

REFRACTORIES FOR BLACK LIQUOR GASIFICATION

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Abstract: *Improved alkali resistant refractories are needed for biomass and black liquor gasification (BBLG). One particularly harsh application is linings for gasifiers used in the treatment of black liquor (BL). Black liquor is a water solution of the non-cellulose portion of the wood (mainly lignin) and the spent pulping chemicals (Na_2CO_3 , K_2CO_3 , and Na_2S). Development of new refractory materials for the black liquor gasification (BLG) application is a critical issue for implementation of this technology. FactSage® thermodynamic software was used to analyze the phases present in BL smelt and to predict the interaction of BL smelt with different refractory compounds. The modeling included prediction of the phases formed under the operating conditions of high temperature black liquor gasification (BLG) process. At the operating temperature of the BLG, FactSage® predicted that the water would evaporate from the BL and that the organic portion of BL would combust, leaving a black liquor smelt composed of sodium carbonate (70-75%), potassium carbonate (2-5%), and sodium sulfide (20-25%). Exposure of aluminosilicates to this smelt leads to significant corrosion due to formation of expansive phases with subsequent cracking and spalling. Oxides (ZrO_2 , CeO_2 , La_2O_3 , Y_2O_3 , Li_2O , MgO and CaO) were determined to be resistant to black liquor smelt but non-oxides (SiC and Si_3N_4) would oxidize and dissolve in the smelt. The other candidates such as MgAl_2O_4 and BaAl_2O_4 were resistant to sodium carbonate but not to potassium carbonate. LiAlO_2 was stable with both sodium carbonate and potassium carbonate. Candidate materials selected on the basis of the thermodynamic calculations are being tested by sessile drop test for corrosion resistance to molten black liquor smelt. Sessile drop testing has confirmed the thermodynamic predictions for Al_2O_3 , CeO_2 , MgO and CaO . Sessile drop testing showed that the thermodynamic predictions were incorrect for ZrO_2 .*

Keywords: *Black Liquor Gasification, Aluminosilicate, Oxide and Non-oxide Refractories.*

1. INTRODUCTION

Black liquor (BL) is a by-product of the papermaking process. BL is an aqueous solution containing waste organic material which is mainly lignin as well as the spent pulping chemicals which are primarily sodium carbonate and sodium sulfate [1]. Chemical energy can be recovered from BL by burning it as a liquid fuel in a boiler or gasifier. BL is expected to become an increasingly important resource for electric power generation [1, 2]. Recovery boilers have been used successfully by the pulp and paper industry for many years, but they have a number of shortcomings including high capital expense, low efficiency, and potential of explosion [1, 3-4]. Black Liquor Gasification (BLG) is recognized as a technology that can replace fossil fuels to produce electricity, and widely viewed as the technology that will replace the recovery boiler. Similar gasification processes

are used to convert low-cost solids such as biomass or waste liquids like BL into clean-burning gases [5]. The fundamentals of the gasification process have been reviewed elsewhere [6]. Several distinct BLG processes have been proposed, but only two of them have had satisfactory results in plant trials [7]. The first process is the low temperature process (600-700°C) developed by Manufacturing Technology Conversion International, Inc (MTCI) [8]. The other is the high temperature process (900-1000°C) developed by Chemrec [8]. The schematic configuration of a high temperature BBLG reformer run under atmospheric pressure is presented in Fig. 1. Both the high temperature and low temperature processes currently use air for combustion, but when oxygen is used in place of air, substantially higher gasification temperatures up to 1400°C, are possible. Higher temperatures and pressures result in higher overall process efficiencies [9]. The commercial

success of BBLG technology requires the development of improved refractory materials for the protective lining of the gasifier. To date, aluminosilicate or fused cast alumina based materials have been used for this. Both thermodynamic calculations and experience show that these aluminosilicates and fused cast aluminas are not sufficiently resistant to the alkali containing atmospheres for extended operation of gasifiers. The objective of research, currently in progress at University of Missouri - Rolla, is the development of cost-effective materials with improved performance in gasifier environments with primary research on high temperature black liquor gasification, as it is the most severe in regard to refractory stability.

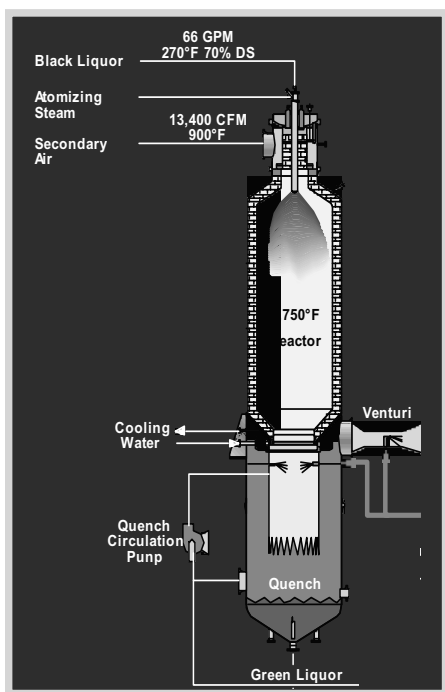


Fig. 1. High Temperature Low Pressure Black Liquor Gasification Refiner [1].

2. THERMODYNAMICS OF INTERACTION OF CANDIDATE REFRACTORIES WITH BLACK LIQUOR SMELT

FactSage® 5.1 is a thermodynamic modeling package that contains a database of thermodynamic properties and performs thermodynamic equilibrium calculation based on Gibbs free energy minimization. As with all thermodynamic models, FactSage® predicts equilibrium and does not take into account

kinetic or microstructural factors. Experiments are necessary to verify the predictions.

2.1. Corroding Smelt

The typical composition of black liquor introduced into the BLG reformer is available in literature [10]. The reported composition was in the form of elemental analysis, but FactSage® can convert this into an equilibrium compound composition (Table 1). The phase/compound composition was modeled at 950°C at a pressure of 1atm.

Table 1. Compound composition of black liquor at T=950°C (wt. %).

Constituents	Na ₂ CO ₃	Na ₂ S	K ₂ CO ₃	C
%	50-55	25-30	1-3	15-20

After the free carbon in black liquor is combusted, the composition of the resulting smelt that would then contact the refractory lining is 70-75% Na₂CO₃ (T_m=858°C), 20-25% Na₂S (T_m=1172°C) and 2-5% K₂CO₃ (T_m=901°C). Formation of sodium sulfate (Na₂SO₄) was predicted by FactSage® when the amount of oxygen introduced to the gasifier was more than the stoichiometric amount necessary to burn the organic portion of black liquor.

FactSage® predicted that about three quarters of the black liquor smelt was composed of sodium carbonate, which would be liquid at the operating temperature of high temperature BL gasifiers. Consequently, the selection of refractory materials for this application must be based upon resistance to molten sodium carbonate; although, interactions with Na₂S and K₂CO₃ should not be ignored. Na₂S should not be as corrosive as the two other components, because it is in solid state at the operating temperature of the BL gasifier. In contrast, Na₂CO₃ and K₂CO₃ are present as a liquid solution that coats the inner surface of the gasifier. No evidence of solubility of Na₂S in liquid was found in available phase diagrams or predicted by FactSage®. Na₂SO₄ melts at 884°C, which was below the operating temperature of BLG; therefore, sodium sulfate should be considered as a liquid part of the smelt in contact with refractory if the condition required for its formation is provided. The analysis that follows has considered only the presence of solid Na₂S.

2.2. Interaction of Aluminosilicates with BL

FactSage® predicts that the main compounds

present in aluminosilicate refractories are corundum, meta-stable aluminosilicate compounds (andalusite, silimanite or kyanite) and mullite. Because the aluminosilicate phases are meta-stable, at 950°C, only the stable compounds (e.g., mullite and alumina) were modeled in this analysis. If these refractory compounds were exposed to black liquor smelt at 950°C and $P_{tot}=1\text{atm}$, the reaction products for corundum would be mainly β'' -alumina ($\text{Na}_2\text{O}\cdot 12\text{Al}_2\text{O}_3$) (~75%) and β -alumina (10%). The reaction products for mullite would be nepheline (~50%) and corundum (~40%). The reaction products are summarized in Table 2. The atmosphere of BLG under these conditions would be mainly composed of CO and H_2 .

To summarize the information presented in Table II, it was predicted that none of the aluminosilicate refractory compounds would be resistant to either Na_2CO_3 or BL smelt at 950°C, the temperature of gasification in high temperature processes. Products formed by the reaction of BL smelt with corundum have a substantially larger volume than the original refractory. For example, mullite refractory exposed to BL at 1000°C, showed about 30% volume expansion and alumina refractory, 13%. Up to 0.7% expansion is reported for α -alumina + β -alumina under the same conditions [11]. Volume expansion promotes crack formation and spalling of the refractory exposing the underlying materials allowing for further attack. In the case of mullite, thermodynamic equilibrium calculations predicted that nepheline, albite, leucite and corundum would form. All of these phases were in the solid state under BLG operating conditions. By the same mechanism as described for corundum, large volume increases accompanied by formation of new phases such as nepheline (about 30%) would be enough to nucleate and propagate cracks in the material structure, decreasing the

lining life due to spallation. The corundum, formed as the reaction product of mullite with BL, would be attacked again by black liquor smelt and corroded by the same mechanism. The vaporization of refractory constituents was negligible under these conditions.

2.3. Interaction of Simple Oxide and Non-Oxide Refractories with Black Liquor

Thermodynamic studies (FactSage®) were performed to predict the behavior of some simple refractory oxides and complex oxides, as well as non-oxides as new refractory materials, against Na_2O , Na_2CO_3 , K_2O , K_2CO_3 , the main components of BL. Simple oxides selected as candidates for use in high temperature BL gasifier are Al_2O_3 , SiO_2 , MgO , CaO , ZrO_2 , Y_2O_3 , La_2O_3 , CeO_2 , Li_2O and BaO . Ellingham Diagrams were plotted (Fig. 2) to check the potential of sodium or potassium metal vapor to reduce the oxide candidates because the existence of alkaline metal vapor in the gasifier atmosphere was probable. If the free energy of formation of each candidate was less than that for sodium or potassium oxide, that oxide was more stable than sodium (potassium) oxide and sodium (potassium) metal vapor was not able to reduce it. Total pressure (P_1) selected to plot the diagram was 1 atmosphere. Based on the diagram, all of the candidate simple oxides were resistant to sodium metal vapor or potassium at $P_i=1\text{atm}$ and $T=300\text{-}1100^\circ\text{C}$, because they all had free Gibbs energy of formation less than that of sodium or potassium oxide. But this evidence was not sufficient to evaluate the material due to lack of information about new compounds that could be formed. For example, alumina or silica was not reduced by sodium oxide but they were known to form new compounds which may lead to failure. FactSage® was used to predict the behavior of candidate refractory simple oxides against the main components of BL at $T=900\text{-}1000^\circ\text{C}$.

Table 2. Products of the reaction between black liquor smelt and aluminosilicate refractories at 950°C

Reaction Products Refractory Compounds	Corundum	β'' -alumina	β -alumina	K- β'' -alumina	Nepheline	Albite	Leucite
Corundum		×	×	×			
Mullite	×				×	×	×

(×): the phase was formed

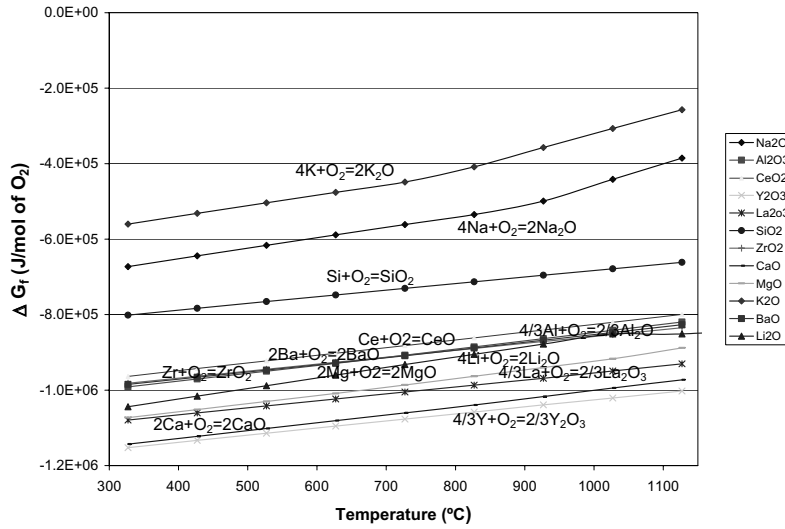


Fig. 2. Ellingham Diagram of candidate simple oxides against sodium oxide.

Table 3. Interaction of refractory simple oxides and non-oxide with BBLG components at T=900-1000°C.

Refractory	Al ₂ O ₃	SiO ₂	MgO	CaO	ZrO ₂	Y ₂ O ₃	La ₂ O ₃	CeO ₂	Li ₂ O	BaO	SiC	Si ₃ N ₄
Na ₂ O	×	×								×	×	×
Na ₂ CO ₃	×	×								×	×	×
K ₂ O	×	×								×	×	×
K ₂ CO ₃	×	×								×	×	×

(×): Reaction occurs

The results are listed in Table 3 which shows that all candidates except Al₂O₃, SiO₂ and BaO were resistant against sodium, potassium oxide and carbonate. Moreover, it is observed that based on FactSage® thermodynamic data base, SiC and Si₃N₄, two non-oxide refractory candidates for BL gasifier applications, were not resistant to BL constituents. SiC is converted to compounds such as Na₂SiO₃, Na₆Si₂O₇, K₂SiO₃ and K₂Si₂O₅;

where some of them were in liquid state at operating temperature of BL gasifier and would dissolve into the smelt. Hydration of MgO and CaO was of high concern especially when the operating conditions of the gasifier included water vapor. The hydration behavior of these oxides as a function of temperature at P_{H₂O} = 1, 20 and 100atm was predict by FactSage®. The results of this study are listed in Fig. 3.

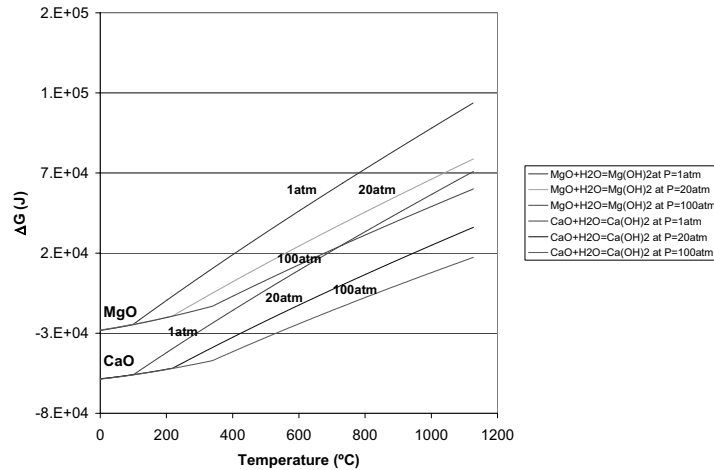


Fig. 3. Hydration behavior of Magnesia.

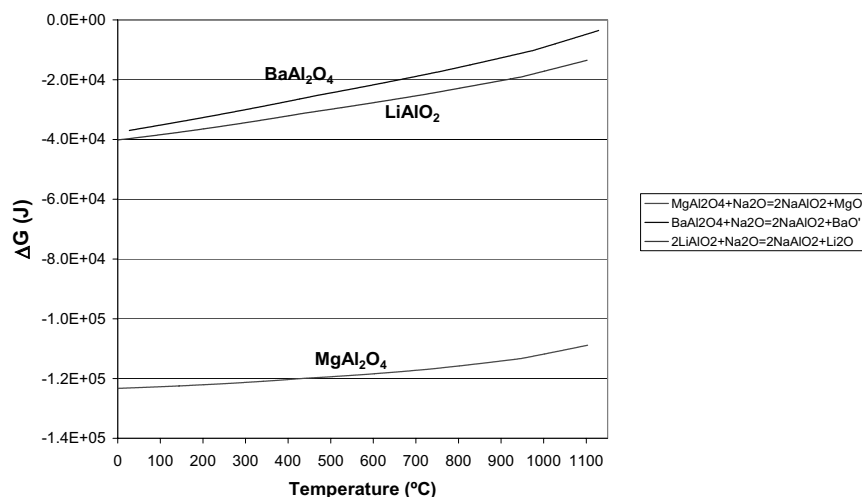
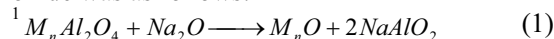


Fig. 4. ΔG for the reaction between three candidate aluminates with sodium oxide.

A temperature gradient exists across the refractory lining from 950°C; the hydration depends on penetration of water vapor into the depth of the refractory lining through porosity, cracks or joints. Fig. 3 shows that even at $P_{H_2O} = 100\text{atm}$, magnesia doesn't hydrate until the temperature was lower than 470°C but under the same conditions, calcia hydrates at about 950°C. Therefore, magnesia would be applicable to BLG but calcia would exhibit the problem of hydration, because diffusion of water vapor into the refractory lining to reach the limiting hydration temperature was much more probable for calcia than magnesia.

2.4. Interaction of Aluminates with Black Liquor

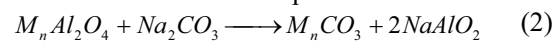
Behavior of aluminates in alkaline atmospheres was of high importance. The aluminate candidates for this application were $MgAl_2O_4$, $BaAl_2O_4$, $LiAlO_2$ and the equation for the main corrosion reaction of these oxides with sodium oxide was as follows:



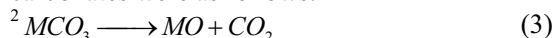
The change in the free Gibbs Energy (ΔG) of reaction versus temperature is plotted and presented in Fig. 4. The data for this diagram was provided from the FactSage® data base. None of the aluminates were resistant to sodium oxide in the range of temperature 0-1100°C, because the ΔG of reaction with sodium oxide for all of them was negative. It could be

¹ M: Mg, Ba, Li
 $n_{(Mg, Ba)}=2, n_{(Li)}=1$

concluded that barium aluminate was the most resistant and magnesium aluminate was the least resistant. Because sodium was in the form of sodium carbonate in BL and in the working conditions of high temperature gasifiers, prediction of the behavior of these aluminates to sodium carbonate was important.



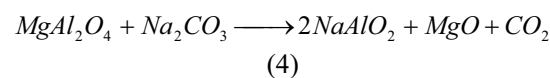
The range of temperature over which the carbonates were stable should be known. The reaction equations for stability of the considered carbonates were as follows:



The reaction equations of candidate aluminates with sodium carbonate are as follows:

ΔG for dissociation of carbonates as a function of temperature in the range of 300-1100°C based on FactSage® thermodynamic data base is presented in Fig. 5.

All considered carbonates as reaction products of aluminates with sodium carbonate are stable except magnesium carbonate which would dissociate at 400°C under $P_t = 1\text{atm}$. The same happened to calcium carbonate but at higher temperature, 850°C. Therefore from $T = 400^\circ\text{C}$, the equation for the reaction of magnesium aluminate with sodium carbonate should change to the reaction as follows:



² M: Mg, Ba, Ca, Li, Na, K
 $n_{(Mg, Ba, Ca)}=2, n_{(Li, Na, K)}=1$

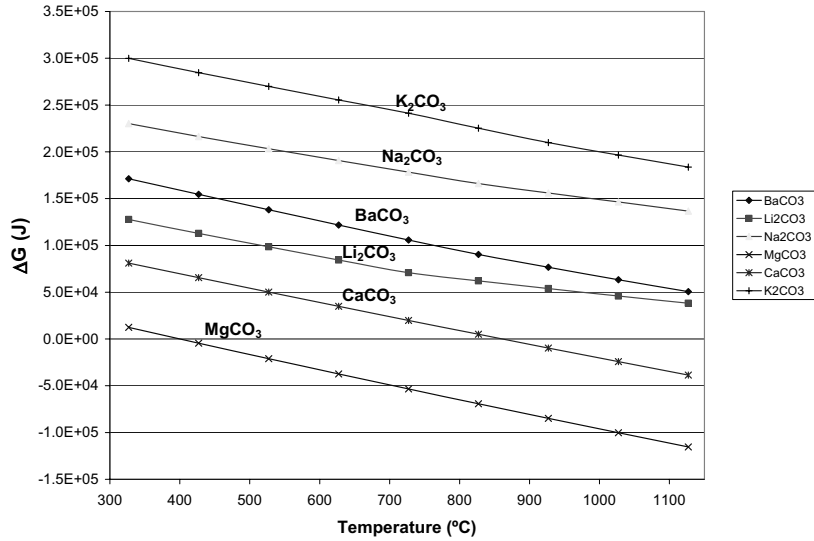


Fig. 5. ΔG of dissociation of carbonates versus temperature.

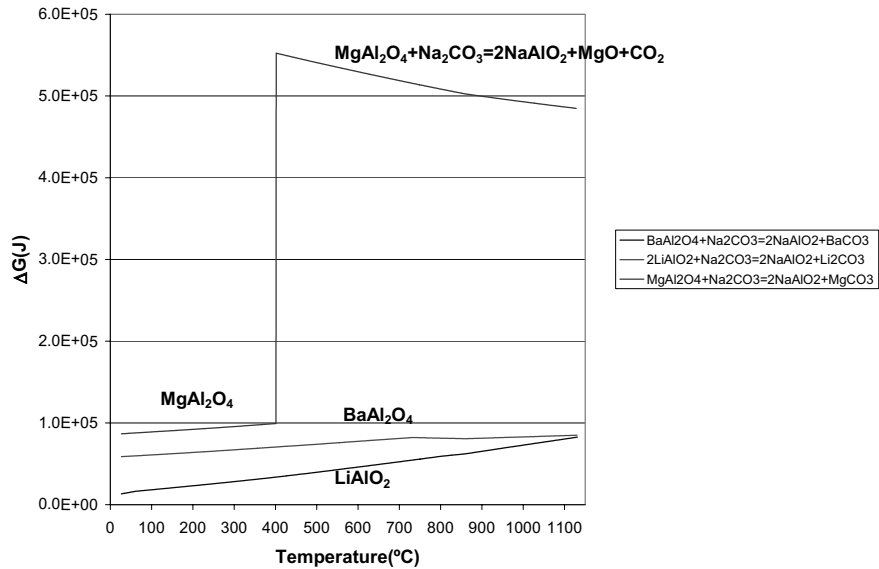


Fig. 6. ΔG of reactions between aluminates and sodium carbonate.

It was observed that sodium and potassium were in carbonate form and not oxide at the operating temperature of BLG. Following the reactions, thermodynamic stability of aluminates against sodium carbonate can be evaluated based on the FactSage® data base.

Fig. 6 is the result of this modeling in the form of ΔG of reaction versus temperature. Based on this Fig., all candidate aluminates were stable against sodium carbonate and among them magnesium aluminate spinel was the most resistant, because it had the highest change of free Gibbs energy from the reaction with sodium

carbonate. It was hard to decide whether to propose these aluminates for the lining of high temperature gasifiers because, although they were resistant to sodium carbonate, they were corroded by sodium oxide. Thermodynamic modeling shows that sodium was stable in the form of sodium carbonate and sodium sulfide at the operating conditions of the high temperature BLG but it seemed to be risky to use these refractory materials because the existence of sodium oxide was possible, due to introduction of water vapor into the gasifier or unstable operating conditions.

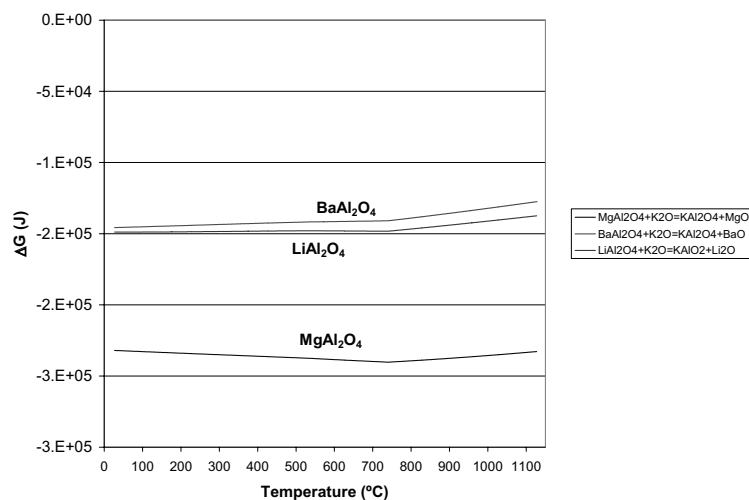


Fig. 7. ΔG of reactions between aluminates and potassium oxide.

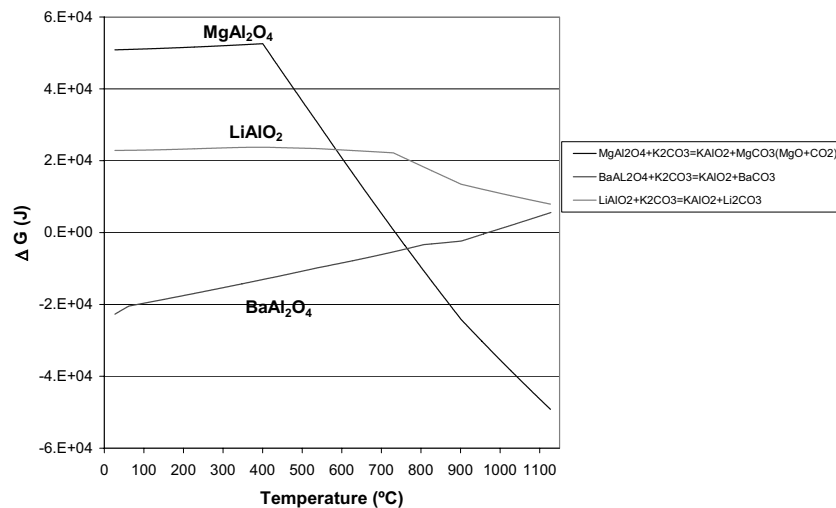
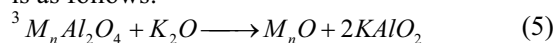


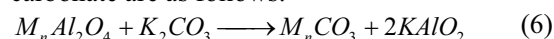
Fig. 8. ΔG of reactions between aluminates and potassium carbonate.

FactSage® showed that the aluminates were not resistant to potassium containing compounds which were part of BL smelt; therefore, studying the reaction behavior of aluminates with K_2O and K_2CO_3 was considered important. The main reaction of the aluminates with potassium oxide is as follows:



Free Gibbs energy change of the reaction as a function of temperature is plotted in Fig. 7. It was observed that none of the aluminates

resisted potassium oxide and, among them, barium aluminate was the most and magnesium aluminate was the least resistant. Reaction equations of aluminates with potassium carbonate are as follows:



ΔG of reactions between aluminates and potassium carbonate versus temperature are plotted in Fig. 8. Among the three aluminates, only lithium aluminate was resistant to potassium carbonate and the use of barium and magnesium aluminates in exposure to potassium carbonate was not advisable. It can be summarized that all three aluminates were resistant to sodium carbonate, but not sodium

³ M: Mg, Ba, Li
 $n_{(Mg, Ba)}=2, n_{(Li)}=1$

oxide. None of the aluminates were resistant to potassium oxide, but lithium aluminate was resistant to potassium carbonate. Experimental analysis was necessary to verify the result of the thermodynamics. Sessile drop tests were employed to study the wetting behavior of the materials by BL as well as the corrosion resistance.

3. EXPERIMENTAL VERIFICATION OF INTERACTION OF CANDIDATE REFRACTORIES WITH BLACK LIQUOR SMELT

Contact angle of sodium carbonate was measured on high purity high density 2-4 cm by 0.5-1 cm thick pucks of the candidate oxides using a sessile drop furnace. Measurements were made in argon atmosphere at the melting point of sodium carbonate. Fig. 9 is a plot of contact angle between the candidate oxides and sodium carbonate measured to date. Cerium oxide had the highest contact angle (8 degrees), but it was still wet by the sodium carbonate. It was expected that the sodium carbonate would wet all oxide refractories. After the contact angle was measured, the sessile drop furnace was heated to 1000°C and held at temperature for 3 hours to allow reactions to initiate. The sample was cooled, removed and sectioned along the diametric plane using kerosene as a cutting fluid. Half of the sample was used for scanning

electron microscopy with electron dispersive spectrometry to determine reaction depth and half was used to x-ray diffraction to determine reaction products if present. It was not possible to determine the depth of reaction with scanning electron microscopy, as the contrast between the original oxides and the reaction products was not high enough to accurately estimate a reaction depth. In addition, energy dispersive spectrometry could not adequately detect sodium, a relatively light element close to the detection limit of the apparatus. Additional methods are being investigated, including elemental mapping. X-ray diffraction was able to determine the reaction products. The depth of beam penetration was varied by controlling the angle of incidence. A low angle of incidence was used to show that the surface coating was indeed sodium carbonate. This was found to be true for all materials. Increasing the angle of incidence penetrated the surface more showing sodium carbonate, the original oxide and any reaction products. In some cases it was possible to further increase the angle of incidence to show the original oxide below the reaction zone. Fig. 10 shows the formation of reaction products between sodium carbonate and alumina as predicted by Fact Sage. Fig. 11 shows the formation of reaction products between sodium carbonate and zirconia which was not predicted by Fact Sage but predicted by Yamaguchi [12].

Contact Angle between Candidate Materials and Na₂CO₃ at 880°C
(Average of 5-7 measurements, 1 standard deviation error bars)

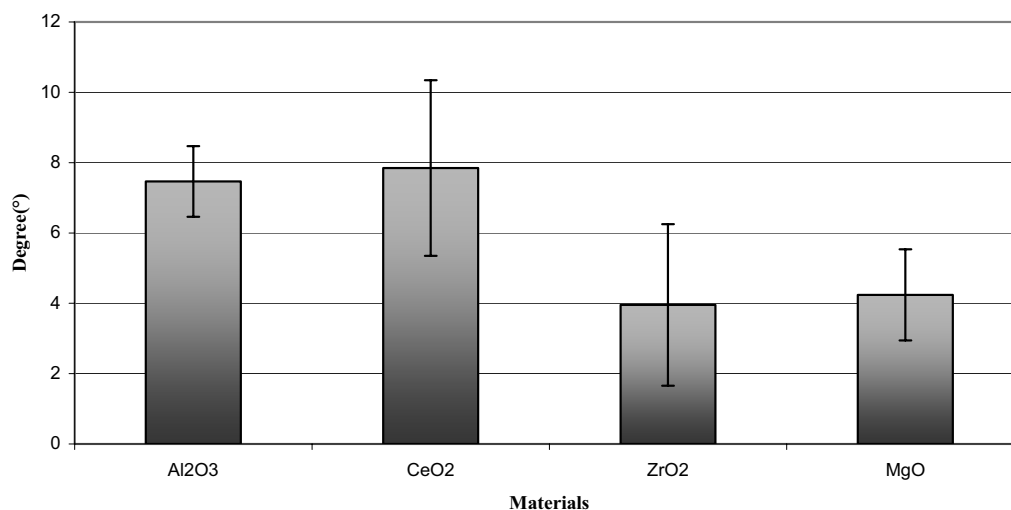


Fig. 9. Contact Angle of Na₂CO₃ on dense candidate oxides.

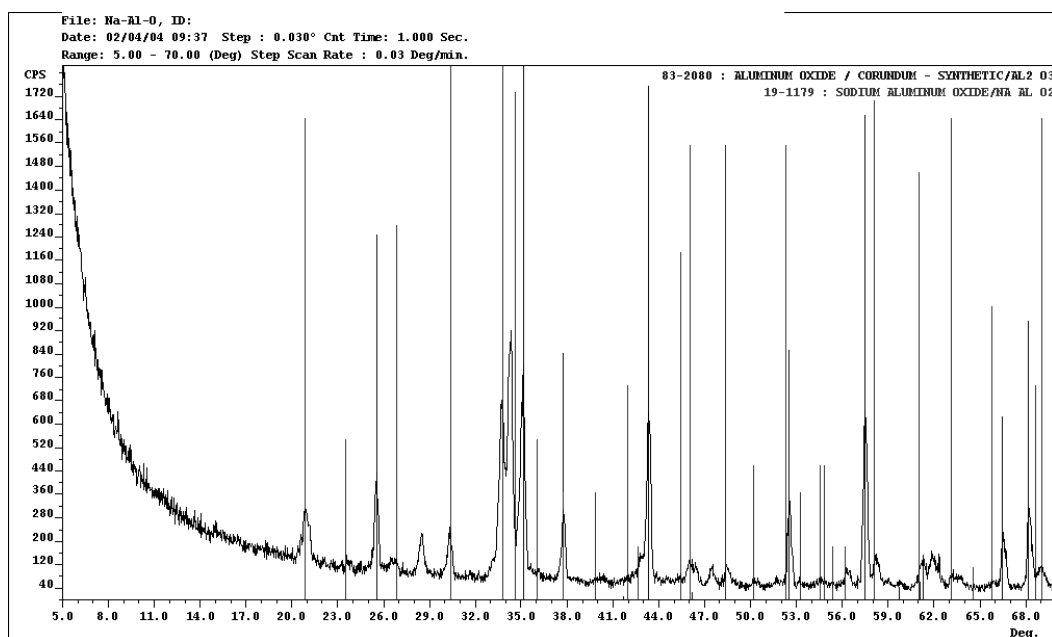


Fig. 10. X-ray diffraction pattern showing reaction product (sodium aluminate) and original corundum.

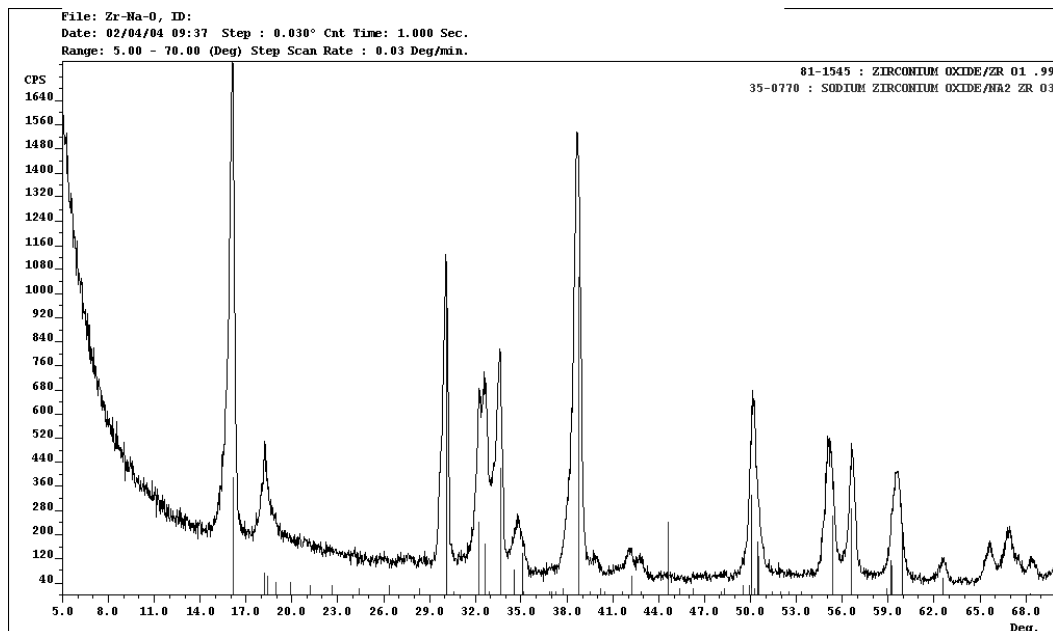


Fig. 11. X-ray diffraction pattern showing reaction product (sodium zirconium oxide) and original zirconia.

Figs. 12 and 13 show the lack of reaction products with magnesia, calcia and ceria as predicted by FactSage®.

4. CONCLUSION

Worldwide growth of black liquor production as a new source of energy and electricity necessitates the development of new refractory materials resistant to the harsh operating

conditions of black liquor gasifiers. These materials would contribute considerably in allowing energy production with this new technology. Thermodynamic analysis based on FactSage® showed that oxides such as magnesia, ceria and zirconia or aluminates such as barium and lithium aluminate may have satisfactory stability against BL but alumina and aluminosilicates would be corroded.

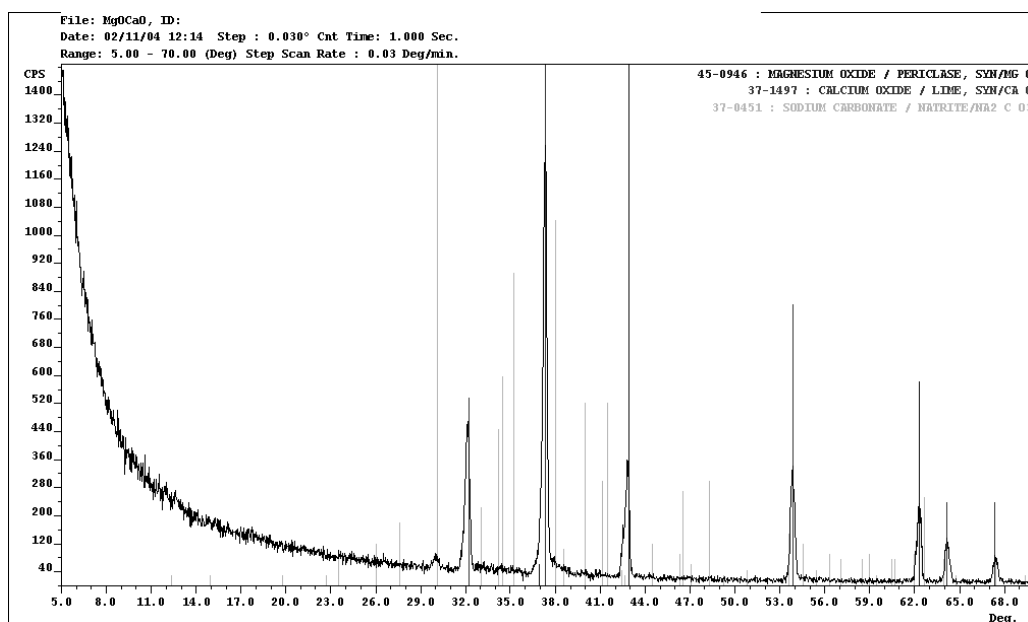


Fig. 12. X-ray diffraction pattern showing lack of reaction product with original magnesia, calcia and Na_2CO_3 .

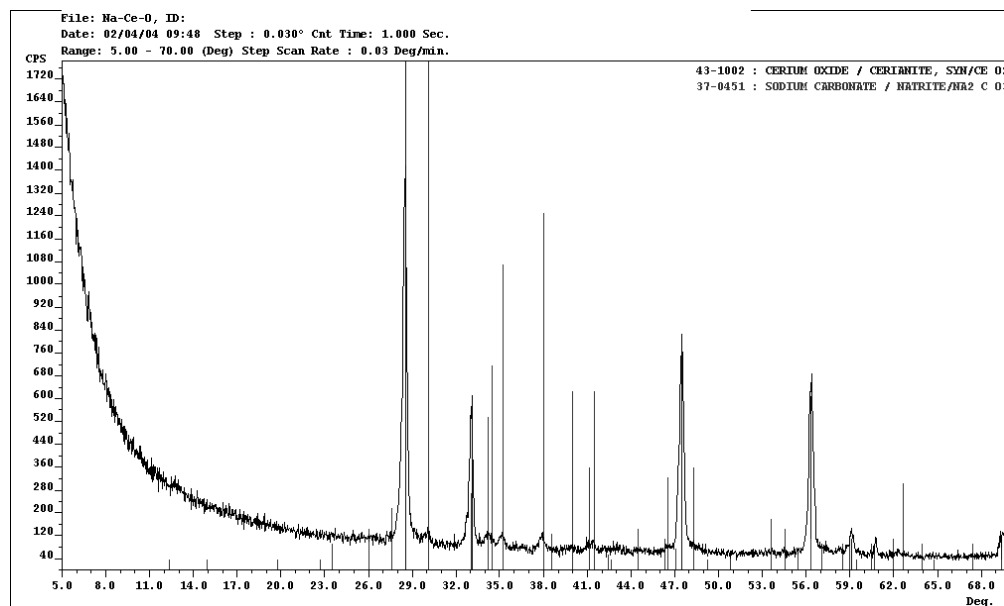


Fig. 13. X-ray diffraction pattern showing lack of reaction product with original ceria and Na_2CO_3 .

All non-oxides investigated were dissolved in BL. Sessile drop testing has confirmed the thermodynamic analysis for the oxides alumina, magnesia, calcia and ceria, but zirconia formed sodium zirconium oxide which was not predicted by FactSage®.

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