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Citric acid as anti-hydration additive for magnesia containing refractory castables

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Abstract

Magnesia hydration is a key concern in refractory castable processing. The volumetric expansion that follows this reaction can result in cracks or even explosion during the first heating-up. Citric acid (CA) and other chelants can significantly reduce MgO hydration rate in aqueous suspensions by forming an insoluble magnesium citrate protective coating on the magnesia particles' surface. In the present work, the performance of CA as an anti-hydration additive in refractory castables was evaluated by hydration tests, mechanical strength and apparent volumetric expansion (AVE) measurements and thermogravimetry. The results attained have shown that CA effectiveness depends strongly on the amount added and by the interaction with other raw materials in the composition, in particular calcium aluminate cement.

Keywords: Refractory castables; Magnesia; Hydration; Chelants; Citric acid

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1. Introduction

The volumetric expansion that follows magnesia hydration is related to the density mismatch between the magnesium oxide ($\rho = 3.5$ g/cm^3) and its hydroxide ($\rho = 2.4$ g/cm^3), which can result in cracks during the processing steps.[1–4] The wide technological interest in magnesia containing refractory castables has triggered various research papers focusing on the magnesia hydration process [5–7], the variables involved [1,4,8,9] and on magnesia anti-hydration techniques (MAHT) [10–17]. The results reported have shown that by reducing the magnesia hydration rate, major improvements in castable mechanical strength can be attained [15–17].

Recently, authors have pointed out citric acid (CA, $C_6H_8O_7$) and other chelant compounds as promising anti-hydration additives for MgO sinter suspensions [18]. In aqueous medium, citric acid dissociates resulting negative ions (Cit^{n-}, n = 3, 2 or 1, depending on the suspension's pH) with great chemical affinity by the positive ones, leading to the formation of inert compounds. Because in the first stage of MgO hydration $MgOH^+$ species are formed on the surface of the particles [5,7,18], the citrate ions are rapidly adsorbed, resulting in a low solubility magnesium citrate protective coating, as schematically shown in Figure 1. This coating significantly reduces the quantity of $Mg(OH)_2$ formed, the hydration rate and the volumetric expansion of the sample in the hydration tests (50 °C, during 7 days in high humidity environment) [18].

In order to highlight aspects related to processing conditions, macroscopic features and possible interaction with other raw materials (calcium aluminate cement, for example), in this paper the role of CA as an anti-hydration additive in magnesia containing castables was evaluated. Mechanical strength and apparent volumetric expansion (AVE) measurements were carried out in samples containing different CA contents during their exposition to a high humidity environment (7 days at 50 °C). Thermogravimetry was used to access the $Mg(OH)_2$ formation rate. MgO-free and MgO-and-CA-free samples were also tested as references.

2. Materials and techniques

A high-alumina vibratable refractory castable containing 6 wt% of magnesia sinter ($D_{50} = 15$ μm, 98 wt% of MgO,

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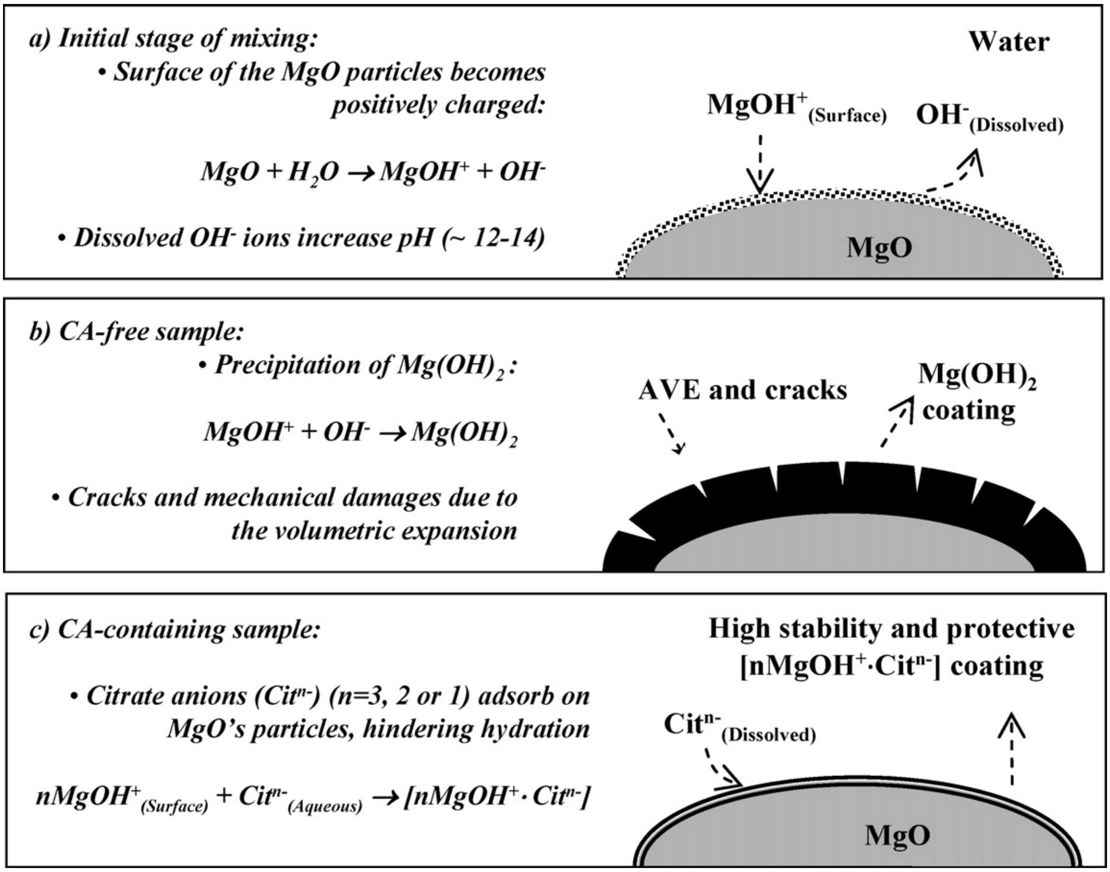

Figure 1. Schematic representation of the citric acid anti-hydration mechanism [18].

Magnesita S.A., Brazil), 6 wt% of calcium aluminate cement (CA25, Almatis, USA)), 5.7 wt% of water and 0.25 wt% of a polyethyleneglycole based dispersant (Basf, Germany) was used as the main composition. 0.1 wt% and 0.2 wt% of citric acid (CA, Sigma) was added to this castable. These amounts were previously defined based on the maximum CA content that could be added without significant modification in the castable flowability. Further compositions, a) without-MgO-and-without-CA (reference composition I), b) with-MgO-and-CA-free (reference composition II) and c) without-MgO-and-with-CA (reference composition III), were also tested. A detailed description of these compositions can be found in Table 1.

Mixing and water addition were carried out in a paddle mixer for 10 minutes. Compositions were cast under vibration in cylindrical molds, 40 × 40 mm, for the drying tests and mechanical strength measurements, and 70 × 70 mm ones, for the apparent volumetric expansion (AVE) evaluation [4]. The initial curing time was carried out in an acclimatized chamber Vöetch 2020 at 10 °C for 24 h. These conditions were selected in order to assure a minimal mechanical strength of the samples for cement hydration and demolding, with no significant magnesia reaction. Afterwards, samples were kept at 50 °C in an environment with R.U. close to 100% for 7 days. During this period, the mechanical strength and the apparent volumetric expansion of the samples were evaluated every 24 h.

The splitting tensile strength of green and humid samples was performed according to the ASTM C496-96 standard in

Table 1
Magnesia sinter suspensions and refractory castable compositions studied.

Raw materials	MgO containing samples (wt%)	Reference samples (wt%) MgO-and-CA-free (Reference I)	MgO-free (Reference III)
Fused* and calcined alumina** ($D_{Part} \geq 100$ μm, $D_{Max} = 5760$ μm)	88	94	94
Calcium aluminate cement **	6	6	6
Magnesia sinter (98 wt% MgO, $D_{50} = 15$ μm)***	6	0	0
Water	5.7	5.7	5.7
Citric acid	0; 0.1 and 0.2	0	0.2
Dispersant (polyethyleneglycole based)	0.25	0.25	0.25

Elfusa (Brazil), ** Almatis (USA), *** Magnesita S.A. (Brazil).

MTS TestStar II equipment. A constant loading rate of 42 N/s (1000 kPa/min) was used.

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

$$Vi = (H \times \pi \times (D_i\text{-}2t)^2)/4 \qquad (1)$$

$$AVE = 100\% \times (V_E\text{-}V_0)/V_0 \qquad (2)$$

Equation 1 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. Further description of this technique can be found in the literature [4,15–17].

In order to highlight the decomposition of hydrated compounds, the drying tests were conducted up to 600 °C with a 10 °C/min heating rate, for samples previously dried at 50 °C for 24 h,. A thermogravimetric apparatus was used for this purpose where mass variations and the temperature profile at the samples' surface were simultaneously recorded. Percentage mass loss rate (wt%/min) versus samples' temperature curves were used for the drying behavior evaluation [19].

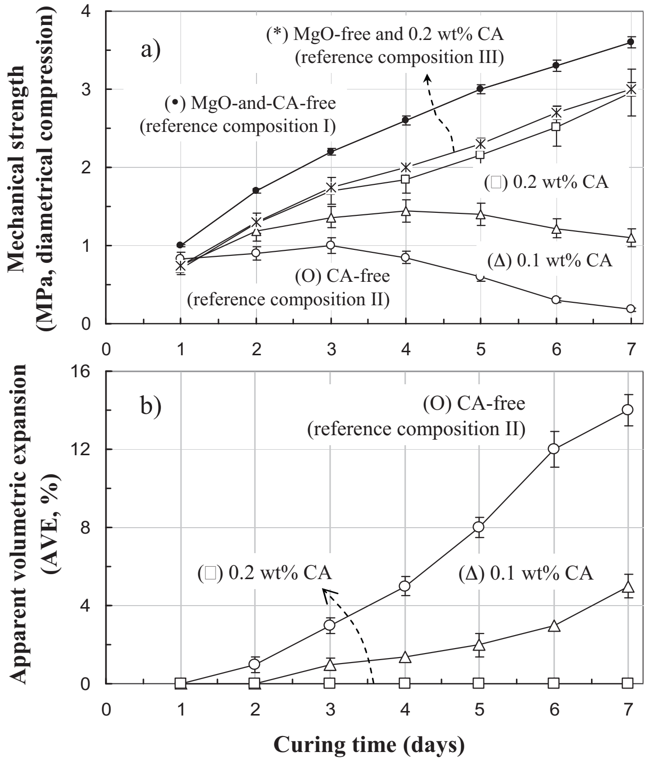

Figure 2. a) Mechanical strength and b) apparent volumetric expansion (AVE) of samples containing different amounts of citric acid at 50 °C, in humid environment.

3. Results and Discussions

In order to understand the impact of the MgO hydration in the castables' strength and the benefits induced by the CA addition, firstly it is necessary to analyze the properties evolution of a magnesia-and-CA-free high-alumina castable bonded with calcium aluminate cement (Figure 2a, reference composition I). Calcium aluminate cement hydration is based on dissolution and precipitation processes and due to this the strengthening of these castables is time-temperature dependent. For temperatures above 20 °C, the maximum strength can be attained after 2 or 3 days of curing, whereas for the lower ones, the process can last several weeks [19]. As no mechanical damage is expected by cement hydration, the strength of these materials increased continuously during the evaluation time. On the other hand, in the CA-free magnesia containing formulation (reference composition II), a not so steep initial increase in mechanical strength is also observed due to the cement hydration. At this stage, magnesia shows a low degree of hydration that is not sufficient to result in mechanical damage. Over the following days, nevertheless, the volumetric expansion can no longer be accommodated in the porosity of the structure and the mechanical strength decreases [4,15]. After this stage, the AVE increases (Figure 2b) and macroscopic cracks are detected.

The 0.1 and 0.2 wt% CA addition to the magnesia-containing castables resulted in: a) samples much stronger than the CA-free one (reference II), b) with mechanical strength levels close to those observed for the MgO-free-CA-containing composition (Figure 2a, reference composition III) and, c) a remarkable reduction in the progress and final AVE levels (Figure 2b). The drying behavior of these samples after hydration (Figure 3) points out two interesting aspects: 1) The drying rate peaks related to the free-water release (below 200 °C) for the CA containing samples were shifted for higher temperatures, which is an indication of less porous and permeable structures, consequently with no hydration cracks [4,19]; 2) Because a significant reduction in the intensities of

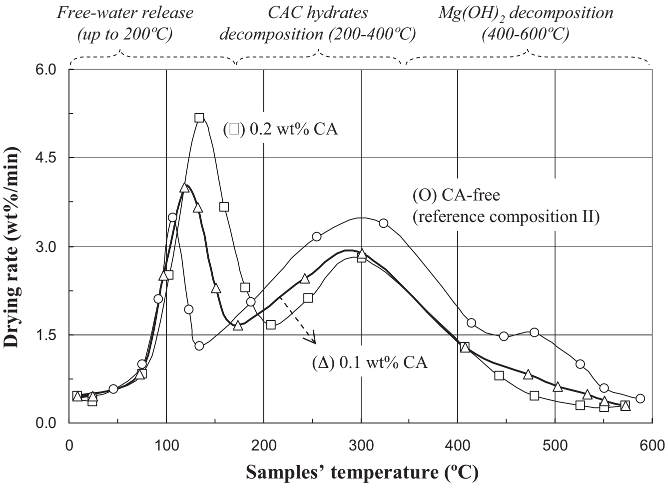

Figure 3. Drying behavior of castables containing different amounts of citric acid after 7 days at 50 °C, in humid environment.

the $Mg(OH)_2$ decomposition peaks was also observed (400-600 °C), these results highlight the effectiveness of CA to reduce MgO hydration rate under these conditions.

The anti-hydration effect was more effective for the 0.2 wt% containing samples than for the 0.1 wt% one, pointing out that the amount of CA added to the composition is a key-issue. This effect can be understood by considering that for the castable compositions, the CA content added was shared amongst the surface of the magnesia particles and all the other raw materials present. Therefore, there is a minimum amount of CA required to coat the MgO particles effectively.

It is also important to evaluate whether a further addition of CA to the composition could lead to even better results. Concerning this aspect, two important effects were observed. Firstly, as mentioned above, CA additions carried out above 0.2 wt% resulted in a significant loss of flowability. Secondly, samples containing 0.2 wt% CA (the MgO containing one and the MgO-free reference composition III) presented mechanical strength levels lower than the MgO-and-CA-free one (Figure 2b, reference composition I). Due to the fact that the damage caused by the magnesia hydration was reduced by CA addition (as seen in Figure 3), this result can be associated to the effects of the CA addition on the cement hydration. The literature reports chelants as setting delayers for the calcium aluminate and Portland cements [20,21]. Based on their affinity for Ca^{2+} and Al^{3+} ions, chelants can inhibit the hydrates precipitation increasing the fresh castable workability. However, because this effect can also reduce the rate of strengthening, in the present case, the addition of greater amounts of CA could mask the benefits attained by reducing MgO hydration.

4. Remarks

Citric acid (CA) additions reduced the deleterious effects of MgO hydration in refractory castables. Samples containing up to 0.2 wt% of CA presented a three-fold mechanical strength increase compared to the CA-free ones and close values to those observed for MgO-free reference composition. By the apparent volumetric expansion (AVE) measurements and thermogravimetry evaluations during the hydration tests, the CA addition reduced the MgO hydration rate under the test conditions (7 days at 50 °C, in a high humidity environment). By varying the CA content on the composition, it was observed that the efficiency of this technique depends on the addition of a proper amount of chelant. The CA amount also affected the hydration of the calcium aluminate cement used as a binder, reducing the final level of mechanical strength of the castable. However, this mechanical strength decrease was much less significant than the one caused by magnesia hydration in the CA-free composition. Compared to other anti-hydration techniques, especially those based on microsilica addition, the CA one presented a more efficient performance to inhibit magnesia hydration and does not leave harmful residues that could decrease the castable refractoriness.

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