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Novel Technological Route to Overcome the Challenging Magnesia Hydration of Cement-free Alumina Castables

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Due to the expansive behavior associated with the brucite $[Mg(OH)_2]$ formation, magnesia hydration is a challenging subject in the refractory castable area. Although various anti-hydration techniques have been suggested in the literature, a technological solution for this issue has not yet been presented. Instead of inhibiting brucite formation, speeding up its formation could be a suitable microstructural engineering resulting in the $Mg(OH)_2$ accommodation in the castable pores and increasing the green mechanical strength of the castables, without crack formation. Therefore, acetic acid was selected and added as a hydrating agent, affecting the amount of brucite generated and also its morphology. As an overall result, the reaction was accelerated and provided some structural flexibility to the $Mg(OH)_2$. This interesting alternative route can result in technological advances on the understanding and use of higher magnesia amounts in cement-free refractory castable compositions.

1 Introduction

Magnesia hydration is a usual scientific and technological subject in the refractory area due to the challenges associated with its expansion behavior. When in contact with water, MgO is prone to react leading to brucite $[Mg(OH)_2]$ formation and a remarkable 2,5-fold volumetric expansion [1–2]. This reaction restricts the use of magnesia in the matrix of refractory castables as it affects various processing steps, such as mixing, moulding, curing and drying [2–3].

In order to master the expansion and inhibit cracking formation, two main mechanisms are commonly considered:

- a physical approach, in which the porosity available can accommodate the volumetric change and
- a chemical route, aiming to reduce or even avoid brucite generation.

Although various anti-damage or anti-hydration techniques were presented in the literature [4–6], a definite technological solution is not yet clear. Thus, to the best of our knowledge, there is a gap in the literature

and industrial procedures, mainly concerning the evolution of free-cement MgO-containing castables. Using magnesia hydration as a bonding mechanism, instead of hindering brucite generation, can provide a novel technological alternative for the production of new classes of refractory castables, as long as its formation is properly controlled and accommodated in the microstructure, reducing the open porosity without leading to mechanical damage.

A different and not common technique to explore the bonding potential of MgO is related to the use of hydrating agents. This sort of additives is commonly applied to speed up the magnesia hydration for the commercial production of brucite, which is widely used as a flame retardant in polymers [7, 8]. The hydrating agents affect the morphology and particle distribution of brucite and thus might accommodate the associated expansion. Among different additives, magnesium acetate seems appropriate as the acetate ion (CH_3COO^-) plays an important role in increasing the MgO hydration rate, owing to its

ability to form Mg^{2+} complexes [9]. For typical hydration in water, the brucite crystals show a spherical morphology, indicating that they precipitate on the surface of MgO particles (Fig. 1a). Conversely, in the presence of magnesium acetate, the brucite crystal precipitation seems to take place in the solution, apart from the magnesia particles, resulting in platelets (Fig. 1b) [9]. This aspect points out the possibility of mastering the $Mg(OH)_2$ morphology and consequently to accommodate it in the castables' structure.

Studies conducted by *Filippou et al.* [9] also indicated the potential of acetic acid (CH_3COOH) as a MgO hydrating agent, pointing out that it can accelerate the brucite formation (and the amount formed) and change its typical morphology. The ability of acetic acid to generate Mg^{2+} complexes plays a key role in the magnesia hydration, as these ions can be released in the solution, leading to the magnesium hydroxide formation not only in the MgO surface particles, but also throughout the whole supersaturated suspension. As a consequence, the hydration is faster and homogeneous. Swift

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precipitation can result in a large amount of nuclei, all of them presenting small overall growth and consequently minute expansion, whereas a slower one, such as MgO in water without any additives, leads to a fewer and bigger nuclei, that when expanded with preferential orientation would crack the surrounding packed structure.

Considering these aspects, the objective of this work was to evaluate the acetic acid interaction in high-alumina free-cement fine magnesia-containing refractory castables, during curing and drying steps. Instead of inhibiting the brucite formation, this reaction was intentionally induced in order to result in a binding effect and also change the morphological features, aiming to accommodate the particles in the microstructure and reduce the castables' porosity without leading to mechanical damage. This technological proposal seems to be very promising for the refractory area, inducing a novel approach to cope with magnesia hydration by using its expansion behavior as a positive aspect to fill in the castable pores and improve its green mechanical properties.

2 Materials and techniques

Two different MgO sources (supplied by *Magnesita Refratários S. A. BR*) were selected:

- dead-burnt (DBM, with specific surface area of $1,1 \text{ m}^2/\text{g}$, $D_{50} = 7,8 \mu\text{m}$, 98 mass-% of MgO, $\text{CaO}/\text{SiO}_2 = 2,5$) and
- caustic (CM, with specific surface area of $24,6 \text{ m}^2/\text{g}$, $D_{50} = 16,6 \mu\text{m}$, 98 mass-% of MgO, $\text{CaO}/\text{SiO}_2 = 5,2$).

The idea of adding CM to the castable was based on its cheaper cost and faster reaction likelihood. Vibratable alumina-magnesia castable compositions were designed according to Alfred's particle packing model ($q = 0,26$). Coarse tabular alumina was used as aggregates ($D \leq 6 \text{ mm}$, *Almatis/US*) and the matrix comprised 6 mass-% of magnesia (DBM or CM), 7 mass-% of reactive alumina (CL370, *Almatis*) and fine ($\leq 200 \mu\text{m}$) tabular alumina (*Almatis*). The castable dispersion was carried out by adding 0,2 mass-% of a polycarboxylate based dispersant (*BASF/DE*). The designed castables were prepared in a R02E *Eirich* mixer. The water content required for suitable mixing and moulding (initial vibration flow level of 80 %) was 4,1 mass-% for the DBM-based composition and 5,1 mass-% for the CM-containing one. This

remarkable difference was the first indicative of the difficulty of adding caustic magnesia to castables due to its high specific surface area and consequent MgO hydration trend. One must also note that no hydraulic binder (such as calcium aluminate cement or hydratable alumina) or microsilica was added, as the target was to use MgO hydration to induce particle bonding and result in a novel binder alternative for refractory castables. The selected acetic acid (*AcA*, *Synth/BR*) contents were 0,1 or 0,2 mass-%. AcA-free (0 mass-%) composition was also prepared as a reference.

The curing behavior of these castables was evaluated by elastic modulus (MOE) measurements as a function of time (up to 7 days). Prismatic samples ($25 \text{ mm} \times 25 \text{ mm} \times 150 \text{ mm}$) were cast under vibration and carefully demoulded after three hours of curing at $50 \text{ }^\circ\text{C}$ in a climatic chamber (relative humidity = 80 %). These measurements were conducted according to ASTM C 1198-91 using the resonance bar technique (*Scanelastic equipment*, *ATCP/BR*), which is based on the sample excitation and by the detection of the cor-

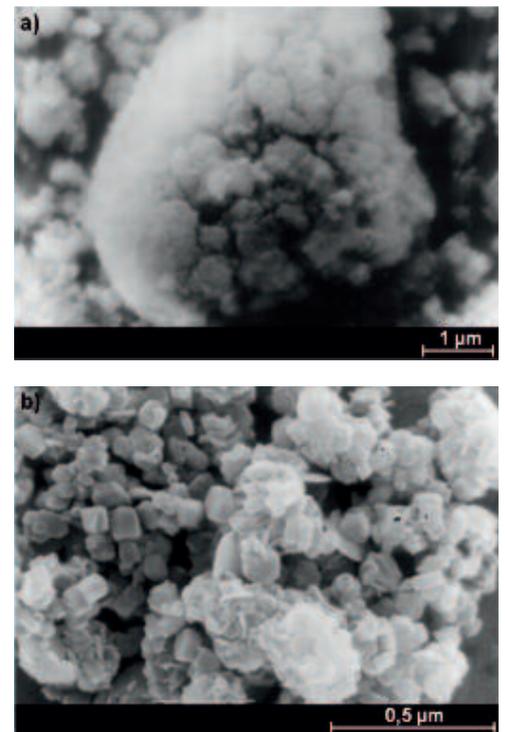


Fig. 1 (a) Spherical particles (pure water conditions) or (b) small plates (magnesium acetate solution) of magnesium hydroxide [9]

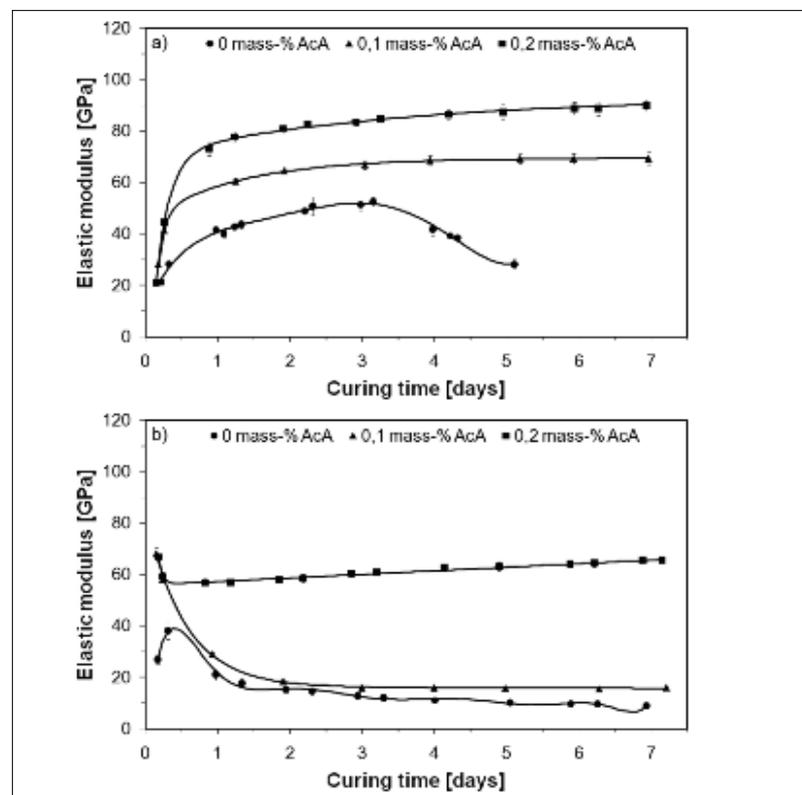


Fig. 2 Elastic modulus as a function of the curing time (at $50 \text{ }^\circ\text{C}$ in humid environment) for (a) dead-burnt or (b) caustic magnesia-containing refractory castables, without acetic acid (0 mass-% AcA) or with 0,1 or 0,2 mass-% of AcA

respondent vibration spectrum, using piezo-electric transducers.

In order to evaluate the brucite formation, thermogravimetric analysis [10] were conducted (after 1 day of curing at 50 °C; 5 K/min up to 650 °C) in cylindrical samples (40 mm × 40 mm) and the hydration degree was measured considering the mass of water released during drying in the 250–500 °C range (related to brucite formation) and the theoretical mass of water required for full MgO hydration. Therefore, the percentage of MgO (actual amount compared to the overall content) particles that hydrated could be analyzed.

Besides castables, aqueous acetic acid suspensions were also prepared in order to point out the effect of this additive on the brucite formation and morphology. Thus, 10 g of caustic (CM) were mixed with 100 ml of water under constant rotation for 1 h at 50 °C. The MgO hydration was also evaluated in a solution of 0,2 mol/l of acetic acid in water. After mixing, the suspensions were vacuum filtered and the solids were washed in distilled water and dried at 110 °C for 1 day. The short washing step does not lead to any relevant changes in the particles' size or shape, due to the low solubility of magnesium hydroxide and the previous intensive mixing for 1 hour at 50 °C under intensive stirring in a low content water suspension. The resultant morphology was then analyzed by scanning electron microscopy (SEM, Philips XL-30 FEG/NL).

3 Results and discussions

Fig. 2 shows the *in situ* elastic modulus evolution with curing time for the dead-burnt (a) or caustic (b) MgO-containing castables with (0,1 or 0,2 mass-%) or without (0 mass-%) acetic acid (AcA). Regardless of the magnesia source, although after different time lengths, the castables with no acetic acid presented a drop in the elastic modulus values concerning curing time and consequently cracking, due to brucite formation. This behavior was observed earlier for the CM composition, due to its higher reactivity. Nevertheless, by adding only 0,1 mass-% of AcA, an outstanding increase in the MOE was observed for the DBM composition (Fig. 2a) with no further decrease in the elastic modulus and no cracks after 7 days. With 0,2 mass-% of AcA, the values were even more remarkable, attaining almost 90 GPa at

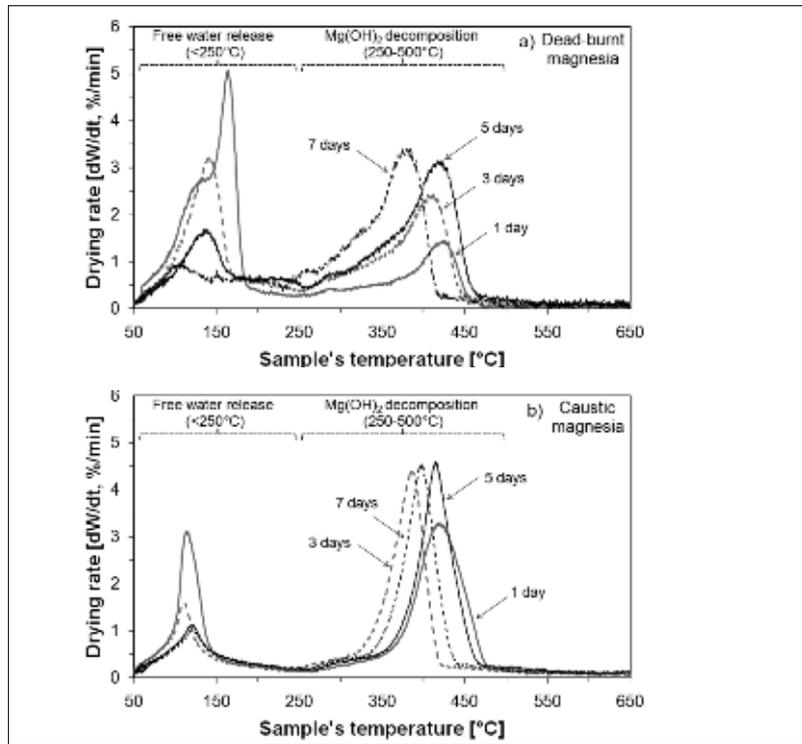


Fig. 3 Drying rate profiles as a function of sample's temperature after 1, 3, 5 or 7 days of curing at 50 °C for castables containing: a) dead-burnt (DB) or b) caustic magnesia (CM). The analyses were conducted up to 650 °C under a heating rate of 5 °C/min

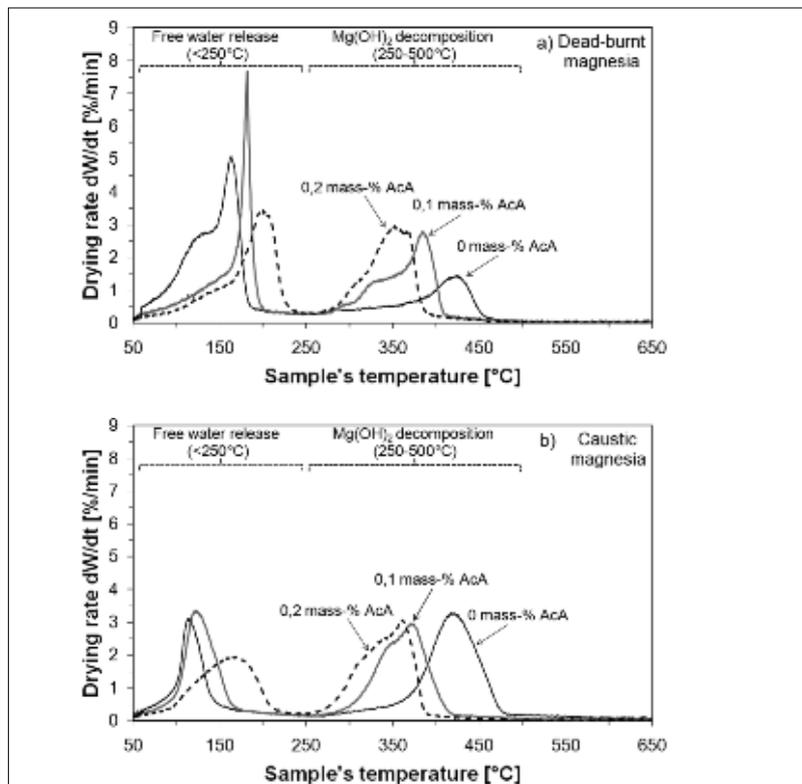


Fig. 4 Drying rate profiles as a function of sample's temperature after 1 day of curing at 50 °C for castables containing: a) dead-burnt or b) caustic magnesia-containing refractory castables, without acetic acid (0 mass-% AcA) or with 0,1 or 0,2 mass-% of AcA. The analyses were conducted up to 650 °C under a heating rate of 5 °C/min

Tab. 1 Hydration degree for the dead-burnt (DBM) or caustic (CM) magnesia-based castables, using different acetic acid contents (0, 0,1 or 0,2 mass-%)

	Hydation Degree [%]		
	0 mass-% AcA	0,1 mass-% AcA	0,2 mass-% AcA
DBM	18,78	32,89	43,10
CM	55,62	59,46	59,67

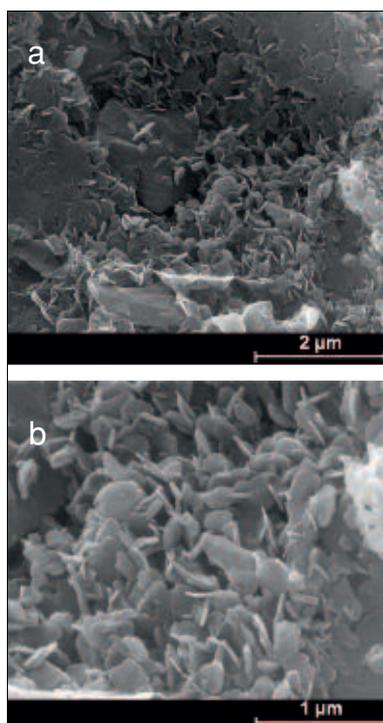


Fig. 5 a–b SEM images of Mg(OH)₂ crystals precipitated in the matrix of caustic magnesia containing castables without acetic acid after 1 day of curing at 50 °C and 1 day of drying at 110 °C

the end of the experiment. For the CM castable (Fig. 2b), 0,2 mass-% of AcA was required in order to avoid MOE decrease as a consequence of physical integrity loss related to the *in situ* Mg(OH)₂ formation. Despite the need of higher acetic acid content to react with caustic magnesia (CM), at the beginning of the measurements, a significant increase in the MOE was observed when compared to the AcA-free composition. This result points out that for the CM composition the highest value of the elastic modulus was achieved in the first hours after moulding, before the initial E measurements.

In order to better understand the different results attained for the dead-burnt (DBM) or caustic (CM) magnesia, thermogravimetric analysis were conducted and the drying rate was calculated according to *Innocentini et al.*

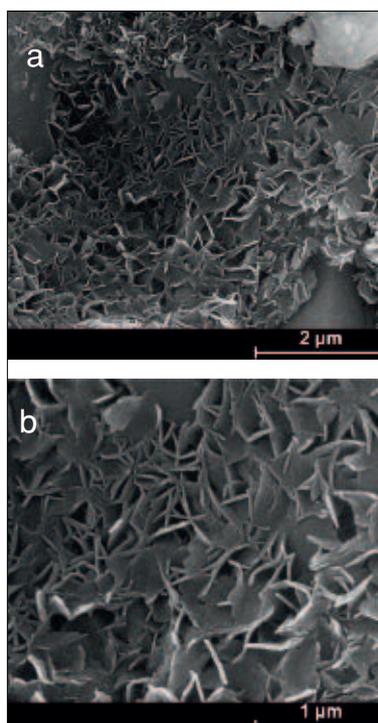


Fig. 6 a–b SEM images of Mg(OH)₂ crystals precipitated in the matrix of caustic magnesia containing castables with 0,2 mass-% of acetic acid after 1 day of curing at 50 °C and 1 day of drying at 110 °C

[10], after curing the castables for 1, 3, 5 or 7 days at 50 °C. According to Fig. 3, regardless of the MgO source, two different peaks were detected: the first one was associated with the release of free-water (below 250 °C) and another related to brucite decomposition (above 250 °C). The area below the peaks is proportional to the amount of free-water or brucite. Increasing the curing time, higher brucite peaks (and lower free-water ones) were detected, indicating the increase in its content. Comparing to the dead-burnt source, the hydration of caustic magnesia was faster, showing a higher brucite peak after 1 day of curing and a consequent decrease in the elastic modulus (Fig. 2). Displacements in the top peak drying rate temperature is usually associated to the permeability of the sample, which changes over time

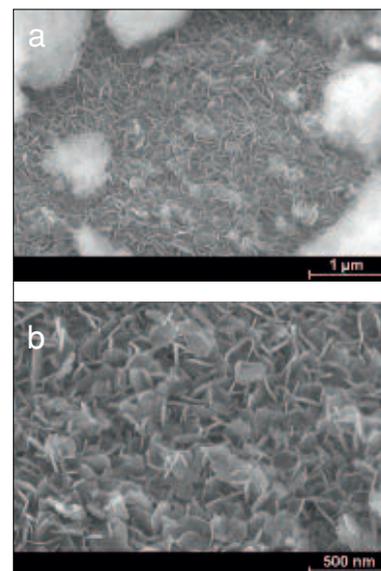


Fig. 7 a–b SEM images of Mg(OH)₂ crystals obtained from the hydration of caustic magnesia at 50 °C during 1 h in an aqueous solution

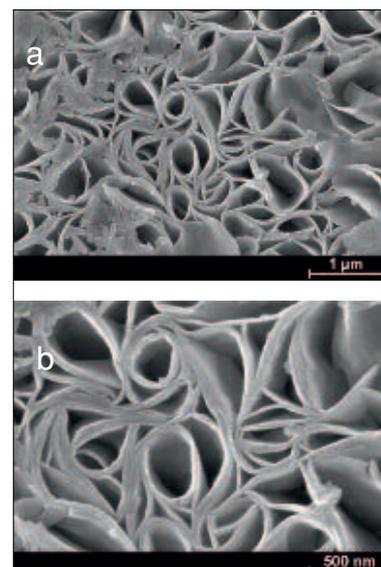


Fig. 8 a–b SEM images of Mg(OH)₂ crystals obtained from the hydration of caustic magnesia at 50 °C during 1 h in an aqueous solution of 0,2 mol/l of acetic acid

due to the decrease in porosity or crack formation.

The effect of acetic acid addition (AcA) for both MgO sources was also evaluated by thermogravimetric analysis, as shown in Fig. 4. For the DBM-based composition, the increase in the AcA content led to higher brucite decomposition peaks, pointing out that this additive induced the Mg(OH)₂ formation. On the other hand, for the CM-con-

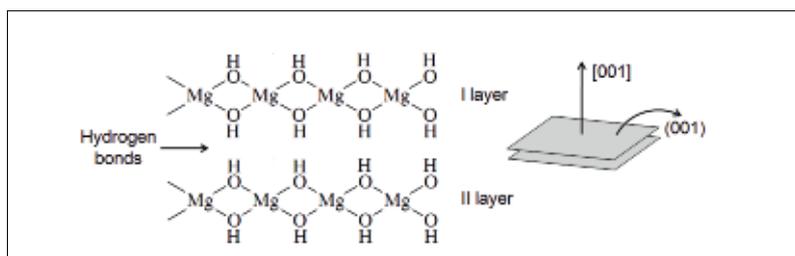


Fig. 9 Schematic representation of the magnesium hydroxide layered structure and the [001] direction

taining castable, all brucite decomposition peaks were very similar in terms of area and height, showing a less intense effect of AcA on caustic magnesia, as this source is already very prone to brucite generation, due to its higher specific surface area. Based on these curves, the hydration degree was then calculated and the results are presented in Tab. 1. By increasing the acetic acid content, a higher hydration degree was attained, mainly for the DBM source (which shows a lower likelihood for natural hydration), indicating that it induced and sped up the brucite formation and, thus, led to greater elastic modulus values.

In order to figure out why the castables did not crack even with higher brucite content (DBM with 0,1 or 0,2 mass-% AcA and CM with 0,2 mass-% AcA), CM compositions without (0 mass-%) or with 0,2 mass-% of acetic acid were analyzed by SEM. Whereas for the AcA-free castable (Fig. 5) rigid and tangled platelets were attained, the addition of 0,2 mass-% of AcA (Fig. 6) led to a more open and homogeneous structure. For the AcA-containing castable, they looked more flexible, indicating a resilient structure, able to absorb a higher brucite content (Tab. 1), but without the drawback of cracking.

With the objective of confirming this morphology change, water or acetic acid-based suspensions were produced and examined by SEM after 1 day of drying at 110 °C. Figs. 7 and 8 indicate distinct $Mg(OH)_2$ morphologies, attesting the platelet shape for the AcA-free aqueous suspension and highlighting the flexible $Mg(OH)_2$ morphology for the acetic acid containing solution. Therefore, the lack of crack formation for the AcA-containing castables and the increase in their elastic modulus during curing was associated to the faster brucite formation effect, coupled with a resilient structure able to inhibit stresses build-up. Furthermore, as acetic

acid accelerates the brucite generation, the likelihood for crack formation is reduced as the castable's structure is not yet rigid at initial setting steps and thus any stress can be easily accommodated.

According to the literature [11], the chemical activity of Mg^{2+} ion ($a_{Mg^{2+}}$) is greater than its solubility ($S_{Mg^{2+}}$), whereas the activity of hydroxyl ions (a_{OH^-}) is lower than its solubility (S_{OH^-}) by a 2,3 factor. As a consequence, after brucite precipitation, the Mg^{2+} ions are not released in the solution, but a portion of the OH^- ions can be dissolved. In order to maintain the electroneutrality, the hydroxyl ions are partially replaced by the solution's acetate ions (CH_3COO^-). During magnesia hydration, the MgO cubic structure changes and a $Mg(OH)_2$ hexagonal structure takes place. Considering that the magnesium hydroxide closely packed layers occur in the [001] direction (Fig. 9) and that the ion CH_3COO^- radius is roughly 3-fold higher than the OH^- one [11], its replacement would inhibit the crystal growth in this direction, as the $Mg(OH)_2$ layers are linked by weak hydrogen bonds. Therefore, the crystal growth could preferentially take place in parallel directions to the (001) plane, resulting in morphological changes, as highlighted in Fig. 8.

4 Conclusions

The attained results pointed out that, although challenging, there is a technological route to overcome the magnesia hydration drawback related to crack formation during curing. The trick to master the MgO hydration is to speed up the reaction and to provide some structural flexibility degree to its particles, therefore able to absorb the generated stresses. This resilient MgO -based material, induced by acetic acid addition, might be the key to increasing the use of magnesia as a binding agent in refractory castables. The higher brucite formation that takes place due

to the presence of acetic acid may affect the castables' drying step as a higher amount of chemically-bonded water would be released. This aspect will be addressed in a forthcoming publication by the authors.

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