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The role of hydraulic binders on magnesia containing refractory castables: Calcium aluminate cement and hydratable alumina

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Abstract

Previous work by the authors has shown that the effects of calcium aluminate cement (CAC) and hydratable alumina (HA) can modify the magnesia hydration behavior in aqueous suspensions. As a consequence of these studies, the present paper highlights how varying the content of these binders can affect magnesia hydration in refractory castables using pH, apparent volumetric expansion, mechanical strength and porosity measurements and hydration–dehydration tests. Furthermore, as mechanical strength, porosity and refractoriness also play an important role in these materials, binder-free, magnesia-free and magnesia-and-binder-free samples were also tested as references. It was found that the deleterious effects of magnesia hydration can be greatly minimized by the binder and its selection content.

Keywords: Refractory castables; Calcium aluminate cement; Hydratable alumina; Magnesia hydration; Anti-hydration technique

1. Introduction

1.1. Magnesia containing refractory castables

Magnesia containing castables present high refractoriness and alkaline slag and thermal shock resistances due to their high melting point (2800 °C) and ability to generate *in situ* spinel ($MgAl_2O_4$) when combined with Al_2O_3 [1]. Nevertheless, magnesia can also easily react with water, forming magnesium hydroxide ($Mg(OH)_2$ or brucite) [2–5]. If this reaction occurs before castable hardening (raw materials or during the mixing, for instance), it results in porosity after brucite decomposition (during the first heat-up in the 400–600 °C interval), reducing the mechanical strength [5]. On the other hand, if carried out at the curing and drying steps, the three fold volumetric expansion that follows magnesia hydration induces compressive stresses and mechanical damages to the structure [4,6].

It was reported that with the use of anti-hydration techniques (MAHT), these drawbacks can be avoided and the benefits of magnesia addition could be maximized [5–7]. Among the best described MAHT, microsilica addition [6] and the binder content control [8,9] are the most effective. Microsilica is an amorphous submicron-sized form of SiO_2 added to castable formulations in order to improve the packing of particles and flowability. Besides these benefits, during the mixing and curing of castables, it partially dissolves as silicilic acid ($HSiO_3$), due to the highly alkaline pH of this type of castable (usually above 10) [10]. This acid reacts with the $Mg(OH)_2$ layer on the surface of the MgO particles forming a water insoluble and protective hydrated magnesium silicate ($MgHSiO_4$) coating [11,12], that halts the hydration reaction [6]. The binder content control, on the other hand, is associated to the reactions occurring when calcium aluminate cement (CAC) or hydratable alumina (HA) hydrate in the presence of magnesia.

1.2. Binder content control as MAHT

Calcium aluminate cement and hydratable alumina are the most used binders in refractory castable formulations, promoting hardening and suitable mechanical strength for demolding and before sintering. Both binders' setting mechanisms are based on hydration reactions. The CAC initially dissolves in water releasing Ca^{2+}, Al^{3+} and OH^- ions. After a period of saturation,

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these ions combine to form low solubility calcium aluminate hydrates (such as $CaO{\cdot}Al_2O_3{\cdot}10H_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$), that precipitate as needle-like shape crystals, restraining the particles displacement and hardening the structure [16–18]. Hydratable alumina, on the other hand, comprises a high surface area (above 150 m^2/g) amorphous transition alumina phase, known as ρ-alumina. In contact with water, the ρ-alumina partially dissolves, rapidly generating a pseudo-boehmite and boehmite gel. This gel reduces the porosity of the structure and, after a time usually shorter than 1 h (at temperatures above 20 °C) it crystallizes (bayerite, $Al(OH)_3$), bonding the particles [16,17]. These hydration reactions can significantly affect the magnesia hydration.

During its hydration, CAC greatly increases the castables' pH due to the release of OH^- in the water (Eqs. (1) and (2)) [14,15]. Due to the chemical equilibrium shifting principle, this excess of OH^- ions favors the magnesia hydration, as shown in Eq. (3) [2,3]:

$$Ca(AlO_2)_2 + 4H_2O \rightarrow Ca^{2+} + 2Al(OH)_4{}^- \quad (1)$$

$$Al(OH)_4 \rightarrow Al^{3+} + 4OH^- \quad (2)$$

$$MgO + H_2O \rightarrow MgOH^+ + OH^- \rightarrow Mg(OH)_2 \quad (3)$$

Investigations carried out in CAC–magnesia aqueous suspensions have shown that the greater the CAC content, the higher the suspensions' pH and the amount of brucite generated, for a given time–temperature condition (7 days at 50 °C, in a humid environment) [8]. Consequently, for the low CAC content ones, smaller apparent volumetric expansions (AVE) were observed.

When tested in the same conditions, HA–magnesia aqueous suspensions presented a different behavior [9,18,19]. Above a certain HA content (5 wt.%), no evidence of magnesia hydration was observed. In this case, two effects contributed to halting the hydration: 1) HA hydration results in a lower increase in suspensions' pH and 2) the Al^{3+} ions release allowed the formation of a protective coating of hydrotalcite ($Mg_6Al_3(OH)_{16}(CO_3{\cdot}4H_2O)$) on the surface of the magnesia particles. Hydrotalcite (HDTC) belongs to a class of clay-like synthetic minerals known as double layered hydroxides and it is formed when Al^{3+} and Mg^{2+} ions are simultaneously dissolved in an alkaline aqueous medium [20,21]. The HDTC presents low solubility in water (in alkaline environment) and great mechanical strength due to the hydrogen bonds present in its structure. Once it is formed at the surface of the magnesia particles, it makes the water diffusion difficult and halts magnesia hydration [9].

Based on these previous investigations [8,9], the present work aimed to apply the binder content control as a MAHT in refractory castables. Magnesia containing refractory castable compositions, designed with different amounts of CAC or HA, were systemically tested. In order to investigate its effectiveness, AVE, mechanical strength, porosity and pH measurements were correlated to hydration–dehydration tests evaluated by thermogravimetry. Besides this, because the effects of varying the binder content can also play an important role in the mechanical strength, porosity and refractoriness, binder-free, magnesia-free and magnesia-and-binder-free samples were also tested as references.

2. Materials and techniques

A vibrated high-alumina refractory castable composition containing 6 wt.% of magnesia (Magnesita S.A., Brazil) and different amounts of calcium aluminate cement (CA14M, Almatis, US, 0–12 wt.%) or hydratable alumina (Alphabond 300, Almatis, US, 0–6 wt.%) were used in the tests. Reference compositions, where, magnesia or magnesia-and-the-binders were replaced by calcined alumina, were also evaluated. A detailed description of the compositions is shown in Table 1.

Mixing and water addition were carried out in a paddle mixer for 10 min. Compositions were cast under vibration in cylindrical molds: 40 mm × 40 mm, for drying, hydration tests, mechanical strength and porosity measurements, and 70 mm × 70 mm, for the apparent volumetric expansion (AVE) evaluation. The initial curing time was carried out in an acclimatized chamber Vöetch 2020, at 8 °C for 24 h. These conditions were applied in order to assure a suitable mechanical strength for the samples' demolding, with a minor magnesia reaction [4]. The hydration tests were carried out in samples thermally treated at 50 °C, in a humid environment, for 7 days. During this length of time, the mechanical strength, porosity, dehydration profile and apparent volumetric expansion of the samples were evaluated every 24 h.

In parallel, just after mixing, the pH of castables' samples was recorded every 10 s, during 24 h and at room temperature (25 °C).

The drying tests were conducted up to 600 °C in green humid samples, under a 10 °C/min heating rate, using a thermogravimetric apparatus [22]. Mass changes and the temperature profile inside the furnace and at the samples' surface were simultaneously recorded. Percent mass loss rate (dW/dt, wt.%/min) versus the samples' temperature curves were used in the drying behavior evaluation [4,6,22].

The AVE test consists of measuring the dimensions of a 70 mm × 70 mm cylindrical sample during the humidity exposure over 7 days. The AVE is calculated considering the initial volume of the samples as a reference and can be described by the following equations:

$$V_i = \frac{(H \times \pi \times (D_i - 2t)^2)}{4} \quad (6)$$

$$AVE = 100 \times \frac{(V_E - V_0)}{V_0} \quad (7)$$

Eq. (6) is used to calculate the volume of cylindrical samples at a particular time, where V_i is the volume; H, the height; D, the diameter and t the mold wall thickness. For the AVE parameter; V_0 is the initial volume of the sample and V_E is the correspondent volume after hydration and expansion. A detailed description of this technique can be found in the literature [4,6,8,9].

Table 1
Refractory castable compositions studied.

Castables' compounds	Raw materials			wt.%		
				Binder and MgO containing	Binder-free*	Binder-and-MgO free*
Matrix ($D_P < 100$ μm)	*CAC compositions*	Calcined aluminas (A1000SG, Esy-pump 1000)[a]		15–3	15	21
		Calcium aluminate cement (CA14M)[a]		0–12	0	0
		Magnesia (D_{50} = 15 μm, 98 wt.% MgO)[b]		6	6	0
		Additives	Water	5.5	5.5	5.5
			Dispersant (Polyethylene glycol)[d]	0.2	0.2	0.2
	HA compositions	Calcined aluminas (A1000SG, Esy-pump 1000)[a]		15–9	15	21
		Hydratable alumina (Alphabond 300)[a]		0–6	0	0
		Magnesia (D_{50} = 15 μm, 98 wt.% MgO)[b]		6	6	0
		Additives	Water	6	5.5	5.5
			Dispersant (polyethylene glycol)[d]	0.4	0.2	0.2
Aggregates ($D_P \geq 100$ μm)	While fused alumina[c]			79	79	79

[a] Almatis (US).
[b] Magnesita S.A. (Brazil).
[c] Elfusa (Brazil).
[d] Bayer (Germany).
* Reference compositions.

The splitting tensile strength was measured according to the ASTM C496-96 standard in a piece of MTS TestStar II equipment. A constant loading rate of 42 N/s (1000 kPa/min) was used. The porosity of the samples was measured by the Archimedes' method, using kerosene as an immersion fluid. Both techniques used samples previously dried at 110 °C for 24 h.

3. Results and discussion

3.1. CAC and magnesia containing compositions

Fig. 1 shows the thermogravimetry analyses of the castable samples containing different CAC contents after 7 days at 50 °C in a humid environment. Thermogravimetry has been used commonly in order to follow magnesia hydration in aqueous suspensions and refractory castables [4,6,8,9]. The mass loss rate versus temperature profiles for CAC and MgO containing castables is comprised of four main peaks [4]. Those below 230 °C represent an overlapping of free-water release and decomposition of certain CAC hydrated compounds (such as $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$ and alumina gel) [19]; the higher temperature ones are related to the decomposition of more stable CAC hydrated compounds (230–400 °C, $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and $Al(OH)_3$, in this case [4,15,22–24]) and brucite (400–600 °C) [2–4]. The areas underneath the peaks are proportional to the amount of CAC hydrates or brucite formed during the curing period. Fig. 1a shows that, with the increase in the CAC content, more CAC hydrates ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and $Al(OH)_3$, in this case [15,23,24]) and brucite were generated, reducing the amount of free-water in the samples (the binder-free sample will be analyzed in the following sections). Because all these

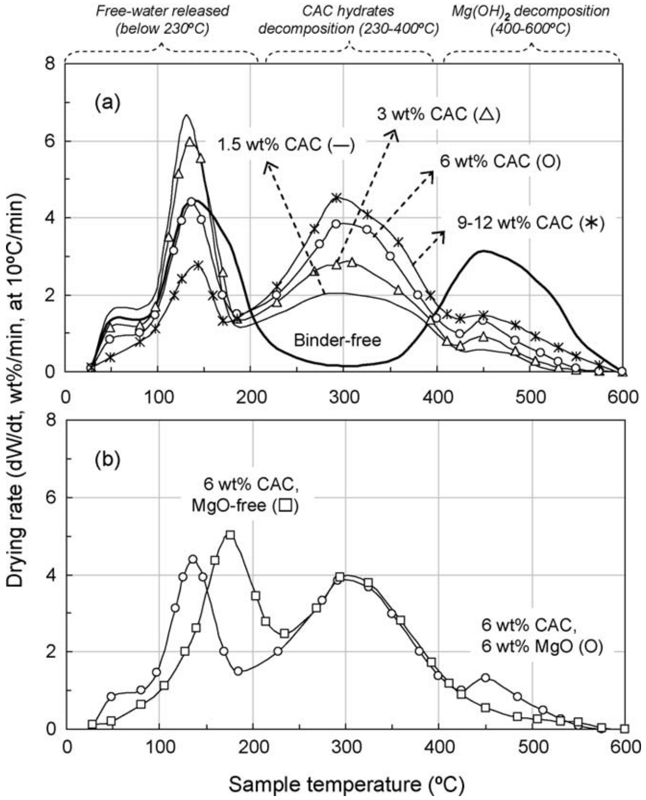

Fig. 1. Thermogravimetry (10 °C/min) of castables containing a) 6 wt.% of magnesia and different amounts of calcium aluminate cement (CAC) and b) 6 wt.% of CAC and magnesia-free reference sample (both after 7 days at 50 °C, in R.U. ≅ 100%).

samples contained the same amount of magnesia, these results indicated that, due to the CAC content increase, magnesia hydration rate was significantly enhanced. This behavior was related to the evolution of castables pH after mixing (at 20 °C during 24 h).

It can be seen in Fig. 2a that all the CAC containing compositions presented initial pH values near to 9.7 (attained before the beginning of CAC hydration). After an initial induction period, the castables' pH begins to increase, reaching a plateau at higher pH levels. The higher the CAC contents, the faster the pH increase and the higher the levels attained after 24 h. Similar results can be found in the literature, relating this behavior to the massive dissolution of Ca^{2+}, Al^{3+} and OH^- ions in the water [13–15]. As previously shown in Eqs. (1)–(3), this increase in the medium's pH, enhances the driving force for magnesia hydration (the faster and the more intense the pH increase, the greater the magnesia hydration driving force). Therefore, regarding the results of Figs. 1a and 2a, it can be pointed out that, for the systems studied, one of the main effects of CAC addition in magnesia containing castables was the increase of the brucite formation rate due to the high alkaline environment.

The amount of brucite in refractory castables cannot be seen as the only variable that leads to the AVE increase. CAC hydration begins a few hours after the mixing, whereas, for magnesia, it can last some days, depending on the curing conditions [4]. This difference in the hydration kinetics presents two important consequences. 1) As can be seen in Figs. 1b and 2a (dotted line), respectively, CAC hydration and the correspondent castable pH were not affected by the magnesia. 2) The faster reaction allows CAC to set the structure and rapidly fill the porosity, reducing the room available for the brucite expansion. Therefore, competition is observed among the extra-volume generated by magnesia hydration, the porosity available to accommodate it and the mechanical strength needed to prevent damage to the structure. In Fig. 3a–c, respectively, the results of this competition were evaluated considering the evolution of AVE, mechanical strength and porosity for the castable samples containing magnesia and different amounts of CAC (0–12 wt.%), as a function of the curing time (up to 7 days at 50 °C, in a humid environment).

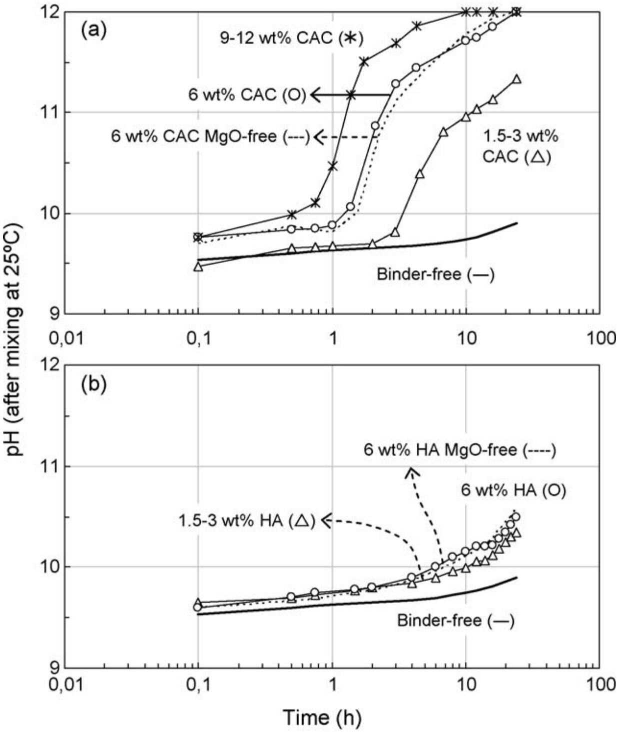

Fig. 2. pH after mixing (at 25 °C) of MgO containing castables prepared with different amounts of a) calcium aluminate cement (CAC) or b) hydratable alumina (HA) (the dotted lines show the pH change for MgO-free reference compositions).

For the samples containing 1.5–3 and 12 wt.% of CAC, lower values of AVE, a continuous mechanical strength increase and the porosity reduction along the curing period can be observed; for the 6–9 wt.% ones, on the other hand, there was an initial increase in the mechanical strength and porosity reduction, followed by a great AVE increase and mechanical strength degradation after the fourth day of exposure. As, for the magnesia-free reference samples (Fig. 4a), the mechanical strength continuously increased with the CAC content and a low porosity and no AVE changes were observed, the different effects caused by CAC content variation should be analyzed as a whole, as summarized in Table 2.

For the low CAC content samples (1.5–3 wt.%), the low AVE levels can be understood considering that, despite the poor mechanical strength increase, the small amount of brucite generated could be easily accommodated in the porosity. The high CAC content composition (12 wt.%) presented a high magnesia hydration degree and porosity reduction, but in spite of it, the AVE values were the smallest among the CAC containing composition, due to the higher mechanical strength developed by the high cement amount. For these cases, one of the variables that helps to minimize AVE was attained (respectively, low brucite content and high mechanical strength). For the medium CAC content ones (6–9 wt.%), on the other hand, a harmful combination of alkaline pH, high magnesia hydration degree, porosity reduction and intermediate mechanical strength favored the AVE increase.

These results indicate that the control of the CAC content in the castable formulation may be suitable, but it is not an effective way to minimize the deleterious effects of magnesia hydration. Nevertheless, the benefits of using low (below 6 wt.%) or high (above 9 wt.%) CAC amounts must be carefully considered due to the potential side effects that can be induced. The low CAC containing castables are highly sensitive to the curing and heat-up conditions due to the low mechanical strength levels developed [22–25] and require the addition of drying additives, such as polymeric fibers, in order to reduce the explosive spalling likelihood [26]. For the high CAC containing ones, on the other hand, low refractoriness phases can be formed (such as $12CaO.7Al_2O_3$) due to the excessive amount of CaO [1]. Based on these aspects, it is reasonable to consider that the CAC content control could present better results if it was applied in combination with other anti-hydration techniques, such as the microsilica addition [6].

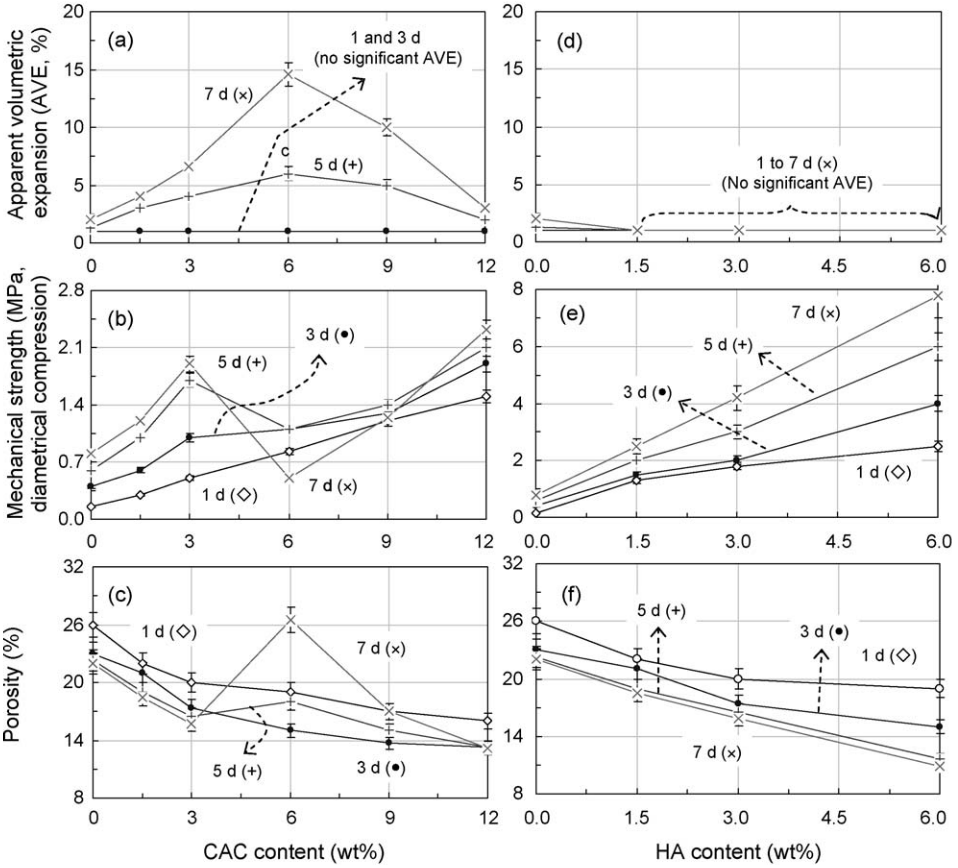

Fig. 3. Effect of different calcium aluminate cement (CAC) or hydratable alumina (HA) on castables' apparent volumetric expansion (a and d), mechanical strength (b and e) and porosity (c and f).

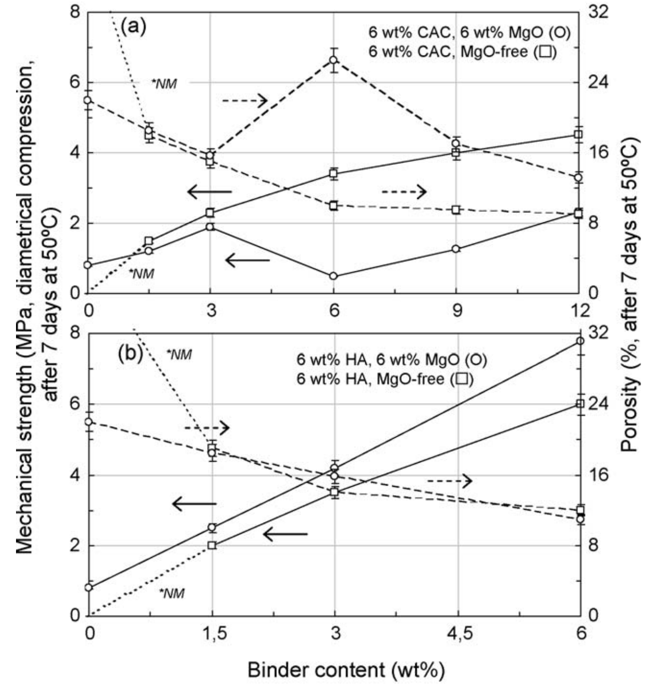

Fig. 4. Mechanical strength and porosity of MgO-free reference castables (MgO-free) containing 6 wt.% of a) calcium aluminate cement (CAC) or b) hydratable alumina (HA) (both kept in humid environment, at 50 °C, for up to 7 days. *NM = not-measurable).

3.2. HA containing compositions

The drying behavior of HA containing castables differs significantly from the CAC containing ones [26,27]. Due to the hydrated compounds formed and the low permeability level of the structure, during the dewatering of the HA containing castables, the free-water release, the alumina gel and the boehmite decomposition are overlapped in a single broad peak from room temperature up to 300 °C. Above this temperature, in the 300–500 °C range, the decomposition of the bayerite was detected [27]. Considering these aspects, it can be pointed out in Fig. 5a that only minor differences were observed in the thermogravimetry results for the different HA containing samples (1.5–6 wt.% HA, Fig. 5a), for the low temperature dehydration reactions (below 300 °C). The comparison with the magnesia-free reference sample (Fig. 5b) shows that no significant magnesia hydration occurred and that these results were mainly due to the HA content.

Concerning castable mechanical properties, two important aspects must be highlighted. Although no noteworthy AVE changes were observed (Fig. 3d), mechanical strength levels (Fig. 3e) up to 2.5 times higher and lower porosity (Fig. 3f) than that detected for the CAC containing equivalent composition were attained. Moreover, compared to the magnesia-free sample (Fig. 4b), the HA–magnesia composition resulted in superior mechanical strength values. These aspects indicate

Table 2
Effects of different binder contents on magnesia hydration.

Effects generated by binder on:	Compositions tested (different binder content)						
	Binder-free	*Low* (1.5-3 wt.%)		*Medium* (6-9 wt.%)		*High* (12 wt.%)	
	–	*CAC*	*HA*	*CAC*	*HA*	*CAC*	*HA*
pH increase	Very low	Low	Low	High	Low	High	-
Driving force for magnesia hydration	High	Low	Very low	High	Very low	High	-
Magnesia hydration degree	High	Low	Very low	High	Very low	High	-
Porosity reduction	Low	Low	High	High	High	High	-
Mechanical strength increase	Low	Intermediate	High	Intermediate	Very High	High	-
Apparent volumetric expansion (AVE)	Small	Small	Non detectable	Great	Non detectable	Intermediate	-
Efficiency as Magnesia anti-hydration technique (MAHT)	Moderated (lack of mechanical strength before testing)	Low (did not increase MgO hydration rate, but did not halt it)	High (halted MgO hydration)	None (increased MgO hydration rate)	Very high (halted MgO hydration rate and improved mechanical strength)	Low (inhibited the damages by AVE but may reduce refractoriness)	-

that, by replacing CAC by HA, not only magnesia hydration and its effects were greatly reduced, but also interesting benefits were attained in the castable properties, as also reported in the literature [28].

This behavior can be attributed to two main causes. Firstly, as seen in Fig. 2b, it can be observed that the HA addition did not change the castable's pH so intensely as the CAC did. Therefore, the driving force for magnesia hydration was not significantly increased. Secondly, the combination of magnesia and HA results in the hydrotalcite (HDTC) formation. HDTC is mainly detected when the ion ratio Mg^{2+}/Al^{3+} is close to 4:1.7 (different ratios result HDTC and boehmite or HDTC and brucite [20,21]). Due to this, the HDTC is preferably formed on the surface of the magnesia particles, where the Mg^{2+} concentration is higher [9,19,28]. Because of its low solubility in alkaline environment and the hydrogen bonds [20,21], a protective coating on the surface of the magnesia particles is formed, halting the hydration reaction and, simultaneously, bonding the castables' matrix particles strongly. As it is formed, no more Mg^{2+} ions will be available in the suspension and no further HDTC will be produced. As the amount of HDTC generated in these conditions was below the detection limit of the thermogravimetric apparatus used (in the literature, the XRD technique was used for this purpose [9]), no significant modifications in the castables' dewatering behavior were detected.

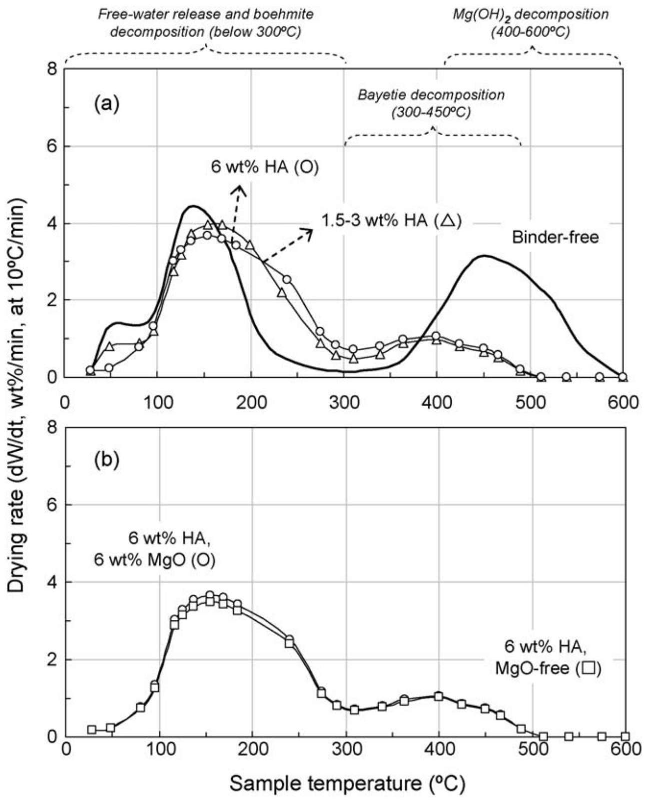

Fig. 5. Thermogravimetry (10 °C/min) of castables containing a) 6 wt.% of magnesia and different amounts of hydratable alumina (HA) and b) 6 wt.% of HA and magnesia-free reference sample (both after 7 days at 50 °C, in humid environment).

Compared to the CAC containing compositions, the control of the HA content resulted in important benefits with two minor side effects. 1) For the higher HA content, low water and a dispersant amount increase (5.5–6.0 wt.% and 0.2–0.4 wt.%, respectively) were required in order to improve the castables' flowability. 2) The well known difficulties for drying HA containing castables [26,27] can be solved by using polymeric fibers as drying additives, as shown elsewhere [26]. Nevertheless, because this binder does not present calcium in its chemical composition, no low melting point compound is expected (actually, the *in situ* spinelization can be favored), increasing the castables' refractoriness [28].

3.3. Binder-free composition

The binder-free magnesia containing composition presented an unexpected and potentially useful behavior. Observing the results presented in Figs. 1, 3 and 4, it can be pointed out that, in spite of the greatest magnesia hydration degree among all the compositions tested, this particular one presented a low AVE value and a continuous strengthening with the curing time. As no significant mechanical strength gain was observed for the magnesia-and-binder-free reference (samples did not attain enough strength to be demolded, Fig. 4), it indicates that magnesia hydration can present a binding effect.

Two main points must be highlighted. Initially, the highest magnesia hydration degree presented by the binder-free sample can be associated to the greater supply of water for the magnesia particles (no competition with the CAC) and to the absence of Al^{3+} to form hydrotalcite. Secondly, binder-free castables (also known as zero-cement) usually present high porosity levels, as described in the literature [29] and as shown in Figs. 3 and 4. For binders-containing castables, a significant fraction of the porosity is occupied by the hydrated phases during curing and the hardened structure presents higher rigidity [30]. Therefore, the volumetric expansion that follows magnesia hydration cannot be suitably accommodated and compressive stresses can lead to AVE changes and mechanical damages.

For the binder-free structures, on the other hand, there is extra room to fit the volume generated and the lack of mechanical strength allows small levels of internal deformation without changing the AVE. Finally, the pores filled in by the brucite reduce the porosity leading to an increase in mechanical strength. These results suggest that, after a proper optimization, this effect could be used to develop a corrosion resistant, high refractoriness and competitive costs for the magnesia-based binder system. This hypothesis is currently under investigation.

4. Conclusions

Magnesia hydration and the apparent volumetric expansion were significantly affected by the nature and the content of the binder used in the castable compositions. It was observed that magnesia hydration resulted in less intense damages in compositions with low (1.5–3 wt.%) and high (12 wt.%) CAC contents. In the first case, because the low CAC content did not increase the castables' pH so intensively, the driving force for magnesia hydration was reduced and, additionally, the extra volume generated by the MgO hydration could be suitably accommodated. For the 12 wt.% CAC, the high mechanical strength developed minimized the damages caused by the magnesia hydration. The compositions with the CAC contents 6–9 wt.% range presented the highest levels of damage caused by a combination of high pH, lower porosity and intermediate values of mechanical strength, resulting in a high magnesia hydration degree and not high enough mechanical strength to restrict the volumetric expansion. Due to the drawbacks pointed out as a result of either the low or high CAC amounts, it is reasonable to consider that the CAC content control should be applied in combination with other magnesia anti-hydration techniques in order to attain better results.

The replacement of the CAC by hydratable alumina resulted in interesting benefits. Due to the generation of hydrotalcite (HDTC) in the particles surface, magnesia hydration was halted, no significant AVE was observed and the mechanical strength values were at least 2.5 times higher than the CAC containing equivalent ones and 30% greater than the magnesia-free reference were attained. Based on these results, the use of HA instead of CAC can be pointed out as one powerful magnesia anti-hydration technique. Furthermore, its calcium-free composition naturally induces its use for *in situ* spinel containing castables.

Acknowledgements

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