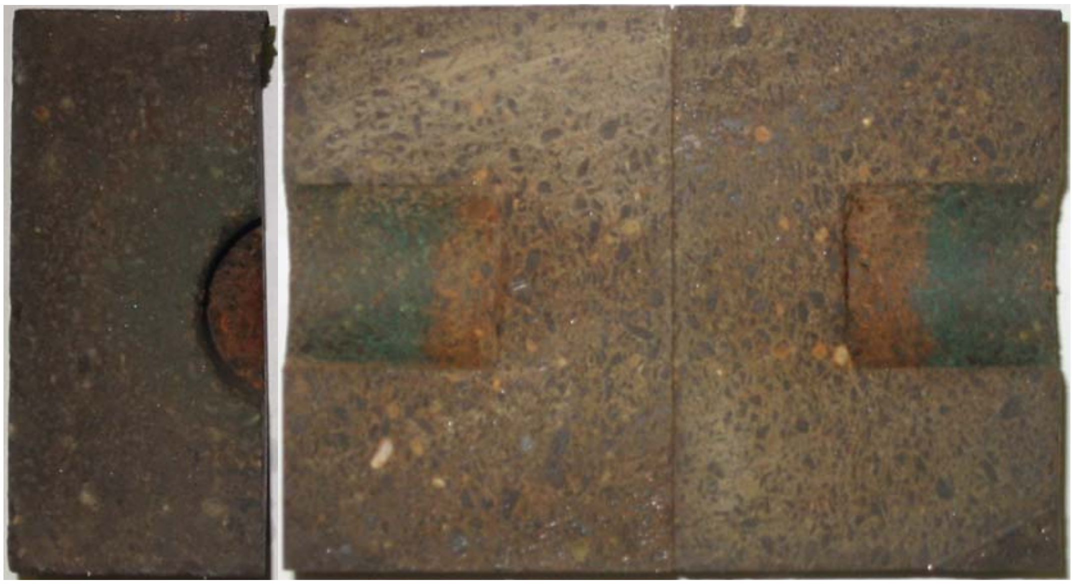

Figure 7 Cup Sample after smelt test.

Two additional 80% magnesia 20% alumina samples (28 and 29, not presented in table) were prepared based on magnesia concrete mixes. In both cases the blocks cracked during drying at 100°C as shown in Figure 8 and Figure 9 so not further testing was carried out.

Figure 8 M80 XA after drying at 100C.

Figure 9 M80 NC-O after drying at 100C.

Task 1.4

Refractory materials are being evaluated and modeled to be used in the pulse combustors, shown in Figure 10, that are failing at Big Island and Trenton.

Figure 10 Picture of failed pulse combustor tube sheet.

An enlargement showing the critical delamination at a depth of 5-6” into the 11” thick by 5’ diameter panel is shown in Figure 11. The delamination eventually could lead to blockage of the heat exchanger tubes and necessitates refractory replacement. Material properties of two possible replacement materials have been measured and a finite element model of the tube sheet has been developed.

Figure 11 Enlargement showing critical delamination failure at 5-6" in depth and accompanying transverse cracking.

Two models were developed for the tube sheet as shown in Figure 12. The multi-hole model has a central hole at R = 381 mm, θ = 60° surrounded by six other holes. The single hole model has a single hole at R = 381 mm, θ = 60°. Very little difference was found in the state of maximum stress in the vicinity of the holes so the single hole model was used for all iterative modeling as shown in Table 3.

The boundary conditions used in all models are shown in Figure 13. Standard properties from handbooks were used when properties were not known. Once again the bane of modeling raised its ugly head. The properties of refractories needed for modeling have not been measured. Failure was determined to occur due to the restraint of the anchors. Figure 14 shows the principal stresses in the vicinity of an anchor. Figure 15 shows the effect of the holes on the stress distribution. Additional work is required to finalize these models and determine more accurate results.

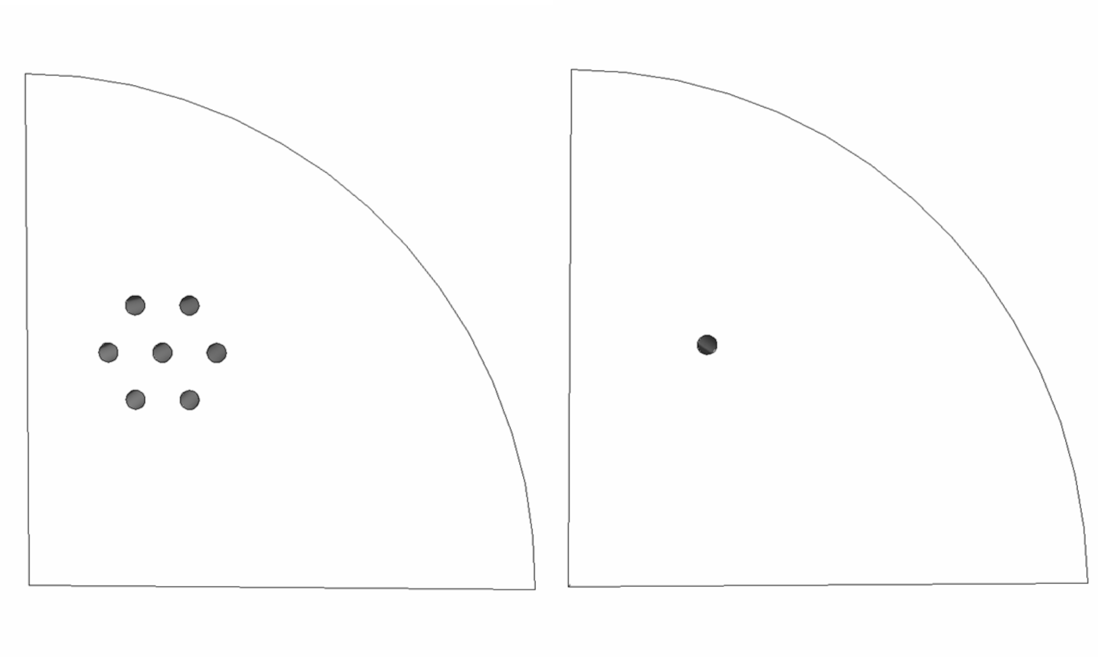

Figure 12 Two models-multi-hole (left) and single-hole (right)

Table 3 Comparison of maximum principal stress and displacemnt for 2 models.

	Stress	Displacement
Model-1	5.45 MPa	4.81 mm
Model-2	5.42 MPa	4.80 mm

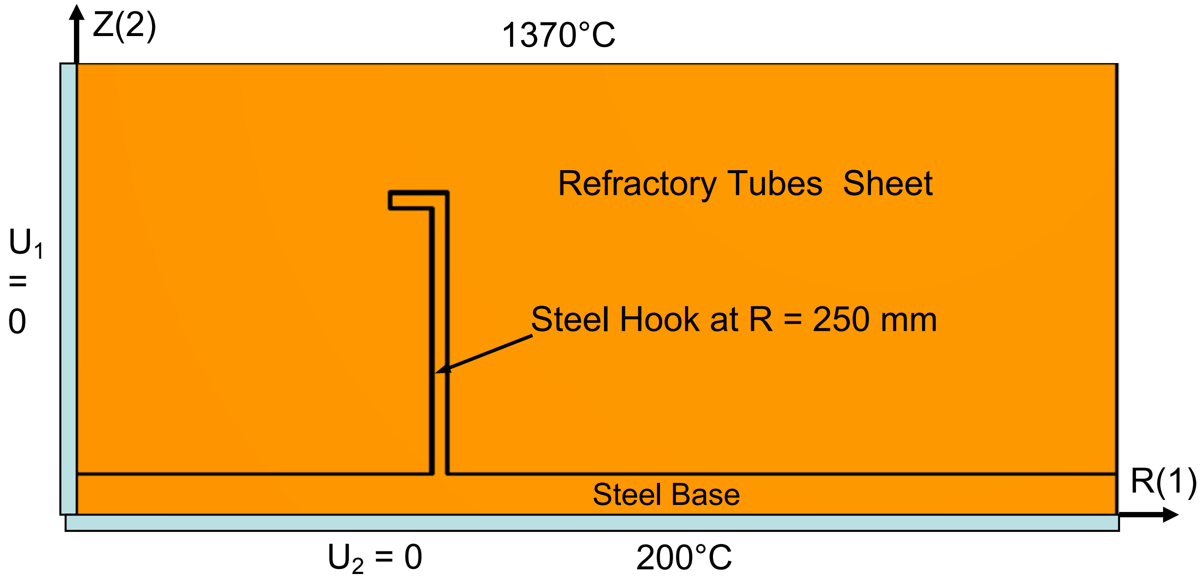

Figure 13 Boundary Conditions

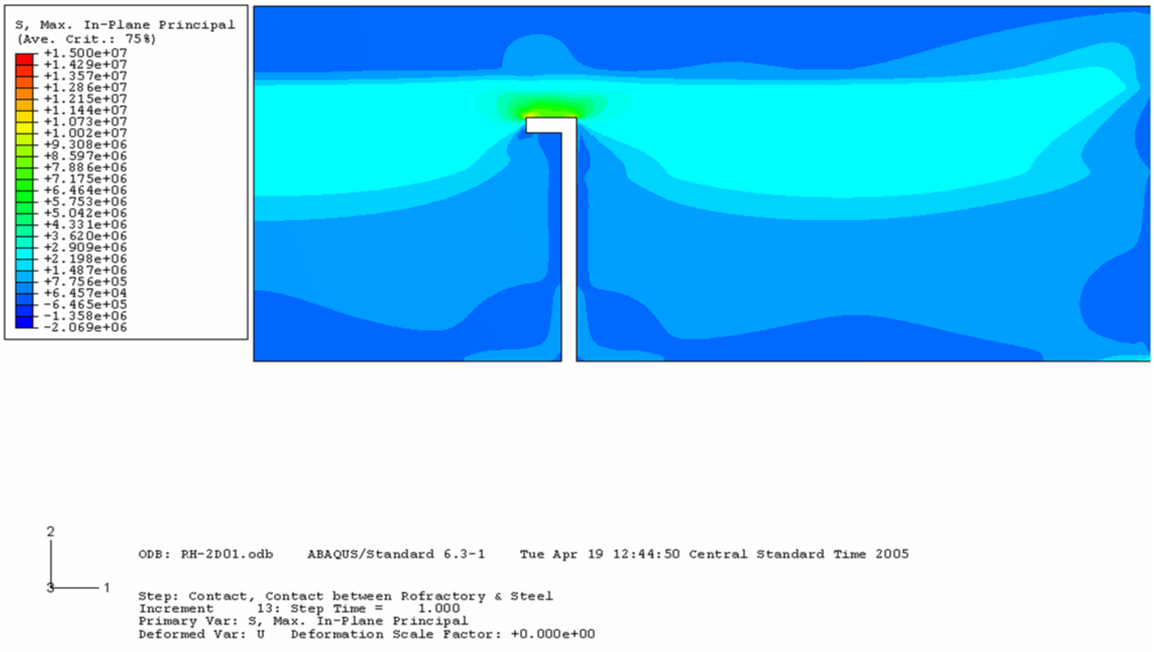

Figure 14 Principal stress distribution in viciity of anchor.

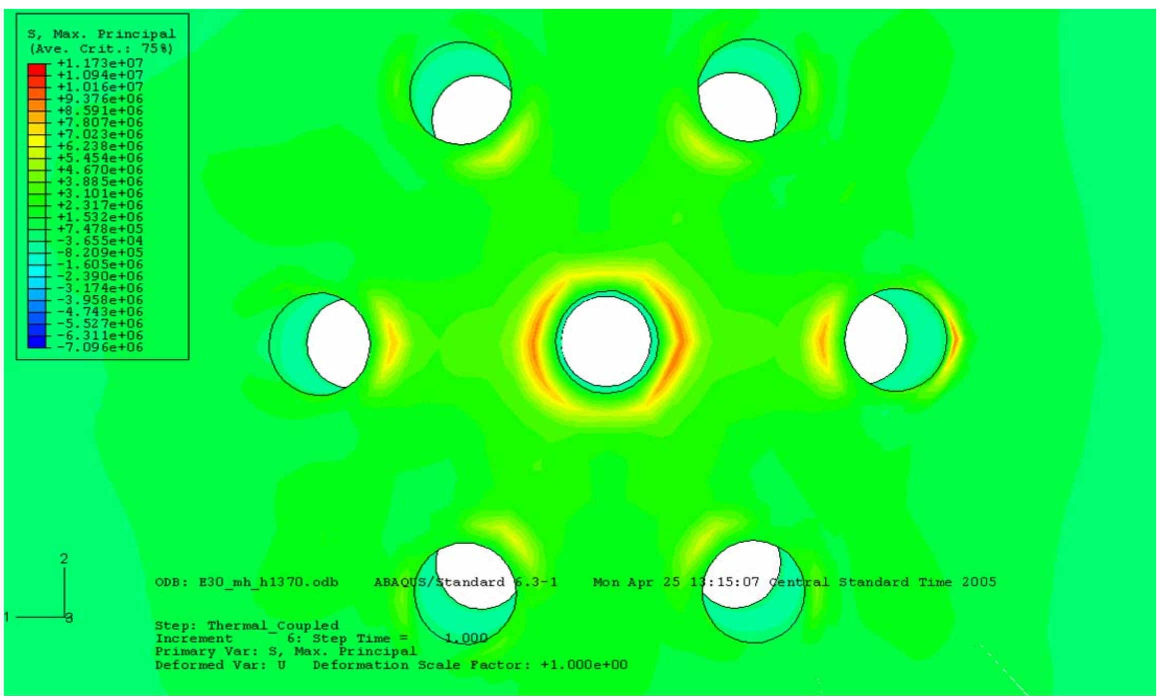

Figure 15 Principal stress distribution in the vicinity of holes.

Refractory materials were evaluated for replacement of the current refractory. A 90% zirconia 10% alumina material currently used for burner ports in the chemical industry is preliminarily recommended for use in the pulse combustor. MOR and CCS were measured with the results shown in Table 4. Thermal expansion and shrinkage were measured as shown in Figure 16.

Table 4 AZ-10 MOR an CCS resuilts

ASTM C-133-97(2003)							
Sample:	AZ10						
Test:	CCS						
Fired to:	RT						
	Density (g/cc)	Mass (g)	Width (in)	Depth (in)	Height (in)	Load (#)	CCS (psi)
A	3.14	401.8	1.98	1.98	1.99	14300	3,650
B	3.10	395.7	1.99	1.98	1.98	13500	3,430
C	3.10	388.5	1.99	1.98	1.94	13750	3,490
AVERAGE	**3.11**	**395.3**	**1.99**	**1.98**	**1.97**	**13850**	**3500**
STANDARD DEVIATION							**110**
Fired to:	700C						
A	3.07	388.6	1.98	1.98	1.97	14300	3,650
B	3.08	395.2	1.98	1.99	1.99	13500	3,430
C	3.06	379.2	1.99	1.98	1.92	15000	3,810
AVERAGE	**3.07**	**387.7**	**1.98**	**1.98**	**1.96**	**14267**	**3600**
STANDARD DEVIATION							**190**
Fired to:	1400C						
A	3.02	382.6	1.99	1.98	1.96	22000	5,580
B	3.07	376.5	1.98	1.98	1.91	17100	4,360
C	3.05	379.9	1.98	1.98	1.94	21400	5,460
D	3.08	381.7	1.98	1.98	1.93	20200	5,150
AVERAGE	**3.05**	**380.2**	**1.98**	**1.98**	**1.94**	**20175**	**5100**
STANDARD DEVIATION							**550**
Test:	MOR	Span (in):	7.00				
Fired to:	RT						
	Density (g/cc)	Mass (g)	Length (in)	Depth (in)	Heigth (in)	Load (#)	MOR (psi)
A	3.12	2282.2	11.27	2.01	1.97	325	437
B	3.15	2288.9	11.27	2.00	1.97	321.5	435
C	3.06	2289.2	11.26	2.00	2.03	359	457
AVERAGE	**3.11**	**2286.8**	**11.27**	**2.00**	**1.99**	**335**	**440**
STANDARD DEVIATION							**12**
Fired to:	700C						
A	3.00	2269.5	11.26	2.00	2.05	285	356
B	3.04	2519.0	12.05	2.01	2.09	426	509
C	3.05	2208.5	11.27	2.01	1.95	352	484
AVERAGE	**3.03**	**2332.3**	**2.01**	**1.95**	**352.00**	**354**	**450**
STANDARD DEVIATION							**82**
Fired to:	1400C						
A	3.03	2267.0	11.25	2.02	2.01	538	692
B	3.08	2425.3	11.62	2.01	2.06	651	801
AVERAGE	**3.05**	**2346.2**	**11.44**	**2.02**	**2.04**	**595**	**750**
STANDARD DEVIATION							**77**

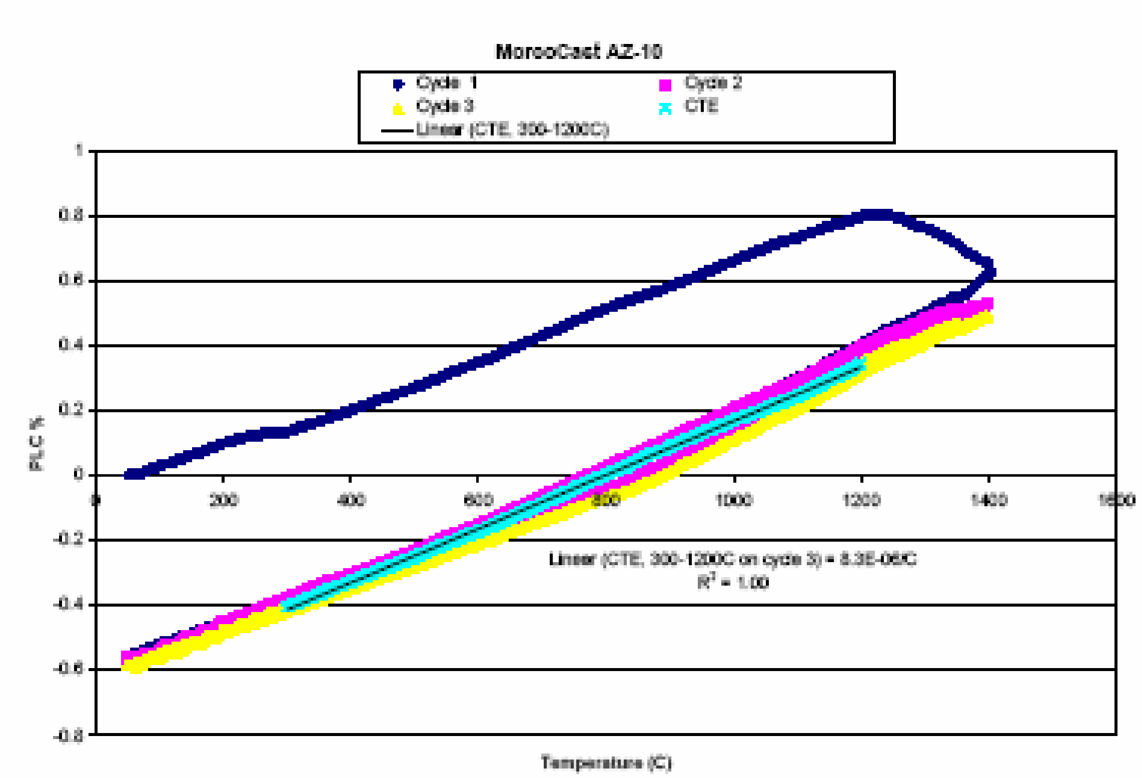

Figure 16 CTE and permanent shrinkage of AZ-10.

Task 2.0

See Appendix A.

CONCLUSION

Samples provided by in-kind sponsors were tested using cup testing. The best performing materials in the cup testing were fused cast materials. Currently testing of 2 castables were completed and 1 magnesia brick. The brick performed very well and should be moved into industrial trials. The castables cracked during drying and require additional work.

Computer simulation of existing materials will accelerate materials research in developing these new materials, and it is less costly and time consuming. Finite element modeling was conducted for the damage analysis in this study. Both and HTLP gasifier and the pulse combustor used for LTLP gasification were studied. The pulse combustor requires more work and will be reported on more fully in the next report. AZ-10 refractory has been recommended as a replacement of existing materials based on the model and thermo-mechanical properties measured.

This study presented continuum damage mechanics based analytical model for predicting the failure behavior of refractory lining in high temperature black liquor gasifiers. The damage model accounts for the chemical expansion in addition to mechanical and thermal expansion. A comparison of predicted damage patterns for BLG refractory material with the observed damage pattern in a glass melting furnace refractory brick indicates that this model could be used to evaluate failure behavior of refractory linings in black liquor gasifier.

Chemical reaction and thermal expansion with improper constraints causes the most compressive damage in the refractory structure. Layered damage occurred in the refractory structure due to the tensile damage. Expansion allowance affects the damage of the refractory structure. Tensile damage could be reduced by allowing for larger expansion.

No systematic experimental work has been done so far to characterize the failure behavior of refractory materials in black liquor gasifier. Experimental work is needed to validate the models presented here.

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APPENDIX A -- Modeling of Thermomechanical and Failure Behavior of Refractory Linings in a High Temperature Black Liquor Gasifier

III. Modeling of Thermomechanical and Failure Behavior of Refractory Linings in a High Temperature Black Liquor Gasifier[1]

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Abstract

Refractory failures have impeded the advancement of high temperature black liquor gasification. The failures are controlled by the thermomechanical behavior and the chemical expansion of the refractory lining. Finite element modeling is employed to study the operational performance of alumina refractory linings in a high temperature black liquor gasifier using commercial software, ABAQUS®. The stress and strain distributions, thermomechanical behavior of the refractory linings under thermal loading and chemical attack are investigated. The objective of this study is to help in the design of refractory materials to better serve in high black liquor gasifiers under the operational environment.

Keywords: finite element, black liquor, gasifier, high temperature, alumina, refractory, thermomechanical, chemical expansion

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I. Introduction

High temperature black liquor gasification (BLG) technology has garnered much interest over the last two decades as a potential chemical recovery alternative available to the pulp and paper industry. The BLG technology has higher energy efficiency and generates far more power with overall lower cost than conventional technology. It improves safety by reducing the risk associated with smelt-water explosions. It reduces the wastewater discharges and harmful emissions into the environment.

High temperature black liquor gasifiers are generally cylindrical, range from 1.5 to 25 meters in height and 0.5 to 5 meters in diameter[1], as shown in Figure 1. In the gasifier reactor vessel, there are usually 2-6 coaxial component layers. Refractory linings composed of single bricks are used to protect the exterior metallic part of the gasifier vessel. A dense refractory material lining is designed to be exposed to the highest temperature environment. The second refractory lining is usually chosen with a similar material as a “safety” layer. Subsequent layers are used to provide insulation and expansion allowance. Steel shell is used to provide reaction space and confinement to the refractory linings.

The gasifier generally operates at temperature range from 950 to 1000 ^{o}C. The high temperature and the chemical corrosion conditions make the current refractory materials for the BLG reactor vessel lining inadequate. Refractory failures during operation retarded the application of the BLG technology[2, 3]. Refractories used in the pilot units and commercial high temperature black liquor gasifier system lasted only several months, with a replacement cost up to 1 million dollars and several weeks downtime. Peascoe et al. studied the refractory materials using immersion tests in molten smelt[4]. It was found, sodium aluminum silicates was formed in mullite based refractories and caused volume changes from 8% to 33%. $NaAlO_2$ and MgO were formed in $MgAl_2O_4$ spinel based refractories and caused volume changes from 2.1% to 13%. Alumina refractories had the best corrosion resistant with an expansion ranging up to 0.7%. Alumina refractory is being used in the most recent refractory lining of the commercial high temperature black liquor gasifier at New Burn due to its higher corrosion resistance. However, study is still needed to find more appropriate alternatives to the current BLG refractory material.

Dogan et al.[5] analyzed the failure of refractories taken from commercial coal gasifiers which are similar to the BLG system. They found that several types of failure occurred in the refractories. The failures include: pinch spalling at the brick corners, slabbing of the hot face region which is exposed to the highest temperature (conversely, the cold face is defined as the region at the lowest temperature), cracks parallel to the hot face either from brick interface or in the interior of the brick or both. Study of thermomechanical behavior of refractories would help in understanding the failure behavior of the refractories. However, it is very hard and costly to carry out experiments to study the thermomechanical behavior and chemical reaction of BLG refractory due to high temperature and the corrosion environment involved. Thermomechanical modeling would be an efficient and economical way for the development of new BLG refractory materials.

Very limited work has been done to model the thermomechanical behavior of refractory linings similar to the refractory lining in a BLG system, such as coal gasifiers. Chen[6] studied the thermomechanical behavior of refractory linings for slagging gasifiers.

It was found that thermomechanical behavior in the refractory lining is controlled by the temperature gradient through the lining and the confinement from the surrounding components of the gasifier. Schacht[7] studied the thermomechanical and fracture behavior of cylindrical refractory linings exposed to high temperature. He found that the brick interface separate due to the thermal expansion. High tensile radial stress is produced at the end of the opening possibly leading to a crack starting from the interface and growing into the interior of the brick. The hot face region experienced the highest compressive tangential stress which leads to pinch spalling of the hot face. However, no work has been done to study the thermomechanical behavior of the refractory linings accounting for combined effect of thermal loading and chemical attack, which is the real operational environment of high temperature BLG systems. Due to the chemical reaction of the refractory material and the black liquor smelt, the thermomechanical and failure behavior of refractory in BLG system is more complicated.

In order to understand the failure of BLG refractory thoroughly, an extensive study of the thermomechanical behavior of BLG refractory linings under thermal loading and chemical attack is necessary. In this study, a thermomechanical model accounting for chemical reaction is developed and implemented into the commercial finite element software, ABAQUS[8], so it can be used to simulate the thermomechanical performance of the refractory linings in a high temperature BLG system.

II. Constitutive Relations

A high temperature black liquor gasifier is considered as a long hollow cylinder with a composite wall heated from the centerline uniformly along the axis. The temperature distribution is assumed to vary in the radial direction only. Therefore, the problem is simplified into a two-dimensional model based on the gasifier structural configuration and the assumption of the temperature distribution.

During the operation of a high temperature black liquor gasifier, the thermal behavior, chemical reaction and mechanical behavior are coupled together. Change in temperature in the gasifier structure will affect the reaction rate and the stress-strain distribution, which in turn affects the deformation and fracture behavior of the structure. Tensile cracking or gap formation will change the thermal conductivity of the lining and hence the heat transfer. Therefore any realistic modeling effort should consider the heat transfer, chemical reaction and thermomechanical performance simultaneously.

Heat is generated inside the reactor, and transferred through the refractory lining wall and the steel shell, and then it dissipates to the surrounding environment by radiation and convection. The two-dimensional transient heat conduction through the gasifier wall is derived from the 3-D governing equation given by Hetnarski[9].

$$\rho C \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial \theta^2}\right) + \dot{Q} \tag{1}$$

where $\dot{Q}$ is the heat flow rate, ρ is the density, C is the specific heat, T is the temperature, t is the time, k is the conductivity, and r and θ are the directions.

The boundaries of heat transfer include both the convection and the radiation. Heat flux on a surface due to convection is governed by

$$q = h\left(T - T^A\right) \tag{2}$$

where h is a reference film coefficient, and T^A is an ambient temperature value.

Heat flux on a surface due to radiation to the environment is governed by

$$q = e\sigma\left[\left(T - T^0\right)^4 - \left(T^A - T^0\right)^4\right] \tag{3}$$

where e is the emissivity of the surface, σ is the Stefan-Boltzmann constant (5.67 x 10^{-8} W/m^2K^4), and T^0 is the value of absolute zero on the temperature scale being used.

The refractory linings are composed of bricks. There are interfaces between the bricks and the gasifier component layers. Heat transfer rate, Q_j, through the interface is expressed by the joint conductance, h_j, the apparent contact area, A_a, and the temperature drop, ΔT_j, as[10]

$$Q_j = h_j A_a \Delta T_j \tag{4}$$

Governing equation of the chemical reaction of alumina and black liquor smelt is also needed in the study. Unfortunately, there is no experimental work regarding the reaction rate. The reaction rate of alumina refractory and black liquor smelt components is assumed to be a function of time and temperature. Generally, the chemical reaction can be expressed by the volume change such that the reactive behavior of refractory material is described by the reactive strain as

$$\varepsilon^r = aT^m \cdot bt^n \tag{5}$$

where ε^r is the chemical expansion, a and b are constants and m and n are the parameters related to temperature and time.

The thermal loading and chemical reaction cause reversible thermal expansion and irreversible chemical expansion, respectively. Under constraint, the volume change induces significant stresses in the components. Based on the hypothesis that the mechanical strain $\{\varepsilon^m\}$, the thermal strain $\{\varepsilon^t\}$, and the reactive strain $\{\varepsilon^r\}$ are independent of each other, the total strain can be written in separable form such that

$$\{\varepsilon\} = \{\varepsilon^m\} + \{\varepsilon^t\} + \{\varepsilon^r\} \tag{6}$$

where the notation $\{\ \}$ denotes a tensor quantity.

In the high temperature black liquor gasifier, the component refractory bricks expand more freely in the vertical direction than in the other directions. The stress produced in the vertical direction would be very small compared to other stress components, so the state of plane stress is used in the model. The two-dimensional strain-stress constitutive relations for the plane stress state are given by

$$\varepsilon_{rr} = \frac{1}{E}\sigma_{rr} - \frac{\nu}{E}\sigma_{\theta\theta} + \alpha T + \varepsilon^{r} \tag{7}$$

$$\varepsilon_{\theta\theta} = \frac{1}{E}\sigma_{\theta\theta} - \frac{\nu}{E}\sigma_{rr} + \alpha T + \varepsilon^{r} \tag{8}$$

$$\varepsilon_{r\theta} = \frac{1+\nu}{E}\tau_{r\theta} \tag{9}$$

where ε_{rr} and $\varepsilon_{\theta\theta}$ are the strains in r and θ directions, respectively, $\varepsilon_{r\theta}$ is the shear strain, σ_{rr} and $\sigma_{\theta\theta}$ are the stresses in r and θ directions, respectively, $\tau_{r\theta}$ is the shear stress, E is the Young's modulus and ν is the Poisson's ratio.

In the finite element computation, the coupling of the thermal behavior and mechanical behavior is achieved by

$$\begin{bmatrix} K_{UU} & K_{UT} \\ K_{TU} & K_{TT} \end{bmatrix} \begin{bmatrix} \Delta U \\ \Delta T \end{bmatrix} = \begin{Bmatrix} R_U \\ R_T \end{Bmatrix} \tag{10}$$

where ΔU is the incremental displacement due to both thermal and chemical expansions, ΔT is the incremental temperature, K_{ij} are submatrices of the fully coupled Jacobian matrix, and R_U and R_T are the mechanical and thermal residual vectors, respectively.

III. Computational Model

Figure 2 identifies the component layers and bricks, the brick joints and the geometry of the two-dimensional model for the BLG refractory lining problem. Region "ABCD" in Figure 2 is modeled in the study. The model is composed of two layers of refractory lining, one layer of insulation fiber and steel shell. The inner diameter of the reactor is 2.4 m. The thickness of each refractory lining is 152 mm. The thickness of fiber layer is 20 mm. The thickness of the shell is 30 mm. The interface between adjacent layers is considered to be intact initially but capable of separation and sliding. In each refractory lining, there is one-half refractory brick. The left hand side of the brick of the inner refractory lining and the right hand side of the brick of the outer refractory lining are defined to be at the centerline of the brick. The other side of the brick is defined as the brick joint. The centerline of the brick is fixed without rotation during the operation of the brick. Dry brick joints are used in the model. That is, a joint could transfer a compressive load across it and remain intact but it would open under any tensile stress so the load at the joint would be released.

Alumina material is selected for both the working and back-up refractory linings, a fiber layer is used as insulation, and a carbon-steel is used for the container shell. The thermal and mechanical properties of those materials are usually non-linear and temperature dependent. The refractory material is treated as an elastic-plastic material. The properties of alumina are highly temperature dependent. However, only a limited experimental data is available. Some thermal properties of the refractory are obtained with varying temperature by Hemrick's[11] as given in Table 1. Other properties of the refractory are $E =$ 103 GPa at 23 ^{o}C and $E =$ 81 MPa at 900 ^{o}C. The Young's modulus at other temperatures will be linearly interpolated based on the above two values. The room temperature properties of the refractory are $\rho =$ 3480 kg/m^3, $\alpha =$ 8.7 x 10^{-6}/K and $\nu =$ 0.24, yield strength, $\sigma_{yield} = 200$ MPa and ultimate strength $\sigma_{ultimate} = 220$ MPa. The room temperature linear elastic-plastic properties for the carbon steel are $\rho =$ 7800 kg/m^3, $k = 55$ W/mK, $C = 500$ J/gK, $\alpha =$ 13 x 10^{-6}, $e =$ 0.8, $E =$ 210 GPa, $\nu =$ 0.3 and the yield strength, $\sigma_{yield} = 300$ MPa. A fiber material which could be compressed up to 80% in volume (Figure 3) is used in the model. Due to the lack of data, simple temperature independent thermal and mechanical material properties for the fiber material are used; $\rho =$ 300 kg/m^3, $k =$ 0.2 W/mK, $C = 2900$ J/gK and $\alpha \approx 0$.

Gap conductance of the interface of refractory linings is given as an average value of 1000 W/m^{2}K (when the two surfaces are contacted tightly) and zero (when the gap between two contacted surfaces exceeds 100 mm) based on the work of Gmelin et al.[12] This value would have very little effect on the temperature, stress and strain distributions in the geometry studied. A small drop in temperature between the interfaces would be expected in the model. The same value is taken for the gap conductance of the interface between component layers due to its insignificant effect.

A coupled thermal-mechanical user interface model accounting for chemical reaction is developed and implemented into a finite element code, ABAQUS[8]. Increments of temperature and displacement are calculated based on equation (10). A FORTRAN language programmed user subroutine UEXPAN[8] is developed to model the chemical expansion and implemented to interface with the main finite element code. Both the thermal expansion and chemical expansion are defined as functions of temperature and time in the subroutine. Plane stress elements CPS4T[8] are used for all the components of the BLG system. The mesh was chosen following refinement studies in which one mesh (1307 nodes) matched a finer mesh (2765 nodes) with respect to maximum stress components to within 4 %. Finer mesh of 2765 nodes and 2261 elements are employed in the finite element model. In order to better capture the stress response, a finer mesh is used in the inner surface region of the refractory linings which is exposed to the highest temperature, as shown in Figure 4. Cylindrical coordinate system is used in the model. R in Figure 4 is referred to as radial direction and θ in Figure 4 is referred to as tangential direction.

The inner surface of the reactor is heated up to 950 ^{o}C at a constant heating rate of 20^{o}C per hour. The ambient temperature (surrounding the steel shell) is 23 °C in the beginning of heating and increases to 49°C at the end of heating. The value of absolute zero, $T^0 = -273$ ^{o}C and a convection coefficient, $h =$ 30 W/m^2 K is used to describe the motion of the surrounding air outside the steel shell.

The chemical reaction is assumed to occur only when temperature is above 850 ^{o}C. The reaction rate changes linearly with the temperature. Chemical reaction rate at 850 ^{o}C is assumed to be 6 x 10^{-5}/h. The chemical reaction will be completed when the volume change of corroded alumina reaches 130%. It is also assumed that the chemical reaction wouldn't affect other properties of the refractory.

IV. Results and Discussion

Temperature distribution in the refractory lining is important to the development of strain and stress in the refractory. Thermal gradient produced through the thickness of the refractory lining would cause differential strain in the refractory therefore resulting in stresses in it. Figure 5 shows the comparison of the tangential stresses in the inner refractory lining and the outer refractory lining at the same moment (time t) during the operation. It is found that the stress in the inner refractory lining is significantly larger than in the outer refractory lining. Therefore, only the thermomechanical behavior and the chemical expansion of the inner refractory lining are presented in the following studies. Moreover, because the behavior of the refractory under tension and compression is different, strain and stress components in both tangential and radial directions are analyzed.

Figure 6 shows the tangential strain distributions in the inner refractory lining. The strains at the surface and the interior of the brick at the end of heating and after 3 months service are presented. For both time ranges, different amounts of expansion are developed through the thickness of the brick. The strains decrease approximately linearly from the hot face to the cold face at the end heating. This is caused by the thermal gradient in the refractory lining[13]. However, nonlinear strain distribution appears in the refractory brick after 3 months service. Very high tangential strains appear in the region between hot face and at a depth of about 50 mm from the hot face. The strains in the rest of the brick after 3 months are similar to the strains at the end of heating. This is because the temperature exceeds 850 ^{o}C up to the depth of about 50 mm from the hot face. This results in considerable chemical expansion in this region which is the so called reaction zone. Note that the highest tangential strain on the surface of the brick after 3 months is close to the end of the reaction zone because of the development of plastic strain in the region.

Figure 7 shows the radial strain distributions in the inner refractory lining. The strain distribution at the end of heating is similar to that of the tangential strain. However, extremely high radial strains, much larger than the tangential strains in the same region, are developed in the reaction zone after 3 months. Strains in the rest of the brick after 3 months are similar to the strain at the end of heating. This is due to the chemical expansion and less constraint in the radial direction than the tangential direction. As a result, a very large expansion gradient is produced at the end of reaction zone after 3 months. This differential expansion will cause significant stresses which would damage the refractory material.

Figure 8 shows the tangential strain history of the inner refractory lining. The minimum tangential strain is on the cold face of the refractory lining. It increases during heating due to the thermal loading, and then decreases slightly due to the compression of the fiber and the temperature drop in this region[13]. The maximum tangential strain is at the end of the reaction zone. It increases until about 800 hours of operation at which time the fiber layer is fully compressed. During heating, due to the combined effect of thermal loading and chemical reaction, the strain increases at a much higher rate. The tangential strain history of the brick corner is also shown in Figure 8. The strain in this region begins to decrease after about 320 hours of operation due to the development of the plastic strain.

Figure 9 shows radial strain history of the inner refractory lining. The minimum radial strain is on the cold face of the lining. It increases during heating due to the thermal loading, and then decreases slightly until about 400 hours because of the temperature drop in this region due to the compression of the fiber layer during this period[13]. The minimum radial strain reaches steady state after the full compression of the fiber. However, the pressure on the cold face increases due to the confinement from the steel shell. The mechanical strain is fairly small compared to the thermal strain. The maximum radial strain is on the hot face. It increases nearly linearly throughout the operation although the refractory lining is confined from the outside. The hot face can expand inward when spalling occurs at the corners of the brick.

The expansion of the refractory lining and the confinement from the surrounding structures induces significant stresses in the refractory lining. Figure 10 shows the tangential stress distribution in the inner refractory lining. Compressive tangential stress is developed in the high temperature region, about 40 mm deep from the hot face at the end of heating. Almost no tangential stress is developed in the rest of the brick at the end of heating. These results indicate that the brick joint opening takes place from the cold face and extend up to the region about 40 mm from hot face. Ultimate compressive tangential stress is reached in the unopened portion of the brick after 3 months, which means that spalling occurs in this region. Tangential stress on the brick surface after 3 months is very small due to the brick joint opening. Very high tensile tangential stress is developed in the interior of the brick at the end of the reaction zone after 3 months. This is caused by the considerable differential expansion in this region by the chemical reaction. As a result, crack in radial direction could possibly develop in the interior of the brick due to this high tensile tangential stress.

Figure 11 shows the radial stress distribution in the inner refractory lining. Radial stress in the inner lining brick is very small at the end heating due to expansion allowance. High tensile radial stress is developed on the surface of the brick at the tip of the brick joint opening at the end of heating. As a result, cracks parallel to the hot face would initiate at this point. Significant radial stress is developed after 3 months due to the extremely large differential expansion caused by chemical reaction. Very high tensile radial stress is developed in the interior of the brick at the end of the reaction zone. This means the slabbing crack would initiate either from the tip of brick joints opening during heating and propagate inward towards the center of the brick after heating, or starts in the interior of the brick during long term service. Very high compressive radial stress is developed on the surface of the brick after 3 months due to the high compressive tangential stress and the pressure from the second refractory lining.

From the foregoing stress and strain analysis, the following four failure modes of the inner refractory lining are envisioned as outlined in Figure 12:

(1) Pinch spalling at the brick corners or spalling of the entire hot face.

(2) Cracking parallel to the hot face from the interface.

(3) Cracking parallel to the hot face in the interior of the brick.

(4) Radial cracks in the interior of the brick.

The failure modes observed from the real gasifier refractory bricks relate to the thermomechanical and chemical expansion study presented above.

Based on above results, it can also be observed that the chemical reaction of the smelt and refractory dominates the developments of strain and stress and hence the failure in the refractory lining. Better corrosion resistance will improve the performance of the refractory material in a high temperature BLG system.

V. Conclusions

A coupled thermal-mechanical model accounting for the chemical reaction is developed for refractory linings in a high temperature black liquor gasifier. This model is implemented into a commercial finite element code. The stress and strain distributions, time dependent thermomechanical behavior of the refractory lining under thermal loading and chemical attack are evaluated. The chemical reaction of the black liquor smelt and the refractory dominates the stress and strain development in the refractory lining. Four possible failure modes of the refractory lining are surmised by the stress and strain analysis. The model helps understand the failure behavior of the refractory lining in a high temperature black liquor gasifier system.

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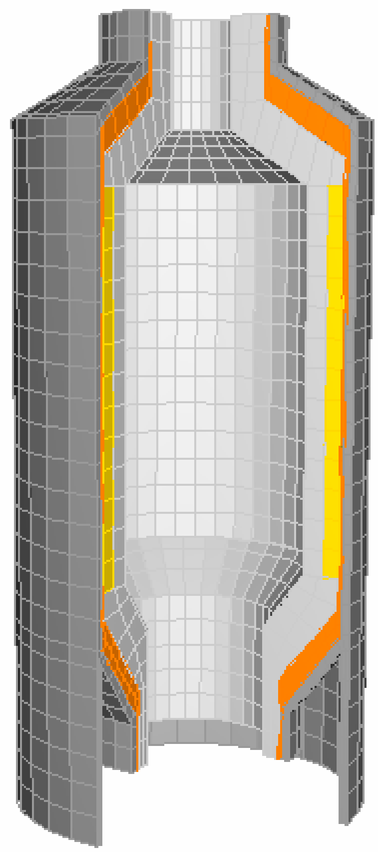


Figure 1. Schematic construction of a typical high temperature gasifier.

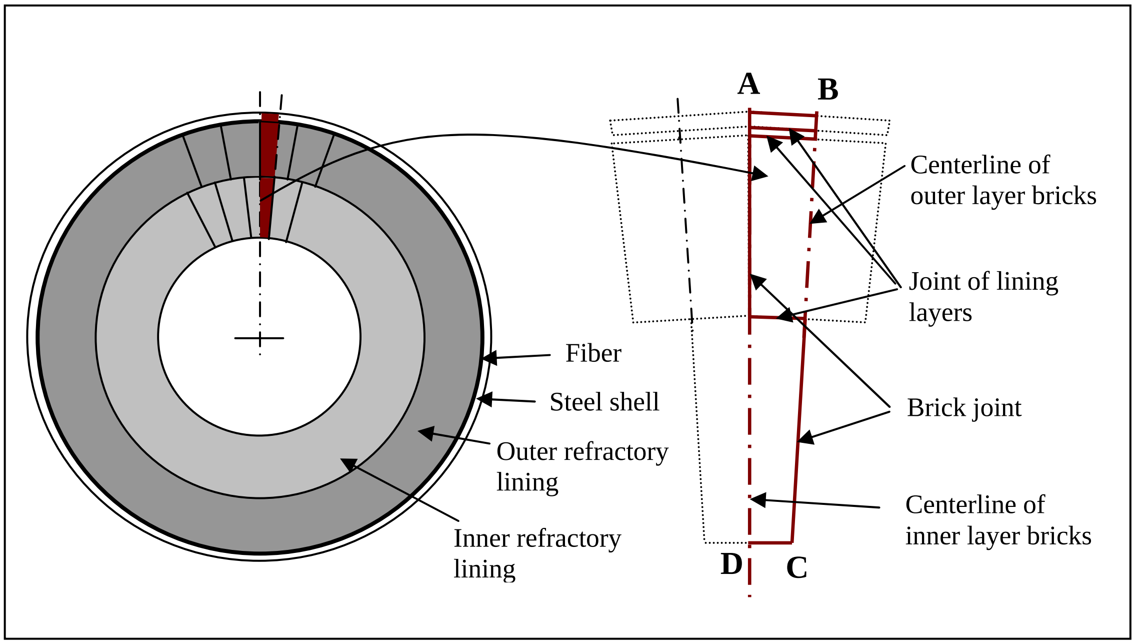


Figure 2. Idealized black liquor gasifier model.

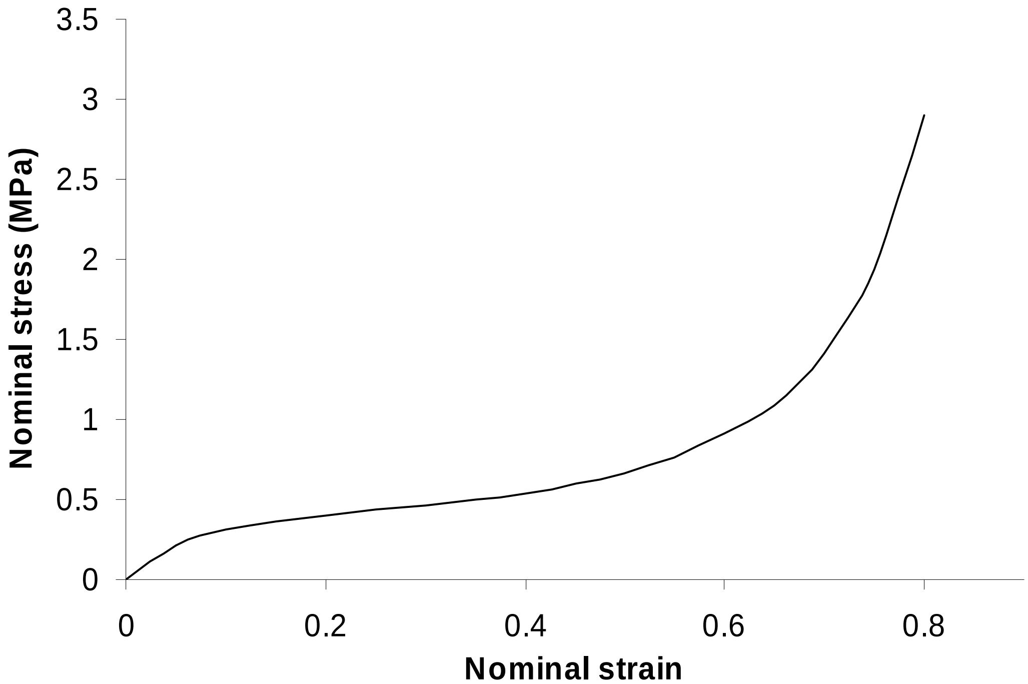


Figure 3. The compression of fiber material.

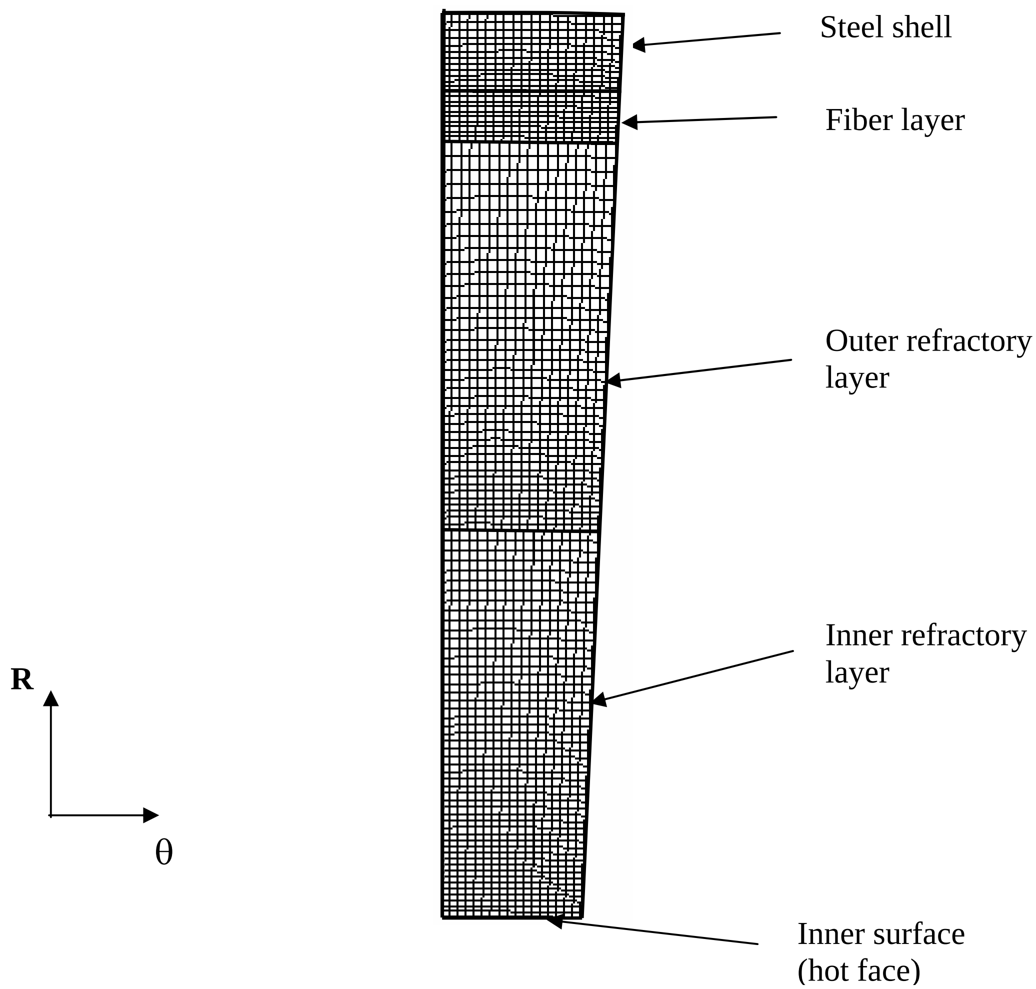
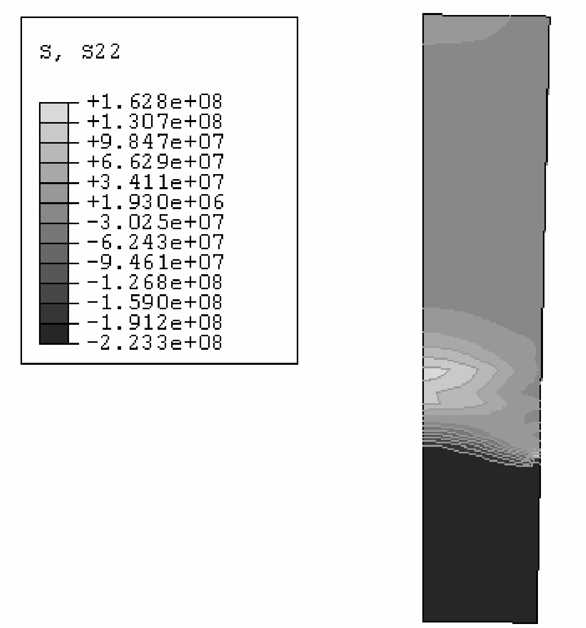
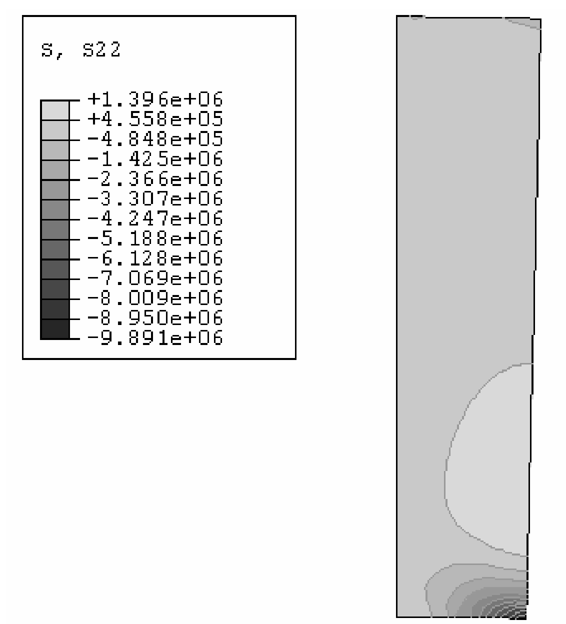


Figure 4. Illustration of assembles and meshes of the model.



(a) Stress in inner refractory lining



(b) Stress in outer refractory lining

Figure 5. Comparison of the tangential stresses in the inner and outer refractory linings at time t.

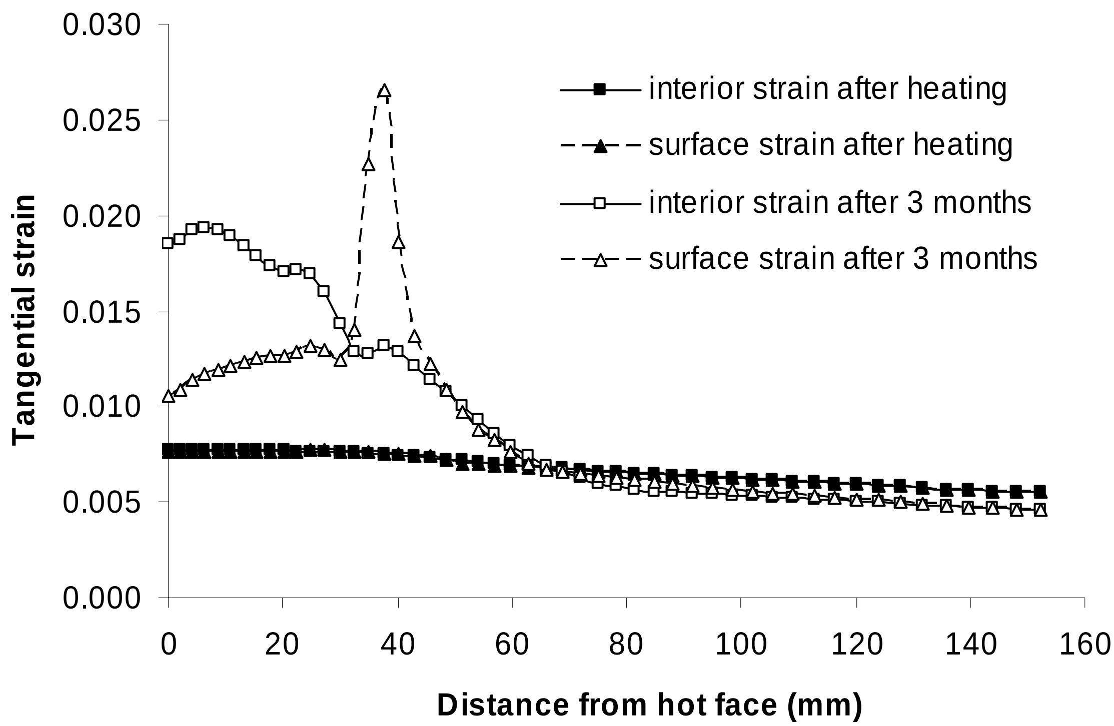


Figure 6. Tangential strain distribution in the inner refractory lining.

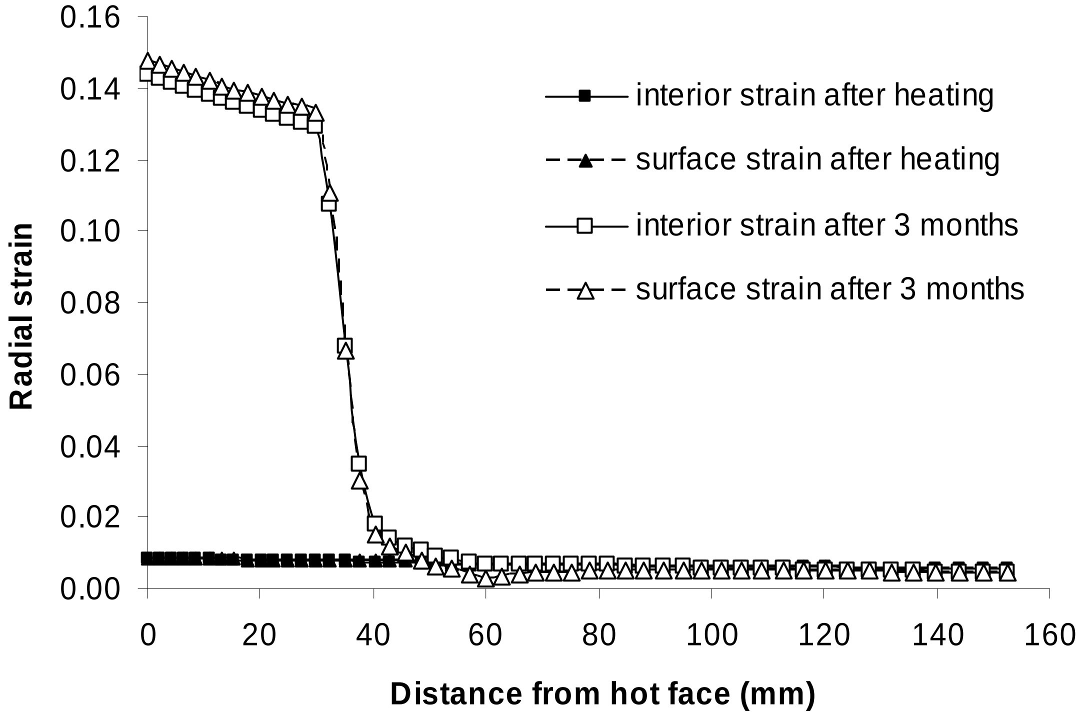


Figure 7. Radial strain distribution in the inner refractory lining.

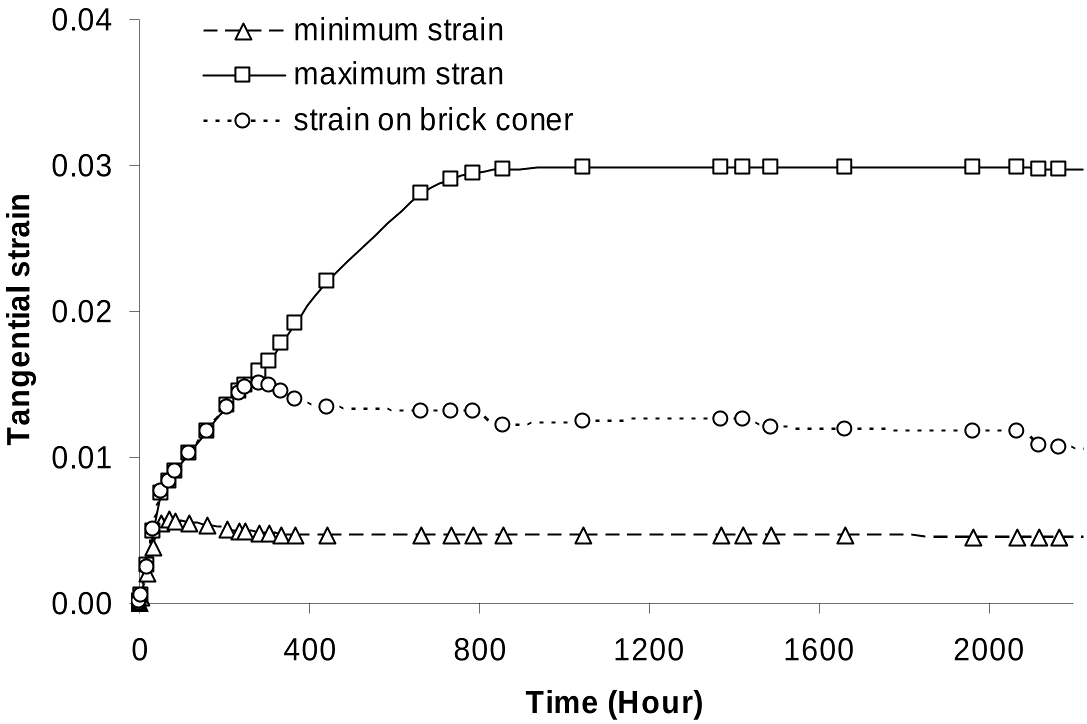


Figure 8. Tangential strain history in the inner refractory lining.

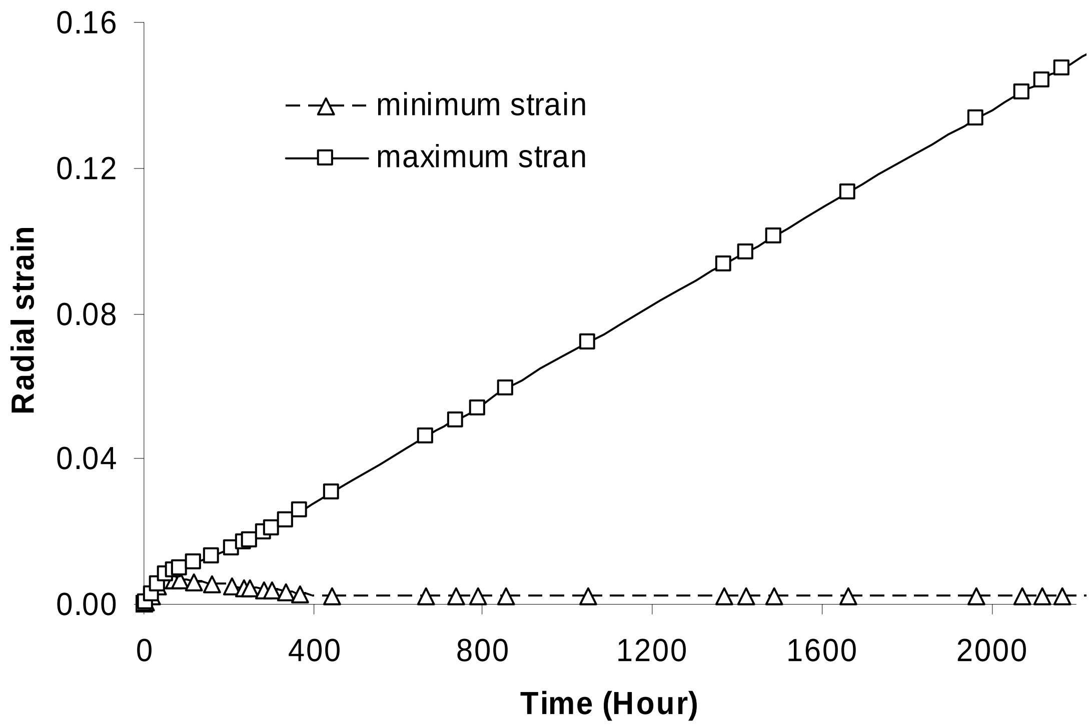


Figure 9. Radial strain history in the inner refractory lining.

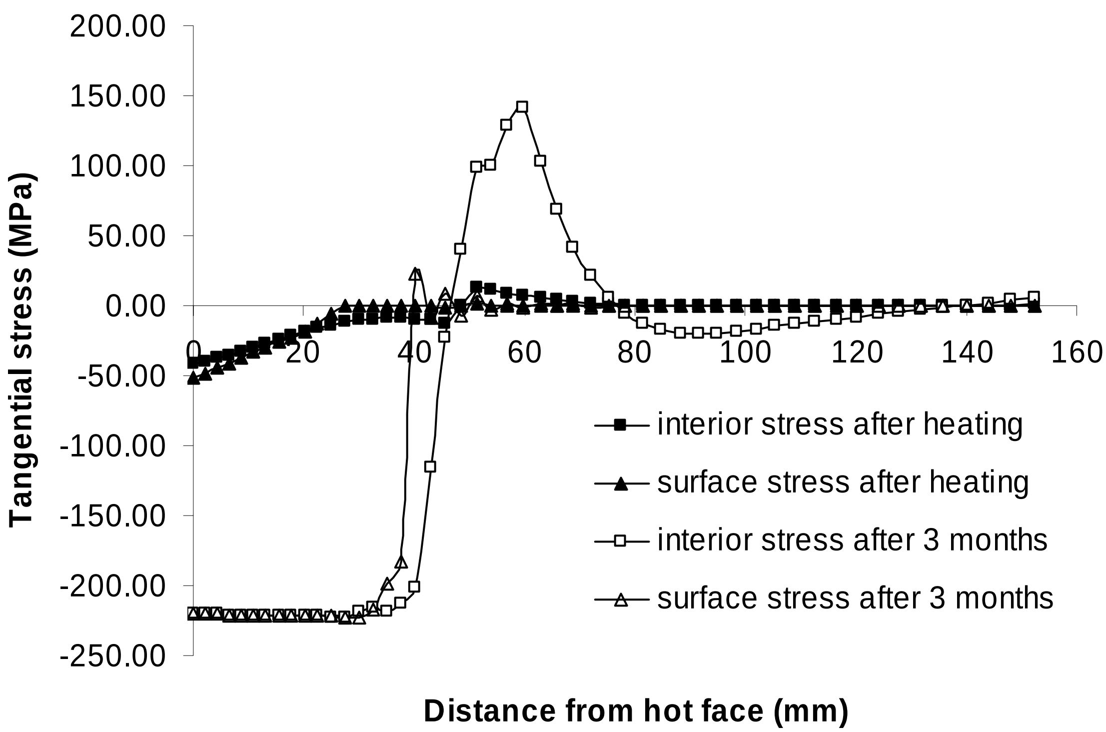


Figure 10. Tangential stress distribution in the inner refractory lining.

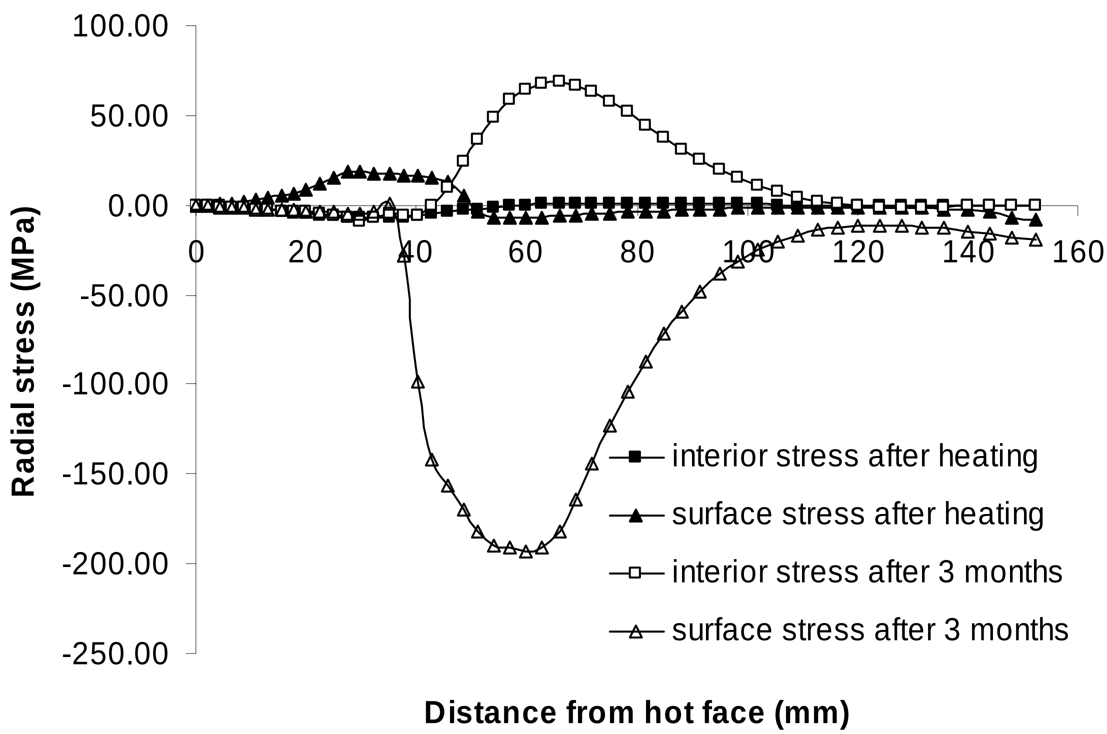


Figure 11. Radial stress distribution in the inner refractory lining.

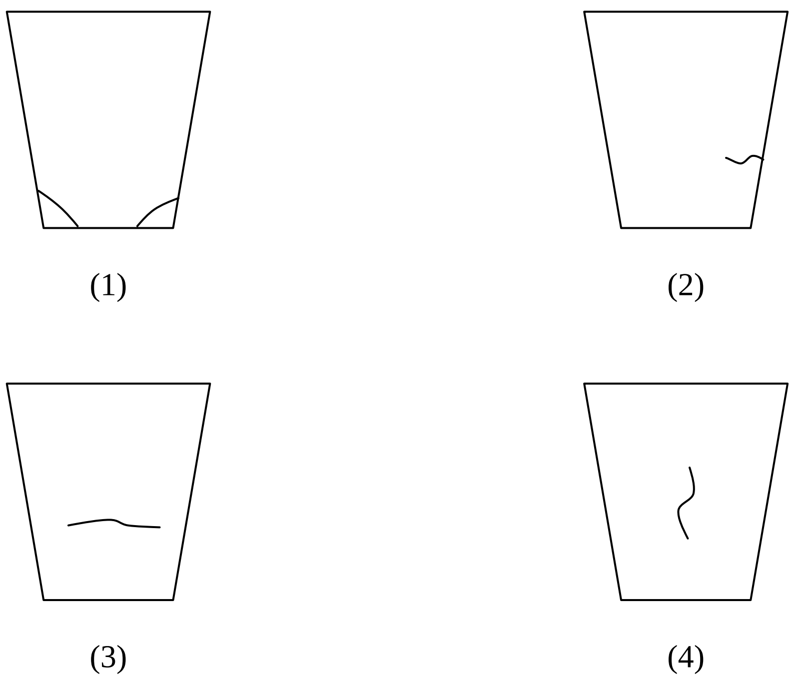


Figure 12. Possible failure modes due to the stress in the inner refractory lining. (1). Pinch spalling at the brick corners or spalling of the entire hot face. (2). Cracking parallel to the hot face from the interface. (3). Cracking parallel to the hot face in the interior of the brick. (4).Radial cracks in the interior of the brick.

Table 1. Temperature dependent properties of alumina used in the model

Temperature (^{o}C)	**Thermal conductivity (W/m K)**	**Specific heat (J/g K)**
23	**9.34**	**778**
100	**9.28**	**916**
200	**8.29**	**1010**
300	**7.55**	**1080**
400	**6.75**	**1130**
500	**5.81**	**1170**
600	**4.37**	**1210**
700	**4.65**	**1220**
800	**4.76**	**1240**
900	**4.86**	**1250**
1000	**5.21**	**1270**