REACTION BEHAVIOR OF MAGNESIUM ORTHOTITANATE AND CALCIUM TITANATE WITH COMPOUNDS OF PORTLAND CEMENT AND THEIR USE IN A CHROME-FREE REFRACTORY

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ABSTRACT

In this work magnesium orthotitanate (Mg_2TiO_4) and calcium titanate ($CaTiO_3$) were submitted individually to a reaction with CaO, Ca_2SiO_4, Ca_3SiO_5, $Ca_3Al_2O_6$ and $Ca_4Al_2Fe_2O_{10}$ in an electric furnace at 1450°C for 2.5 hours. The powder X-ray diffraction analysis revealed the formation of calcium titanate during the reaction of magnesium orthotitanate with most of the Portland cement phases. By other hand, calcium titanate was not affected when in contact with Portland cement phases. These results opened a great possibility in exploring both phases in a new chrome-free refractory. In a second step of this research, a magnesia-magnesium orthotitanate-calcium titanate refractory brick was produced and compared with a standard magnesia-spinel refractory brick. Both formulations were evaluated in 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 associated with scanning electronic microscopy. Refractories of magnesia-magnesium orthotitanate-calcium titanate system presented excellent coat adherence result maintaining the same level of thermal spalling resistance when compared with a standard magnesia-spinel refractory.

INTRODUCTION

Chrome-free refractories for the burning zone of cement rotary 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. By this way, several refractory phase systems have been alternatively evaluated; most of them based in magnesia-alumina spinel and dolomite systems. In table I it is presented comparative data for the three refractories mostly used in transition and burning zones of cement rotary kilns [1]. Magnesia-alumina spinel refractories present a poor coat adherence resistance once, in contact with Portland cement, these refractories generate calcium aluminate phases [2]. Dolomite refractories, on other side, present low spalling and hydration resistance.

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

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

To diminish these problems many developments were conducted to improve refractories for cement rotary kilns. New systems were developed, such as: magnesia-zirconia, magnesia-spinel-zirconia, magnesia-calcia-zirconia, magnesia-hercynite and magnesia-galaxite [3-7]. 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 [8]. Presently, titania is another oxide under study. Makino et al [9] evaluated compositions from the system MgO-TiO_2-Al_2O_3 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 $MgO-TiO_2-Al_2O_3$ 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.

This research is divided in two stages. In the first one the authors evaluated the reaction products when Portland cement phases reacted with refractory phases. In the second stage, refractory bricks were formulated with the refractory phases initially evaluated in the first stage.

EXPERIMENTAL METHOD

Refractory Phases Evaluation

In this study the authors investigated the reaction between Portland cement phases and refractory phases, more precisely magnesium orthotitanate (Mg_2TiO_4) and calcium titanate ($CaTiO_3$). The procedure was similar as described in the paper of Radovanovic [10]. A mixture of 5 grams of refractory phase and 5 grams of Porltand cement phase was pressed in a tablet shape and submitted to a thermal treatment at 1450°C for 2.5 hours. After this treatment all reacted tablets were de-agglomerated and the powder was evaluated by X-ray analysis. The Portland cement phases evaluated were CaO, Ca_3SiO_5 (C_3S), Ca_2SiO_4 (C_2S), $Ca_3Al_2O_6$ (C_3A), $Ca_4Al_2Fe_2O_{10}$ (C_4AF). These phases were obtained from analytical reagents after mixture and different heat treatments.

Refractory Bricks Evaluation

Two refractory compositions were evaluated. One composed of magnesia with 15% by weight of an electrofused magnesia-alumina spinel aggregate (named MA) and another one also composed of magnesia with 15% by weight of an electrofused aggregate containing magnesia, magnesium orthotitanate and calcium titanate (named MTC). 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 SO_x in reducing atmosphere, thermal spalling resistance test, apparent porosity, bulk density, true specific gravity, water absorption, total porosity, chemical analysis, elastic modulus, linear thermal expansion coefficient and coating adherence test.

Resistance to SO_x attack in reducing atmosphere was based on the work by Tokunaga et al [11]. 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 (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.

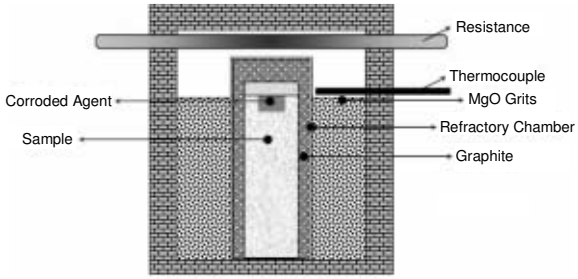


Fig. 1. SO_x attack in reducing atmosphere.

For thermal spalling resistance evaluation 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 thermal 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 [12].

For coating adherence test it was used the same furnace shown in figure 1, 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 bricks and inserted in the furnace. On the top face, a 30-gramme Portland cement tablet 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.

For the determination of linear 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.

RESULTS AND DISCUSSION

Refractory Phases Evaluation

Tables 2 and 3 present results obtained by X-ray analysis after reactions between Portland cement phases and refractory phases (Mg_2TiO_4 and $CaTiO_3$).

Tab. 2. Mineralogical results after reaction of Portland cement phases and Mg_2TiO_4.

	Mg_2TiO_4
CaO	MgO (+++), $CaTiO_3$ (+++), CaO (+),$Ca(OH)_2$ (+)
C_3S	MgO (+++), $CaTiO_3$ (+++), $Ca_3MgSi_2O_8$ (++)
C_2S	MgO (+++), $CaTiO_3$ (+++), $CaMgSiO_4$ (++)
C_3A	MgO (++), $CaTiO_3$ (+++), $CaAl_2O_4$ (+), C_3A (+), Mg_2TiO_4 (-)
C_4AF	$CaTiO_3$ (+++), Mg_2TiO_4 (++), C_4AF (+), Non Identified Phase (+)

(+++) High intensity, (++) Medium intensity, (+) Low intensity, (-) Traces

Tab. 3. Mineralogical results after reaction of Portland cement phases and $CaTiO_3$.

	$CaTiO_3$
CaO	$CaTiO_3$ (+++), CaO (+++), $Ca_3Ti_2O_7$ (-), $Ca(OH)_2$ (-)
C_3S	$CaTiO_3$ (+++), γ-C_2S (+), C_3S (++), $Ca_6Si_4(OH)_4O_{16}$ (-)
C_2S	$CaTiO_3$ (+++), γ-C_2S (+++)
C_3A	$CaTiO_3$ (+++), C_3A (++)
C_4AF	$CaTiO_3$ (+++), $CaFe_2O_4$ (++), C_3A (+), $CaFeO_4$ (+), Non Identified Phase (++)

(+++) High intensity, (++) Medium intensity, (+) Low intensity, (-) Traces

Reactions between Portland cement phases and Mg_2TiO_4 showed decomposition of magnesium orthotitanate, liberating MgO and TiO_2. In any case TiO_2 reacts with calcia present in each Portland cement phase resulting in a refractory calcium titanate phase. It looked promised to promote coat adherence in refractories for burning zone of cement rotary kiln.

By other side, calcium titanate shows a more stable behavior during reaction with Portland cement phases. In any case calcium titanate didn't decompose, maintaining its integrity after reaction. Calcium titante wouldn't promote coat adherence in refractories, but its high thermal expansion coefficient ($14.1x10^{-6}$ °C^{-1}) allows a thermal expansion balance when magnesium orthotitanate ($10x10^{-6}$ °C^{-1}) is present.

Refractory Bricks Evaluation

Table 4 shows chemical analysis results, water absorption, apparent porosity, bulk density, true specific gravity, total porosity, 4-points bending strength, elastic modulus, linear thermal expansion coefficient and SO_x attack of refractories MA and MTC.

Tab. 4. Chemical analysis results, water absorption, apparent porosity, bulk density, true specific gravity, total porosity, 4-points bending strength, elastic modulus, linear thermal expansion coefficient and SO_x attack.

	MA	**MTC**
MgO (%)	88.24	92.29
Al_2O_3 (%)	9.12	0.73
CaO (%)	0.84	2.31
TiO_2 (%)	0.03	2.93
Fe_2O_3 (%)	0.64	0.63
SiO_2 (%)	0.72	0.70
Na_2O (%)	0.41	0.39
K_2O (%)	0.01	0.01
Water Absorption (%)	6.1 $\pm$ 0.5	5.1 $\pm$ 0.4
Apparent Porosity (%)	17 $\pm$ 1	14 $\pm$ 2
Bulk Density (g/cm^3)	2.9 $\pm$ 0.1	3.0 $\pm$ 0.1
True Specific Gravity (g/cm^3)	3.57 $\pm$ 0.01	3.64 $\pm$ 0.01
Total Porosity (%)	18.8	17.6
4-Points Bending Strength (MPa)	7.1 $\pm$ 0.6	13.6 $\pm$ 0.5
Elastic Modulus (GPa)	35.4	128.3
Thermal Expansion Coefficient (x 10^{-6} °C^{-1})	12.8	13.7

The results shown in table 4 indicate that refractory compositions presented very similar impurity levels (Fe_2O_3, SiO_2, Na_2O, K_2O) and bulk density results. Apparent and total porosities are also lower. The MTC refractory composition has 4-points bending strength and elastic module much higher than those for bricks of the MA composition. Linear thermal expansion coefficients are also coherent for each composition.

K_2O penetration analysis showed a similar behavior for MA and MTC refractories (figure 2). Penetration occurs up to 45 mm from the bottom of the hole and reduces significantly after that. Results for penetration of sulphur 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 formulation presented better performance and penetration up to 60 mm.

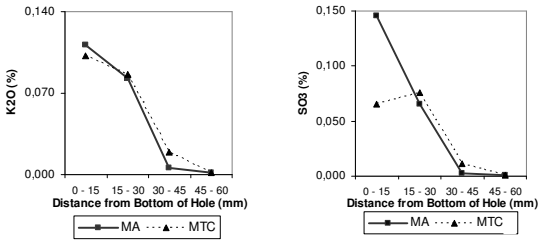


Fig. 2. Penetration results of K_2O and SO_3.

A comparison of the results obtained by Prange et al [12] against the results obtained in this work for loss of mechanical strength after thermal shock from 950°C to room temperature and with 10, 30 and 50 cycles can be seem in figure 3. MTC composition presented similar behavior when compared with MA and much better properties than magnesia and dolomite refractories. Even MTC refractories, with a high MgO content, presented adequate thermal spalling resistance.

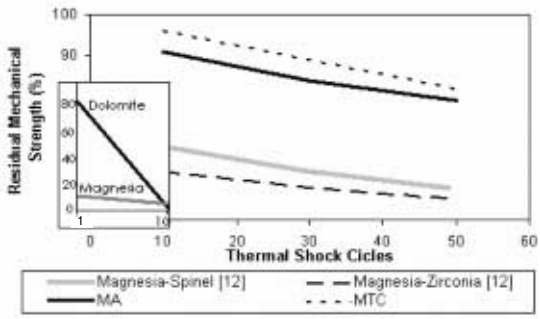


Fig. 3. Comparative thermal spalling resistance of different refractories.

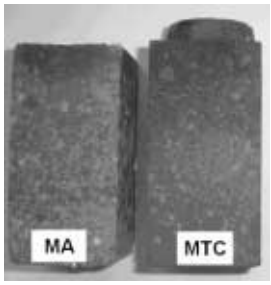
Coating adherence results are presented in figure 4. After 40 hours at 1450°C only MTC composition presented adherence in Portland cement. MA composition didn't present any adherence at all. X-ray diffraction results of the reacted first 10 mm from the surface of refractory showed a considerable amount of calcium titanate and no presence of magnesium orthotitanate, suggesting its total decomposition. These results are consistent with the individual reaction of each Portland cement phase and refractory phases showed in table 2 and 3.

CONCLUSIONS

✓ Magnesium orthotitanate (Mg_2TiO_4) leads to the formation of $CaTiO_3$ after reaction with the clinker of Portland cement, liberating periclase in the refractory system. This reaction promotes good coat adherence.

✓ Calcium titanate ($CaTiO_3$) is stable when in contact with Portland cement phases. Calcium titanate helps to control the linear thermal expansion coefficient of the refractory formulation.

✓ Refractories produced with magnesium orthotitante and calcium titanate is suitable for use in the burning zone of cement rotary kilns.



	MA	MTC
C_3S	+	+
C_2S	+	+
$CaAl_2O_4$	+	
$CaTiO_3$		++
$MgAl_2O_4$	-	

(+++) High intensity,
(++) Medium intensity,
(+) Low intensity, (-) Traces

Fig. 4. Coating adherence result and X-ray analysis of the first 10 mm reacted. X-ray results don't show periclase phase.

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