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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 materials 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 spinels 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

Worldwide growth of black liquor production as a new source of energy and electricity necessitates the development of new refractory materials resistant to harsh operating conditions of black liquor gasifiers. Black liquor is a by-product of the papermaking process. Black liquor 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 sulfide [1]. Chemical energy can be recovered from black liquor by burning it as a liquid fuel in a boiler or gasifier [1, 2]. Black Liquor Gasification (BLG) is widely viewed as the technology that will replace the recovery boiler in the pulp and paper industry [3]. Similar gasification processes are used to convert low-cost solids such as biomass or waste liquids into clean-burning gases [3]. Combustion of these gases has the potential to partially or fully meet the energy needs for pulp and paper plants, reducing or eliminating dependence on electricity generated commercially by the combustion of fossil fuels [4]. The fundamentals of the gasification process have been reviewed elsewhere [4]. The scope of this project will be on high temperature process (900-1000°C) developed by Chemrec [5]. The operating conditions of the process were studied in Task 1.0 and thermodynamic analysis was performed based upon the results of this study.

Thermodynamics showed that the composition of black liquor smelt that would contact the refractory lining is 70-75% Na_2CO_3 ($T_m=858^\circ\text{C}$), 20-25% Na_2S ($T_m=1172^\circ\text{C}$) and 2-5% K_2CO_3 ($T_m=901^\circ\text{C}$) [6]. To date, aluminosilicate or fused cast alumina-based materials have been used in this application. Both thermodynamic calculations and experience show that these aluminosilicates are not sufficiently resistant to the alkali containing atmospheres for extended operation of gasifiers. Thermodynamic analysis showed that oxides such as magnesia, ceria and zirconia or aluminates such as barium and lithium aluminate may have satisfactory stability against black liquor smelt. Non-oxides such as SiC and Si_3N_4 were dissolved by black liquor smelt and were not candidates for this application. The objective of task 1.2 was to verify the results of thermodynamics by experiments.

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.

FactSage® thermodynamic modeling software can convert the elemental analysis composition of the black liquor to compound composition. This results show that at 950°C, black liquor smelt flowing on the refractory lining installed on the gasifier vessel shell is composed of 70-75% sodium carbonate, 20-25% sodium sulfide and 2-5% potassium carbonate. Sodium and potassium carbonate are molten at 950°C while sodium sulfide is in solid state if it is assumed that there is no solution between sodium sulfide and carbonates. Obviously, the selection of refractory materials for this application should be based upon resistance to molten Na_2CO_3 although Na_2S and K_2CO_3 should not be ignored.

Thermodynamic data shows that none of refractory compounds in the alumino-silicate system are resistant to black liquor. At 950°C, corundum converts to β'' -alumina, β -alumina and K- β -alumina while mullite converts to nepheline, albite, leucite and corundum in contact with Black Liquor. All these phase transformations are associated with large volume expansion. Also thermodynamic data shows that simple oxides including ZrO_2 , CeO_2 , La_2O_3 , Y_2O_3 , Li_2O , MgO and CaO are resistant to black liquor but non-oxides such as SiC and Si_3N_4 are oxidized and dissolved in black liquor. Ellingham diagram presents us with the fact that all candidate refractory simple oxides are resistant to both sodium and potassium metal vapors at operating temperature of BLG and none of them are reduced to metallic form.

The other candidates for BLG application are aluminates including MgAl_2O_4 , BaAl_2O_4 and LiAlO_2 . FactSage database showed that none of the aluminates were resistant to sodium oxide in the range of operating temperature of high temperature black liquor gasifier although all three are resistant to sodium carbonate. They form NaAlO_2 in contact with sodium oxide. It was observed that none of the aluminates were resistant to potassium oxide and potassium carbonate except lithium aluminate which was stable with potassium carbonate. The reaction product of aluminates with potassium oxide or carbonate was KAlO_2 .

EXPERIMENTAL

Sessile drop testing was employed to measure the contact angle between the candidate refractory materials and black liquor components. The thermodynamics of interaction of the materials with black liquor smelt was studied before [6]. The schematic of the equipment used for sessile drop testing is presented in Figure 1. The system was designed for the precise determination of the contact angle of liquid droplets on solid substrates under controlled conditions of temperature and atmosphere. The main features of the system are the sessile drop furnace, the controlled atmosphere and the image acquisition system. The furnace was a horizontal tube furnace, resistant heated with Ni-chrome wire with a high-purity, dense and impermeable mullite reaction tube. Each candidate material substrate was placed on an alumina D-tube which was positioned at the center of the hot zone. The experiments were carried out in argon atmosphere. Sample temperature was controlled to within $\pm 5^\circ\text{C}$ as measured with a K-type thermocouple. An optical-quality, fused quartz window permitted observation of the in-situ sessile drop and video recording of the interface interaction behavior between the substrate and the smelt.

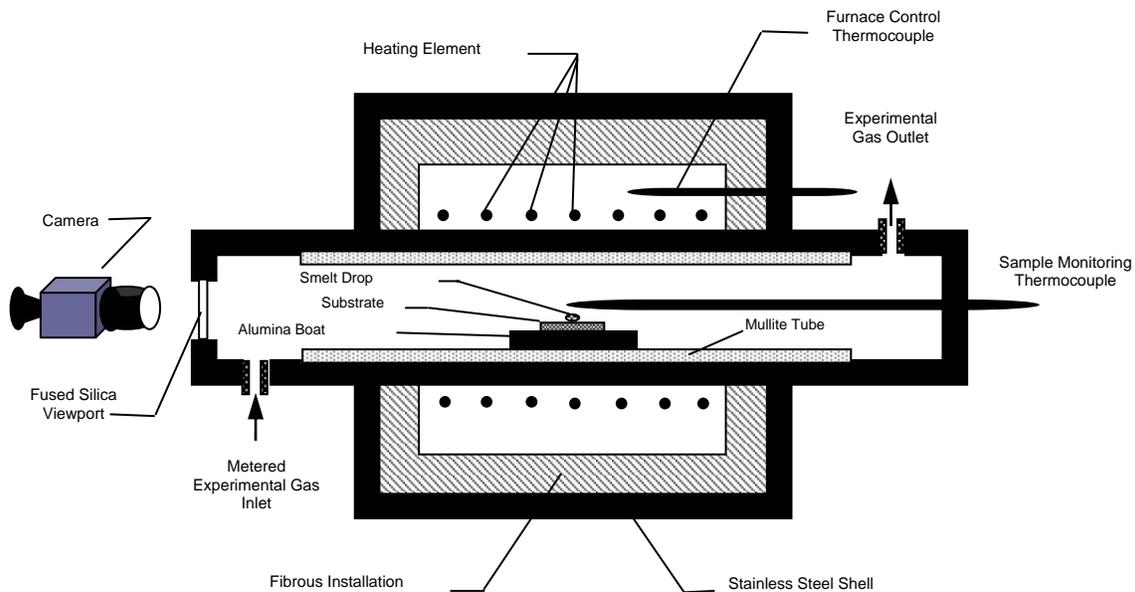


Figure 1: Sessile drop test equipment to measure the contact angle

In sessile drop experiments, smelt powder (0.2-0.3 g), sodium carbonate and potassium carbonate, was formed into 1/4" diameter cylindrical geometry by uniaxial pressing using a 1/4" stainless steel die. The formed smelt powder was placed on the substrate and the liquid drop was formed by heating the drop to 1000°C in 2.5 hours and maintained at 1000°C for 10 hours. Long soaking time was selected to overcome the kinetic barrier and let the sample to react with the smelt if there was no thermodynamic barrier. The image of the sessile drop was recorded by a digital camera and the contact angle was measured at the temperature of complete melting of the drop using enlargement of a photograph extracted from recorded video film of entire test. The average of the 5-7 values was taken as the contact angle.

After cooling from the final sessile drop test temperature (1000°C), the interaction between the solidified smelt and the substrate was examined by thin film x-ray diffraction. If the results of thin film analysis were not satisfactory, the mixture of the powder of each candidate with smelt powder was heated to 1000°C under the same conditions as the sessile drop test. The reaction products were grinded to “-200” mesh powder and analyzed by x-ray diffraction. The interface was also examined in a scanning electron microscope (SEM; Hitachi S-570) and with energy dispersive spectroscopy (EDS) by sectioning the substrate across the interface but 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. Moreover, because sessile drop test is not an appropriate test to do kinetic studies on corrosion and compare the resistance of different materials, a simulative corrosion test such as finger test will be used to study the resistance of different materials to react with black liquor smelt. If x-ray diffraction analysis doesn't show any reaction of the material with black liquor or the constituents, kinetic studies of the reaction don't seem meaningful. In this case, only microstructural features such as porosity, grain size or impurity will affect the corrosion kinetics.

The substrates of Al_2O_3 , MgO and CeO_2 candidate materials were formed in 3/4" diameter and 0.2-0.4" height of high purity powder (>99.5%), sintered at 1600°C for 2hrs to get to about 95% of the theoretical density with almost no open porosity. The substrates of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), Y_2O_3 , ZrO_2 , MgAl_2O_4 , BaAl_2O_4 , LiAlO_2 were fabricated in cylindrical shape with 1.5" diameter and 0.1-0.2" height with 97% of theoretical density and no open porosity. The surface of each substrate was grinded by sand paper and then polished by diamond paste down to 1 μm to form a smooth surface required to measure the contact angle.

RESULTS AND DISCUSSION

Figure 2 shows a schematic of smelt/specimen interface and measurement of the contact angle. The part of the substrate used to be analyzed by x-ray diffraction and studied by SEM is shown as well.

Figure 3 shows the x-ray diffraction pattern of the black liquor sample from Weyerhaeuser BLG plant in North Carolina. This pattern verified the results of thermodynamics and showed that black liquor smelt is mainly composed of sodium carbonate and sodium sulfide. Potassium carbonate was not detected definitely due to either insufficient amount of that in the composition or background noise in the pattern. Sodium oxide is another phase which may exist in black liquor smelt. The other phase that may match the peaks of pattern obtained from the black liquor smelt is sulfur oxide graphite (C_2SO_3) which was not expected by thermodynamics.

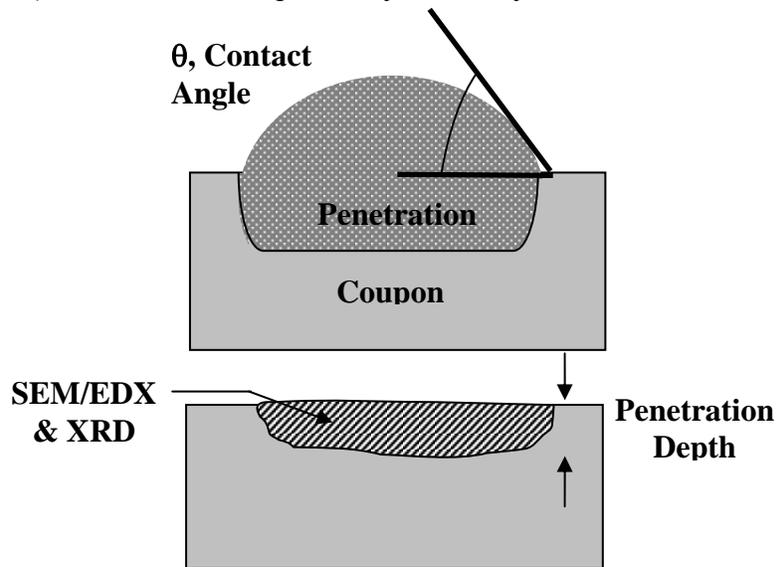


Figure 2: Schematic of contact angle measurement and part of sample analyzed by XRD and SEM/EDX

Sessile drop test was accomplished with sodium carbonate and potassium carbonate since they are in liquid state at operating temperature of black liquor gasification but sodium sulfide is not.

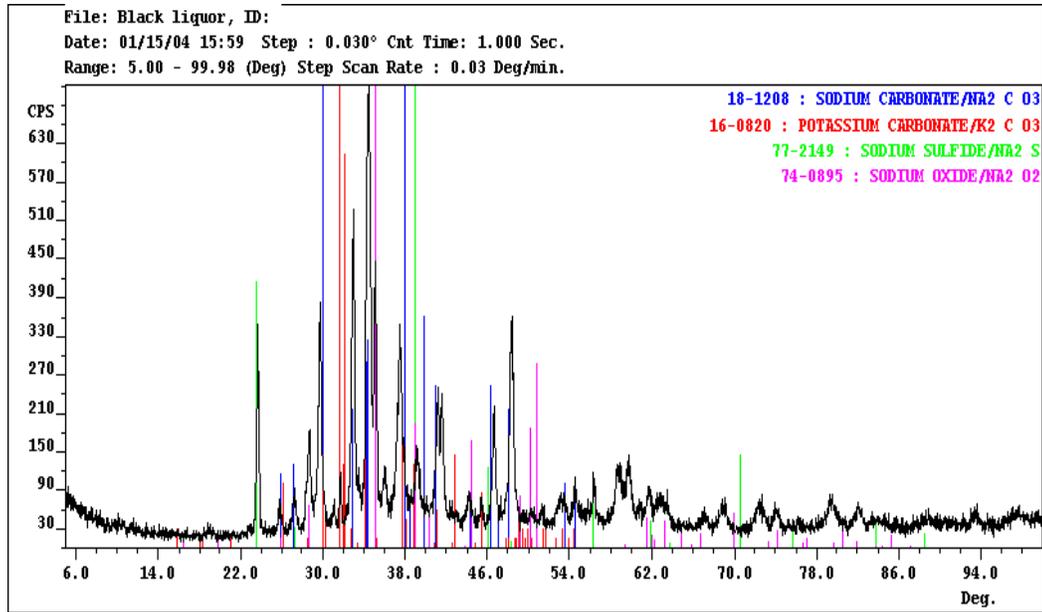


Figure 3: X-ray pattern of black liquor smelt

Figure 4 is a presentation of measured contact angle between the candidate materials and sodium carbonate under argon atmosphere at 1000°C. $MgAl_2O_4$ (spinel) specimen had the highest contact angle (13 ± 1 degrees), but it was still wet by the sodium carbonate. It was expected that the sodium carbonate would wet all oxide refractories. Figure 5 shows Na_2CO_3 drop on spinel substrate at the time it was completely melted and when the measurement was accomplished. Figure 6 shows Na_2CO_3 drop on mullite substrate under the same conditions. The difference of wetting behavior of spinel and mullite with Na_2CO_3 is considerable and distinguishable clearly.

**Contact Angle between Candidate Materials and Na_2CO_3 at 880°C
(Average of 5-7 measurements, 1 standard deviation error bars)**

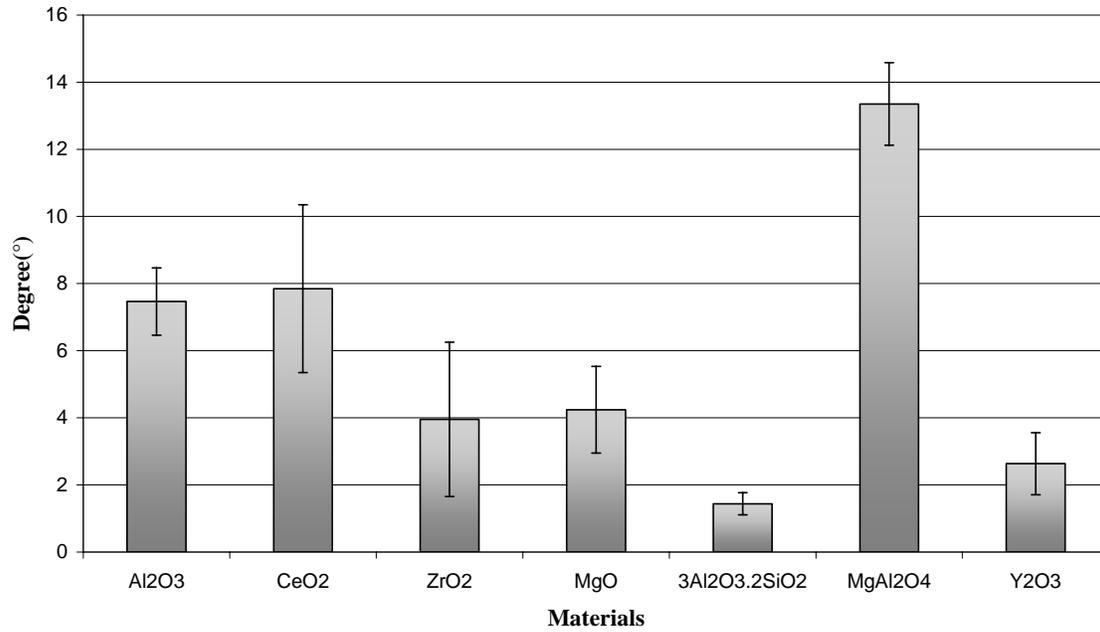


Figure 4: Contact Angle of Na_2CO_3 on dense candidate materials

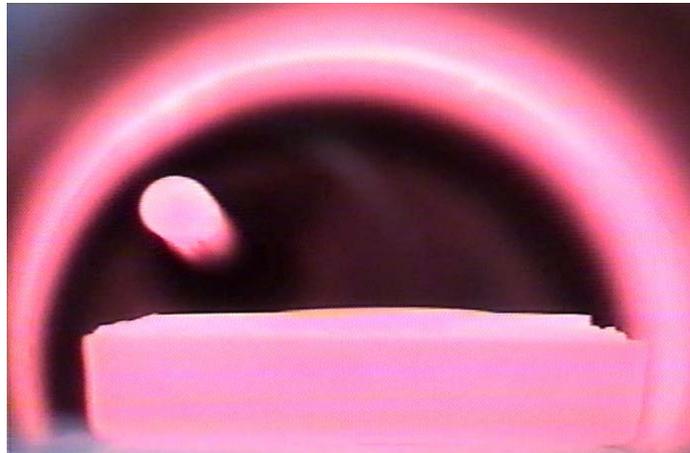


Figure 5: Na_2CO_3 drop on MgAl_2O_4 specimen after melting



Figure 6: Na_2CO_3 drop on mullite specimen after melting

Figure 7 is a plot of contact angle between the candidate oxides and potassium carbonate measured to date. In this case magnesium oxide showed the highest wetting angle of about 10 ± 2 degrees.

The contact angle measurement between lithium aluminate and barium aluminate with sodium carbonate and potassium carbonate are in process.

Contact Angle between Candidate Materials and K_2CO_3 at 920°C
(Average of 5-7 measurements, 1 standard deviation error bars)

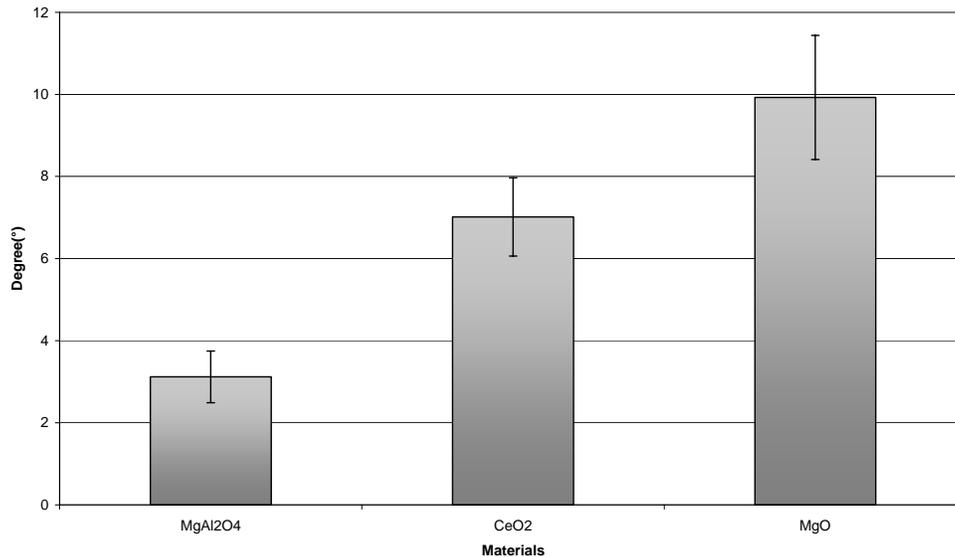


Figure 7: Contact Angle of K_2CO_3 on dense candidate materials

X-ray diffraction was used 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. The surface coating was sodium carbonate for the specimens didn't react. Increasing the angle of incidence increased surface penetration 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

Figure 8 shows the formation of reaction product, sodium aluminate, between sodium carbonate and alumina as predicted by Fact Sage®. Figure 9 shows the formation of reaction product, sodium aluminum silicate, between sodium carbonate and mullite as predicted. Formation of sodium zirconate which was not predicted by Fact Sage® but predicted by Yamaguchi [7] due to reaction between zirconia and sodium carbonate was observed (Figure 10). Figures 11 and 12 show the lack of reaction products with magnesia, calcia and ceria as predicted by FactSage®. Figure 13 shows that yttrium oxide in contact with sodium carbonate formed sodium yttrium oxide which thermodynamics didn't predict. It is observed in Figure 14 that magnesium aluminate spinel precipitated magnesium oxide and formed sodium aluminate in contact with sodium carbonate which is not in agreement with the thermodynamics. It seems that the kinetics of reaction is slow between spinel and sodium carbonate at 1000°C because the reaction layer at the surface of the substrate after sessile drop test was very thin and a relatively thick transparent layer of sodium carbonate smelt was solidified at the surface. X-ray diffraction didn't show any reaction between lithium aluminate and sodium carbonate which agrees with the thermodynamics (Figure 15) but barium aluminate formed barium carbonate and sodium aluminum oxide (Figure 16). It is predicted that barium aluminate dissociated to barium carbonate and aluminum oxide at the first step and then sodium carbonate reacted with aluminum oxide and formed sodium aluminate. The materials which didn't show any reaction with sodium carbonate or were among the promising candidates were also tested with potassium carbonate to measure the contact angle and evaluate their reactivity with potassium carbonate. The results showed that both magnesium oxide and cerium oxide were resistant to potassium carbonate as they were resistant to sodium carbonate (Figure 17 and 18) which verified the results of thermodynamic studies. Magnesium aluminate spinel reacted with potassium carbonate and formed magnesium oxide and potassium aluminum oxide as reaction products (Figure 19). Therefore spinel was probably dissociated to magnesium oxide and aluminum oxide first and the reaction between aluminum oxide and potassium carbonate formed potassium aluminate. Also thermodynamics showed that spinel would not be resistant to potassium carbonate. Both lithium aluminate and barium aluminate showed no reaction with potassium carbonate as was predicted by Factsage® (Figure 20 and 21).

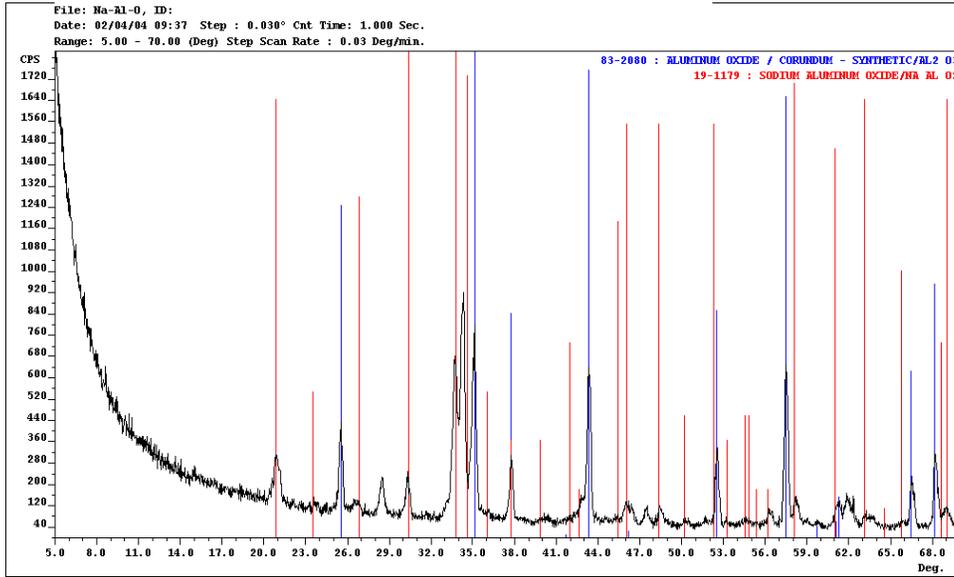


Figure 8: X-ray diffraction pattern showing reaction product sodium aluminate, and original corundum

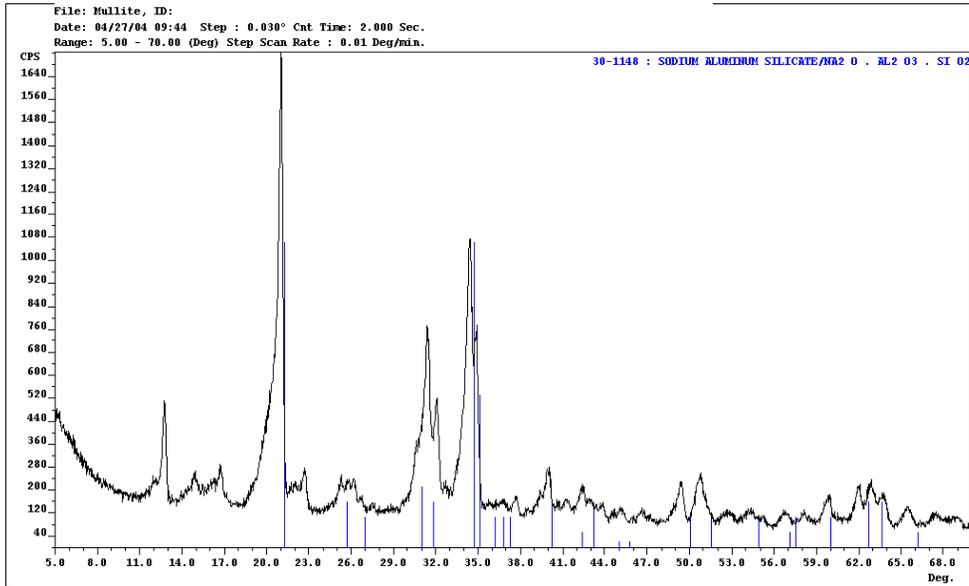


Figure 9: X-ray diffraction pattern showing reaction product sodium aluminum silicate in mullite specimen

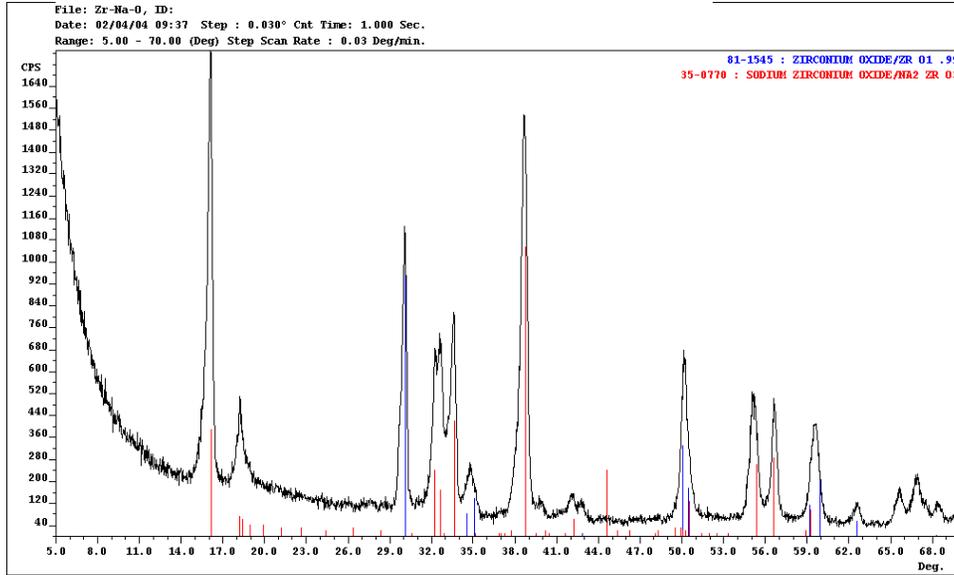


Figure 10: X-ray diffraction pattern showing reaction product sodium zirconium oxide, and original zirconia

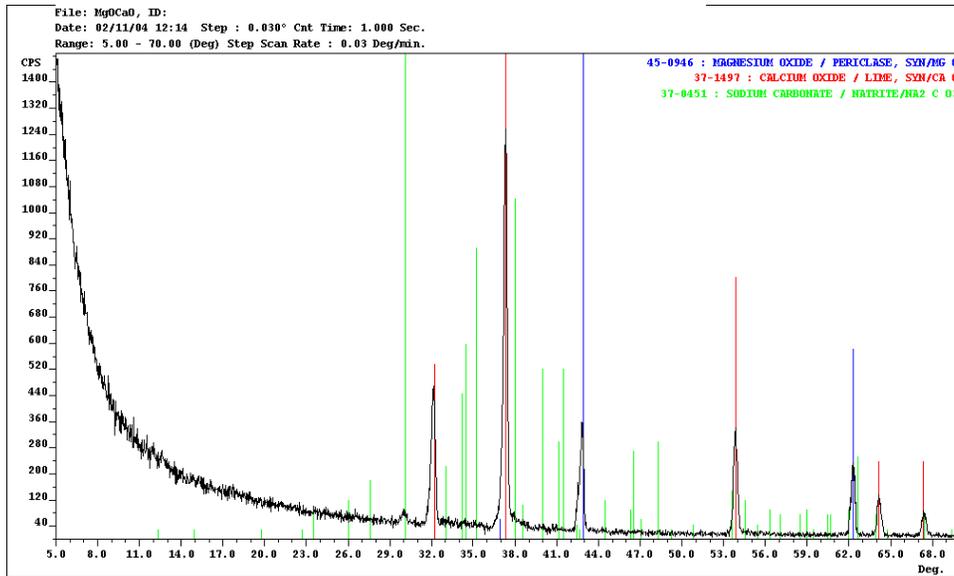


Figure 11: X-ray diffraction pattern showing lack of reaction product with original magnesia, calcia and Na₂CO₃

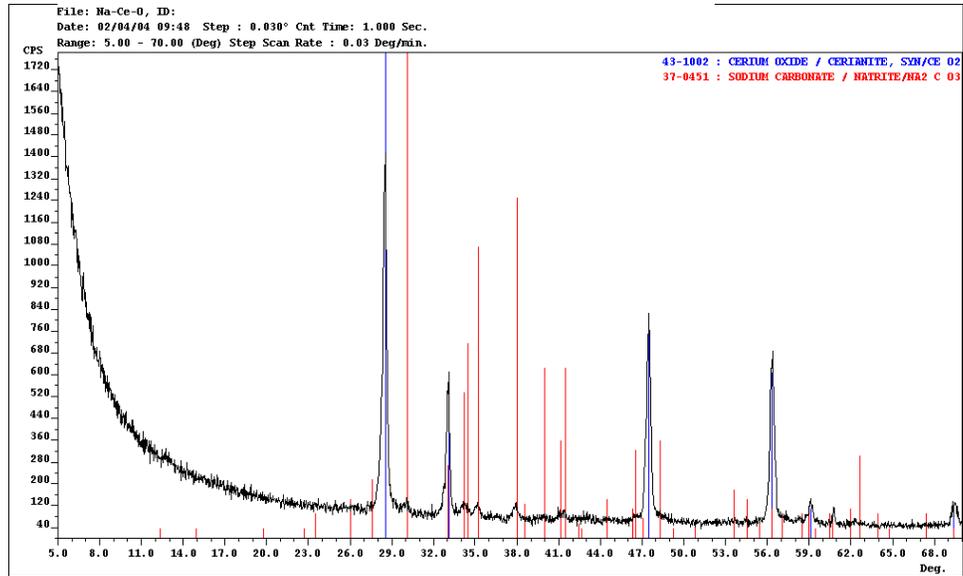


Figure 12: X-ray diffraction pattern showing lack of reaction product with original ceria and Na_2CO_3

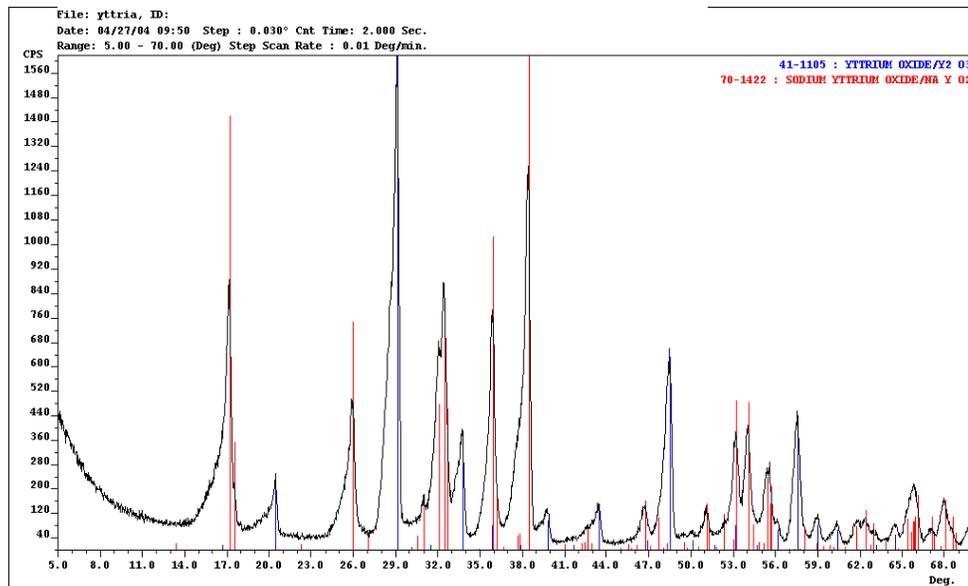


Figure 13: X-ray diffraction pattern showing reaction product sodium yttrium oxide, and original yttrium oxide

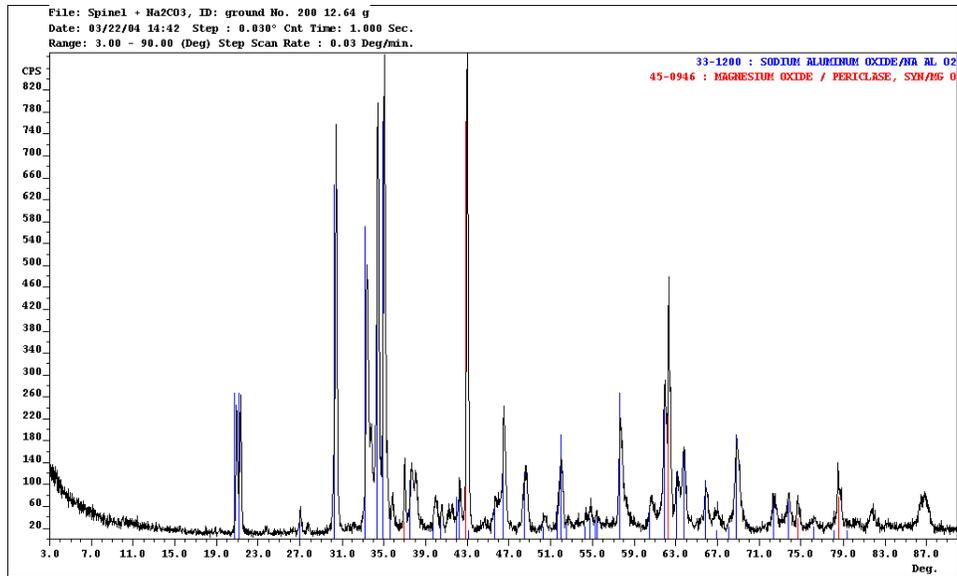


Figure 14: X-ray diffraction pattern showing reaction products sodium aluminum oxide and magnesium oxide in spinel specimen

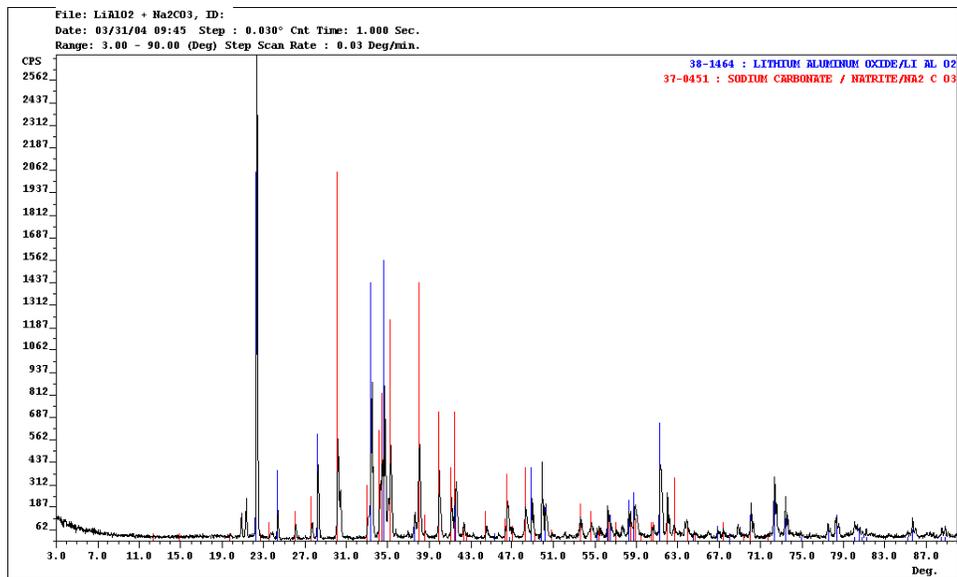


Figure 15: X-ray diffraction pattern showing lack of reaction product with original lithium aluminate and Na_2CO_3

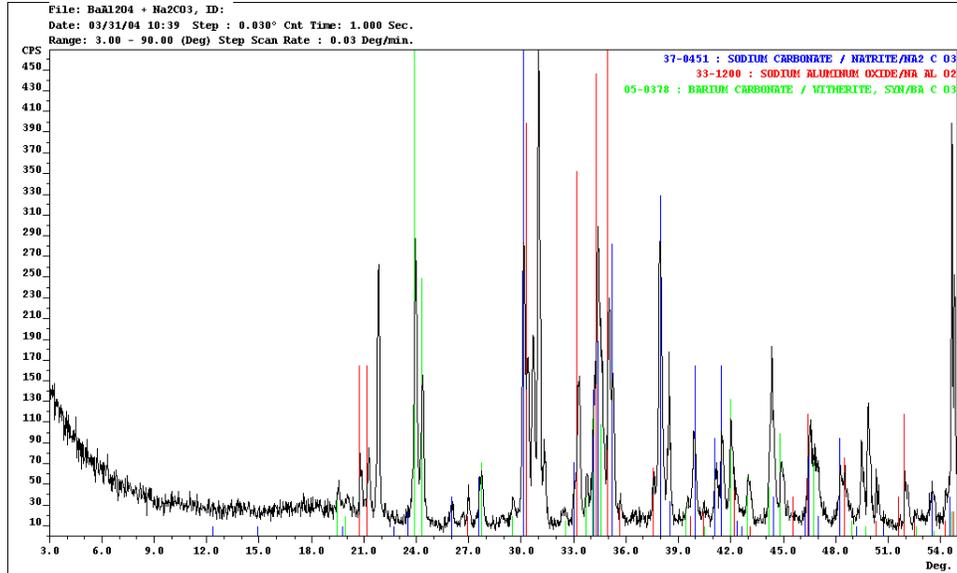


Figure 16: X-ray diffraction pattern showing reaction products, sodium aluminum oxide, barium carbonate and original Na_2CO_3 smelt in barium aluminate specimen

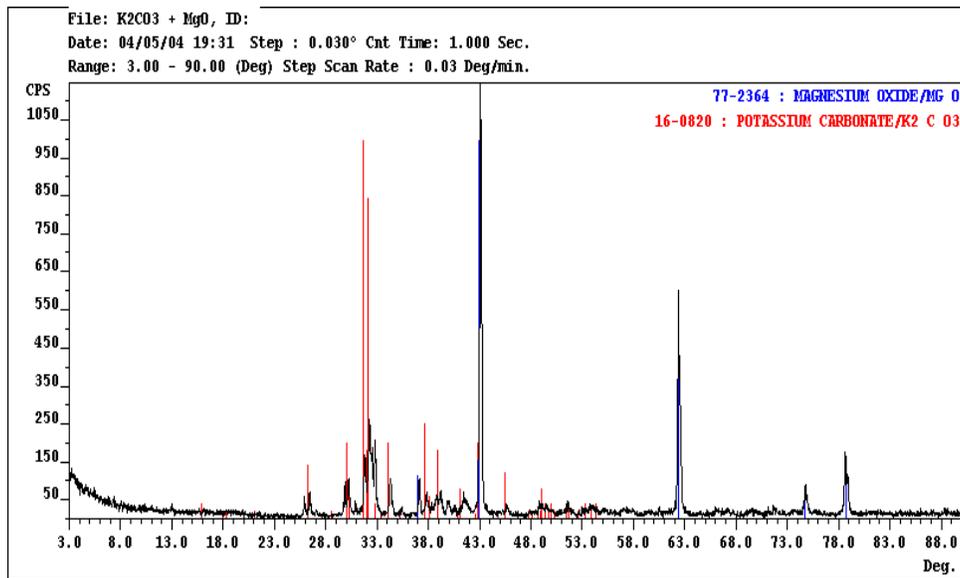


Figure 17: X-ray diffraction pattern showing lack of reaction product with original magnesium oxide and K_2CO_3

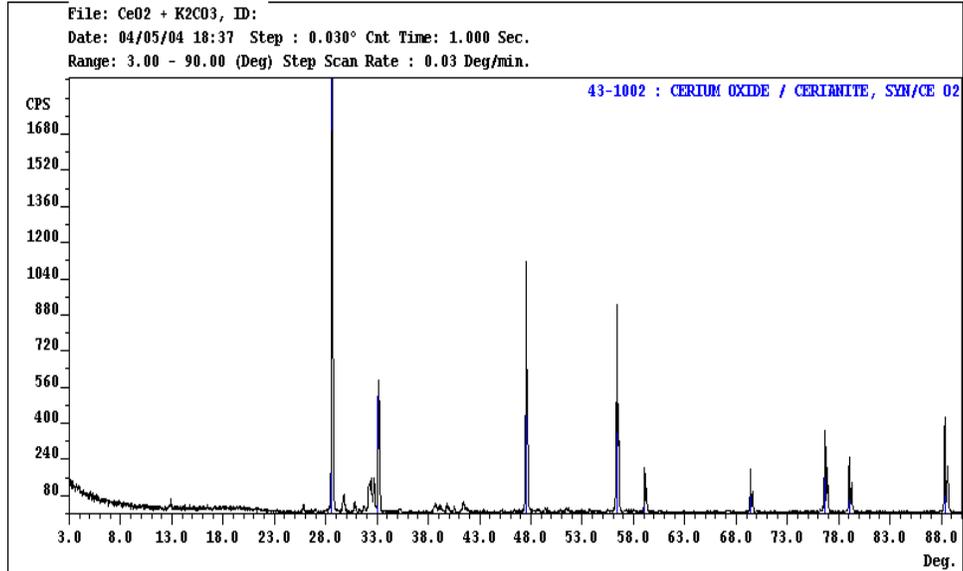


Figure 18: X-ray diffraction pattern showing lack of reaction product with original cerium oxide and K_2CO_3

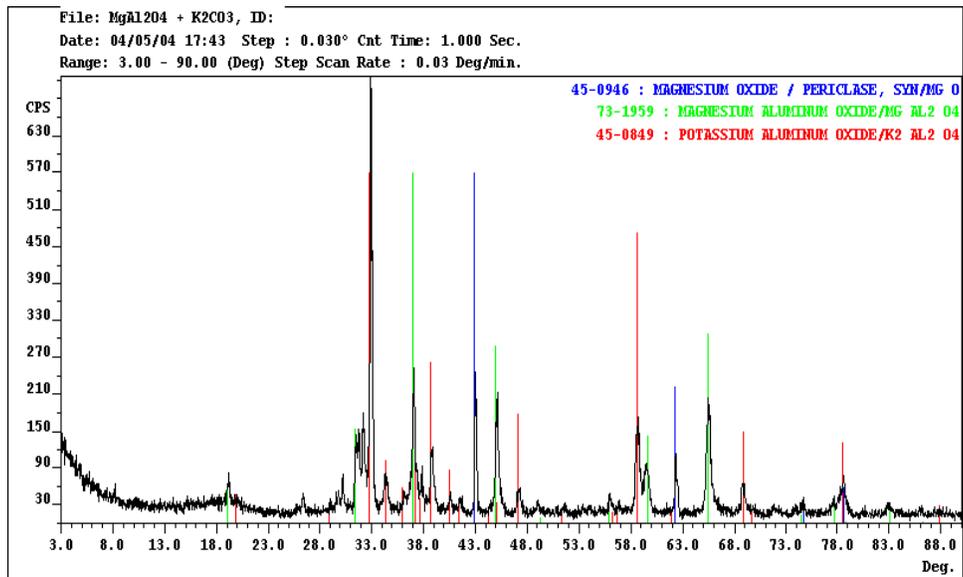


Figure 19: X-ray diffraction pattern showing reaction product potassium aluminum oxide and magnesium oxide, and original spinel

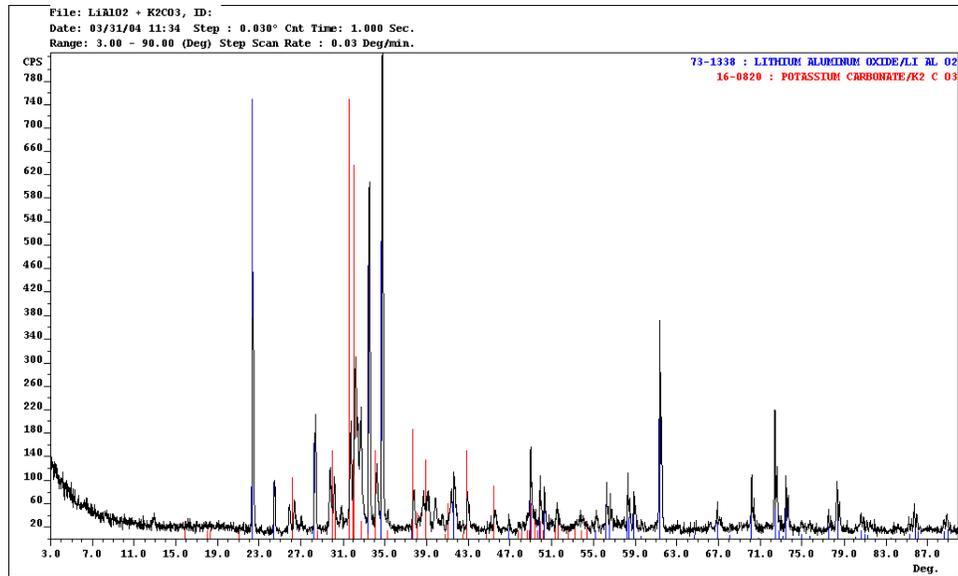


Figure 20: X-ray diffraction pattern showing lack of reaction product with original lithium aluminate and K_2CO_3

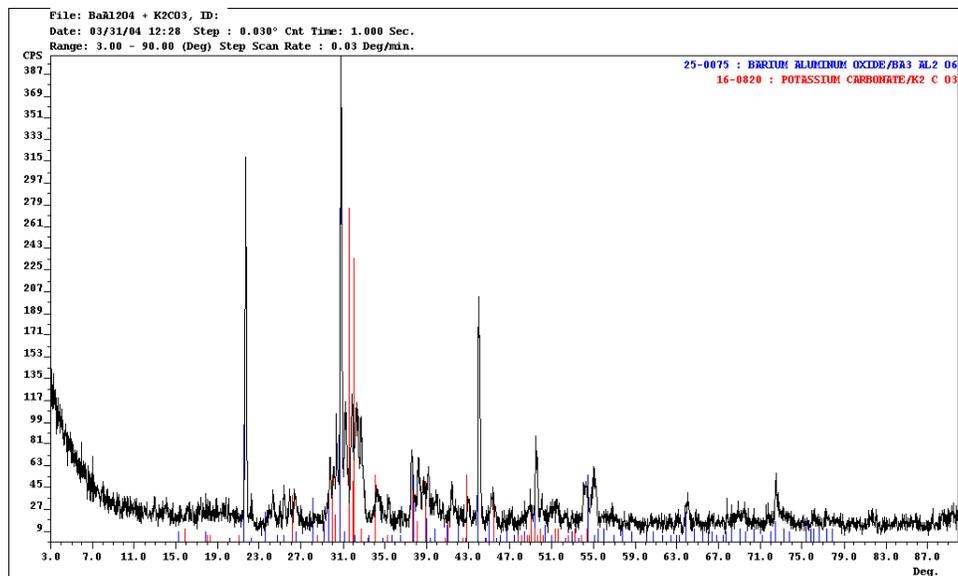


Figure 21: X-ray diffraction pattern showing lack of reaction product with original barium aluminate and K_2CO_3

The summary of the results from x-ray diffraction analysis of different samples is also presented in Table I in addition to the results of thermodynamics for comparison. The results of thermodynamics were obtained only based on FactSage® data base.

Table I: Results of thermodynamics (FactSage®) and XRD analysis at 1000°C

Candidate Material	Na ₂ CO ₃ (Thermodynamics)	K ₂ CO ₃ (Thermodynamics)	Na ₂ CO ₃ (XRD)	K ₂ CO ₃ (XRD)
Al ₂ O ₃	X	X	X	?
3Al ₂ O ₃ .2SiO ₂	X	X	X	?
CeO ₂				
ZrO ₂			X	?
MgO				
Y ₂ O ₃			X	?
MgAl ₂ O ₄		X	X	X
LiAlO ₂				
BaAl ₂ O ₄			X	

(x): Reaction occurred, (?): No experiment,

CONCLUSION

The results of thermodynamics (FactSage®) and experiment were in agreement for Al_2O_3 , $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite), CeO_2 , MgO , LiAlO_2 , and were not in agreement for ZrO_2 , Y_2O_3 , MgAl_2O_4 , BaAl_2O_4 candidate materials. Therefore experimental work is always necessary to evaluate the materials for any application and thermodynamics is not sufficient. So far magnesium aluminate spinel showed the highest contact angle with sodium carbonate (13 ± 1 degrees) while magnesium oxide showed the highest contact angle with potassium carbonate (10 ± 2 degrees). Although cerium oxide and magnesium oxide didn't show high contact angle with sodium carbonate and potassium carbonate but they didn't show any reaction with either one of the smelts. Therefore if a high purity material with the least amount of impurity is used for making refractory out of MgO and CeO_2 with dense microstructure, they can be promising candidates for application in black liquor gasifiers.

MgAl_2O_4 can still be a good candidate for BLG application although powder x-ray diffraction verified the reaction of sodium carbonate and potassium carbonate with spinel. Because sessile drop test showed relatively high contact angle with sodium carbonate and very thin reaction layer although spinel didn't have a high contact angle (3 ± 1) with potassium carbonate.

Lithium aluminate should be considered as a promising candidate as well because it reacted neither with sodium carbonate nor with potassium carbonate (powder mixture). Contact angle between lithium aluminate and barium aluminate with both sodium carbonate and potassium carbonate will be measured by sessile drop test and reported later.

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LIST OF ACRONYMS AND ABBREVIATIONS

BLG=Black Liquor Gasification

LPLT=Low Pressure Low Temperature

HPLT=High Pressure Low Temperature

LPHT=Low Pressure High Temperature

HPHT=High Pressure High Temperature

T_m=melting point temperatura

SEM=Scanning Electrón Microscope

EDS=Energy Dispersive Spectroscopy

XRD=X-Ray Diffraction

T=Temperature