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# Chelants to inhibit magnesia (MgO) hydration

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## Abstract

Magnesium oxide (MgO) presents excellent refractoriness and high resistance to basic slag. However, in the presence of water, MgO undergoes an expansive hydration reaction generating $Mg(OH)_2$, which can lead to swelling and cracking. In this work, additives called chelants were added to dead burnt magnesia suspensions in order to check their effectiveness as inhibitors of the magnesium oxide hydration. Zeta potential, ionic conductivity, pH and temperature measurements were used to provide information related to the magnesia surface and the chelant adsorption. Assessment of the hydration degree and volumetric expansion provided indications of the amount of $Mg(OH)_2$ formed, as well as its likelihood to damage the ceramic bodies. The results showed that citric acid can inhibit hydration to some extent, whereas ethylenediamine tetraacetic acid (EDTA) was more effective in preventing volume expansion. An addition of 0.3 wt% of these chelants was sufficient to prevent hydration and avoid expansion.

*Keywords:* Magnesia; Refractory castables; Hydration; Chelants

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## 1. Introduction

Magnesia based refractory castables present a wide technological interest because they associate versatility, high refractoriness and resistance to basic slag [1,2]. Additionally, systems containing $Al_2O_3$ and MgO provide in situ spinel ($MgAl_2O_4$) formation, which can improve thermal shock resistance [3]. However, in the presence of water, MgO undergoes an expansive hydration reaction as a result of the different densities between the magnesium oxide ($\rho = 3.5$ g/cm$^3$) and the corresponding hydroxide formed ($\rho = 2.4$ g/cm$^3$), $Mg(OH)_2$, also known as brucite [4]. This expansion represents the main challenge in magnesia containing castables, since it may lead to swelling and cracking, damaging the refractory integrity [2,5].

Many studies have been carried out to understand the hydration mechanisms of magnesia [6–10] in order to develop anti-hydration techniques. [11–15] Nevertheless, the results attained are quite diverse due to differences in the magnesia source, purity, temperature, hydration time and the chemical environment where the hydration is performed.

Magnesia is generally obtained by calcining or sintering magnesite ($MgCO_3$) or brucite at moderate to high temperatures. There are different processing routes, leading to magnesium oxides with distinct reactivity. When the MgO is reactive or the environment becomes more favorable to hydration, its reaction mechanism is similar to that of hydratable aluminas (or $\rho$-alumina) [6,10,16]. Conversely, when it is less reactive, as the dead burned (or sintered) magnesia, the hydration mechanism is based on the dissolution and precipitation process, which can be compared to that of calcium aluminate cements [6,8]. These features can be summarized by the reaction steps below [8–10]:

Firstly, the magnesia surface is protoned by $H^+$ ions originated from water dissolution Eq. (1) and the MgO-alkaline oxide plays an electron donor role:

$$MgO_{(Solid)} + H_2O \rightarrow MgOH_{(Surface)}{}^{+} + OH_{(Aqueous)}{}^{-} \qquad (1)$$

After that, negative $OH^-$ ions are electrostatically attracted to the positive $MgOH^+$ surface and adsorbed Eq. (2):

$$MgOH_{(Surface)}{}^{+} + OH_{(Aqueous)}{}^{-} \rightarrow MgOH^{+}\cdot OH_{(Surface)}{}^{-} \qquad (2)$$

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Afterwards, in the dissolution step, $Mg^{2+}$ and $OH^-$ are gradually released to the aqueous medium Eq. (3) and remain dissolved until their concentrations reach the supersaturation point, when magnesium hydroxide finally precipitates Eq. (4).

$$MgOH^+ \cdot OH_{(Surface)}{}^- \rightarrow Mg_{(Aqueous)}{}^{2+} + 2OH_{(Aqueous)}{}^- \tag{3}$$

$$Mg_{(Aqueous)}{}^{2+} + 2OH_{(Aqueous)}{}^- \rightarrow Mg(OH)_{2(Solid)} \tag{4}$$

According to Eqs. (1)–(4) and to the model proposed, it can be suggested that, to prevent hydroxide formation, it is necessary to decrease the rate of MgO dissolution and/or $Mg(OH)_2$ precipitation. This may be attained by adding molecules which can be adsorbed on the magnesia surface, building up a protective coating and inhibiting the dissolution step from taking place. Chelants are good candidates for this purpose.

Chelants are a group of molecules that present various negative sites in the same molecule and due to this, could be adsorbed onto the positively charged magnesia surface (Fig. 1) [17]. Considering this aspect and the mechanism proposed for magnesia hydration, the greater the number of negative sites, the higher the absorption of the additive and the more efficient the coating is. Moreover, these molecules are characterized by their high affinity for metal ions (such as $Mg^{2+}$ and $Ca^{2+}$), forming complexes with them. Thus, these $Mg^{2+}$ complexes in a solution could inhibit the hydroxide precipitation step. Bearing this in mind, this article aims to evaluate how the presence of different chelants influences the kinetics of MgO hydration reaction by zeta potential, ionic conductivity, pH and temperature measurements. The hydration degree, as well as the apparent volumetric expansion (AVE), was also assessed.

## 2. Materials and methods

Aqueous suspensions of dead burned magnesia ($CaO/SiO_2 = 2.54$, $D90 < 75\ \mu m$ and 98.7 wt% MgO – Magnesita S.A., Brazil) with 12.5 and 67 wt% of solid content were used for the experiments. Different p.a. compounds were evaluated as chelant additive candidates: citric acid (CA), tartaric acid (TA), sodium citrate (Cit) and ethylenediamine tetraacetic acid (EDTA) (Satelite Químicos, Brazil).

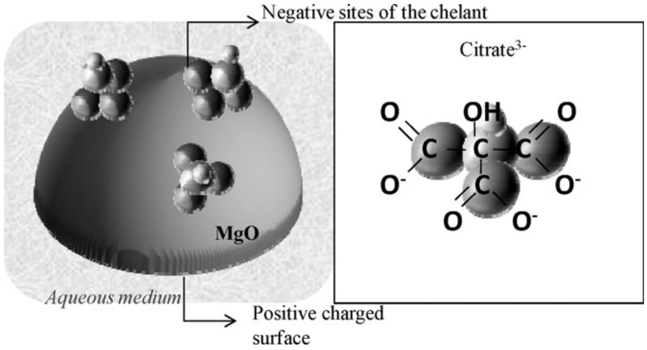

Fig. 1. Sketch for the chelant (citric acid) adsorption on the positively charged magnesia surface.

The 12.5 wt% suspensions were useful to evaluate the hydration kinetics of MgO by means of zeta potential, ionic conductivity, pH and temperature (heat evolution) measurements. Whenever used, the amount of chelants was 0.3 wt%.

The data were recorded as a function of time with the help of zeta potential, ionic conductivity, pH and temperature sensors connected to an automatic acquisition system (ESA 9800, Matec Applied Sciences, UK). Data acquisition started immediately after the sensors were inserted into the MgO and MgO–chelant suspensions. With the aid of a thermal bath, the suspensions were kept at 50 °C during the experiments, enabling faster hydration kinetics than at room temperature [2,5].

The zeta potential analyzer is able to measure the mobility of the particles when an electric field is applied to them. Computer software then converts this mobility into the electrical potential of the particles on their shear plane, which is the so-called zeta potential. For this calculation, the software uses information from particle properties (density and concentration) and solvents (density and dielectric constant). Zeta potential measurements give an indication of how the magnesia surface interacts with water and also with the chelant molecules. Conductivity and pH measurements provide data related to the concentration of ionic specimens and $OH^-$ in solution, respectively.

Dead burned magnesia suspensions with higher solid contents (67 wt%) were used to measure the hydration degree (HD) and the apparent volumetric expansion (AVE) of the formulations. The suspensions were cast into 40 mm × 40 mm cylindrical molds and kept at 50 °C in an acclimatized chamber (Vötsch, model 2020) in a moisture-saturated environment (approx. 100% RH) for 7 days, which is enough time for the hydration reaction effects to be visible [2].

The hydration degree was calculated based on the weight loss of the samples between 200 and 800 °C [1]. In this temperature range, only water molecules bonded as $Mg(OH)_2$ were decomposed. The HD was determined according to Eq. (5), where $M_{Initial}$ is the initial mass, $M_{Final}$ is the final mass and 0.31 is the ratio between the molecular weight of MgO and $Mg(OH)_2$.

$$HD = 100 \times \frac{M_{Initial} - M_{Final}}{0.31 \times M_{Initial}} \tag{5}$$

Physical damage caused by MgO hydration was evaluated using the measurements of the apparent volumetric expansion (AVE) [2,5,13–15]. The AVE values were obtained by measuring the dimensions of the samples before and after being exposed to the hydration condition. The molds used in this test had a thin-wall, made of a special non-adherent polymeric material. In these molds, the samples were free to expand without any significant restriction, enabling the measurement of the samples' dimensions reliably while expanding [2]. The AVE was calculated considering the initial volume of the samples as a reference, as described by Eqs. (6)

and (7).

$$V_i = \frac{\pi H_i (D_i - 2t)^2}{4} \tag{6}$$

$$\mathrm{AVE} = 100 \times \frac{V_E - V_0}{V_0} \tag{7}$$

The volume of the cylindrical shapes was calculated from measurements taken at several points in the specimens, where $V_i$ is the volume; $H$ is the height; $D$ is the diameter and $t$ is the mold wall thickness. For AVE, $V_0$ was the initial volume of the sample and $V_E$, the respective volume after hydration and expansion.

## 3. Results and discussion

### 3.1. Hydration in plain MgO suspensions

Fig. 2 shows the zeta potential, ionic conductivity, pH and temperature for the plain MgO suspensions. The high positive value of zeta potential at the beginning of the experiment suggests that magnesia surface protonation (Eq. (1)) takes place as soon as it comes in contact with water. At the same time, $OH^-$ ions are released to the aqueous medium, which explains the relatively high initial values of the ionic conductivity and pH. After that, the dissolution step starts (Eq. (2)) and the positive charges ($MgOH^+$ on surface) are gradually neutralized by the adsorption of negative ions ($OH^-$), decreasing the zeta potential. Carrying on the dissolution process, $OH^-$ anions are desorbed from the MgO surface, releasing magnesium ions into the solution (Eq. (3)). As a consequence, the ionic conductivity and pH continuously increase due to the higher concentration of $Mg^{2+}$ and $OH^-$ ions, respectively.

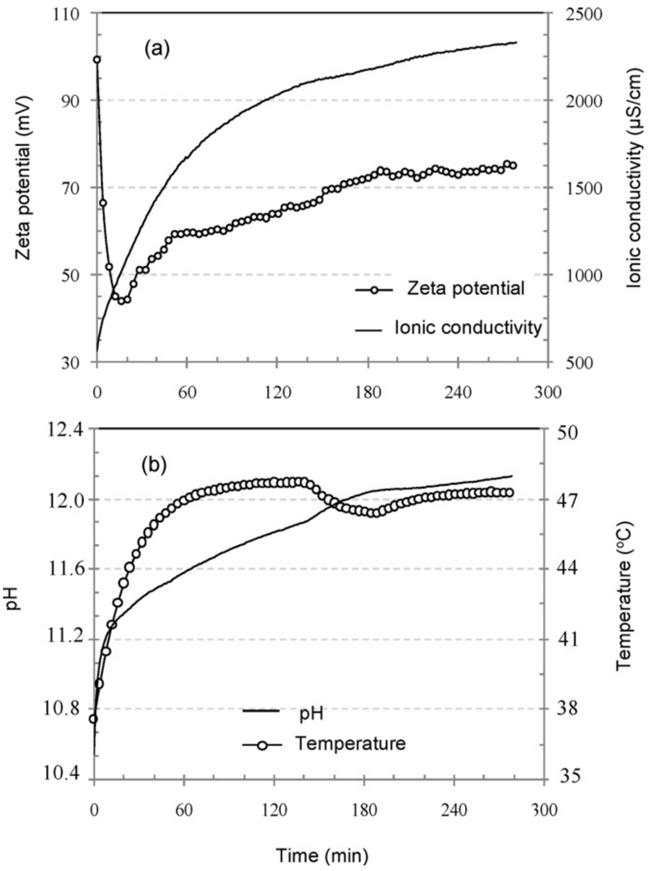

Fig. 2. (a) Zeta potential/ionic conductivity and (b) pH/temperature for magnesia sinter suspensions (12.5 wt% solids) as a function of the time.

The ionic conductivity and pH profiles show that the rate of ion release into the solution decreases over time, reaching the equilibrium condition, which could induce the end of the dissolution step. However, since magnesium hydroxide is the most stable species in this system, the process will progress until $Mg(OH)_2$ precipitates. The precipitation step (Eq. (4)) occurs when the super saturation of the solution is reached. This step shifts the equilibrium of the system, favoring further protonation of the magnesia surface, thereby increasing the zeta potential again. Additionally, Fig. 2b shows that after stabilizing the suspension in the thermal bath (at around 70 min), the temperature remains constant for a period of time, but then it drops again after approximately 140 min. Simultaneously, the pH profile's slope increases, suggesting a re-dissolution phenomenon on the surface of the magnesia particles. The temperature drop indicates that it is an endothermic process, requiring energy to be carried out.

According to these results, the hydration of magnesia occurs in a two-step process (dissolution and precipitation), following the Le Chatelier cycle. Moreover, it can be inferred that the initial zeta potential value is useful to provide data at the protonation step, whereas the potential decrease is related to the dissolution step. These statements are valid for the conditions studied here: dead burned MgO, 12.5 wt% solid suspensions at 50 °C.

### 3.2. Hydration in MgO–chelant suspensions

In the presence of chelants there are two dissociation reactions that occur simultaneously in the suspensions: water and chelant dissolution (Eqs. (8) and (9)) [17]. In the case of chelants, these reactions are more complex because they depend on their structure and on how many dissociable groups there are in their molecules:

$$H_2O \rightarrow H_{(\mathrm{Aqueous})}{}^{+} + OH_{(\mathrm{Aqueous})}{}^{-} \tag{8}$$

$$\mathrm{Chel} \rightarrow nH^{+} + \mathrm{Chel}^{(n-)} \tag{9}$$

In the first contact with the water–chelant system, magnesia particles' surfaces become protoned (Eq. (1)) by $H^+$ ions from both water and the chelant dissociation. After that, as the negative ions approach the positively charged MgO surface, two different negative species are available: (i) the $OH^-$ ions due to the water dissociation and (ii) the $\mathrm{Chel}^{(n-)}$ released from the chelant. As seen previously, the $OH^-$ ions adsorbed on the $MgOH^+$ surface are desorbed after some period of time, releasing magnesium cations into the solution (Eq. (3)). However, because these $Mg^{2+}$ ions can be trapped by the chelant, the $\mathrm{Chel}^{(n-)}$ ions could:

Table 1
Chemical stability constants for the magnesium–chelant complexes [17].

| Chelant | Solubility constant ($K_s$) |
|---|---|
| $EDTA^{4-}$ | $2.04 \times 10^{-9}$ |
| $Cit^{3-}$ (same as CA) | $6.31 \times 10^{-4}$ |
| $TA^{2-}$ | $4.37 \times 10^{-2}$ |

(a) Complex the $Mg^{2+}$ ions dissolved by $OH^-$ from water:

$$\text{Chel}^{(n-)} + \text{Mg}^{2+} \rightarrow \text{Mg}_n\text{Chel}_2(\text{Insoluble}) \qquad (10)$$

(b) or adsorb on the MgO surface:

$$\text{MgOH}_{(\text{Surface})}{}^{+} + \text{Chel}_{(\text{Aqueos})}{}^{(n-)} \rightarrow [\text{MgOH}^{+}\cdot\text{Chel}^{(n-)}]_{(\text{Surface})} \qquad (11)$$

Thus, depending on the stability constant of the complex formed and the energy reduction caused by the $\text{Chel}^{(n-)}$ adsorption on the MgO surface, either Eq. (10) or (11) can prevail.

The complexation trend (Eq. (10)) can be inferred by the stability constant ($K_s$) of the complex compound, as presented in Table 1 for the chelants studied here [17]. The higher the $K_s$ value, the more stable the complex formed. The predominance of the adsorption (Eq. (11)) can be assessed by the zeta potential behavior: increasing chelant adsorption on the MgO surface will result in lower potential values. This phenomenon occurs due to the neutralization of the positive $MgOH^+$ sites on the magnesia surface by the negative $\text{Chel}^{(n-)}$.

Although the relationship presented above is valid for chelants, it is important to note that if other molecules are present in the suspension, a similar effect can be observed. For instance, polymers, which possess lateral negative groups, also reduce the zeta potential, but are not bonded to the magnesia surface. Therefore, care must be taken when analyzing more complex systems.

If the complexation of $Mg^{2+}$ ions in the solution prevails, then the equilibrium of Eq. (10) shifts to the right (products), favoring the dissolution process, as more $Mg^{2+}$ ions are consumed in the reaction. The higher the dissolution, the more rapidly the suspension attains super-saturation, accelerating the precipitation of $Mg(OH)_2$ and increasing the hydration degree. On the other hand, if the chelant adsorption on the MgO surface prevails, less $Mg^{2+}$ is brought into the solution, which inhibits precipitation of $Mg(OH)_2$ (less hydration). For this reason, if a protective coating were formed on the magnesia particles, the dissolution reaction will stop. However, in real systems both reactions (complexation and adsorption) can occur simultaneously and it is necessary to minimize the complexation and maximize the adsorption in order to reduce the MgO hydration. This balance can be attained by selecting chelants with higher adsorption capacity and which can generate stable complexes (Table 1).

EDTA is the chelant that generates the most stable complex (the highest $K_s$ value, Table 1). However, the highest initial zeta potential values (Fig. 3) indicate low degree of surface adsorption. Therefore, the complexation reaction is favored and magnesia dissolution takes place, reducing the zeta potential. After a while, a plateau value is attained for some minutes, but then it begins to rise again. This further increase can be associated to the re-protonation of the magnesia surface activated by the precipitation of $Mg(OH)_2$.

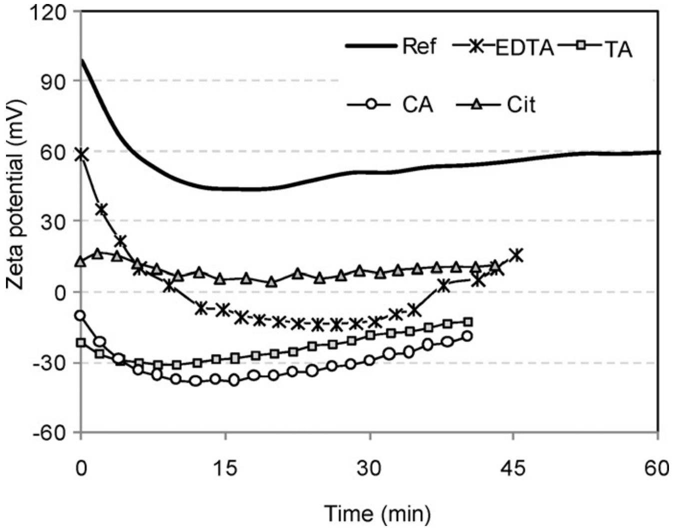

Fig. 3. Zeta potential for magnesia suspensions (12.5 wt% solids) containing different chelant agents as a function of the time.

Conversely, citric acid (CA) and tartaric acid (TA) additives present the highest adsorption on the magnesia surface, as can be predicted from their low $K_s$ values (Table 1). The adsorption leads to the neutralization of the positive charges on the MgO surface, resulting in a negative zeta potential (Fig. 3). Although citric and tartaric acids adsorb very strongly on the surface and present $K_s$ values lower than EDTA, they do not prevent the dissolution completely. This is indicated by the decrease in the initial zeta potential over time, followed by an increase due to the re-protonation step (Fig. 3).

Sodium citrate (Cit) did not present an adsorption as strong as that from CA and TA (Fig. 3). Nevertheless, it can also be an effective additive, since it keeps the zeta potential nearly as constant as a function of time. This result suggests a small degree of dissolution and re-protonation for the magnesia particles which minimize hydration.

### *3.3. Physical and mechanical aspects related to hydration in MgO–chelant suspensions*

In order to study the physical and mechanical aspects related to hydration, concentrated magnesia suspensions (67 wt%) were tested. Hydration degree (HD) and apparent volumetric expansion (AVE) measurements for magnesia suspensions containing different chelants are presented in Fig. 4. The reference sample (chelant-free) and those containing TA and CA showed the same trend for HD and AVE. However, for the samples containing Cit and EDTA, quite distinct behaviors were observed.

Tartaric acid and citric acid improved the hydration resistance of the MgO, as predicted by the zeta potential experiments (Fig. 3). Fig. 5 shows that the amount of visible cracks decreases in the following sequence: Ref > TA > CA. The highest expansion was observed for sodium citrate, along with the lowest hydration (Fig. 4). This apparent contradiction may be explained by Fig. 5, where the sample Cit presents a large crack, which may have affected the AVE measurement.

According to the discussions on the zeta potential results, EDTA can be pointed out as the chelant which is most prone to complexation. This characteristic favors magnesia hydration, which is confirmed by the highest HD shown in Fig. 4 among those chelants containing suspension. As a large number of complexes forms in the solution, they can be thoroughly spread throughout the sample volume. These complexes act as nuclei for the precipitation of $Mg(OH)_2$, thereby generating a very homogeneous structure, which is effective in accommodating the volume expansion (Fig. 6). Therefore, a lower AVE may be expected, with very few cracks (Fig. 5).

In order to better visualize the effects of EDTA, scanning electron microscopy (SEM) was performed (Fig. 7). Although

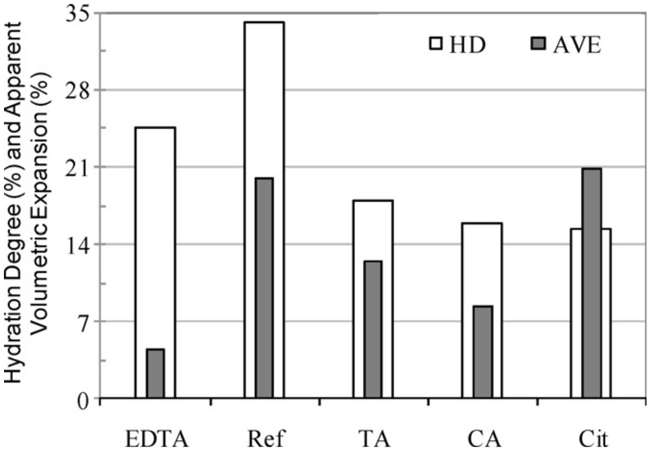

Fig. 4. Hydration degree (HD) and apparent volumetric expansion (AVE) for magnesia suspensions without CAC (67 wt% solids) containing different chelants (0.3 wt%) after curing at 50 °C for 7 days.

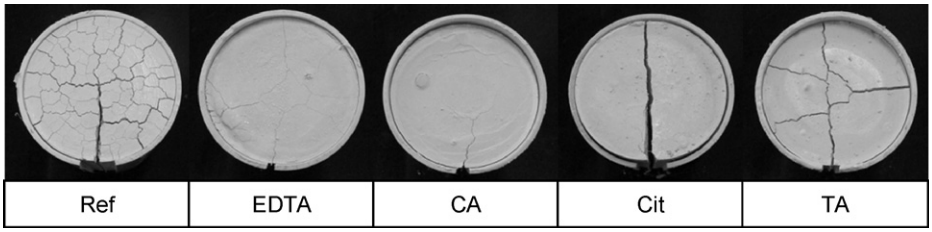

Fig. 5. Photograph of magnesia suspensions without CAC (67 wt% solids) containing different chelants (0.3 wt%) after curing at 50 °C for 7 days.

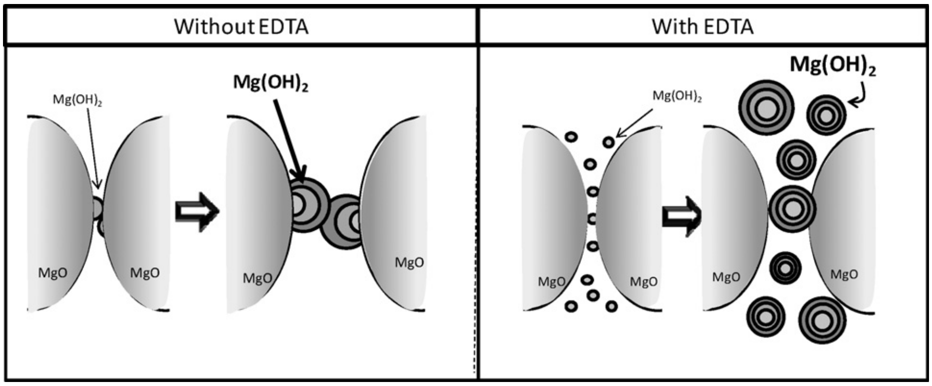

Fig. 6. Schematic representation of magnesia hydration in the (a) absence or (b) presence of EDTA.

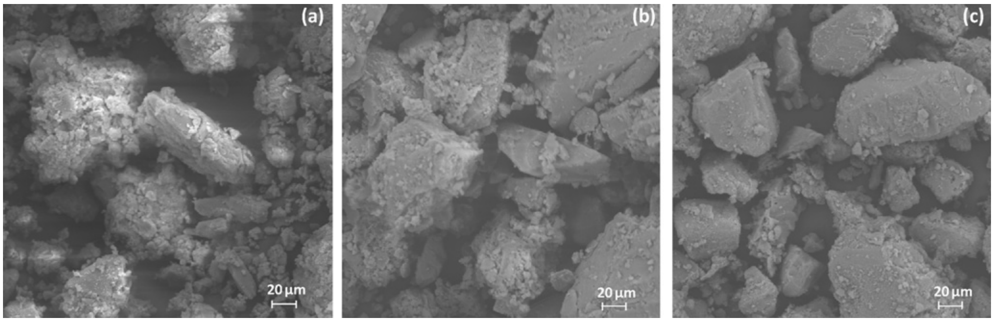

Fig. 7. Scanning electron microscopy of magnesia samples: (a) without chelant or in the presence of chelants (b) citric acid and (c) EDTA.

the images did not show the exact crystalline habit of $Mg(OH)_2$, it is clear that the crystals formed in the sample without chelants (Fig. 5a) are quite different from the others. This distinction is evident for EDTA, which presents crystals with well defined faces (Fig. 7c). A similar mechanism was also reported in the literature [8] for magnesia hydration in the presence of magnesium acetate. This additive also presents high affinity for the complexation of $Mg^{2+}$ ions, thus increasing MgO dissolution and the hydration degree.

## 4. Conclusions

The hydration process of magnesia is carried out according to the Le Chatelier cycle, involving successive steps of protonation of the MgO surface, dissolution of $Mg^{2+}$ ions and precipitation of $Mg(OH)_2$. The chelants can affect this process in two ways: complexing the dissolved $Mg^{2+}$ ions and/or adsorbing on the MgO surface. Tartaric acid (TA) and citric acid (CA) adsorb on the MgO surface and reduce its trend to hydration. CA was more effective than TA, leading to a lower hydration degree (HD) and apparent volume expansion (AVE). Sodium citrate (Cit) significantly reduced HD, however, AVE may be negatively affected due to a heterogeneous precipitation of $Mg(OH)_2$. EDTA has a high affinity to $Mg^{2+}$ ions, favoring the formation of complexes. Although it did not prevent the MgO from hydrating, a very low AVE value was observed. This volume stability was due to the formation of a homogeneous structure of $Mg(OH)_2$ crystals, which accommodates the volume expansion.

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