IMPROVEMENT OF AN ELECTROFUSED MGO-CAZRO$_3$ REFRACTORY MATRIX BY THE ADDITION OF HERCYNITE SPINEL AND MAGNESIUM-ALUMINIUM SPINEL FOR THE CEMENT INDUSTRY

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ABSTRACT
The development of innovative chrome-free basic bricks based on electrofused MgO-CaZrO$_3$ technology using as ceramic bonding two different types of spinel (hercynite and magnesium-aluminium spinel) to improve their properties is presented. Microstructural, physical, mechanical, and thermal properties of electrofused MgO-CaZrO$_3$ matrix were determined. Static and dynamic resistance tests by chemical attack of cement raw constituents were carried out. The results showed that thermo-mechanical properties of new bricks significantly improved with increasing spinel content. Microstructural analysis revealed that the spinel phase aided to develop a strong bond between the magnesia and calcium zirconate refractory phases. Finally, this refractory matrix exhibits a good thermal stability and excellent chemical resistance against cement raw meal.

Keywords: MgO-CaZrO$_3$ refractories, Hercynite, Magnesium aluminium spinel, rotary cement kiln.

INTRODUCTION
Recently, the substitution of fossil fuels by the use of secondary fuels and industrial waste (eg. used tires, coal ash and sewage sludges), associated with the modernization and improvements of the cement rotary kiln themselves have drastically affected the performance life of the refractory bricks. Those changes have driven the refractory industry to create and develop improved refractory lining products[1].

Newest refractory trends, for improving the properties of lining are related to the optimization of the matrix by careful design of the phase combinations and the microstructure characteristics. There is no doubt that, one of the main microstructural characteristic that has to taking into account for contributing to the development of a reliable refractory matrix is the bond. By increasing the bonding strength, the resistance against many kinds of stresses during performance and structural spalling would be improved. In addition, a high strength brick frequently has been linked to a rigid matrix; however cement rotary kilns require refractory bricks with sufficient structural flexibility and stress absorbent to prevent cracking and peeling off from the hot face.

By other hand, MgO-CaZrO$_3$ materials are well known to be compatible phases, do not form a liquid phase up to temperatures higher than 2060ºC and they are highly resistant in aggressive basic environments and atmospheres with high alkali contents at temperature up to 1400ºC. In this kind of refractory matrix, the formation of a so-called elastic direct bonding between MgO and CaZrO$_3$ and the high refractoriness of CaZrO$_3$ (2340ºC), allow to reach a high hot mechanical strength and excellent corrosion resistance against alkali, earth alkali oxides and basic slags[2-14]. Kozuka et al. in Japan have studied the behavior of magnesia-calcium zirconate refractory bricks in rotary cement kilns. The conclusion of this study proved that the bricks showed superior corrosion resistance and good coating adherence but peeled off easily in high stressed areas[15,16].

According to the above mentioned, the objectives of this research are the study, development and the evaluation of physical, mechanical, thermo-mechanical and chemical properties, as well as microstructural characteristics of a new free-chrome refractory brick composes of a matrix made of electrofused magnesia-calcium zirconate (MgO-CaZrO$_3$) with little addition of magnesium aluminate spinel (MgAl$_2$O$_4$) and hercinite (FeAl$_2$O$_4$) acting as bonding linkage. Due to the importance of the development of a strong bonding structure in the refractory matrixes, the influences of varying the amount of both spinel phases (MgAl$_2$O$_4$ and FeAl$_2$O$_4$) on the refractory matrix were established. Additionally, static and dynamic resistance tests to chemical attack by cement raw meal were carried out.

EXPERIMENTAL PROCEDURE
Raw material

Since, raw material characteristics play an important role in getting suitable final refractory properties; the use of high purity raw material was a necessary issue (even in industrial scale). The chemical composition of the raw material used for the development of new refractory bricks is given in table 1. For the sintered magnesia a wide particle size distribution (coarse, intermediate and fine grains) was used; for electrofused magnesia-calcium zirconate mixture only coarse and intermediate grains were used. Fine particle grains (‹45μm) were utilized for ZrO$_2$, MgAl$_2$O$_4$ and FeAl$_2$O$_4$. The addition of a fine particle size for spinel and zirconia is due to a well known superior reaction force with the surrounding matrix. The crystalline phases identified by XRD analysis for the starting raw meal were: MgO (periclase-MgO), MgO-CaZrO$_3$ (periclase-MgO, calcium zirconate-CaZrO$_3$ and non-stequiometric calcium zirconate-CaO$_{0.15}$ZrO$_{0.85}$O$_{1.85}$), MgAl$_2$O$_4$ (periclase-MgO and spinel-MgAl$_2$O$_4$), FeAl$_2$O$_4$ (hercinite-FeAl$_2$O$_4$) and ZrO$_2$ (baddeleyite-ZrO$_2$).

Refractory matrix

In order to evaluate the effect of magnesium aluminate and hercynite spinels on an electrofused MgO-CaZrO$_3$ matrix, nine refractory formulations were studied; the first one without addition of spinel (formulation 1) and the rest with variations in the spinel contents. The refractory formulations are shown in table 2. The addition of a small quantity of fine zirconia particles in all formulations responds mainly to avoid free lime in the refractory matrix and promotes the formation of an *in. situ.* calcium zirconate phase.

Preparation and characterization of refractory bricks

Mixtures with compositions according to the proportions given in table 2 were prepared. Dextrine was added to bind the mixtures and for providing maximum stability of the green samples dur-

Tab. 1: Chemical composition of raw materials.

Compositions (% by weight)						
Raw Material	MgO	ZrO_2	CaO	Al_2O_3	Fe_2O_3	SiO_2
Sintered MgO	98.91	–	0.85	0.08	0.05	0.11
Elecrofused MgO-$CaZrO_3$	50.00	36.43	13.57	–	–	–
$MgAl_2O_4$	34.00	–	0.20	64.0	1.0	0.40
$FeAl_2O_4$	4.6	–	0.19	49.06	45.78	0.13
ZrO_2	–	97.72	–	–	–	2.10

Tab. 2: Refractory formulations.

Compositions (% by weight)					
Refractory formulation	MgO	$CaZrO_3$	Mg Al_2O_4	$FeAl_2O_4$	ZrO_2
MZ	85.5	14.0	–	–	0.5
2MA	83.0	14.0	2.5	–	0.5
3MA	81.9	14.0	3.6	–	0.5
4MA	80.7	14.0	4.8	–	0.5
5MA	79.5	14.0	6.0	–	0.5
6H	83.0	14.0	–	2.5	0.5
7H	81.9	14.0	–	3.6	0.5
8H	80.7	14.0	–	4.8	0.5
9H	79.5	14.0	–	6.0	0.5

ing subsequent handling prior to firing. The powders were uniaxial pressed into a metallic mould obtaining refractory bricks of 228x114x76 mm. After pressing, green compacts were sintering at 1650ºC for 7 h in an industrial tunnel kiln. Physical properties such as apparent porosity, bulk density, cold crushing strength, cold modulus of rupture and hot modulus of rupture at 1260°C were measured based on ASTM standards. Phase analyses of the sintered samples were carried out by X-ray diffraction study (Philips X'pert) using Cu-Kα radiation in the diffraction range of 5–90°. Sintered samples morphology was examined using scanning electron microscope (JSM-6490, Joel) with an energy dispersive scanning attachment for qualitative and quantitative microanalysis.

Static and dynamic chemical attack test by clinker raw meal powders (see table 3) were executed for evaluating corrosion resistence and coatability of free-spinel MgO-$CaZrO_3$ matrix and MgO-$CaZrO_3$ matrixes with spinel addition. The static method intends to make raw meal contact with the refractory and evaluates clinker adherences by heating. Using a crucible (114x114x76 mm) made of refractory brick, a hole was bored in the sample brick with the dimensions Φ50x50 mm and filled it with clinker raw meal. The crucible sample was heated in an gas furnace for 4 h at 1450 ºC. The adherence of the clinker on the refractory was determined according to the following criteria: nill adherence (clinker pellet is removed by inverting the sample up side down), moderate adherence (clinker pellet is removed by slightly hitting) and strong adherence (clinker pellet is practically fused with the refractory).

For the dynamic method a laboratory rotary kiln was lined with the refractory to be tested. The temperature was increased to 1450 ºC with an air/O_2 burner. The raw meal (the amount of 3–5 kg) was fed continually during 4 h rotating the kiln to 1 r.p.m. After the test, the degree of penetration and the microstructure damage of the refractory was evaluated by electronic microscopy on polished sections.

Tab. 3: Chemical composition of clinker raw meal.

Compositions (% by weight)						
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O
44.79	11.86	3.03	1.60	0.88	0.47	0.24

RESULTS AND DISCUSSION

Physical properties

Physical properties from each refractory formulation are provided in table 4. According to the results an average magnitude of apparent porosity for the refractory formulations was established around 17-18%. Whereas the porosity of refractory bricks manifests itself in different coating adhesion levels, the average magnitude reached in this study was suitable because it permits a desirable good coating adherence avoiding thermal overloads on the brick hot face.

The results obtained for cold crushing strength shown an increase tendency in magnitude with spinel addition and a maximum cold crushing strength magnitude corresponding to 3MA formulation for magnesium aluminate spinel ($MgAl_2O_4$) and 9H formulation for hercynite spinel. This behaviour can be explained in porosity terms, since according to those values 3MA and 9H refractory formulations registered the minimum porosity magnitude.

For cold and hot modules of rupture the addition of both magnesium aluminate and hercynite spinels resulted in higher magnitudes compared to MZ formulation. In addition, it was found that the most favourable spinel content to reaches the maximum value in both cold and hot modules of rupture was 2MA formulation for $MgAl_2O_4$ addition and 8H formulation for $FeAl_2O_4$ addition.

X-ray diffraction analysis

The X-ray diffraction (XRD) study obtained from each refractory formulation revealed the presence of the same phases prior to sintering. This indicates that there were no new phases formed. However, the diffraction patterns of formulation 2MA and 6H did not detect spinel phase peak intensity due to the small amount used (see table 5).

Microstructural analysis

Figure 1 shows a SEM image of the sintered microstructure of the formulation without spinel content (MZ). It can be observed a homogeneous microstructure matrix forms by two well-distributed phases. Using energy dispersive spectroscopy analysis (EDS) were identified as magnesia (grey grains) and calcium zirconate (white grains). At higher magnification an excellent bond linkage between MgO and $CaZrO_3$ grains was observed.

Tab. 4: Physical properties of the refractory bricks.

Brick Type	Properties				
	Apparent porosity (%)	Bulk density (g/cm^3)	Cold crushing strength (MPa)	Modulus of rupture (MPa)	Hot modulus of rupture @ 1260ºC (Kg/cm^2)
MZ	18.4	2.94	39.6	9.6	59
2MA	17.7	3.01	54.2	12.7	144
3MA	17.1	3.02	56.5	11.6	126
4MA	18.1	2.98	47.2	8.7	116
5MA	18.6	2.97	49.3	9.5	121
6H	18.4	3.00	44.2	9.7	111
7H	18.2	3.01	49.4	10.5	118
8H	18.1	3.00	47.5	10.4	132
9H	17.9	3.00	55.5	11.2	80

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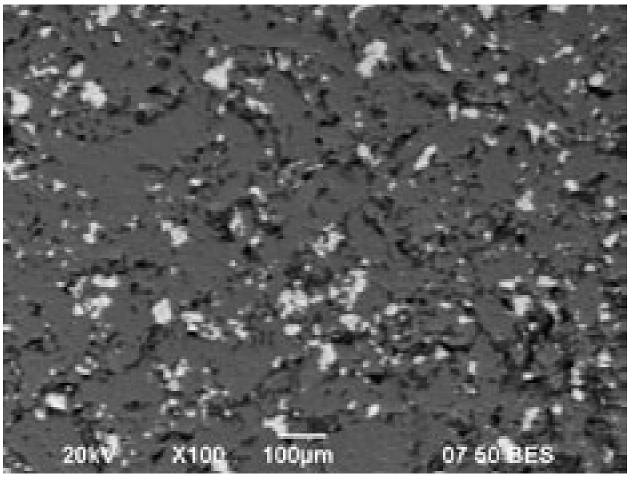

Fig. 1: Sintered microstructure of MZ formulation.

Tab. 5: Physical properties of the refractory bricks.

Brick	Crystalline phases					
	MgO	$CaZrO_3$	N.S $CaZrO_3$	ZrO_2	Mg Al_2O_4	Fe Al_2O_4
MZ	xxxxx	xxx	x	–	–	–
2MA	xxxxx	xxx	x	–	–	–
3MA	xxxxx	xxx	x	–	x	–
4MA	xxxx	xxx	x	–	xx	–
5MA	xxxx	xxx	x	–	xx	–
6H		xxx	x	–	–	–
7H		xxx	x	–	–	x
8H		xxx	x	–	–	xx
9H		xxx	x	–	–	xx

*N.S meaning non stechiometric $CaZrO_3$ ($CaO_{0.15}ZrO_{0.85}O_{1.85}$).

In the figure 2, it was shown a representative microstructure corresponding to the refractory formulations with addition of $MgAl_2O_4$ spinel (2MA, 3MA, 4MA and 5MA). This microstructural analysis revealed as in MZ formulation, the presence of well-distributed magnesia (grey grains) and calcium zirconate grains (light gray grains) in the microstructure as mainly phases. Magnesium aluminate spinel phase was not identified at low magnifications; however, at higher magnifications it was revealed that spinel was located in the boundaries between MgO and $CaZrO_3$ particles acting as a bond linkage among these phases.

It is proposed that spinel phase was localized by diffusion in these specific zones due to its melting temperature is lower than both magnesia and calcium zirconate phases. Besides, the fine particle

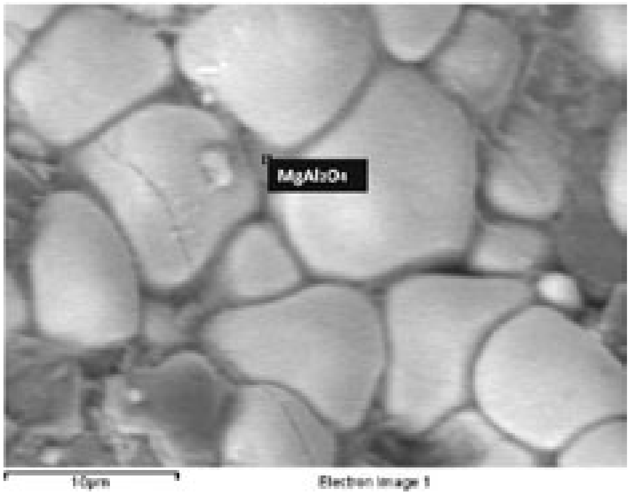

Fig. 3: SEM micrograph of the 5MA formulation. The rectangle indicates the spinel location in the microstructure.

size of spinel phase contributed to the arrangement in those specific zones. A high magnification SEM image for 5MA formulation is shown in figure 3, in which spinel phase was identified in the boundaries between magnesia and calcium zirconate particles. This was corroborated by EDS analysis.

The representative microstructure corresponding to the refractory formulations with addition of $FeAl_2O_4$ spinel (6H, 7H, 8H and 9H) is shown in figure 4.

By this analysis, it can be seen in the microstructure the presence of well-distributed magnesia (gray grains) and calcium zirconate grains (white grains) as mainly phases. Hercynite spinel was also located in the boundaries between MgO and $CaZrO_3$ particles acting as a bond linkage between these phases.

Coatability and corrosion res istance

In table 6 is shown the results obtained by static and dynamic methods for determining the coating adhesion in the refractory formulations. In general, the hot face in every refractory formulation was no corroded by cement liquid phase; however a brown molten phase entered up to a range of 6 to 9 mm depth. In addition, the increase of spinel content leads to a diminished in coating adhesion. This behaviour can be attributed to spinel phases due to their lack of coating adhesion. According to the microstructural analysis corresponding to static and dynamic tests a slightly densification was observed without corrosion evidence. It is important to mention that bonding strength still remained in all formu-

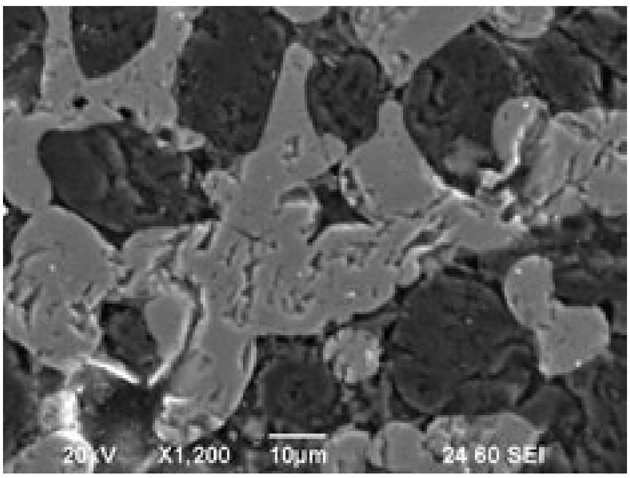

Fig. 2: General microstructure with $MgAl_2O_4$ spinel addition.

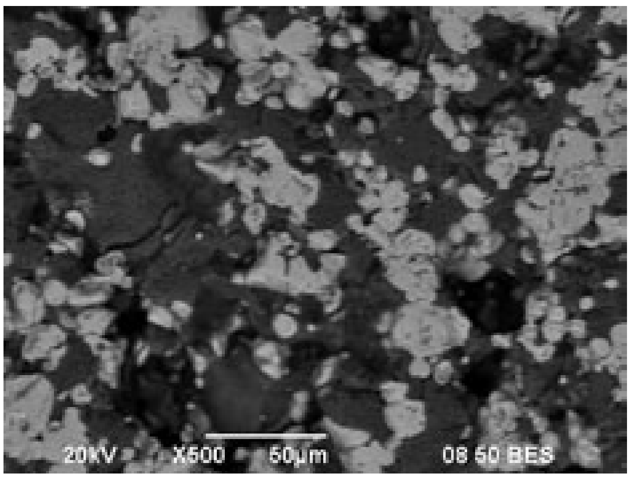

Fig. 4: General microstructure with FeAl2O4 spinel addition.

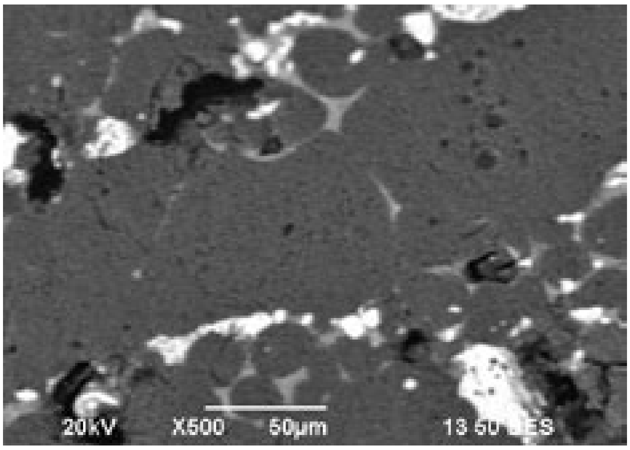

Fig. 5: General microstructure with $MgAl_2O_4$ spinel addition tested with clinker raw meal at 1450 ºC for 4 h.

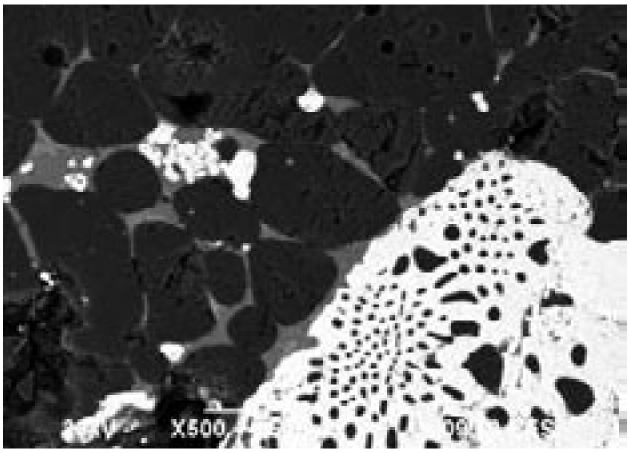

Fig. 6: General microstructure with $FeAl_2O_4$ spinel addition tested with clinker raw meal at 1450 ºC for 4 h.

lations. Figure 5 and 6 revealed a slightly dense microstructure presented in all formulations due to clinker penetration. Besides, a magnesia-calcium zirconate unaltered bonding was presented.

Tab. 6: Adherence test with clinker raw meal.

Formulation	Static test		Dynamic test
	Distance from hot face (mm)	Adherence	Adherence
MZ	9.0	strong	moderate
2MA	6.4	strong	moderate
3MA	5.6	strong	moderate
4MA	5.7	moderate	moderate
5MA	5.7	moderate	moderate
6H	3.6	moderate	moderate
7H	3.4	moderate	moderate
8H	4.3	nill	moderate
9H	5.5	nill	moderate

CONCLUSIONS

This research demonstrated that the addition of magnesium-aluminate and hercynite spinels to the electrofused $MgO-CaZrO_3$ matrix improved their thermo-mechanical properties. The microstructural analysis revealed that both spinel ($MgAl_2O_4$ and $FeAl_2O_4$) were located in the boundaries between MgO and $CaZrO_3$ particles acting as a bond linkage among these phases. Coating adherence was moderate and a general slightly dense microstructure with a magnesia-calcium zirconate unaltered bonding was presented after raw meal clinker attack.

REFERENCES

[1] Bartha, P. and Klischat, H. J; "Classification of magnesia bricks in rotary cement kilns according to specification and service-ability"; ZKG International. 47:277–280, 1994.

[2] J.L. Rodríguez-Galicia, A.H. de Aza, J.C. Rendón-Angeles, P. Pena; "The Mechanism of corrosion of MgO $CaZrO_3$–calcium silicate materials by cement clinker"; Journal of European Ceramic Society. 27:79-89, 2007.

[3] Serena S, Sainz MA, Caballero A; "Corrosion behavior of $MgO/CaZrO_3$ refractory matrix by clinker"; Journal European Ceramic Society. 24:2399–2406, 2004.

[4] Serena S, Sainz MA, Caballero A; "The system clinker–$MgO–CaZrO_3$ and its application to the corrosion behavior of $CaZrO_3/MgO$ refractory matrix by clinker"; Journal European Ceramic Society. 29:2199–2209, 2009.

[5] Edén Rodríguez, G-Alan Castillo, José Contreras, J.A. Aguilar Martínez, Yadira González, Ana-María Guzmán, Laura I. García Ortiz; "Desarrollo de un refractario $MgO-CaZrO_3$ dopado con $MgAl_2O_4$ para la industria cementera"; Ciencias UANL. 15:23–30, 2011.

[6] Edén Rodríguez, G-Alan Castillo, Ana María Guzmán; "Effect of spinel $MgAl_2O_4$ on microstructural and mechanochemical properties evolution in a sintered $MgO-CaZrO_3$ refractory matrix"; Industrial Ceramics. 31:1–5, 2011.

[7] Rodríguez. E.A., Castillo. G.A., and Guzmán A.M; "Development of a chrome-free refractory based on electrofused magnesia-calcium zirconate technology using spinel addition for use in cement rotary kilns"; UNITECR´09 Congress. 072, 2009.

[8] Rodríguez JL, Baudín C, Pena P; "Relationships between phase constitution and mechanical behaviour in MgO–$CaZrO_3$–calcium silicate materials"; Journal of European Ceramic Society. 24:669–679, 2004.

[9] Rodríguez JL, Pena P; "Obtención de materiales de magnesia-circonato dicálcico por sinterización reactiva de mezclas dolomita – circón"; Estudio del procesamiento. Boletín de la Sociedad Española de Cerámica y Vídrio. 40:463–471, 2001.

[10] Rodríguez JL, Rodríguez MA, De Aza S, Pena P; "Reaction sintering of zircon–dolomite mixtures"; Journal of European Ceramic Society. 21:343–354, 2001.

[11] Rodríguez JL, De Aza S, Pena P; "Effect of agglomerate and grain size on the reaction sintering of zircon–dolomite mixtures"; Brit Ceram Trans. 100:181–91, 2001.

[12] J.E. Contreras, G.A. Castillo, E.A. Rodríguez; "About the influence of electrofused FeAl2O4 in a refractory base on MgO-CaZrO3 by sintering on this properties"; UNITECR´03. Osaka, Japan. 2003.

[13] Eden. A. Rodríguez, G. Alan-Castillo, Jose. E. Contreras, Tushar. K. Das; "Microstructure and Properties of Spinel-Magnesia-Zirconia-Calcium Zirconate refractory mixtures"; UNITECR´07 Congress. 612, 2007.

[14] J.E. Contreras, G.A. Castillo, E.A. Rodríguez, T.K. Das, A.M. Guzmán; "Microstructure and properties of hercynite-magnesia-calcium zirconate refractory mixtures"; Materials Characterization. 54:354–359, 2005.

[15] Kozuka, H., Kaita, Y., Tuchiya, Y., Honda, T. and Ohta, S; "New kind of chrome-free (MgO-CaO-ZrO2) bricks for burning zone of rotary cement kiln"; UNITECR. 93, Sao Paulo, Brasil. 1027–1037, 1993.

[16] H. Kozuka, Y. Kajita, Y. Tuchiya, T. Honda and S. Ohta; "Further improvements of MgO-CaO-ZrO2 refractory bricks"; UNITECR´05. 1995.