

Title: Refractory for Black Liquor Gasifiers

Type of Report: Quarterly Report

Reporting Period Start Date: April 1, 2005

Reporting Period End Date: June 30, 2005

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Date Report Issued: July 2005

DOE Award Number: DE-FC26-02NT41491

Name and Address of Submitting Organization:

**Curators of the University of Missouri on behalf of University
of Missouri-Rolla**

Sponsored Programs

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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, ZrO₂ 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 °C.

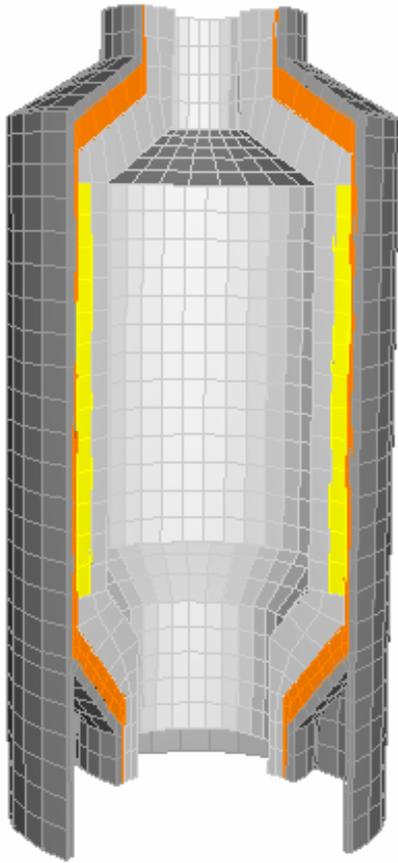


Figure 1 Schematic construction of a typical high temperature gasifier

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 °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 (H₂), carbon dioxide (CO₂), methane (CH₄), nitrogen (N₂), water vapor (H₂O) and hydrogen sulfide (H₂S). The smelt drops are mainly sodium carbonate (Na₂CO₃) and sodium sulfide (Na₂S). 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.

Task 1.4

Refractory materials are being evaluated and modeled to be used in the pulse combustors, shown in Figure 2, that are failing at Big Island and Trenton.



Figure 2 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 3. The delamination eventually would 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 was developed.



Figure 3 Enlargement showing critical delamination failure at 5-6" in depth and accompanying transverse cracking.

Task 2.0

See Appendix A for a complete report on the most recent modeling activities. This work is in addition to the continued refinement of models for both the pulse combustor and the gasifier.

CONCLUSION

Samples provided by in-kind sponsors were tested using cup testing. The best performing materials in the cup testing were fused cast materials. Magnesia brick performed very well and should be moved into industrial trials. The castables cracked during drying and require additional work. New magnesia based castables have been received and are in testing.

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. MorcoCast AZ-10 refractory has been recommended as a replacement of existing materials based on the model and thermo-mechanical properties measured and is currently in industrial trial.

This study presented continuum damage mechanics based analytical model for predicting the failure behavior of refractory lining in cup testing. 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 the cups used 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 – FAILURE ANALYSIS OF A REFRACTORY
CUP UNDER THERMAL LOADING AND CHEMICAL ATTACK
USING CONTINUUM DAMAGE MECHANICS**

FAILURE ANALYSIS OF A REFRACTORY CUP UNDER THERMAL LOADING AND CHEMICAL ATTACK USING CONTINUUM DAMAGE MECHANICS

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ABSTRACT

Refractories are widely used for the linings of furnaces and vessels of the glass-making, steel-making and energy-production industries. The refractory linings are subjected to significant thermal loading and chemical corrosion which lead to spalling and cracking. A continuum damage mechanics based analytical model is developed to study the failure behavior of an alumina refractory exposed to high temperature and corrosive environments. The predicted damage pattern is compared to that observed in brick in a cup test. This work provides a mechanics and material science based method for the failure analysis of refractories. It would serve as a guide in the development of refractories.

INTRODUCTION

Refractories are widely used in the glass-making, steel-making and energy-production industries. However, refractory linings in these applications are usually subjected to high temperature and chemical attack, resulting in volume change and strength degradation which leads to spalling and cracking¹⁻⁴.

Therefore, the study of failure behavior of refractories is very important in the development of refractories. It is very time consuming and expensive to carry out experiments to study the failure behavior of refractories due to the high temperature and corrosion environment. Many studies have been done on the thermomechanical modeling of refractories⁵⁻⁷. Based on the results of the thermomechanical studies, critical regions for the failure of refractories can be identified. However, those studies are still limited to give further understanding of the failure behavior of refractories. Such as how much the material is damaged and when the failure occurs.

In order to understand the failure of refractory materials thoroughly, an extensive study of the failure behavior of refractories under thermal loading and chemical attack is necessary. In this paper, a thermomechanical and continuum damage mechanics based damage model for a refractory cup in a corrosion test will be presented. In addition to the thermal consideration, chemical reaction is also taken into account in the model.

CONTINUUM DAMAGE MECHANICS

Refractories are classified as brittle materials. The failure of refractories due to thermal loading and

corrosion is usually represented by the formation of micro-cracks. Due to the difficulties in describing the evolution of the micro-crack pattern in a failing brittle solid, continuum damage mechanics (CDM) has been used extensively to describe the failure processes of brittle materials such as concrete, rock and glass.

Continuum damage mechanics, regarded as a continuous measurement of internal stiffness degradation of a material, was first introduced by Kachanov⁸ and further developed by Lemaitre⁹, Kachanov¹⁰, and Chaboche¹¹. A scalar variable, D , between 0 and 1 is used to describe the damage. The constitutive law for a damaged material is derived by using the effective stress. The damage variable is described in terms of stiffnesses as

$$D = 1 - \frac{\tilde{E}}{E} \quad (1)$$

where \tilde{E} is the effective elastic modulus of the material, and E is the elastic modulus of the undamaged material. The effective stress in a damaged material under uniaxial load can be expressed as:

$$\tilde{\sigma} = \frac{\sigma}{1 - D} \quad (2)$$

where σ is the normal stress.

Hillerborg, et al.¹² developed a fictitious-crack model to explain both the growth of existing cracks and the formation of new cracks in concrete based on plasticity theory. The formation and propagation of cracks was assumed to start when the tensile stress reaches a critical value. Lubliner, et al.¹³ developed a plastic-damage model to govern the non-linear failure behavior of concrete, in both tension and compression. The model was further developed by Lee and Fenves¹⁴. In this model, isotropic damage variables were used to represent the degradation of elastic stiffness. Tensile and compressive damages were used to describe the failure behavior of the concrete. The effective stress was related to the damaged elastic stiffness and the elastic strain. The plastic strain rate was evaluated by a flow rule, using a scalar plastic potential function.

Saetta, et al.¹⁵ studied the mechanical behavior of concrete under physical-chemical attacks by using a

coupled mechanical and chemical damage model. The mechanical damage variable was defined as the ratio between the area occupied by the voids and the overall section area. The chemical damage was defined as a function of relative residual strength of the material achieved when the chemical reaction is completely developed and the ratio between the actual concentration and the reference concentration of the pollutant. The coupled damage was introduced by combining the mechanical and chemical damage.

Liang¹⁶ developed an inelastic-damage model for a cylindrical refractory lining under thermal loading and chemical attack. The total strain of the lining was defined as the sum of the mechanical strain, thermal strain and reactive strain. The chemical reaction of refractory material was expressed by the reactive strain which is a function of temperature and time. Two damage variables, tensile and compressive damages, were defined to be functions of inelastic strains and temperature. The comparison of the predicted damage patterns and observed damage patterns in a brick from an oxy-fuel glass tank was encouraging.

DAMAGE MODEL FOR REFRACTORY CUP

A preliminary study has been done on the corrosion test of a refractory cup, as shown in Fig. 1. The refractory cup was set in a box furnace flooded with Argon gas. 50 g black liquor smelt was put into the cup. The temperature in the furnace was increased from room temperature to 1000 °C with a heating rate of 1°C/min and then the temperature was held constant for 240 hours. Then the furnace was cooled down to room temperature at a cooling rate of 1 °C/min. After the test, the refractory cup was cut into two parts for the corrosion and failure analysis.



Fig. 1: A refractory cup in corrosion test.

The idealized geometry of the refractory cup used in the model is shown in Fig.2. The outer radius of the refractory cup is 57 mm, the inner radius of the cup is 19 mm, the thickness of the cup is 76 mm and the depth of hole is 38 mm.

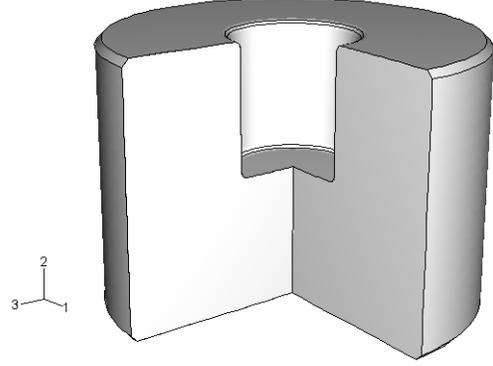


Fig. 2: A cut-away view of the refractory cup used in the model.

Constitutive Relations

In modeling the cracking behavior of the refractory material, the refractory is modelled as an isotropic elastic material. After including the chemical expansion in the stress-strain relations for the refractory, the elastic constitutive relations for the refractory material become

$$\varepsilon_{ij} = \frac{(1+\nu)}{\tilde{E}} \left(\sigma_{ij} - \frac{\nu}{1+\nu} S_{kk} \delta_{ij} \right) + \alpha T \delta_{ij} + \varepsilon^r \delta_{ij} \quad (3)$$

where σ_{ij} and ε_{ij} are the standard stress and strain tensors, ν is the Poisson's ratio, α is the coefficient of thermal expansion, T is the temperature, ε^r is the chemical expansion strain, and δ_{ij} is the Kronecker delta.

The chemical reaction of refractory material is controlled by temperature, time and the depth of penetration. Reactive strain is used to describe the chemical reaction as a function of the temperature, T , time, t , and penetration depth, d .

$$\varepsilon^r = F(T, t, d) \quad (4)$$

Damage Model

Since the failure behavior of a refractory material under tension and compression is different, two damage variables, D_t and D_c , are used to describe the tensile and compressive damages of the refractory. The damage components due to normal principal stresses are assumed to follow a simple linear damage evolution law in which damage is linearly related to the corresponding tensile and compressive principal stress components (σ_i) in a certain stress range:

$$D_i = 0, \quad \text{if } \sigma_i \leq \sigma_{threshold}$$

$$D_i = \frac{\sigma_i - \sigma_{threshold}}{\sigma_{crit} - \sigma_{threshold}}, \text{ if } \sigma_{threshold} < \sigma_i < \sigma_{crit} \quad (5)$$

$$D_i = 1, \quad \text{if } \sigma_i \geq \sigma_{crit}$$

where $i = 1, 2$ which represent tensile and compressive, respectively.

The material degradation is modeled by loss of stiffness as

$$\tilde{E} = (1 - D)E \quad (6)$$

where the total damage, D , is the combination of the tensile and compressive damages.

$$D = 1 - (1 - D_t) \cdot (1 - D_c) \quad (7)$$

COMPUTATIONAL MODEL

A 2-D axisymmetric coupled temperature-displacement finite element model is used to simulate the refractory cup under thermal loading and chemical attack. Commercial finite element package ABAQUS¹⁷ is used for the modeling. A FORTRAN language programmed user material subroutine UMAT¹⁷ is developed and implemented to interface with the main ABAQUS code to simulate the constitutive and damage behavior of the refractory using the approach described earlier.

Due to the unavailability of property data for the tested material, the properties of an alumina refractory material are employed in this model. Some temperature dependent properties of the refractory are given in Table 1. Other properties of the refractory are described below. $E = 103$ GPa at 23 °C and $E = 77$ GPa at 1000 °C, the Young's modulus at other temperatures will be linearly interpolated based on the above two values. The following properties of the refractory are at room temperature: $\rho = 3480$ kg/m³, $\alpha = 8.7 \times 10^{-6}$ /K and $\nu = 0.24$.

Compressive and tensile strengths of alumina refractories at ambient temperature can reach about 3000 MPa and about 200 MPa, respectively. However, it is well known that the strength of refractory materials would be decreased dramatically when exposed to high temperature and chemical corrosion environments. Due to the paucity of knowledge on the strength of refractories under such environments, the threshold compressive and tensile strengths are assumed to be 50 MPa and 10 MPa in the model, respectively. The critical compressive and tensile strengths are assumed to be 300 MPa and 100 MPa as the damage criterion of the refractory material, respectively.

Table 1. Temperature dependent properties.

Temperature (°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

The chemical reaction is taken to be linearly related to all the factors mentioned earlier due to the unavailable experimental data. Reaction is also assumed to occur only at temperatures above 800 °C. The chemical expansion rate is assumed to be 0.006/hour. The depth of the penetration is limited to maximum of 5 mm. The penetration rate is assumed to be 0.05 mm per hour.

RESULTS AND DISCUSSION

In this section, the CDM constitutive model and finite element method described above are employed to predict the damage pattern and growth for the refractory cup in the corrosion test.

Fig. 3 is a picture of the cross section of the refractory cup after the corrosion test. The refractory material reacted with the smelt. A thin layer of reaction zone is created behind the surface of the hole. The volume of the reaction zone increased. Spalling is observed on the reaction surface and cracks are observed starting from the top edge of the hole and directly behind the reaction zone.

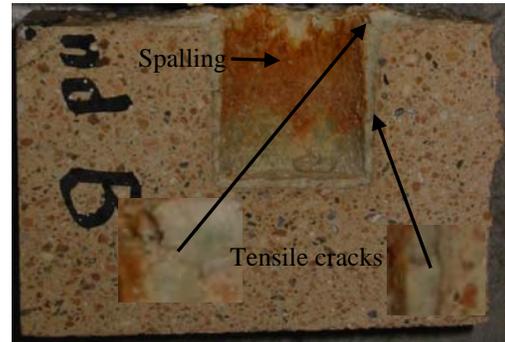


Fig. 3: Cross section of the refractory cup after testing.

Fig. 4 shows the reactive strain in the refractory cup after the test. The curve in the plot is the reactive strain

along the dotted line in the contour pattern. The depth of the reaction zone is about 5 mm from the reaction surface. Reactive strain is the highest on the surface and reduces to zero at the end of the reaction zone. Compared with the picture in Fig. 3, the results shown in Fig. 4 describe the corrosion of the refractory cup very well.

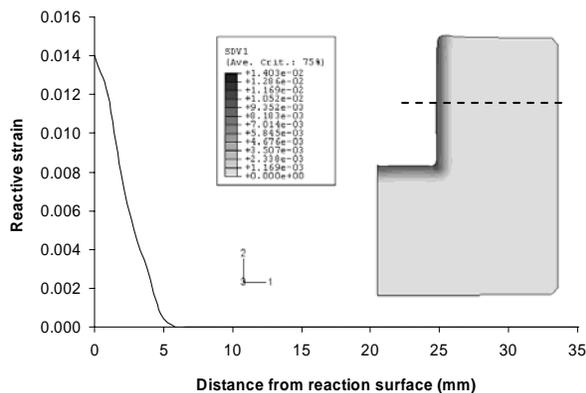


Fig. 4: Reactive strain pattern and numerical result.

Fig. 5 shows the predicted tensile damage in the refractory cup after the corrosion test. Highest tensile damage occurs from the top edge of the hole toward the inside of the cup and then stays in the region right behind the reaction. This result means that the tensile cracks would be developed from the top edge of the hold and behind the reaction zone. Cracks observed in the tested refractory cup shown in Fig. 4 exactly lie on the predicted damaged regions. So the model could be verified based on this.

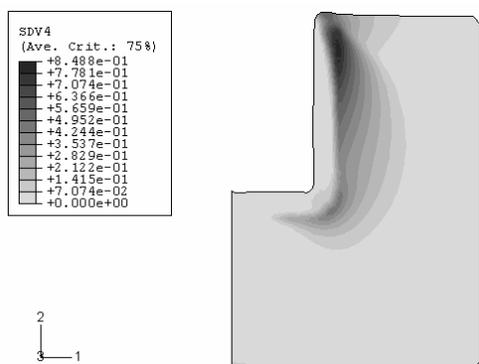


Fig. 5: Predicted tensile damage pattern.

Fig. 6 shows the predicted compressive damage in the refractory cup. Highest compressive damage occurs on the reaction surface, which means the spalling could occur on the surface of the hole. This phenomenon is also observed in the cup after the test, as shown in Fig.3.

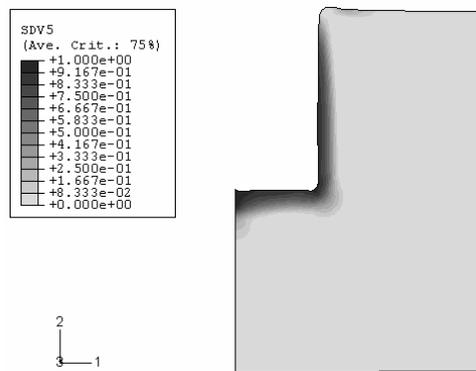


Fig. 6: Predicted compressive damage pattern.

Fig. 7 gives the numerical results of the damage in the cup. The curves in the plot are the damage along the dotted line in Fig. 3. Compressive damage starts from the reaction surface and ends at a depth about 4 mm away from the surface. The maximum compressive damage, which is about 0.85, is on the surface. Tensile damage starts about 2.5 mm away from the reaction surface and ends about 20 mm away from the reaction surface. The maximum tensile damage, which is about 0.7, is right behind the reaction zone. The total damage is dominated by the compressive damage in the reaction zone and by the tensile damage in the remainder of the refractory cup.

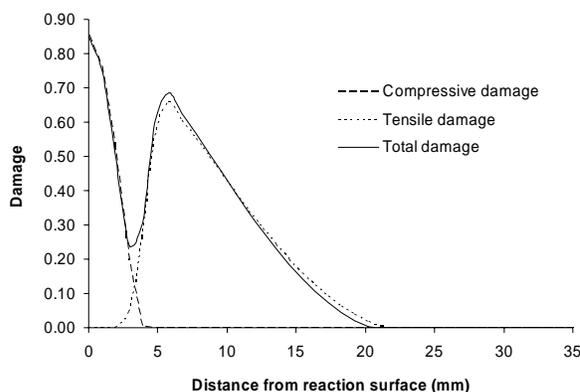


Fig. 7: Through thickness damages.

Fig. 8 shows the history of the maximum reactive strain. The reaction starts after about 10 hours during heating when the temperature is above 800 °C. Then the reactive strain increases linearly until the temperature is lower than 800 °C during cooling. The history of the maximum damage is shown in Fig. 9. However, the growth of damage shows nonlinear behavior due to the degradation of the material stiffness. For the case studied, compressive damage starts after about 35 hours of the test and reaches steady state after about 180 hours. The tensile damage starts

after the occurrence of the compressive damage. The tensile damage is always less than the compressive damage at the same moment. As a result, the maximum total damage is controlled by the maximum compressive damage.

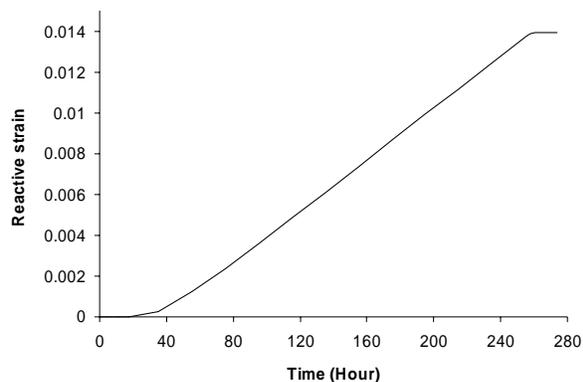


Fig. 8: History of the reactive strain.

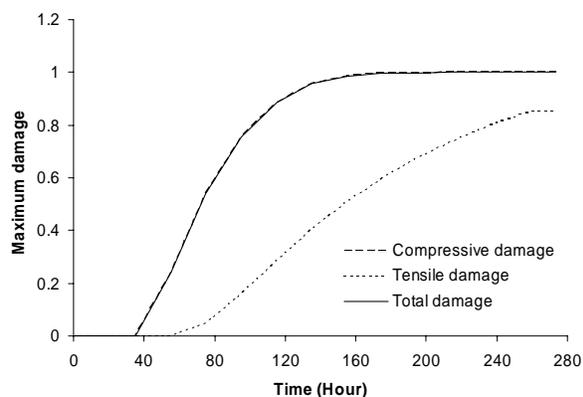


Fig. 9: History of the damages.

CONCLUSIONS

This study presented a continuum damage mechanics based analytical model for predicting the failure behavior of refractory cup under thermal loading and chemical attack. The damage model also accounts for the chemical reaction in addition to mechanical and thermal expansion. Compressive and tensile damages are used to describe the failure behavior of refractory under compression and tension. This work provides a mechanics and material science based method for the failure analysis of refractories. A comparison of predicted damage patterns with the observed damage patterns in refractory cup indicates this model may be appropriate to evaluate the failure behavior of refractory linings.

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