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Magnesia sinter hydration–dehydration behavior in refractory castables

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Abstract

Magnesia (MgO) easily reacts with water when exposed to humidity or during the mixing of refractory castables, resulting a $Mg(OH)_2$ coating layer on a particles' surface. When castables dewater (above 350 °C), this coating begins to decompose, generating porosity and a highly reactive magnesia. Despite the abundant literature concerning magnesia hydration–dehydration mechanisms, few studies were related to refractories. In the present work, aqueous suspensions of thermally treated magnesia sinter were prepared and the influence of the calcination temperature on magnesia reactivity was evaluated by the apparent volumetric expansion (AVE) measurements. Based on these results, the drying behavior of magnesia sinter containing castables was related to mechanical strength and porosity measurements. The effects of re-hydration damages caused by humidity exposition after drying were also investigated.

Keywords: A. Calcination; Magnesia; Hydration; Dehydration

1. Introduction

Magnesia hydration is a major concern regarding its use in refractory castables formulations [1–3]. Besides the rheological difficulties it can impose to castables' processing, two other main side effects have been described in literature. The first one, known as apparent volumetric expansion (AVE) [4], is related to a threefold volumetric expansion that follows magnesia hydration. This expansion is caused by the density mismatches between magnesium oxide ($\rho_{MgO} = 3.5$ g/cm^3) and its hydroxide ($\rho_{Mg}(OH)_2 = 2.4$ g/cm^3) [5–8], and can easily generate intense compressive stress leading to severe mechanical damages. The second one, which was the main objective of this work, is related to the use of partially hydrated magnesia particles in castables' formulations and its consequences on the drying schedule.

Fine magnesia sinter particles react with humidity during storage [9] or with water when the castables are being mixed and cured and rapidly develop a thin, micro-cracked film of $Mg(OH)_2$ on their surfaces [5,6]. This hydroxide layer behaves as a barrier to water diffusion [8] and, under steady temperature and humidity conditions, no further hydration reaction is observed [1,8,9]. The resulting particle is comprised of an anhydrous magnesia core surrounded by a thin micro-cracked brucite layer [8], as schematically shown in Fig. 1a. In castables' compositions, during the first heat-up, the partially hydrated particles will decompose (between 350 and 600 °C), following the general equation:

$$Mg(OH)_2 \rightarrow MgO + H_2O \tag{1}$$

This decomposition reaction can present two main drawbacks: (1) the generation of water vapor in this temperature range can pressurize the structure causing the explosive spalling and (2) the decomposition reaction increases the porosity of the structure, resulting in a highly reactive magnesia (Fig. 1b) [8,10–14]. Besides the high susceptibility to damage by hydration, it can also lead to mechanical strength and thermal cycling resistance reduction and to the slag penetration.

In order to evaluate the extent of hydration–dehydration damages in magnesia sinter used in refractory castables, this paper was divided in two sections: (1) the effect of the calcination temperature (110–900 °C) on the reactivity of partially hydrated magnesia sinter that was investigated using aqueous suspensions and (2) the calcination reactivity results obtained in the first section were related to the drying and humidity effects of magnesia sinter containing castables.

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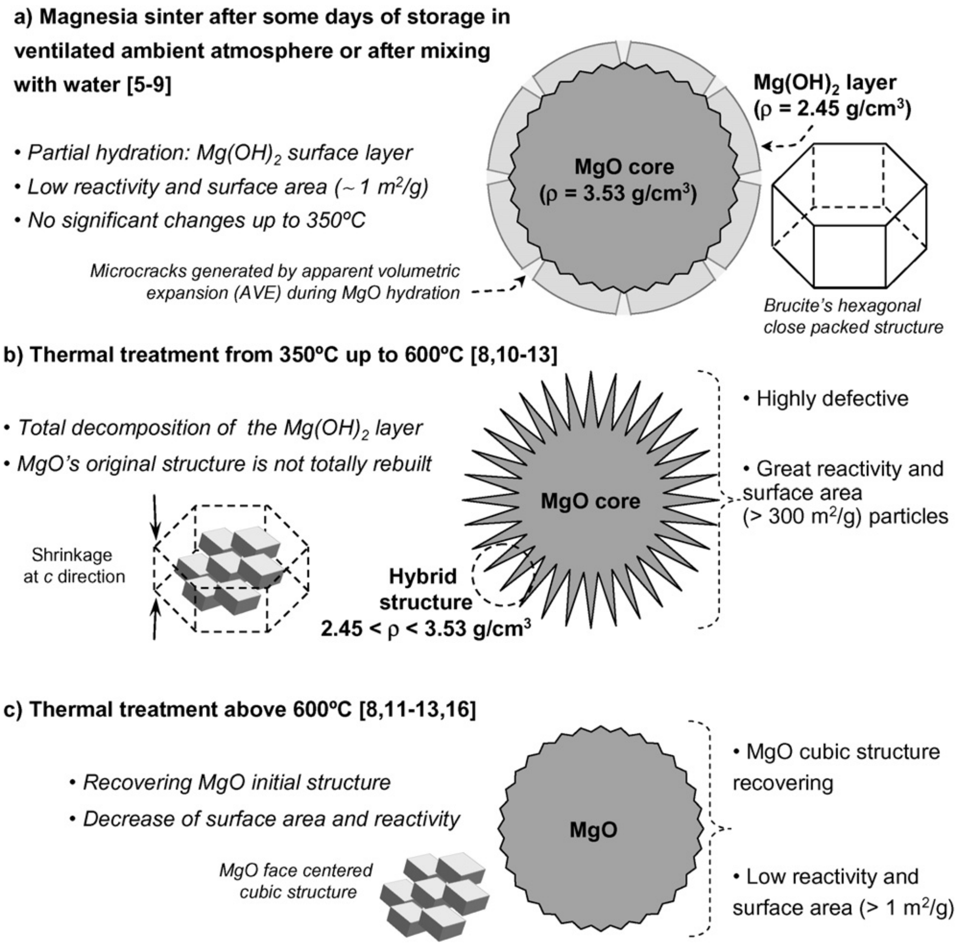

Fig. 1. $Mg(OH)_2$ decomposition mechanism: (a) partially hydrated MgO after humidity or water exposition; (b) after calcination at intermediate temperatures (350–600 °C); (c) after calcination above 600 °C.

2. Experimental procedure

Magnesia sinter (95 wt.% MgO, Table 1) powder samples were initially stored in ventilated environment (25 °C and 50% relative humidity) for 7 days and then thermally treated at different temperatures (50, 110, 350, 400, 500, 600, 700, 800 and 900 °C), for 5 h using a heating rate of 10 °C/min to the exposure temperature. The dehydration kinetics of the sinter and of a high purity magnesium hydroxide (Synth, Brazil, Table 1) was followed by thermogravimetry through the cumulative weight loss (W_D) and the drying rate (dW_D/dt, %/min), defined as

$$W_D\ (\%) = 100 \times \frac{M_0 - M}{M_0} \tag{2}$$

$$\left(\frac{dW_D}{dt}\right)_i = \frac{W_{i+10} - W_{i-10}}{t_{i+10} - t_{i-10}} \tag{3}$$

Table 1
Raw materials tested

Physical and chemical characteristics	Raw materials			
	MgO sinter (as received)[a]	High purity $Mg(OH)_2$[b]	Calcium aluminate cement (CA14M)[c]	Calcined alumina (Esy Pump 1000)[c]
Composition	95 wt.% MgO[d]	99.8 wt.% $Mg(OH)_2$	70 wt.% Al_2O_3/30 wt.% CaO[d]	99.5 wt.% Al_2O_3[d]
Density (g/cm^3)	3.5	2.4	2.9	3.9
Surface area (m^2/g)	1.1	10	1.3	3.3
Particle size (D_{90}, μm)	10	12	90	16

[a] Magnesita S.A. (Brazil).
[b] Synth (Brazil).
[c] Almatis (US).
[d] Typical values.

Table 2
(a) Magnesia sinter suspensions and (b) refractory castable formulation studied

		wt.%
(a) Magnesia sinter suspensions		
Magnesia sinter[a] thermally treated (50, 110, 350, 400, 500, 600, 700, 800 and 900 °C, 5 h hold, at 10 °C/min) after 7 days of storage in ventilated environment		80
Calcium aluminate cement[b]		10
Distilled water		10
		wt.%
(b) Magnesia sinter containing castable		
Matrix ($D_{\text{Particle}} < 100\ \mu\text{m}$)	Calcined alumina[b]	3
	Calcium aluminate cement[a]	6
	Magnesia sinter (as received)[a]	6
Aggregates ($D_{\text{Particle}} \geq 100\ \mu\text{m}$; $D_{\text{Max}} = 5.6$ mm)	White electrofused alumina[c]	84.8
Dispersant agent	Sodium phosphate[d]	0.2

[a] Magnesita S.A. (Brazil).
[b] Almatis (US).
[c] Elfusa (Brazil).
[d] Synth (Brazil).

In the drying Eqs. (2) and (3), M is the instantaneous mass recorded at time t_i during the heating stages and M_0 is the initial mass of the tested sample [15].

After these thermal treatments, aqueous suspensions (80 wt.% sinter, 10 wt.% of calcium aluminate cement and 10 wt.% water) of each thermally treated powder were prepared and vertically cast into 70 mm × 70 mm cylindrical molds specially designed to allow the measurement of the apparent volumetric expansion (AVE) with the magnesia hydration [4]. Details of the formulation are given in Table 2a.

The AVE was calculated considering the initial volume of the samples as a reference, and can be described by the following expressions:

$$V_i = \left(\frac{1}{4}\right) \times H_i \times \pi \times (D_i - 2t)^2 \qquad (4)$$

$$\text{AVE}\,(\%) = 100 \times \frac{V_{\text{E}} - V_0}{V_0} \qquad (5)$$

Expression (4) was used to calculate the volume of cylindrical samples at a particular time; where V_i equals the volume, H_i equals the height, D_i equals the diameter and t equals the mold wall thickness. For the AVE parameter in Expression (5), V_0 is the initial volume of the sample (just after casting) and V_{E} is the correspondent volume after hydration and expansion. The detailed description of the technique and its applications can be found in Ref. [4]. The samples were kept at 50 °C for 7 days in an acclimatized chamber (Vöetsch 2020) with relative humidity close to 100%. During this period, AVE was measured at every 24 h.

For the magnesia sinter containing refractory castables, a vibrated high alumina refractory castable composition containing 6 wt.% of as received magnesia sinter (Magnesita S.A., Brazil, Table 1), 6 wt.% of calcium aluminate cement (CA14M, Almatis, US, Table 1), 5.5 wt.% of water and 0.2 wt.% of a sodium phosphate as dispersant (Synth, Brazil) was used in these tests. An MgO sinter-free composition was used as reference (the amount of MgO sinter was replaced by calcined alumina with a similar particle size distribution, Table 1). A description of the formulations can be found in Ref. [4] and Table 2b. The dry mixing and the water addition were carried out in a paddle mixer for 10 min.

After mixing, formulations were cast under vibration in cylindrical molds for hydration/dehydration tests (40 mm × 40 mm). The curing time was performed in an acclimatized chamber (Vöetsch 2020), at 8 °C for 24 h in 100% relative humidity. These conditions were applied in order to assure a minimal mechanical strength of the samples for demolding and also for minor magnesia hydration [4]. The steps followed during samples processing are described in Fig. 2a.

In order to evaluate the effect of the maximum drying temperature and the castable's susceptibility to moisture after dewatering, samples were initially dried at different temperatures (from 50 °C up to 900 °C, 5 h hold, using a heating rate of 10 °C/min) to the exposed temperature. The amount of water withdrawn at each temperature (free-water plus those chemically bonded to the cement and MgO) was quantified by the parameter W_{DTotal} (wt.%), described in Equation 6 [15].

Part of the samples was used for the mechanical strength and porosity measurements just after drying. The remaining samples were exposed to a 50 °C saturated water vapor environment for 7 days (the apparatus employed is schematically present in Fig. 2b). After this moisture exposure, test samples were dried for 24 h at 110 °C to remove absorbed free-water, then had their mechanical strength and porosity measured. Humidity exposed samples were also re-heated up to 900 °C, for 5 h hold using a heating rate of 10 °C/min to determine the degree of re-hydration of MgO, represented by the W_{H} (wt.%) parameter. In this case, the W_{H} values indicate

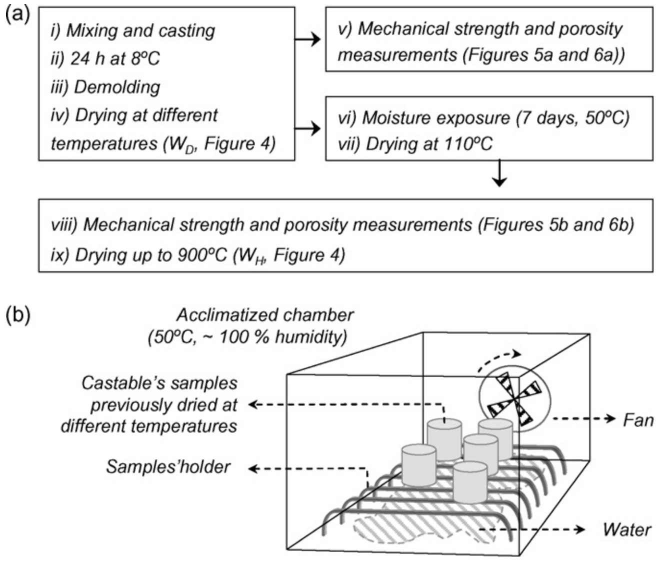

Fig. 2. (a) Steps of the castable processing and (b) schematic view of the apparatus employed to evaluate the effect of moisture exposition (50 °C, 7 days) after castables drying.

the increase in the cement and MgO initial hydration weight due to the exposition to moisture.

The parameters ($W_{\mathrm{D\ Total}}$, wt.%) and (W_{H}, wt.%) were calculated using Eq. (6):

$$W_i\ (\%) = 100 \times \frac{MA - MB}{MA} \tag{6}$$

where W_{i} is one of the water loss parameters ($W_{\mathrm{D\ Total}}$ or W_{H}) and M are the mass values before (B) or after (A) thermal treatment [15].

The splitting tensile strength was obtained according to the ASTM C496-96 standard using MTS TestStar II equipment. A constant loading rate of 42 N/s (1000 kPa/min) was employed. Five specimens for each testing condition were evaluated. The apparent porosity of the samples was measured by the immersion method, using kerosene as immersion fluid.

3. Results and dicussion

3.1. Thermally treated magnesia sinter aqueous suspensions

Fig. 3 displays the thermogravimetric results of the as-received sinter and the high-purity magnesium hydroxide. For the as-received MgO sinter sample, a small peak at 100 °C can be observed, related to the physically adsorbed water; followed by the $Mg(OH)_2$ decomposition one, from 350 °C up to 635 °C (temperature range corresponding to the loss of 10 and 90 wt.% of the initial mass, respectively) [10,11,13]. As the particle size distributions were similar, the high-purity compound decomposed in the same temperature interval, but at a higher rate. This difference was mainly attributed to the amount of hydroxide present in each case. The high-purity compound decomposed stoichiometrically, loosing ~30 wt.% of its initial weight. For the magnesia sinter, on the other hand, only a small quantity of water was lost (~3.9 wt.%), indicating that this material had a small degree of hydration. The apparent volumetric expansion (AVE) values of the thermally treated magnesia sinter suspensions can also be seen, which points out that they were strongly affected by the thermal treatment temperature and humidity exposure. The maximum values were observed by the sinter thermally treated in the range of 350–600 °C; below (as received sample, 110 and 300 °C) and above (700 and 800 °C) this temperature interval, the AVE value was reduced and was absent for the sample heated up to 900 °C.

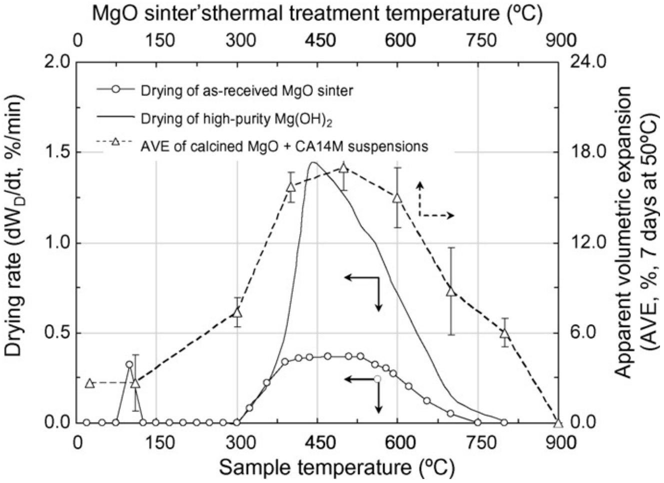

Fig. 3. Drying rate of a 7 days stored sinter and for a high-purity magnesium hydroxides. The apparent volumetric expansion (AVE) results for the thermally treated magnesia sinter suspensions samples are also shown.

Because the AVE results are directly related to the hydration degree of magnesia (the higher the AVE value, the greater the hydration degree [4]), this parameter can be used as a way to evaluate the samples reactivity after thermal treatment. The thermal treatments conducted bellow 350 °C were not able to trigger the $Mg(OH)_2$ decomposition and did not affect significantly the sinter reactivity (only adsorbed water was released, Fig. 1a) [10,11]. On the other hand, for those carried out at calcination temperatures in the range of 350–600 °C, a large increase in the reactivity of magnesia sinter was observed. It can be related to the partial decomposition of the $Mg(OH)_2$ protective layer [8,10,13] and to the defective and high surface area structure formed (Fig. 1b) [8,14]. Finally, at 900 °C, the reactivity of the magnesia particles was reduced by rebuilding the initial MgO cubic crystalline structure (Fig. 1c) [14,16].

These results represent important technological concerns regarding magnesia additions in refractory castables. As is well known, if the calcination of the magnesia sinter (or its precursors, such as magnesium carbonate, $MgCO_3$) is not conducted at the proper temperature, highly reactive particles can be produced, increasing the likelihood of mechanical damages by AVE [8,13,14,16]. Besides this, the castables' firing conditions, such as those presented in this paper, can lead to further magnesia hydration when the refractory lining is in contact with environmental moisture. In the following section, the results presented in Fig. 3 will be correlated with the effects of the maximum drying temperature on castables' mechanical strength, porosity and susceptibility to moisture exposition.

3.2. Effect of maximum drying temperature on green castables mechanical strength and porosity

Fig. 4 depicts the amount of water removed for each maximum drying temperature ($W_{\mathrm{D\ Total}}$) in castables samples. It can be observed that the higher the thermal treatment temperature, the greater the amount of water removed. This aspect is compatible with the refractory castables drying behavior, described in literature [4,15] and highlights two main points: a) at temperatures below 250–300 °C, the increase in $W_{\mathrm{D\ Total}}$ values are related mainly to the withdraw of uncombined water from the castables porous structure. The higher the temperature, the greater is the energy of the water vapor and, consequently, the greater its tendency to be released into the environment [15]. (b) Above 250–300 °C, although there was some free-water remaining, the weight loss is mainly related to the decomposition of the hydrated compounds of calcium aluminate cement and magnesia [4].

Figs. 5 and 6 show the effects of the drying temperature and humidity exposure on green castables mechanical strength and

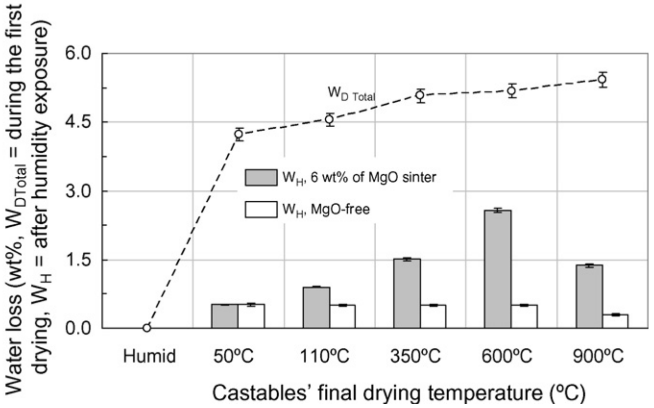

Fig. 4. Amount of water lost at each maximum drying temperature ($W_{D\ Total}$) and gained after humidity exposure (W_H) as measured by heating castable samples up to 900 °C.

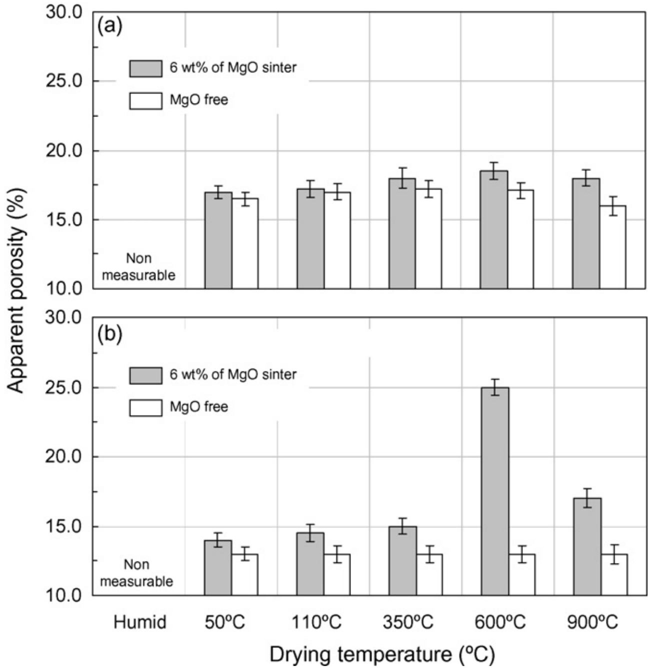

Fig. 6. Samples' porosity (a) after drying and (b) after drying and exposure to humidity.

porosity, respectively. Comparing humidity treated samples, the MgO-containing and MgO-free formulations had an increased mechanical strength when dried up to 110 °C (Fig. 5a), while there was no significant change in porosity (Fig. 6a). Between 110 and 900 °C, a reduction in mechanical strength values and an increase in porosity can be observed. Both effects were more significant in the magnesia containing composition than in the MgO-free one. Finally, for the samples fired at 900 °C, a remarkable increase in mechanical strength was observed for both compositions and the porosity was reduced to values close to the initial values (fired at 110 °C).

The samples' mechanical strength dependence on drying temperature can be associated with the different effects of water withdraw from the castables structure. At low drying temperatures (≤110 °C), only the uncombined water was removed as the cement and magnesia hydrates were not decomposed [4,10,11]. This effect reduces the distance among the castables matrix particles, enhancing the mechanical strength (when compared to the humid samples). Above this temperature, however, the cement and magnesia hydrates begin to decompose (up to 300–350 °C and between 350 and 600 °C, respectively) [4,10,11,15], increasing the samples porosity and reducing their mechanical strength. This effect is particularly important for magnesia containing materials. Besides the fact that these samples have both hydrated compounds and, due to this hydration, a greater porosity increase, the water released by the cement hydrates decomposition enhances the likelihood of damage by magnesia hydration. Above 600 °C, the early stages of sintering contribute to improve mechanical strength and reduce porosity.

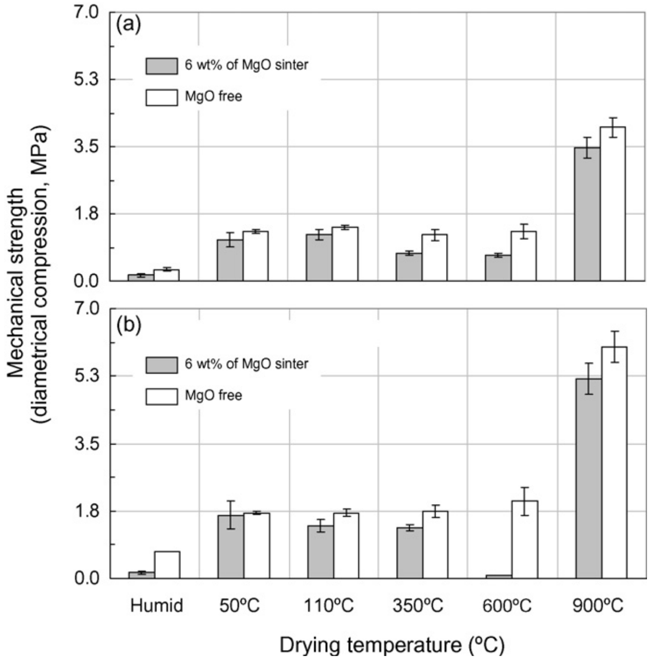

Fig. 5. Samples' mechanical strength (a) after drying and (b) after drying and exposure to humidity.

3.3. *Effect of humidity exposure on castables mechanical strength and porosity after drying*

The effects of humidity exposure after drying the castables on mechanical strength and porosity can be seen in Figs. 5b and 6b, respectively. The different drying temperatures presented a significant effect on the mechanical strength and porosity of the samples after exposure to humidity. Comparing with those tested after drying (Figs. 5a and 6a), all MgO-free samples and those containing magnesia and dried up to 350 °C and at 900 °C had significant increases in the mechanical strength and reduction in porosity; for the MgO-containing one dried at 600 °C an opposite behavior was observed.

These results suggest that, after drying at specifc temperatures, the hydration processes of cement and magnesia could carry on or be resumed if suitable conditions of temperature and humidity were provided. This hypothesis is corroborated by the literature [17] and by the hydration after humidity exposure (W_H) results presented in Fig. 4. It can be noticed that all the samples had a weight gain (chemically bonded water), confirming a further hydration of the cement and of the MgO due to the contact with water vapor. Nevertheless, for the magnesia containing samples, the W_H values were significantly higher and attained their greater values for the 600 °C treated ones. This result can be attributed to the great chemical reactivity of the magnesia after drying at intermediate temperatures (350–600 °C) and, therefore, their greater ability to promote mechanical damages due to the AVE.

For the magnesia containing samples dried up to 350 or at 900 °C, neither mechanical strength reduction nor significant weight increases were observed after humidity exposition. For the samples dried up to 350 °C, this behavior can be explained by the presence of a protective $Mg(OH)_2$ coating produced during the mixing that was not decomposed during the drying up to 350 °C [4,10,11]. The samples fired at 900 °C, on the other hand, had a higher chemical stability due to the thermal treatment conducted at 900 °C. This treatment is thought to partially rebuild the periclase original structure [12–14], causing the strenght increase.

4. Conclusions

Magnesia sinter fine particles can be partially hydrated due to the contact by environmental humidity, during storage, or due to the reaction with water in the castables' mixing step. In both cases, the magnesium hydroxide layer formed on the particles' surface can be preserved while the castables are hardening. Depending on the temperature attained during the drying, this layer was affected in different ways. For lower drying temperatures (below 350 °C), it was not affected and behaved as a protective barrier against further humidity exposure. In the temperature range between 350 and 600 °C, it was partially decomposed, resulting in a high surface area and humidity susceptible surface. Due to its defective crystalline structure, porosity was generated in the castable structure, reducing its mechanical strength. On the other hand, when drying was conducted at 900 °C, the partially decomposed hydroxide layer returned to the MgO periclase original structure, increasing its hydration resistance and mechanical strength.

Significant enhancement in the green castables mechanical properties and humidity susceptibility can be attained by modifications in the drying schedule. If the maximum drying temperature were limited to values below 350 °C, most of the free and chemically bonded water can be withdrawn at the same time, and the $Mg(OH)_2$ protective coating is preserved. In such conditions, no significant modifications in castables' properties were observed. This mechanism is especially suitable for pre-shaped monoliths stored in humid environments or for those that are in contact with water based products; such as paintings, joining mortars, or shotcreted castables, before being heated to the working temperature and sintered. On the other hand, for *in situ* cast linings (such as ladle slaging line, for example), drying must be conducted above 900 °C, to assure the re-building of the MgO original structure with its higher chemical stability.

The results attained also suggest that if the magnesia particles hydration was minimized or interrupted in its early stages (during the mixing or in the first hours of curing), the thickness of the $Mg(OH)_2$ layer formed can be reduced and, consequently, the effects of its decomposition could be less damaging to castables mechanical strength, porosity and high-temperature properties, such as slag penetration. This is the target of the novel magnesia anti-hydration techniques for refractory castables that will be studied in future research by the authors.

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References

[1] A. Kitamura, K. Onizuka, K. Tanaka, Hydration characteristics of magnesia, Taikabutsu Overseas 16 (3) (1995) 3–11.

[2] A. Kaneyasu, S. Yamamoto, A. Yoshida, Magnesia raw materials with improved hydration resistance, Taikabutsu Overseas 17 (2) (1996) 21–26.

[3] A. Yoschida, T. Nemoto, A. Kaneyasu, Evaluation method for hydration resistance of magnesia fine powder and effect of B_2O_3 content in magnesia raw materials, in: Proceedings of UNITECR', , , 2003–2003

[4] R. Salomão, L.R.M. Bittencourt, V.C. Pandolfelli, A Novel Approach for Magnesia Hydration Assessment in Refractory Castables, Ceram. Int. 33 (5) (2007) 803–810.

[5] R.I. Razouk, R.S. Mikhail, The hydration of magnesium oxide from vapor phase, J. Phys. Chem. 62 (1958) 920–925.

[6] G.K. Layden, G.W. Brindley, Kinetics of vapor-phase hydration of magnesium oxide, J. Am. Ceram. Soc. 46 (11) (1963) 518–522.

[7] P.J. Anderson, R.F. Horlock, J.F. Oliver, Interaction of water with the magnesium oxide surface, Trans. Faraday Soc. 61 (516) (1965) 2754–2762.

[8] W. Feitknecht, H. Braum, Mechanisms of hydration of magnesium oxide in water vapor (in German), Helv. Chim. Acta 50 (7) (1967) 2040–2053.

[9] P. Brandão, G.E. Gonçalves, A.K. Duarte, Mechanisms of hydration/carbonation of basic refractories—Part I, Refract. Appl. News 3 (2) (1998) 6–9.

[10] P.J. Anderson, R.F. Horlock, Thermal decomposition of magnesium hydroxide, Trans. Faraday Soc. 58 (475) (1962) 1993–2004.

[11] R.S. Gordon, W.D. Kingery, Thermal decomposition of brucite. I. Electron and optical microscope studies, J. Am. Ceram. Soc. 49 (12) (1966) 654–660.

[12] V.A. Phillips, H. Opperhauser, J.L. Kolbe, Relations among particle size, shape and surface area of $Mg(OH)_2$ and its calcination product, J. Am. Ceram. Soc. 61 (1) (1978) 75–81.

[13] J. Green, Review: calcination of precipitated $Mg(OH)_2$ to active MgO in production of refractory and chemical grade MgO, J. Mater. Sci. 18 (1983) 637–651.

[14] M.G. Kim, U. Dahmen, A.W. Searcy, Structural transformations in decomposition of $Mg(OH)_2$ and $MgCO_3$, J. Am. Ceram. Soc. 70 (3) (1987) 146–154.

[15] M.D.M. Innocentini, F.A. Cardoso, M.M. Akyioshi, V.C. Pandolfelli, Drying stages during the heating of high-alumina, ultra-low cement refractory castables, J. Am. Ceram. Soc. 86 (7) (2003) 1146–1148.

[16] V.S.S. Birchal, S.D.F. Rocha, V.S.T. Ciminelli, The effect of magnesite calcination conditions on magnesia hydration, Miner. Eng. 13 (14) (2000) 1629–1633.

[17] S. Chatterji, Mechanism of expansion of concrete due to the presence of dead-burnt CaO and MgO, Cem. Conc. Res. 25 (1) (1995) 51–56.