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Temperature and common-ion effect on magnesium oxide (MgO) hydration

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Abstract

MgO based refractory castables draw wide technological interest because they have the versatility and installation advantages of monolithic refractories with intrinsic MgO properties, such as high refractoriness and resistance to basic slag corrosion. Nevertheless, MgO easily reacts with water to produce $Mg(OH)_2$, which is followed by a large volumetric expansion, limiting its application in refractory castables. In order to develop solutions to minimize this effect, a better understanding of the main variables involved in this reaction is required. In this work, the influence of temperature, as well as the impact of the chemical equilibrium shifting (known as the common-ion effect), on MgO hydration was evaluated. Ionic conductivity measurements at different temperatures showed that the MgO hydration reaction is accelerated with increasing temperature. Additionally, different compounds were added to evaluate their influence on the reaction rate. Among them, $CaCl_2$ delayed the reaction, whereas KOH showed an opposite behavior. $MgCl_2$ and $MgSO_4$ presented similar results and two other distinct effects, reaction delay and acceleration, which depended on their concentration in the suspensions. The results were evaluated by considering the kinetics and the thermodynamics of the reaction, and the mechanical damages in the samples that was caused by the hydration reaction.

Keywords: A. Suspensions; C. Chemical properties; D. MgO; E. Refractories

1. Introduction

The advances in castables are closely linked to the requirements of end-users. Due to tougher working conditions, new materials have been developed to improve the performance and increase the refractory's working life. In this context, MgO based castables have been developed and studied.

Magnesium oxide is one of the most important raw materials in the refractory industry due to its high refractoriness (melting point of 2800 °C), corrosion resistance in a basic environment, and low cost [1–4]. Moreover, in the Al_2O_3–MgO system, the formation of spinel ($MgAl_2O_4$) can improve the thermal shock resistance [1]. Because of its inherent properties, magnesia/alumina spinel containing refractories are considered an excellent liner for steel production [3,5,6].

MgO based refractory castables, however, have not been widely used due to their hydration and accompanying volume expansion that can double a sample's size [7,8]. This expansion is caused by the different densities between the magnesium oxide ($\rho = 3.5$ g/cm^3) and the corresponding magnesia hydroxide ($\rho = 2.4$ g/cm^3). Because advanced castables are denser, the hydroxide that is formed cannot be accommodated by the residual porosity in the sample. The higher the expansion pressure, when hydration occurs, the greater the mechanical damages caused in the structure, such as cracks or dusting [9–11]. As a consequence, magnesia additions in castables matrixes have been limited to small amounts (below 10 wt%) and/or large particles ($\geq$40 μm) [12]. Moreover, the gas evolution from $Mg(OH)_2$ thermal decomposition that occurs at about 350 °C causes many issues in refractories.

The hydration of magnesia is caused by its contact with liquid water (during mixing and curing steps of castables), water vapor (throughout the drying process), or environmental moisture. In the literature, two main mechanisms for the

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magnesia hydration are found. The first is the shrinking core model proposed by Kitamura et al and the second is based on the dissolution and precipitation process of MgO particles.

In the first mechanism it was studied magnesia samples in the 135–200 °C temperature range [10]. This mechanism can be compared to the hydration reaction of hydratable alumina (or ρ-alumina), well understood in the literature, unlike the magnesia hydration [13,14].

Hydratable alumina, a transition and low crystalline phase of alumina, is produced by a flash calcination of gibbsite at lower temperatures. The attained phase (usually rho) has a high surface area due to its internal porosity and unsaturated bonds left by the release of vapor water during calcination.

Magnesia particles (MgO) are typically obtained from seawater, brines or magnesite ($MgCO_3$). Brazilian refractories are typically obtained by calcining or firing magnesite from brines. There are different processing routes, leading to magnesia with distinct reactivities.

In this study, caustic magnesia, one of the most reactive magnesias, was used. This material has a polycrystalline structure which, according to Kitamura et al, hydrates in two steps. First, the formation of a brucite ($Mg(OH)_2$) layer is carried out at the grain boundaries (which has little room for expansion accommodation) [10,15,16], stressing the structure. As hydration proceeds, the tensions generated by the expansion become strong enough to break grain boundaries, leading to several smaller particles. Thus, both the surface area and the reaction rate increases exponentially until a more stable crystalline structure is attained. At this stage, the reaction rate starts decreasing, and it is primarily influenced by water diffusion through the hydroxide layer [10]. The main feature of this hydration mechanism is the absence of intermediate steps in the reaction, with no dissolution stage before the hydrated phase formation.

The second mechanism was proposed for magnesia hydration at temperatures lower than 90 °C, which is directed at obtaining specific hydroxide morphology for application as flame retardant and smoke-suppressing additives in polymers. This mechanism can be compared to cement hydration. In the cement dissolution step, cement particles are dissolved by water, resulting in Ca^{2+} and $Al(OH)_4^-$ ions. This step is followed by a slow nucleation process which precedes the precipitation of hydrated phases. This stage is known as the "induction period", and remains until the first crystalline hydrates nuclei are formed. After the induction period, precipitation occurs quickly as a result of crystal growth [17].

The mechanism based on the dissolution and precipitation of MgO particles (second hydration method) is well accepted in the literature, although different kinetic models and intermediate steps for the reaction have been proposed. A short compilation of the proposed stages in this mechanism is presented below.

(1) MgO-alkaline oxide plays an electron donator role in water:

$$MgO_{(s)} + H_2O_{(l)} \rightarrow MgOH^+_{(surface)} + OH^-_{(aq)} \tag{1}$$

(2) OH^- anions are adsorbed in the positively charged surface:

$$MgOH^+_{(surface)} + OH^-_{(aq)} \rightarrow MgOH^+{\cdot}OH^-_{(surface)} \tag{2}$$

(3) OH^- anions are desorbed from the surface, releasing magnesium ions into the solution:

$$MgOH^+{\cdot}OH^-_{(surface)} \rightarrow Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{3}$$

(4) Ions concentration reaches the solution supersaturation, at which point the hydroxide starts to precipitate on the oxide surface:

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mg(OH)_{2(s)} \tag{4}$$

Considering Eqs. (1)–(4), the surface of magnesium oxide is hydroxylated in the presence of water, than the OH^- ions are in equilibrium with the $MgOH^+$ sites at the surface of the solid. At this stage in dissolution, Mg^{2+} and OH^- start to be released in the aqueous medium. These ions are kept in solution until their concentration reaches the solution's supersaturation, when the hydroxide precipitation occurs on a hydrated particle surface.

Taking into account reactions (1)–(4), if one wishes to inhibit magnesia hydroxide formation, it is necessary to decrease the rate of one or both of the two following processes; the dissolution (Eqs. (1)–(3)) or precipitation (Eq. (4)).

The solubility of brucite decreases with temperature [17], which implies that analyzing $Mg(OH)_2$ stability over a temperature range is necessary [18,19]. Moreover, based on Eqs. (1)–(4) and the displacement of the chemical equilibrium (common-ion effect) [20], the addition of Mg^{2+} or OH^- ions promote the increase of both the hydroxide formation rate and thus, the mechanical damage caused by hydroxide expansion [19,21]. The addition of OH^- ions is a more complex process than Mg^{2+}, because the presence of OH^- decreases the dissolution process and increases the precipitation one. On the other hand, Mg^{2+} additions favor the precipitation step.

Bearing this in mind, the aim of this article is to clarify how temperature and the presence of different soluble salts influence the kinetics of MgO hydration reactions and their deleterious effects. This will be evaluated by measuring ionic conductivity, oscillatory rheometry, reaction temperature, and apparent volumetric expansion (AVE).

2. Materials and techniques

Aqueous suspensions containing 67.7 wt% of caustic magnesia ($CaO/SiO_2 = 5.18$ and 99 wt% MgO – Magnesita S.A., Brazil) were used for these experiments. The deionized water used to prepare the suspension was cooled to 10 °C to retard hydration of magnesia.

Ionic conductivity measurements as a function of time were carried out at temperatures between 10 and 80 °C using an electrode linked to a data acquisition system (Orion 3Star, Thermo Electron England) and a thermal bath (Fenix, Thermo Electron, Germany). One hundred and fifty grams of suspension was used for the measurements, with the surface of each solution covered with an oil layer to avoid evaporation.

The variables that influence the process of MgO hydration may also be attained using oscillatory rheometry. This test can be evaluated quantitatively considering the viscoelastic changes occurring in MgO suspensions during hydration. By monitoring these changes, it is possible to detect when demolding conditions of MgO based castables are feasible [22]. In the oscillatory test, a sinusoidal time function is used to apply stresses or strains to a sample [23] while viscosity and elasticity data are recorded. This method is particularly suitable for systems that gradually change from a viscous liquid to an elastic solid as a result of a physical or chemical process because the sample structure is not disrupted during the test [23].

The material's response to an applied stress may be expressed in terms of the complex modulus ($G*$), which represents the total resistance of a substance to an applied deformation. The complex modulus involves both the storage or elastic (G') and loss or viscous (G'') moduli according to Eq. (5):

$$G^* = G' + iG'' \tag{5}$$

The G' modulus is related to the storage of energy as potential energy during deformation, and its release after withdrawal of the applied stress. The deformation is recovered completely and instantaneously, whereas G'' indicates the fraction that is irreversibly lost as shear heating in the viscous flow during the deformation of the material. When $G'' > G'$ for all the frequency spectrum, it implies that the material behaves predominantly as a viscous fluid, whereas if $G' > G''$, the elastic solid behavior prevails [24].

The MgO hydration increases both the storage and loss moduli of the suspension, until a transition from a viscous fluid to an elastic solid is observed. Even after this point, the number of connections among particles still increases up to a constant value, named $G'_{\text{equilibrium}}$ [24]. The measurement of both moduli throughout time can be used to assess the setting of suspensions containing MgO.

The oscillatory tests were carried out in a rotational rheometer (RS300, Thermo Haake, Germany) at temperatures from 10 to 50 °C using a CS (controlled stress) mode, in which shear stress (torque) is controlled. The stress and frequency applied during the tests were previously defined by conducting G' measurements as a function of stress (0.01–100 Pa) and frequency (0.01–10 Hz). A linear viscoelastic behavior, characterized by a constant value of G' was observed for all systems up to 1 Hz and 1 Pa, which were chosen as standard values for the following oscillatory tests.

Table 1
MgO suspension compositions.

Suspension	wt%
MgO	77
Water	33

Additives	Content added (wt% added to the MgO suspension)	Maximum solubility (g/100 mL water, 25 °C)
$MgCl_2$	0–20	52
$MgSO_4$	0–14	35.4
$CaCl_2$	0–22.5	73
KOH	0–30	112

G' and G'' moduli were measured as a function of time using a vane type sensor, which shows reduced wall effects and causes minimum disruption of the material structure during the alignment procedure [24]. The MgO suspension was placed in a cylindrical cup, the vane sensor positioned automatically within the suspension, the suspension surface was covered with an oil layer in order to avoid evaporation (drying) and the G' and G'' moduli measurements as a function of the time were carried out.

Different soluble salts of $MgCl_2$, $MgSO_4$, $CaCl_2$ and KOH were added to the magnesia suspension, resulting in the compositions shown in Table 1. Their influence on the kinetics of MgO hydration reaction and the volume expansion were evaluated by measuring the apparent volumetric expansion (AVE), which was taken at different temperatures.

The suspension reaction temperature experiment consisted of measuring the heat released over time, which provided important information on reaction kinetics. A type k thermocouple was inserted in the suspension, which was kept in a calorimeter and linked to an automatic data acquisition system, as shown in Fig. 1a.

The AVE values were obtained by measuring the dimensions of the samples before and after being exposed to the hydration

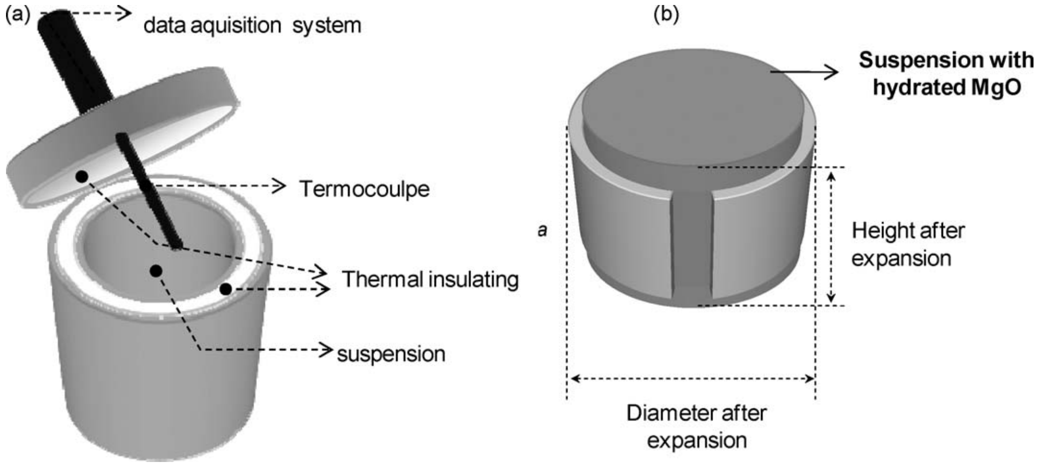

Fig. 1. (a) Experimental apparatus to record the heat evolution during the reaction. (b) Schematic view of the apparent volumetric expansion (AVE) test.

condition (3 days at room temperature). The suspensions were cast in thin-wall cylindrical molds (40 mm × 40 mm) made of a non-adherent polymeric material. In these molds, the samples were free to expand without significant restrictions, allowing a uniform measurement of the samples' dimensions during the test [25]. A schematic view of the apparent volumetric expansion (AVE) test is shown in Fig. 1b.

The AVE is calculated using the initial volume of the sample at time zero (V_0) and the correspondent final volume after hydration and expansion (V_E) by the following equation:

$$\mathrm{AVE} = 100\frac{V_E - V_0}{V_0} \qquad (6)$$

The general equation used to calculate the volume of cylindrical samples at various times including initial (V_0) and final (V_E) was:

$$V_i = \frac{H_i\pi(D_i - 2t)^2}{4} \qquad (7)$$

where V_i is the volume at any time; H, the height; D, the diameter and t the mold wall thickness.

3. Results and discussion

3.1. Temperature effect on the magnesia hydration

Ionic conductivity measurements were carried out for magnesia suspensions at different temperatures to evaluate the ionic species concentration versus hydration time (Fig. 2a).

According to the dissolution/precipitation mechanism for caustic magnesia proposed in the literature [17], the conductivity evaluation shows a maximum value, indicating that there was dissolution before precipitation. The dissolution of solid MgO increases the concentration of the Mg^{2+} and OH^- ions in solution. After a while, the concentration of these ions in water reaches the solubility limit, which is followed by the precipitation of the hydroxide, resulting in the setting of the suspension.

The precipitation mechanism presented is influenced by the four reactions previously presented (Eqs. (1)–(4)), with all occurring simultaneously. The ionic conductivity results obtained show the overall influence of the reactions (the total solution conductivity). The conductivity profile was split and analyzed based on two processes: dissolution and precipitation. The first stage, dissolution, is the combination of the steps where the solid MgO releases Mg^{2+} and OH^- ions in the solution (Eqs. (1)–(3)). In this stage of the process, the main reaction, represented by Eq. (3), favors the conductivity increase. Conversely, the second stage involves the hydroxide formation (Eq. (4)), leading to a conductivity decrease.

Although equipment limitations do not allow tests in the conditions proposed by Kitamura (above 100 °C) [10], in Fig. 2b, the same trend for ionic conductivity above 80 °C were obtained. The results of ionic conductivity showed that both processes, initial dissolution and final precipitation (increase and fall of conductivity, respectively) are strongly influenced by temperature (Fig. 2). Increasingly rapid release of the Mg^{2+} and OH^- ions by MgO into solution occurred with increasing temperature, followed by rapid hydroxide formation.

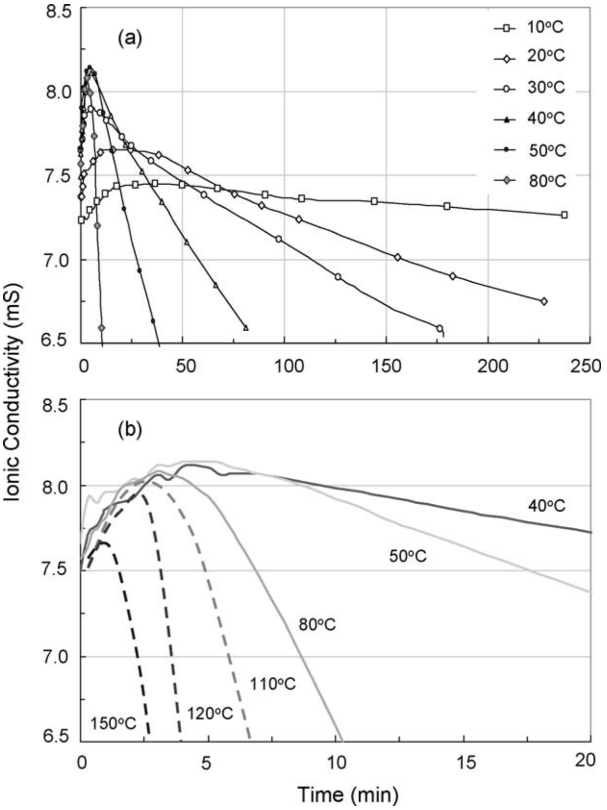

Fig. 2. (a) Ionic conductivity as a function of the time for magnesia suspensions at different temperatures. (b) Ionic conductivity profiles performed in this work (40–80 °C) compared to those carried out by Kitamura (110–150 °C) [10].

Three parameters were analyzed using the conductivity behavior as a function of temperature: (1) elapsed time up to the maximum conductivity value, t_{CM}, which represents the required time for precipitation to start, (2) maximum conductivity attained, C_{Max}, related to the amount of adsorbed ions on the magnesia surfaces and (3) D, the hydroxide precipitation rate evaluated by:

$$D = \frac{C_{Max} - C_f}{t_{CM} - t_f} \qquad (8)$$

where, C_f and t_f correspond to the value of conductivity and the elapsed time at the end of the test, respectively. The end of the test occurs when a constant value is obtained for ionic conductivity or the setting of the suspension is verified.

The change of these parameters (t_{CM}, C_{Max} and D) with the temperature is shown in Fig. 3. The continuous lines are related to the experimental results and the dotted ones represent an extrapolation at temperatures above those where data was taken.

The precipitation rate (D parameter) increased at higher temperatures while t_{CM} decreased. Above 50 °C, the maximum level of conductivity (C_{Max}) decreased slightly, indicating that the adsorption level kept high. These results suggest that increasing temperature led to a higher precipitation rate of the formed compounds. At temperatures above 100 °C, the

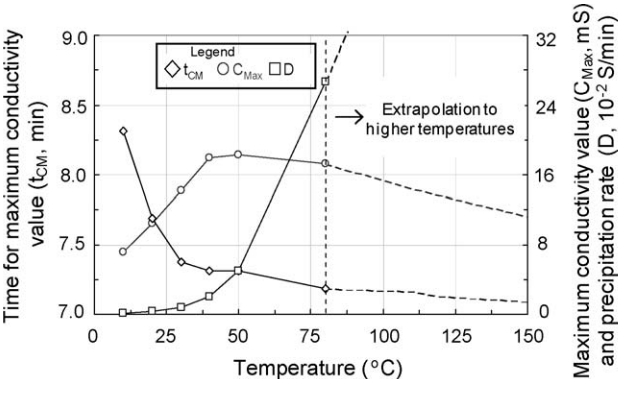

Fig. 3. Time to start the brucite [$Mg(OH)_2$] precipitation (t_{CM}), the precipitation rate (D) and maximum conductivity values (C_M) versus temperature. Solid and dashed lines are based on data and Kitamura's article [10], respectively.

precipitation reaction was intensified due to the presence of water vapor, which besides providing a higher collision among the molecules, made the ionic mobility in the medium more difficult [26].

As soon as MgO is in contact with the water, ionic dissolution starts to take place, increasing the solution conductivity. The conductivity curves (Fig. 2) showed that at temperatures from 10 to 80 °C, the hydration was governed by the dissolution/precipitation mechanism. At temperatures above 80 °C, the dissolution step is so fast that it is hard to evaluate as showed by Kitamura from 110 to 150 °C [10]. It suggests that MgO always undergoes dissolution before precipitation but, depending on the temperature, this step is very difficult to be determined.

Conductivity results indicate that magnesia is hydrated by dissolution/precipitation at a temperatures range between 10 and 80 °C, and that a temperature increase above that range leads to a higher hydration rate, which is indicated by the precipitation rate increase (D parameter). The results do not exclude the possibility of the two mechanisms being carried out simultaneously, because it is not possible to evaluate the hydration degree based on the conductivity decrease. However, the results indicate that higher temperatures induce the precipitation mechanism, whereas, lower ones, favor the dissolution/precipitation mechanism.

Fig. 4 shows the results obtained by oscillatory rheometry tests versus time for different temperatures. The measurement of G' modulus over time was used to assess the setting of suspensions caused by the precipitation of $Mg(OH)_2$ on the particles' surface. The formation of the hydrated layer diminishes the mobility of particles in the suspension, increasing the interaction among them. As a result, the suspension becomes more elastic compared to the initial material. Increasing the temperature caused the time where G' started increasing to be reduced, and caused G' to reach higher levels. These results show that for the same reaction time, the hydroxide content was higher with increasing temperature, indicating the dependence of precipitation with this parameter.

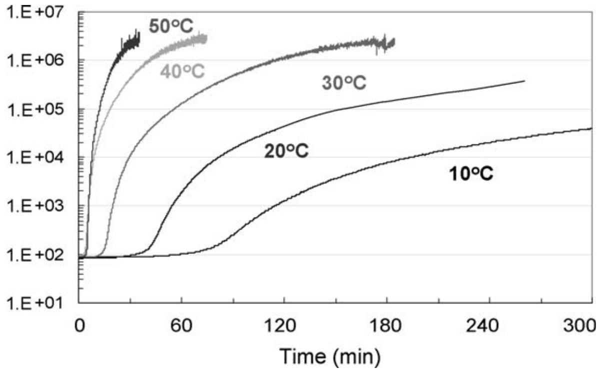

Fig. 4. Storage modulus (G') versus time at different temperatures.

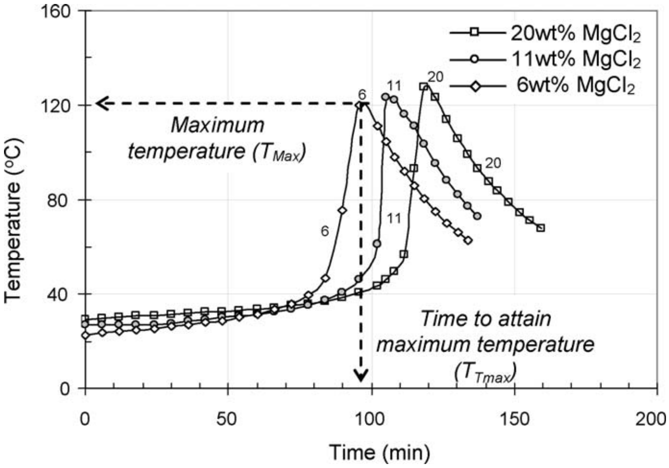

Fig. 5. Heat releasing profile for the MgO hydration reaction.

3.2. Common-ion effect on the magnesia hydration

Two parameters can be analyzed in terms of temperature evolution for the MgO hydration reaction as a function of time: (1) attained maximum temperature, T_{Max}, which is related to the reactants concentration and the mechanical damage potential caused by volumetric expansion, and (2) the elapsed time till reaching the maximum temperature, T_{TMax}, which represents either the delay or the advance of the reaction due to the addition of salts or base (KOH) in the plain suspension. In Fig. 5 the parameters (T_{TMax} and T_{Max}) were determined using MgO suspensions containing different $MgCl_2$ content by means of temperature curves as a function of time.

The behavior of these parameters (T_{TMax} and T_{Max}) and the apparent volumetric expansion (AVE) as a function of concentration of different salts are shown in Fig. 6. The profile of the curves attained for $MgCl_2$ and $MgSO_4$ did not significantly change for the content range evaluated. $CaCl_2$ additions at levels above 1 wt%, however, promoted a noticeable increase in the time to reach the maximum temperature (T_{TMax}), indicating that MgO hydration has been inhibited. Consequently, the addition of high $CaCl_2$ levels (above 1 wt%) should result in a decrease in the damage generated by expansion (AVE) and the heat released (lower T_{Max}). This is confirmed in the AVE curve shown in Fig. 6. The delay of MgO hydration reaction for $CaCl_2$ additions above 1 wt% may be explained by the formation of a protective anion (Cl^-) layer, which is attracted by the positive charge of

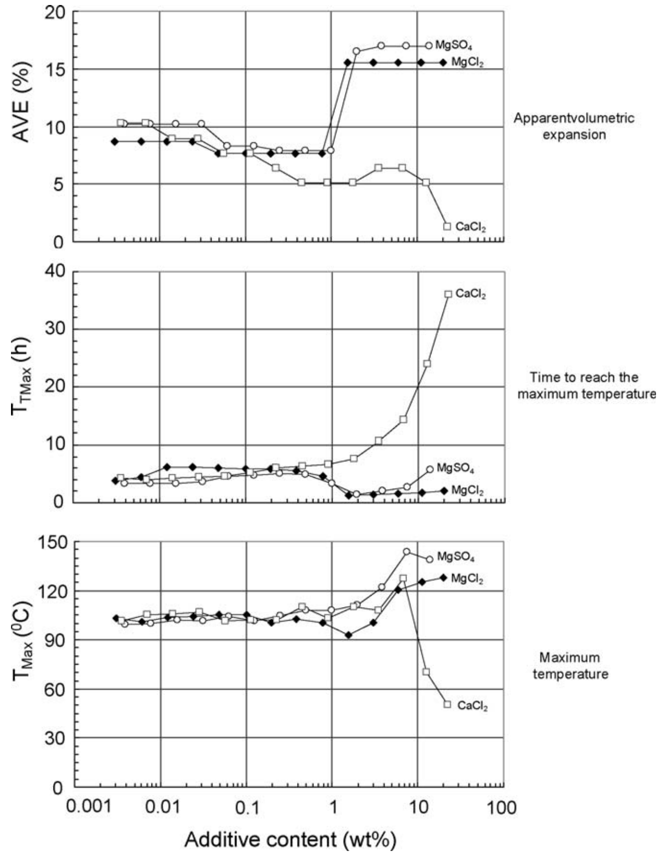

Fig. 6. Apparent volumetric expansion (AVE), time to reach the maximum temperature (T_{TMax}) and maximum temperature (T_{Max}) as a function of the salts concentration added to the caustic magnesia suspension: $MgCl_2$, $MgSO_4$ and $CaCl_2$.

magnesia surface ($MgOH^+$). This inhibits the OH^- attraction [27] and consequently, step 2 (Eq. (2)) – the formation of $MgOH^+.OH^-$.

Concerning the addition of other salts ($MgCl_2$ and $MgSO_4$), the effect of the formation of a protective anion layer, which inhibits the MgO hydration, was less effective. The greater reaction velocity (lower T_{TMax}), the increase of the heat released, and the mechanical damages shown by the high AVE values in Fig. 6 indicated that the effect of a high concentration of Mg^{2+} ions was more effective compared to those promoted by the anions barrier; accelerating the hydroxide formation. Thus, Mg^{2+} cations and anions (Cl^- and $SO_4{}^{2-}$) affect both the kinetics and the thermodynamics of the hydration reaction. Additionally, when $CaCl_2$ was added, the absence of Mg^{2+} or OH^- ions did not induce a supersaturation, as with Mg salts. Thus, if the salt concentration was increased, the anion barrier would be more effective for inhibiting the MgO hydration when compared to salt addition containing common-ion.

The development of a charge at the surface of a particle affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus, an electrical double layer is formed round the particle, which consists of an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated [28,29]. The attraction of the Cl^- ions by the positive charge on the magnesia surface promotes the formation of an electrical double layer, which acts as a repulsive barrier that inhibits the OH^- attraction, protecting the magnesia surface against hydration.

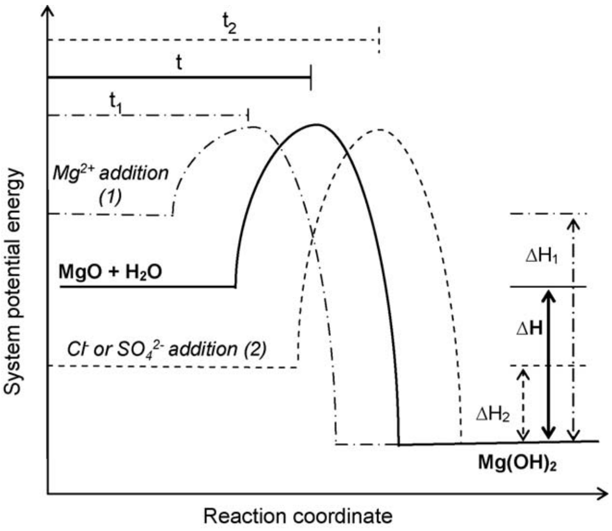

Fig. 7. Schematic representation of the system energy as a function of the reaction coordinate (reaction evolution) for the MgO hydration. The relative times were evaluated and are shown in Fig. 6 as the time elapsed to attain the maximum temperature.

The schematic representation of the system energy and its progress along the hydration reaction pathway is shown in Fig. 7, which is shown to illustrate how the reaction is delayed or accelerated based on the suspension's changes and the results obtained. The addition of Mg^{2+} ions increases the initial energy of the system (reactants), whereas the anion additions (Cl^- or $SO_4{}^{2-}$) reduce the reactants' energy due to the lower potential energy of the particles surface. These changes on the suspension energy for the reaction will result in a reaction acceleration or delay, respectively.

The addition of Mg^{2+} results in a greater heat release, and consequently, the enthalpy change of system (ΔH_1), whereas the anions addition has a smaller heat release (ΔH_2); in reference to the MgO hydration reaction (ΔH). The time necessary to start the reaction is represented as the change in the reaction coordinate (x axis in Fig. 7): Mg^{2+} initiates the reaction in time t_1, whereas the anions delay it (time t_2). These arbitrary times are based on the comparison to the system with no additives (t). This parameter was evaluated, and is shown in Fig. 6 as the time elapsed to attain the maximum temperature.

The various types of ions will have different effects on the electrical double layer. The addition of $MgSO_4$, for example, result in the presence of Mg^{2+} ions that promotes acceleration of the MgO hydration, a mechanism that is more effective than the protective effect by $SO_4{}^{2-}$ ions. In contrast, the addition of $MgCl_2$ promotes a balance between the accelerating and retarding effect of the Mg^{2+} and Cl^- ions, respectively. This can be explained by the smaller size of Cl^- ions that result in better coating of the surface of the MgO particles, inhibiting their hydration when compared to the larger size of the $SO_4{}^{2-}$ ions.

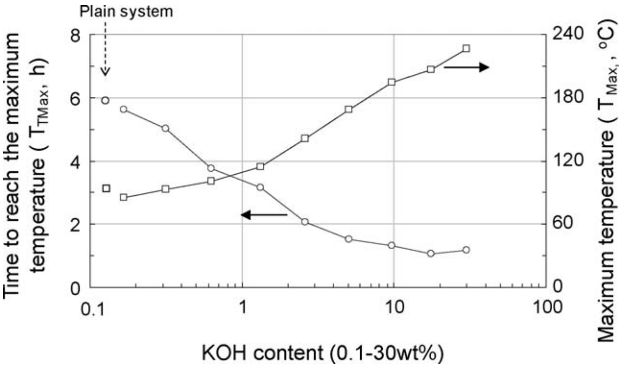

Fig. 8. Time to reach the maximum temperature (T_{TMax}) and the maximum temperature reached (T_{Max}) versus KOH concentration.

In order to isolate the common-ion effect without the anionic protection, a water soluble base (KOH) was added to the aqueous system, as shown in Fig. 8. Based on the concept of displacement of chemical equilibrium, in Eq. (4), the addition of OH^- ions would also promote the formation and precipitation of magnesium hydroxide. In Table 2 shows the characteristics of the suspensions tested and the impact of the different additives investigated ($CaCl_2$, $MgCl_2$, $MgSO_4$ and KOH), based on results verified in Figs. 6 and 8.

In Fig. 8, the increase of OH^- concentration accelerated the reaction kinetics and the related damages. This effect has two important technological implications in castables containing MgO: (1) the main hydraulic binders used in castables release a large amount of OH^- ions during their hydration, resulting in the rapid hydration of magnesia and, (2) the addition of $CaCl_2$ reduces the reaction rate for hydration, but required a high salt concentration (above 10 wt%), making its use unsuitable in refractory castables.

Regarding the application in refractory castables, the higher the curing temperatures, the higher the hydration reaction and the damage generated to the castable material. If one of the hydration reaction steps (dissolution or precipitation) could be delayed, suitable results to control hydration could be obtained. Compounds with a higher affinity to MgO than those tested ($MgCl_2$ and $MgSO_4$) could decrease the dissolution step, and hence, MgO hydration. This effect can be attained by selecting additives which provide stronger chemical adsorption instead of a weaker physical one.

Intrinsic MgO properties in refractory castables applications are of wide technological interest. One of the most important and reactive compound of these system is the calcium aluminate cement (CAC). This makes the study of MgO hydration in the presence of a CAC an important aspect to prevent unwanted side effects during the castable placement and setting. The addition of basic CAC can be responsible for further hydration due to the chemical equilibrium displacement. Thus, it would be interesting to evaluate MgO based castables by replacing the CAC with an alternative binder system in future research.

Table 2
Characteristics of the suspensions tested and the impact of the different additives (for amounts higher than 1 wt%).

	Saturation[a]	Protective layer	AVE	T_{TMax}	T_{Max}
$MgCl_2$	Yes (Mg^{2+})	Yes (Cl^-)	Increase	Decrease	Increase
$MgSO_4$	Yes (Mg^{2+})	Yes (SO_4^{2-})	Increase	Decrease	Increase
$CaCl_2$	No	Yes (Cl^-)	Decrease	Increase	Decrease
KOH	Yes (OH^-)	No	Large Increase	Large decrease	Large Increase

[a] The point at which a solution of a substance cannot dissolve any more, and when additional amounts of this substance will appear as a precipitate.

4. Conclusions

Based on the study of ionic conductivity measurements, magnesia hydration is carried out in two stages: (1) the adsorption of H^+ ions on the surface of magnesium oxide, and (2) the precipitation of magnesium hydroxide. The beginning of the precipitation promotes a greater contact among the particles, which, over time, can result in mechanical stresses and expansion damages to the shaped samples. This behavior is suggested in the oscillatory tests. It was determined that the hydroxide amount increased with the temperature, highlighting its dependence on the precipitation of $Mg(OH)_2$.

Regarding the common-ion effect, the increase of Mg^{2+} or OH^- concentration promoted hydroxide formation at a greater rate along with an increase in temperature, leading to increased mechanical damage (volumetric expansion). On the other hand, depending on the concentration added, the addition of $MgCl_2$ and $MgSO_4$ promoted a protective layer on the MgO particles' surface, depending on the concentration added. This effect was confirmed by the addition of $CaCl_2$, which lead to a delay in hydration.

Regarding the application in refractory castables, the higher the curing temperatures, the higher the hydration reaction and the damage generated. The addition of basic compounds (such as calcium aluminate cement) might be responsible for further hydration due to the chemical equilibrium displacement. Compounds with higher affinity for MgO than those tested could decrease the dissolution step, and hence, hydration of MgO. This effect can be attained by selecting additives which provides stronger chemical adsorption instead of a weaker physical one.

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