EVALUATION OF AGGREGATES FROM MgO-TiO_2-CaO SYSTEM USED IN REFRACTORIES FOR BURNING ZONE OF CEMENT ROTARY KILNS

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ABSTRACT

Chrome-free refractories for the burning zone of rotary cement kilns have been largely studied in the last years, because of the health and environmental problems caused during disposal of used chrome oxide containing refractories. Several refractory phase systems have been alternatively evaluated. In this work, fused aggregates from the MgO-TiO_2-CaO system were added in a magnesia based refractory composition. Physical, thermomechanical and thermochemical tests were comparatively made against a commercial magnesia-spinel refractory. The results indicated that the developed chrome-free refractories containing fused aggregates from the MgO-TiO_2-CaO system are very promising candidates for the burning zone lining of cement rotary kilns.

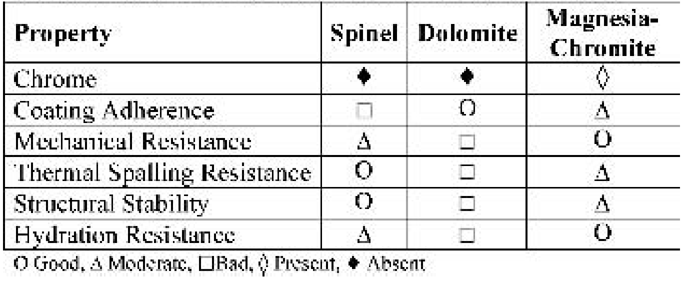
Key-words: refractories, burning zone, cement rotary kilns, magnesia, titania, calcia.

1. INTRODUCTION

Portland cement is the final product of a complex pyroprocessing technology that transforms raw materials rich in SiO_2, CaO, Al_2O_3 and Fe_2O_3 into calcium silicate and aluminate phases. Over the years, driven by cost reduction searches, the technology of Portland cement production has been experienced several changes, mainly by the use of alternative raw materials and fuels. These changes, in addition to the increased thermal loads, imposed constant developments in the refractory linings. At the start of 20th Century, small-sized rotary kilns and shaft kilns employed mostly fireclay and high alumina bricks even in high temperature zones. This practice was maintained until the forties, when the first magnesia and magnesia-chromite refractories for the burning zone of cement kilns appeared. These refractories presented high mechanical, corrosion, hydration and thermal spalling resistance with good structural stability. However, one big issue opposing its use is the presence of chromium (III) oxide in magnesia-chromite refractories. In contact with alkaline salts, the chromium ion becomes hexavalent, in which case it is carcinogenic and harmful to the environment. During the forties dolomite refractories were also employed in burning zone of Portland cement rotary kilns. However, these refractories presented the drawbacks of hydration sensitivity and were also prone to sulphur and CO_2 attack. With the advent of the high production cement rotary kilns the thermal charge changed drastically, demanding new refractory products. In the sixties the precalcination system enabled production of direct bonding basic bricks with high abrasion and chemical attack resistance, but with low flexibility. During the seventies, after the initial success of magnesia-spinel refractories in the Japanese steel industry, these bricks started to be introduced in low and high transition zone of cement rotary kilns. This technology got established during the eighties, especially in Western countries. Even so, dolomite and magnesia-chromite refractories are still being used in the burning zone of cement rotary kilns thanks to their high coating adherence capacity. During the nineties, new refractory technologies were developed, aiming mainly at chrome-free bricks with general improvement to properties [1-4].

What can be observed today is a constant concern with the development of new chrome-free refractories, mainly based on two systems: magnesia-spinel ($MgAl_2O_4$) and dolomite. In table I it is presented comparative data for the three refractories mostly used in transition and burning zones of cement rotary kilns [5]. The main advantage of magnesia-spinel refractories is the thermal spalling resistance, once the thermal expansion difference between magnesia and magnesia-alumina spinel aggregates creates a proper amount of voids in the microstructure, thereby improving this property [6]. Despite their improved overall properties, these refractories display a poor coating adherence, which limits their use in burning zones. On other hand dolomite refractories present low spalling and hydration resistance, but excellent coating adherence.

Table 1. Properties of refractory lines used in transition and burning zones of cement rotary kilns [5].



Property	Spinel	Dolomite	Magnesia-Chromite
Chrome	♦	♦	◊
Coating Adherence	□	O	Δ
Mechanical Resistance	Δ	□	O
Thermal Spalling Resistance	O	□	Δ
Structural Stability	O	□	Δ
Hydration Resistance	Δ	□	O

O Good, Δ Moderate, □Bad, ◊ Present, ♦ Absent

Apart from the technologies mentioned in the previous paragraph, today there are new refractories based on new systems, such as: magnesia-zirconia, magnesia-calcia-zirconia, magnesia-spinel-zirconia, magnesia-hercynite ($FeO•Al_2O_3$) and magnesia-galaxite ($MnO•Al_2O_3$) [7-11]. Great efforts are concentrated in $MgO-Al_2O_3-ZrO_2$ and $CaO-MgO-ZrO_2$ systems. Despite its hydration problem, research findings point out that dolomite-magnesia-zirconia bricks as the best refractory system for the burning zone of cement rotary kilns. Magnesia-spinel-zirconia is quite a recent new development and its results have been promising. Magnesia-hercynite initially presented good results attached to low cost production and chrome-free technology; although it demands excellent furnace operation and shows limitations regarding use of fuel waste and alternative sources of raw materials. In a well controlled furnace magnesia-hercynite presents good coating adherence, once high viscous phases, such as calcium-ferrite and calcium-aluminate are formed in the interface refractory-cement. In addition, hercynite is not corroded by alkaline chlorites and provides thermal spalling resistance even in low quantities [12]. Presently, titania is another oxide under study. Makino et al. [13] evaluated compositions from the system $MgO-TiO_2-Al_2O_3$ (MTA) as substitute for chromite and spinel in cement rotary kilns. Preliminary results showed a better thermal spalling resistance than magnesia-chromite, but worse than magnesia-spinel. Samples from MTA system were attacked by a mixture of cement with the addition of 10% of calcium sulphate. Results were very similar to magnesia-chromite refractories and better than magnesia-spinel refractories. In general, refractories from MTA system are presenting good potential for use in cement rotary kilns.

Motivated by these last results, in this work it was evaluated the effects of electrofused aggregates from $MgO-TiO_2-CaO$ (MTC) system when employed in refractories for the burning zone of cement rotary kilns. One of the advantages of this type of aggregate is the absence of free calcia in its composition, which eliminates the hydration problems.

2. EXPERIMENTAL METHOD

In this study, three refractory compositions were evaluated. One composed of magnesia with 15% by weight of an electrofused magnesia-alumina spinel aggregate (named MA) and two other magnesia based compositions also containing 15% by weight of MTC phase system aggregates (named MTC 1 and MTC 2). Refractory bricks with dimensions of 228 x 114 x 63 mm were produced by mixing raw-materials prepared in a typical industrial granulometric distribution for maximum packing, pressing, drying and sintering at 1550°C for 6 hours. Samples were extracted from the refractory bricks and submitted to several tests including: resistance to attack by SOx in reducing atmosphere, thermal spalling resistance test, apparent porosity, bulk density, true specific gravity, water absorption, total porosity, chemical analysis, elastic modulus, thermal expansion coefficient and coating adherence test.

Resistance to SOx attack in reducing atmosphere was based on the work by Tokunaga et al. [14]. Samples with dimensions of 60 x 60 x 200 mm were extracted from refractory bricks, and a hole with 35 mm in diameter and 20 mm deep was made in one of 60 x 60 mm sides. In this hole, a corrosive mixture, consisting of 35% of $CaSO_4•2H_2O$, 35% of K_2SO_4 and 30% of KCl, was inserted. A protection from the refractory brick itself was placed over the hole and the set was introduced in an electric furnace, as shown in **Figure 1.** The test was conducted by cycling for three times the temperature from 1300°C down to 800°C. After the test, the samples were cut into sections at 15 mm intervals, starting from the bottom of the hole. Each cut section was submitted to chemical analysis.

For thermal spalling resistance evaluation, the method described by Prange et al. [15] was used. Samples with dimensions of 110 x 25 x 25 mm were extracted from refractory bricks and placed in an electric furnace preheated to 950°C. After 1 hour these samples were removed from the furnace and cooled down in the air. This procedure was repeated, to supply samples with 10, 30 and 50 shocks. After test, four specimen of each sample were subjected to a 4-points bending test, and with the rupture results of the samples without thermal shock it has been possible to plot a graph of the residual mechanical strength percentage against the number of thermal cycles.

Coating adherence test was based on the works of Honda and Ohta [16] which took into account a thermal gradient between the hot and cold face of the refractory and the residency time in the test temperature. To guarantee an adequate thermal gradient, the same furnace shown in **Figure 1** was used, replacing the graphite in the internal chamber for fused magnesia. Prismatic samples with dimensions of 80 x 40 x 40 mm were extracted from refractory

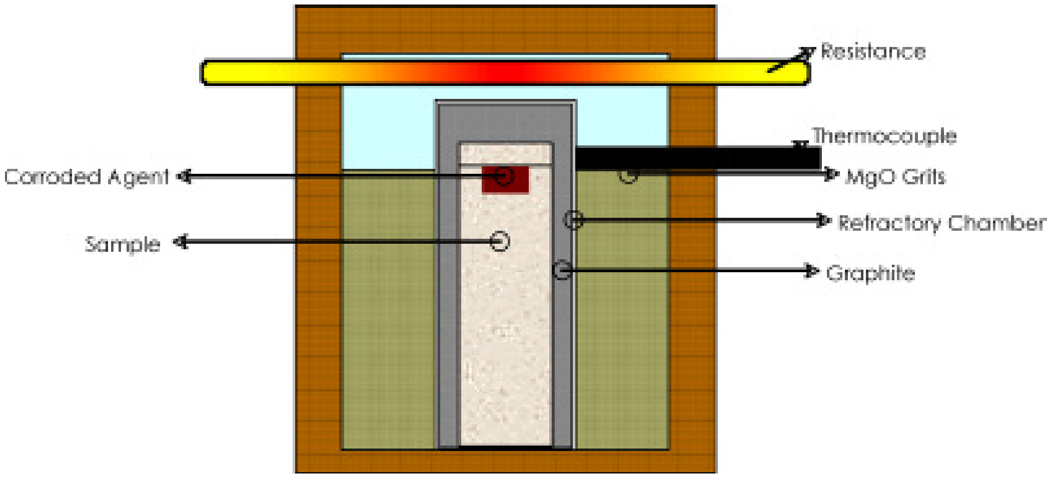


Figure 1. SOx attack in reducing atmosphere furnace scheme.

bricks and inserted in the furnace. On the top face, a 30-gramme Portland cement tablet, with chemical analysis shown in **Table 2**, was placed. The set was heated up to 1450°C for 20 hours and cooled down up to room temperature. After that the tablet was replaced by a new one and the set was then heated up again to 1450°C for a further 20 hours. After testing, refractory samples were evaluated by x-ray diffraction and scanning electronic microscopy.

For the determination of thermal expansion coefficient, samples with nominal dimensions of 50 mm in diameter and 50 mm in height were extracted from refractory bricks. In each sample, between the superior and inferior faces, a central and longitudinal 12 mm hole was made. Each formulation was placed inside Netzsch equipment, model RUL 421E, where a minimum constant load of 0.02 MPa and a heating rate of 5°C/min were applied up to a temperature of 1200°C. This procedure made the equipment work like a dilatometer.

The elastic modulus measurement was made using impulse/resonance method in Grindo Sonic equipment in samples of 25 x 25 x 150 mm extracted from the refractory bricks.

Table 2. Chemical analysis of Portland cement (percentage values by weight).

SiO_2	TiO_2	Fe_2O_3	Al_2O_3	Cão	MgO	Na_2O	K_2O
19.7	0.33	3.41	5.12	62.3	8.00	0.27	0.90

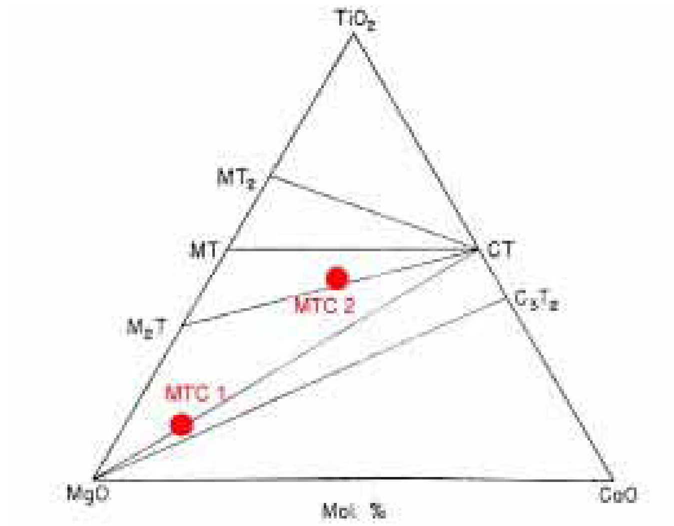


Figure 2. Phase diagram of MgO-TiO_2-CaO system, showing compositions evaluated in this work.

3. RESULTS AND DISCUSSIONS

The MTC aggregates chosen for this work are shown in the phase diagram showed in **Figure 2**, where Alkemade lines can be seen. The electrofused aggregate with MTC 1 composition presented, as its main phases, periclase, calcium titanate ($CaTiO_3$) and a solid solution of $MgAl_2O_4$ and Mg_2TiO_4 ($MgAl_2O_4$•Mg_2TiO_4). On the other hand, the aggregate MTC 2 presented calcium titanate ($CaTiO_3$), a solid solution $MgAl_2O_4$•Mg_2TiO_4 and $MgTiO_3$. **Table 3** shows the results of chemical analysis and the number of phases present in each aggregate calculated using the x-ray diffraction and scanning electronic microscopy results.

Table 4 shows chemical analysis results, water absorption, apparent porosity, bulk density, true specific gravity, total porosity, 4-points bending test results, elastic modulus and thermal expansion coefficient of refractories produced with MA, MTC 1 and MTC 2 aggregates.

The results shown in table III indicate that all refractory compositions presented very similar impurity levels (Fe_2O_3, SiO_2, Na_2O, K_2O) and bulk density results. True specific gravity is directly proportional to calcium titanate content; the increase in $CaTiO_3$ content leads to a higher true specific gravity. Apparent and total porosities are also lower. The MTC 1 and MTC 2 refractory compositions have 4-points bending strength and elastic module much higher than those for bricks of the MA composition. Thermal expansion coefficients are also coherent for each composition. In MA refractories the presence of MgO with a thermal expansion coefficient of 13.5x10^{-6} °C^{-1} and magnesia-alumina spinel with a thermal expansion coefficient of 7.6x10^{-6} °C^{-1}, generated a refractory with an intermediate thermal expansion coefficient of 12.8x10-6 °C-1. Substituting spinel for MTC aggregates produced refractories with slightly higher thermal expansion coefficients. MTC 1 aggregates have a significant quantity of MgO and $CaTiO_3$ with thermal expansion coefficient of 14.1x10^{-6} °C^{-1} [17]. In this way, MTC 1 aggregates present higher thermal expansion coefficient when compared with MA aggregates. On the other hand MTC 2 aggregates present $CaTiO_3$ and Mg_2TiO_4, the latter with a thermal expansion coefficient of 10x10^{-6} °C^{-1} [18]. As a consequence, the use of MTC 2 aggregates generated refractories with a lower thermal expansion coefficient when compared with MTC 1 refractories.

Figures 3, 4 and 5 present results of SOx attack in reducing atmosphere. K_2O penetration analysis showed a similar behavior for MA and MTC 1 refractories. Penetration occurs up to 45 mm

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Table 3. Chemical and mineralogical results from MA, MTC 1 and MTC 2 aggregates (percentage by weight).

	MA	MTC 1	MTC 2
TiO_2	0.02	15.7	55.8
SiO_2	0.22	0.78	0.68
Fe_2O_3	0.13	0.29	0.78
CaO	0.17	9.93	21.4
MgO	32.0	70.7	18.9
Na_2O	0.30	0.09	0.07
Al_2O_3	67.1	2.53	2.35
Mineralogical Composition	100% $MgAl_2O_4$	70% MgO 24% $CaTiO_3$ 6% $MgAl_2O_4$•Mg_2TiO_4	51% $CaTiO_3$ 39% $MgAl_2O_4$•Mg_2TiO_4 10% $MgTiO_3$

Continued From Page 16

Table 4. Chemical analysis results, water absorption, apparent porosity, bulk density, true specific gravity, total porosity, 4-points bending test results, elastic modulus and thermal expansion coefficient.

	MA	MTC 1	MTC 2
MgO (%)	88.24	92.29	85.81
Al_2O_3 (%)	9.12	0.73	1.05
CaO (%)	0.84	2.31	3.26
TiO_2 (%)	0.03	2.93	8.01
Fe_2O_3 (%)	0.64	0.63	0.63
SiO_2 (%)	0.72	0.70	0.83
Na_2O (%)	0.41	0.39	0.38
K_2O (%)	0.01	0.01	0.02
Water Absorption (%)	6.1 + 0.5	5.1 + 0.4	4.1 + 0.2
Apparent Porosity (%)	17 + 1	14 + 2	12 + 1
Bulk Density (g/cm^3)	2.9 + 0.1	3.0 + 0.1	3.1 + 0.2
True Specific Gravity (g/cm^3)	3.57 + 0.01	3.64 + 0.01	3.69 + 0.01
Total Porosity (%)	18.8	17.6	15.9
4-Points Bending Test (MPa)	7.1 + 0.6	13.6 + 0.5	11 + 1
Elastic Modulus (GPa)	35.4	128.3	94.1
Thermal Expansion Coefficient (x 10^{-6} °C^{-1})	12.8	13.7	13.2

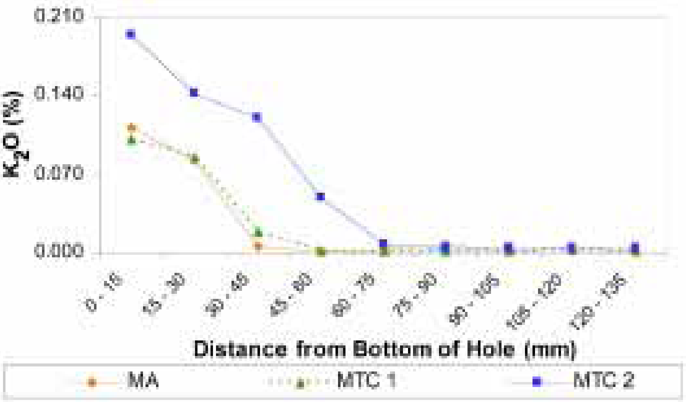


Figure 3. K_2O penetration results of refractories attacked in reducing atmosphere.

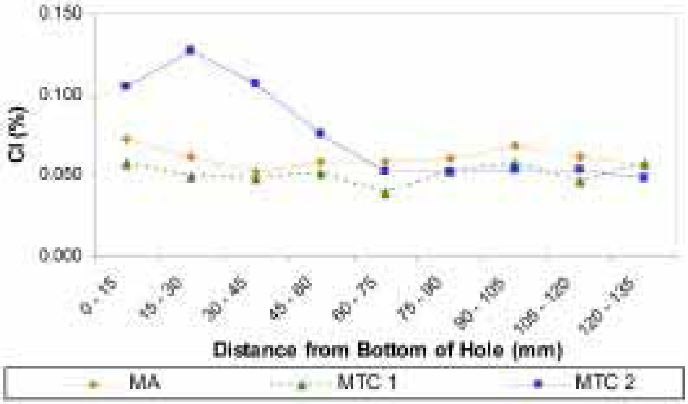


Figure 5. Chlorine penetration results of refractories attacked in reducing atmosphere.

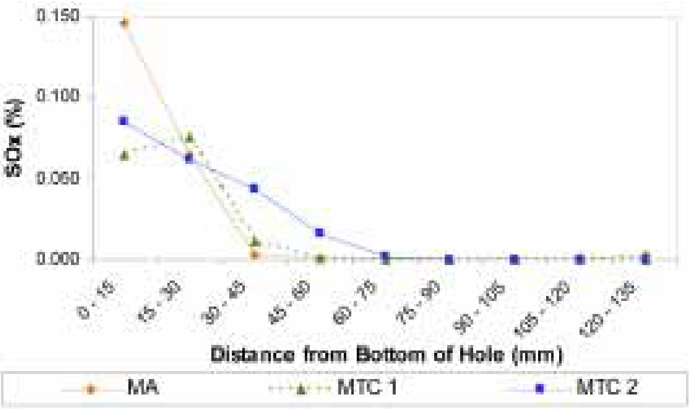


Figure 4. SOx penetration results of refractories attacked in reducing atmosphere.

from the bottom of the hole and reduces significantly after that. MTC 2 refractories showed a strong penetration of K_2O up to 75 mm from the bottom of the hole.

Results for penetration of sulphur and chlorine showed a strong concentration in MA refractories in the first 15 mm, after that there is a strong decrease up to 60 mm in depth. Refractories from MTC 1 formulation presented better performance and penetration up to 60 mm. In contrast, MTC 2 refractories presented high sulphur and chlorine penetration up to 75 mm in depth.

In general, MTC 2 composition refractories presented higher potassium, sulphur and chlorine penetrations (up to 75 mm from the bottom of the hole). Even with the lowest apparent and total porosity, MTC 2 is the least promising composition in relation to attacks by these elements.

The results obtained for loss of mechanical resistance after thermal shock from 950°C to room temperature and with 10, 30 and 50 cycles are presented in **Figure 6**. MTC 1 and MTC 2 refractories presented similar behavior when compared with MA refractories. A comparison of the results obtained by Prange et al. [15] against the results obtained in this work can be seen in **Figure 7**. Even though the curves for magnesia-spinel refractories have mechanical resistance values lower than those obtained for MA composition the slopes of the curves are very similar. It must be pointed out that all compositions evaluated in this work displayed much better properties than magnesia and dolomite refractories. Even MTC 1 refractories, with a high MgO content, presented adequate thermal spalling resistance.

When magnesia-alumina spinel is added in MgO refractory compositions, the low thermal expansion coefficient induces the creation of a proper amount of voids due to the difference between MgO and $MgAl_2O_4$ thermal expansion coefficients. These defects are responsible for a better thermal spalling results, but cause higher porosity, lower mechanical resistance and lower elastic modulus values. Aggregates from MgO-TiO_2-CaO system investigated in this work presented thermal expansion coefficients equivalent to MgO which enabled the production of refractories with low porosity, and higher mechanical resistance and elastic modulus values without compromise thermal spalling resistance.

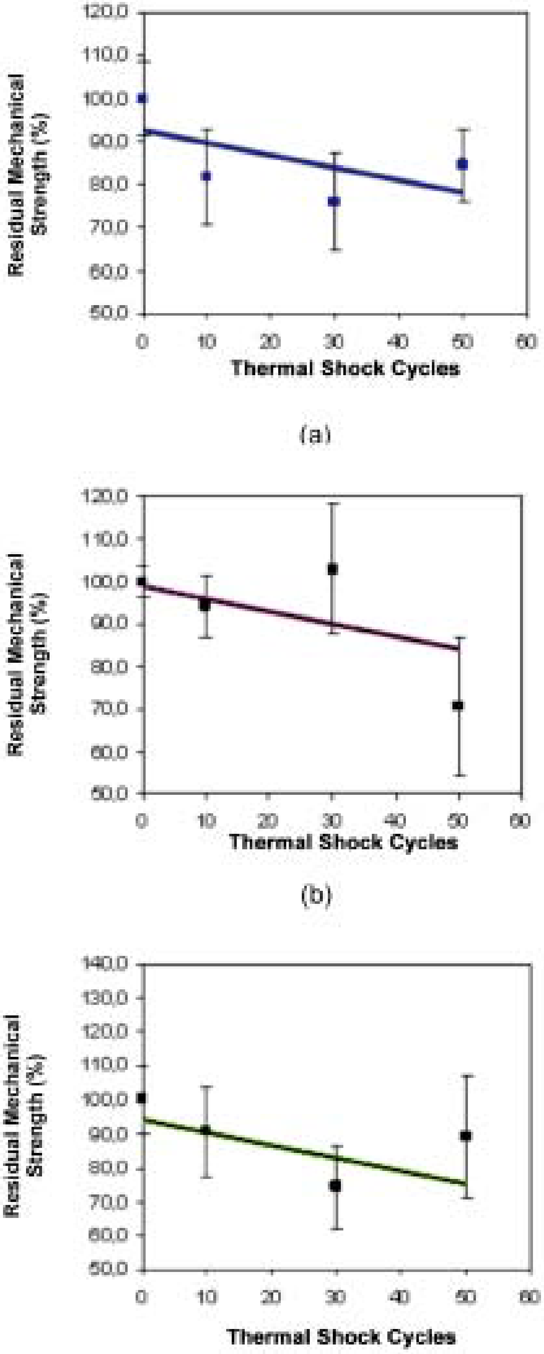


Figure 6. Loss of resistance results after thermal shock in refractories of formulations (a) MA, (b) MTC 1 and (c) MTC 2.

Coating adherence results are presented in **Figure 8.** After 40 hours at 1450°C only MTC 1 and MTC 2 compositions presented adherence in Portland cement. MA composition didn't present any adherence at all. X-ray results of the first 10 mm reacted from the surface of refractory are showed in T**able 5**, where MgO peaks were excluded.

Portland cement reacts with spinel producing $CaAl_2O_4$ as demonstrated in **Equation 1**.

$$MgAl_2O_4+Ca_3SiO_5 \rightarrow MgO+CaAl_2O_4+Ca_2SiO_4 \quad (1)$$

Degradation of alumina-magnesia spinel aggregates when in contact with Portland cement phase is showed in SEM of **Figure 9** (a). As pointed out in previous reports [19-21] reaction products formed in this reaction generate low temperature liquid phase turning difficult the coating adherence.

In the MTC 1 composition the formed Mg_2TiO_4 reacts with Ca_3SiO_5 resulting in two different reaction products depend on the quantity of Mg_2TiO_4 in contact with Ca_3SiO_5. When the quantity of Mg_2TiO_4 is superior than Ca_3SiO_5 the reaction products are $CaTiO_3$, merwinite and periclase as showed in **Equation 2** and **Figure 9b**. Near the surface of refractory, where the quantity of Mg_2TiO_4 is higher, the reaction products are $CaTiO_3$, Ca_2SiO_4 and periclase as hypothesized in **Equation 3** and **Figure 9c**.

$$3Mg_2TiO_4+2Ca_3SiO_5 \rightarrow 3CaTiO_3+5MgO+Ca_3MgSi_2O_8 \quad (2)$$

$$Mg_2TiO_5+Ca_3SiO_5 \rightarrow CaTiO_3+2MgO+Ca_2SiO_4 \quad (3)$$

MTC 2 compositions present large quantities of Mg_2TiO_4 which upon reaction with Ca_3SiO_5 results in $CaTiO_3$, Ca_2SiO_4, periclase and a phase rich in magnesia, iron oxide and alumina as showed in **Figure 9d**.

Reaction products of **Equations 2 and 3** can be solid or even a high viscous phase at 1450°C, promoting the coating adherence in refractory.

4. CONCLUSIONS

- The compositions investigated in MgO-TiO_2-CaO system presented interesting results regarding the development of alternative refractories for the burning zone of cement rotary kilns. The presence of Mg_2TiO_4 leads to the formation of merwinite/Ca_2SiO_4, per-

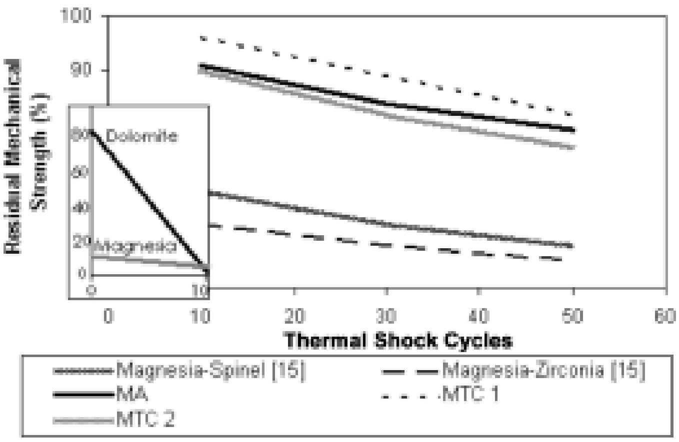
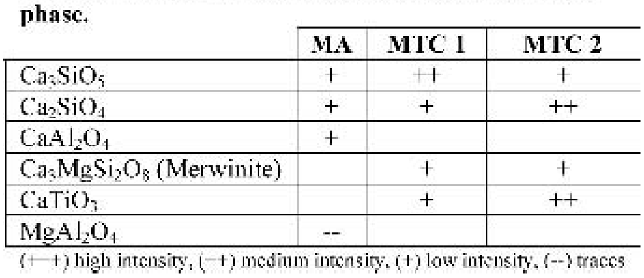


Figure 7. Comparative thermal spalling resistance of different refractories.

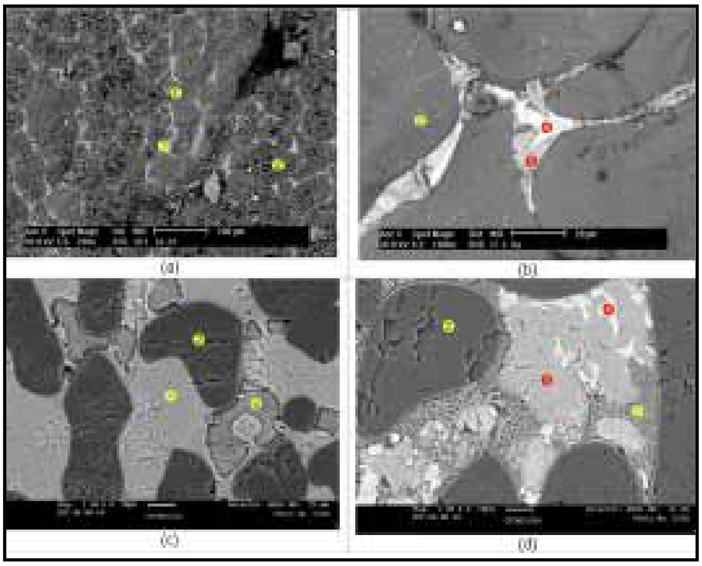
Figure 8. Reaction between Portland cement and MA, MTC 1 and MTC 2 refractories, showing adherence in MTC 1 and MTC 2 compositions.

Table 5. X-ray diffraction results, excludin periclase phase.



	MA	MTC 1	MTC 2
Ca_3SiO_5	+	++	+
Ca_2SiO_4	+	+	++
$CaAl_2O_4$	+		
$Ca_3MgSi_2O_8$ (Merwinite)		+	+
$CaTiO_3$		+	++
$MgAl_2O_4$	--		

(+++) high intensity, (++) medium intensity, (+) low intensity, (--) traces



❶ $MgAl_2O_4$ ❷ MgO ❸Cement ❹ $CaTiO_3$ ❺ $Ca_3MgSi_2O_8$ ❻ Ca_2SiO_4
❼ Phase rich in Mg, Al, and Fe

Figure 9. SEM of (a) MA, (b and d) MTC 2 and (c) MTC 1 compositions after reaction with Portland cement at 1450°C for 40 hours.

iclase and $CaTiO_3$ after reaction with the clinker. These phases allow the adherence of MTC 1 and MTC 2 compositions to Portland cement.

- MTC 1 and MTC 2 refractories presented excellent thermal spalling resistance comparable to MA refractories, despite of their higher thermal expansion coefficients. The mechanism by which this property turned out to be superior is not yet understood.

- MTC 2 refractories presented low resistance when attacked by a corrosive agent composed of 35% of $CaSO_4{\bullet}2H_2O$, 35% of K_2SO_4 and 30% of KCl. On the other hand, MTC 1 refractories presented comparable resistance when compared with MA refractories.

5. ACKNOWLEDGMENTS

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