

# Effects of Additivation During MgO Calcination on Properties of MgO Powders and Magnesium Phosphate Cements

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Magnesium phosphate cement are materials prepared by reacting magnesium oxide with water-soluble phosphates such as mono-ammonium dihydrogen phosphate, which solidified at ambient temperature through the formation of hydrated phases in the material. However, MgO has a high reactivity and requires calcination to reduce its surface area, facilitating the practical application of magnesium phosphate cement. Because it is a process with large energy consumption, the sintering cost is very high when implemented at a large scale. Since the final stages of solid-state reaction are rarely reached, the addition of some components is beneficial from a calcination point of view, as they can lead to the formation of low melting liquid phases. In this study, effects of the inorganic activation of MgO on the properties of cements in terms of phase formation, microstructure, setting time, pore size distribution and mechanical properties were evaluated. The additivation considerably improved the properties of MgO powders, and Na<sub>2</sub>O-PbO-SiO<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> was the most efficient additive to reduce de BET surface area (about 5-6 times). Cements produced using doped MgO without calcination at high temperatures or the use of higher levels of retarding and dispersing additives, showed better physical (porosity approximately 5 times lower and density approximately 38% higher) and mechanical properties (approximately 9 times higher) than the pastes produced with MgO calcined without additives (traditional method).

**Keywords:** CBPC, cement, magnesium phosphate, inorganic additives, properties.

## 1. Introduction

Chemically bonded phosphate ceramics (CBPCs) are ceramics formed from the reaction between metal cations and water-soluble phosphates. Materials such as magnesium phosphate cements (MPC) have attracted significant attention of researchers, therefore, understanding the effects of dosage parameters, such as water content<sup>1</sup>, MgO/NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> ratio<sup>2</sup>, retardant content<sup>3</sup> or calcination possibilities<sup>4</sup>, on phase formation is essential for obtaining cementitious matrices with improved performance and durability<sup>5</sup>. The lower density of CBPCs compared to Portland cement results in products with high strength/weight ratio, an important criterion for the selection of materials<sup>6-9</sup>.

To obtain magnesium and ammonium phosphate cements with desirable properties, it is necessary to control the rate of heat evolution during their setting reactions. If this rate is high enough, large amounts of ammonia can be released, and disruption of the formed gel, interfering with crystallization processes and forming hydrated phases in these cements<sup>6,10,11</sup>.

A method to control the increase in temperature and heating rate is through the calcination of MgO. MgO powders with a small particle size (about 18 - 78 nm), obtained by precipitation, present high reactivity and solubilization rates,

and the use of these powders without prior calcination causes difficulties during cement processing, since exothermic reactions occur rapidly, leading to a poor surface finish, high porosity, and low mechanical strength<sup>12</sup>.

Rezaei et al.<sup>13</sup> calcined MgO at 700°C for 2 hours, yielding unsatisfactory results. Other authors<sup>14</sup> calcined the MgO at temperatures between 700 °C and 1100 °C and found that the calcination temperature had a significant effect on strength values for shorter residence times (2 hours), whereas the strength of samples subjected to 6 hours of calcination did not change much between the temperature range of 700–900 °C. Some authors have shown that calcination of MgO to 1300 °C reduces the porosity of individual grains and also increases particle size<sup>6,12,15</sup>.

Thermal treatment MgO is an important research topic, because this process has high energy consumption and monetary costs when implemented at a large scale. The energy demand and the resource extractive activity are some of the environmental issues that have generated major interest in modern society<sup>16</sup>.

The final stages of solid-state sintering are rarely realized during the calcination of powders, and only a pre-sintering stage that leads to the formation of aggregates is reached, owing to the bad initial packing of the powder particles and/or the low temperature of sintering<sup>10</sup>.

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Therefore, certain types of impurities with low-melting-point are beneficial for calcination because they lead to the formation of liquid phases that optimize the densification process of compacts via two mechanisms: i) particle rearrangement and packing and ii) solution precipitation.

In MgO powders with larger amounts of impurities (e.g., CaO, SiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>), densification is accelerated and occurs at lower temperatures because of the formation of liquids in the SiO<sub>2</sub>-CaO-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system<sup>17</sup>. However, the presence of liquid phases does not guarantee a successful calcination. Three aspects must be considered: the solubility of the solid in the liquid, wettability of the liquid in the solid, and diffusivity of the solid in the liquid. In general, it is desirable for the liquid to wet the particles and for the solid to have a high solubility. Under these conditions, the capillary forces of the liquid act on the solid particles, partially eliminating porosity and reducing the interfacial area. A high diffusion of solids in the liquid is desirable, as it results in a higher densification rate compared with the pore elimination process in the solid state<sup>18</sup>.

Therefore, sintering in the presence of liquids occurs as follows. During heating, the surface area of the particles decreases primarily via solid-state diffusion mechanisms. Immediately after the formation of the first liquid phase, the capillary forces on the surface of the particles bring them together, which results in an increase in the packing of the particles, and the liquid present is released to fill the remaining pores within and between the formed aggregates. In this stage of particle rearrangement and packing, the elimination of porosity causes an increase in the viscosity of the aggregate-liquid system. Consequently, the densification rate of this process decreases with time<sup>18</sup>.

Depending on the sintering temperature and type of additive used, an intermediate step occurs, with a predominance of solution-precipitation mechanisms. As the rate of densification via particle rearrangement decreases, solubilization and diffusion effects dominate. In this second stage, the solubility of the particles within the liquid varies inversely with their size; that is, the larger the particle, the lower its energy and, therefore, the lower its solubility. Differences in solubility establish concentration gradients within the liquid that favor the transport of material from smaller to larger particles via diffusion through the liquid. This mechanism leads to the progressive growth of larger particles at the expense of smaller particles. The solution-precipitation processes not only contribute to the growth of particles during sintering at high temperatures but also promote the densification of aggregates via particle rearrangement and accommodation<sup>18</sup>.

Notably, the aforementioned steps are similar to those that occur during the initial stages of calcination of compact by liquid phase formation. The difference between the calcination and sintering processes is that during calcination, the final stages of sintering rarely occur; this is because of two reasons: i) the need for a high amount of liquid to be formed at high temperatures, and ii) the low initial packing of the powder when compared to a compact.

The oxide formation process can also determine whether the conditions for a well-crystallized material are created during the calcination of non-precursor powders, such as Mg(OH)<sub>2</sub>,

The dissolution should be fast enough to form a gel in the saturated state but slow enough to allow the gel to crystallize. In other cases, ceramics are not formed either because of the formation of precipitates (very fast dissolution) or owing to the very low dissolution of the oxide used (Fe<sub>2</sub>O<sub>3</sub>)<sup>6</sup>. Zawrah<sup>19</sup> and Itani et al.<sup>20</sup> reported that the relative density and flexural strength of calcined MgO compacts increase with the addition of 0.5 mol% P<sub>2</sub>O<sub>5</sub>. They attributed this behavior to the presence of liquids from the MgO-P<sub>2</sub>O<sub>5</sub> system with high binding ability located at the grain boundaries.

In the present study, effects of the use of different types of additives on the fundamental properties of sintered MgO powders as well as on the phases and properties of magnesium phosphate cement are evaluated.

## 2. Materials and Methods

### 2.1. Materials

#### 2.1.1. Magnesium Oxide

Magnesium oxide (basic component) supplied by Buschle & Lepper S.A needed to be calcined at 900 °C and 1100 °C due to its high surface area. MgO was calcined using a Termolab BL 260/03 furnace, with a heating rate of 10°C/min, and the dwell time was fixed at 2 hours. The furnace was cooled at a rate of 15 °C/min and, after calcination, the MgO powders were deagglomerated and passed through a 100 mesh sieve.

#### 2.1.2. Ammonium Dihydrogen Phosphate (ADP)

Ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>), or ADP, reacts with magnesium oxide in the presence of water in an acid-base reaction and is the source of phosphate anions to reaction that, when it occurs, releases a small amount of ammonia into the atmosphere. Therefore, a higher amount of ADP is associated with a higher strength MPC paste, provided the amount of phosphate hydrates is sufficient to surround the MgO grains thoroughly<sup>21</sup>. The ADP used, provide by LabSynth had a surface area of 0.68 m<sup>2</sup>/g, unitary mass of 0.79 kg/dm<sup>3</sup>, and specific gravity of 1.87 kg/dm<sup>3</sup>.

#### 2.1.3. Boric acid (H<sub>3</sub>BO<sub>3</sub>)

The presence of retardants increases the setting time and reduce the intensity of exothermic reactions during the initial setting and hardening stages, delaying the setting time reactions, improving the workability conditions, giving the necessary time for the reactions to occur and effectively form phosphates<sup>21</sup>. Therefore, chemical retardants are utilized in large-scale mixing operations. Commercial boric acid (provide by LabSynth) containing approximately 98% H<sub>3</sub>BO<sub>3</sub> was used in this study.

### 2.2. Methods

#### 2.2.1. Materials characterization

The materials were characterized by X-ray diffraction (Rigaku Geigerflex ME 210GF2 Diffractometer, configured with CuK $\alpha$  radiation, 40 kV of voltage, 100 mA of current, 10-80° 2 $\theta$  scanning, and 4 °/min of scanning speed),

X-ray fluorescence (Philips PW1480 X-ray Fluorescence Spectrometer), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (Philips SEM, model XL 30 FEG, gold coating) to evaluate the phase and chemical compositions. Relevant physical parameters such as the particle size distribution (Horiba model CP5000), mercury porosimetry (Porosizer 9320, Micromeritics), specific surface area estimated by BET (using a Micromeritics Gemini 2370 V1.02 equipment), and specific gravity (Helium Pycnometer Accupyc 1330 V2.01 from Micromeritics) were determined.

### 2.2.2. Inorganic liquid-phase-forming additives

To increase the setting time, reduce the porosity of the cements, and improve the mechanical properties, different additives forming liquid preparations (Table 1) were added prior to the calcination of the MgO powders. These additives were chosen based on the raw materials known to form liquids at temperatures below 1000 °C.

These additives were used at a molar concentration of 0.5%. The proportion of each oxide in the mixtures is stoichiometric. As an example, Na<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> is 1:1 (mol). By mass, additive A contains 30.39 m% Na<sub>2</sub>O and 69.61 m% P<sub>2</sub>O<sub>5</sub>.

The general procedure for the additivation of the powders consisted of the following steps: raw materials (MgO + additives) were weighed at the desired concentrations, packed in plastic bags, shaken vigorously for 5 min, and passed through a 100-mesh sieve for homogenization. Next, the homogenized powder, called “MgO + Additive,” was calcined at 900 °C and 1100 °C with a heating rate of 10 °C/min and a dwell time of 2 hours. After calcination, the powders were deagglomerated and passed through a 100-mesh sieve.

To determine the linear firing shrinkage, 4 (four) flat test pieces using 5.0 g of material per test piece were prepared from MgO powders, respectively, with and without additive L. The compaction pressure, in both cases, was 45 MPa. After compaction, the test pieces were oven-dried at 110 ± 5 °C until constant weight, fired at 1100 °C for 1 h (heating at 3 °C/min up to 600 °C, and at 5 °C/min from 600 °C to 1100 °C), and naturally cooled.

**Table 1.** Liquid phase forming additives used in the calcination of MgO powders.

Additive Identification	Additive Oxide	Additive Content (%mol)*
Additive A	Na <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub>	0.50
Additive B	K <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub>	0.50
Additive C	B <sub>2</sub> O <sub>3</sub>	0.50
Additive D	Na <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub>	0.50
Additive E	Bi <sub>2</sub> O <sub>3</sub>	0.50
Additive F	MnO <sub>2</sub>	0.50
Additive G	Bi <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	0.50
Additive H	Bi <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub>	0.50
Additive I	Na <sub>2</sub> O-CaO-PbO-SiO <sub>2</sub>	0.50
Additive L	Na <sub>2</sub> O-PbO-SiO <sub>2</sub> -Bi <sub>2</sub> O <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	0.50

\* %mol, in relation to the MgO content.

The linear shrinkage was calculated from the change in length (with a resolution of 0.05 mm), upon firing, of the flat test pieces.

### 2.2.3. Dosage and molding of specimens

Based on the results obtained in the previous MgO calcination step, the composition demonstrating the best performance in terms of the setting time and apparent density (MgO + additive L) was chosen for subsequent studies. From the doped powders, cement samples with 55% MgO and 45% NH<sub>3</sub>H<sub>2</sub>PO<sub>4</sub> (by mass) were prepared, and the amount of retardant (boric acid) was calculated as a function of the total mass of MgO, based on the studies of Yang and Wu<sup>22</sup> and Ribeiro et al.<sup>3</sup>, with a fixed content of 15%.

The “reference proportion” used in the molding of the specimens was 1.00: 0.82: 0.15: 0.60 (MgO: ADP: boric acid: H<sub>2</sub>O). Cylindrical specimens of magnesium phosphate cement pastes using MgO produced with different types of additives were molded. The results obtained were later compared to those of the reference sample, which was the cement produced with MgO that was calcined without the addition of any component at the same temperature.

### 2.2.4. Characterization of Magnesium Phosphate Cements (MPC)

To characterize the compositions, indirect measurements of setting time were performed as proposed by Hall. In addition, the compositions were characterized by X-ray diffractometry (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), mechanical strength testing, and mercury intrusion porosimetry (MIP).

#### 2.2.4.1. Setting time

According to the Brazilian standard NBR NM 65<sup>23</sup>, measurement of the setting time should be performed using the Vicat apparatus. However, recent studies<sup>3-5,24-26</sup> have shown that the setting time for magnesium phosphate cements can be indirectly determined by calorimetry assays. These authors observed a direct relationship between the results obtained by calorimetric measurements and using the Vicat apparatus. Since the formation of the hydrated phases in cements is an exothermic reaction, the temperature measurements during hardening results in indirect data that can provide comparative values of setting time. In this study, a Raytec MT infrared pyrometer was used to perform such measurements at random time intervals until a reduction in the mixture temperature could be verified.

As a further qualitative measure of the reaction rate, the setting time of the mortar was monitored with two characteristic times, denoted  $t_1$  and  $t_2$ . These times served to indicate the heat evolution rate,  $t_1$  being the time at which the maximum rate of temperature increase occurred, and  $t_2$  the time at which the maximum temperature  $T_{max}$  was attained, as illustrated in Figure 1. Because the CBPC formation reaction is sufficiently exothermic, the amount of material directly affects in the reaction kinetics. In the present work were used 40 ml of MPC paste to the calorimetric measurements of the setting time.

#### 2.2.4.2. Apparent porosity and density

The apparent porosity and density were verified using the technique based on the Archimedes principle.

The samples were weighed while they were still dry ( $M_s$ ). They were then left immersed in water for 24 hours until they became fully saturated, after which the immersed mass ( $M_i$ ) and the wet mass ( $M_u$ ) were determined. Thus, the apparent porosity ( $P_A$ ) and the apparent density ( $D_A$ ) were calculated according to Equations 1 and 2. The  $\rho_L$  is the liquid density (in this in case, the water,  $\rho_L = 1.0 \text{ g/cm}^3$  at  $25 \text{ }^\circ\text{C}$ ).

$$\%P_A = 100 \times (M_u - M_s) / (M_u - M_i) \quad (1)$$

$$D_A = \rho_L \times (M_s) / (M_u - M_i) \quad (2)$$

### 2.2.4.3. Mechanical strength

The values of axial compression correspond to the average of 3 values for each magnesium phosphate composition and mortar age (3, 7 and 28 days after molding), and were obtained with an Instron 5500R universal testing machine and a load of 1.5 mm/min. The values that differed by more than 5% from the average were discarded and were substituted for the results of new samples.

## 3. Results and Discussion

### 3.1. Characterization of MgO calcined in the presence of additives

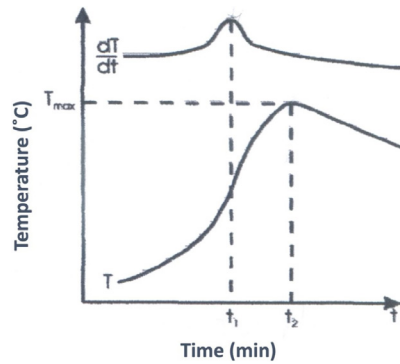
After calcination, the doped powders (with additives, according to Table 1) exhibited a BET surface area lower than that of MgO calcined without additives at the two evaluated temperatures, as summarized in Table 2. Although a reduction in the surface area of MgO powders was observed with all additives, the additives E, G, H, and L were more efficient in this regard. Therefore, subsequent tests were performed with MgO calcined with additive L ( $\text{Na}_2\text{O-PbO-SiO}_2\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ).

Figures 2A and 2B show the LFS and LFSR curves of the pressed precipitated MgO powders, respectively, with and without additive L ( $\text{Na}_2\text{O-PbO-SiO}_2\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ). Both samples presented similar density values ( $\text{approximately } 1.26 \text{ g/cm}^3$ ).

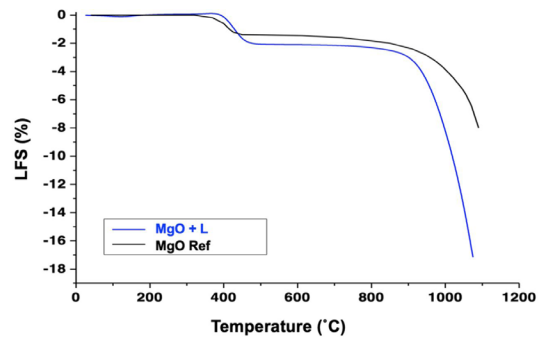
**Table 2.** Specific surface area ( $\text{m}^2/\text{g}$ ) of reference MgO powders (precipitated, without calcination) and those calcined without additives and in the presence of different additives, at  $900 \text{ }^\circ\text{C}$  and  $1100 \text{ }^\circ\text{C}$ .

MgO + Additive	Calcination Temperature	
	$900 \text{ }^\circ\text{C}$	$1100 \text{ }^\circ\text{C}$
Precipitated (without calcination)	46.02	
MgO-Ref (without additives)	23.14	7.87
MgO + Additive A	21.23	7.14
MgO + Additive B	19.66	5.92
MgO + Additive C	20.08	6.10
MgO + Additive D	19.62	5.60
MgO + Additive E	4.51	1.52
MgO + Additive F	13.34	4.76
MgO + Additive G	4.65	1.52
MgO + Additive H	4.63	1.48
MgO + Additive I	9.01	3.17
<b>MgO + Additive L</b>	<b>4.50</b>	<b>1.38</b>

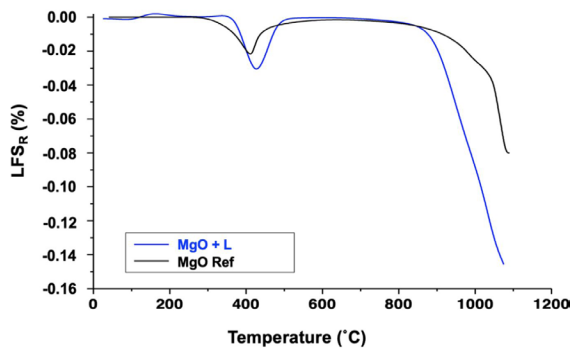
For the MgO sample with additive L, there is a rapid increase in the LFS<sub>R</sub> at approximately  $900 \text{ }^\circ\text{C}$ , the temperature at which the formation of liquid phases begins, assisting the sintering mechanisms of the material. For the MgO sample without an additive, a lower rate of LFS is observed, as the sintering mechanisms will only be activated at temperatures of approximately  $950 \text{ }^\circ\text{C}$ . That is, the additive  $\text{Na}_2\text{O-PbO-SiO}_2\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$  promotes the formation of liquids and leads to the growth of MgO particles, decreasing the specific surface area of these powders and probably increasing the setting time of the cements to more adequate values.



**Figure 1.** Schematic illustration of indirect measurement of setting time by calorimetry<sup>1,14,16</sup>.



(A)



(B)

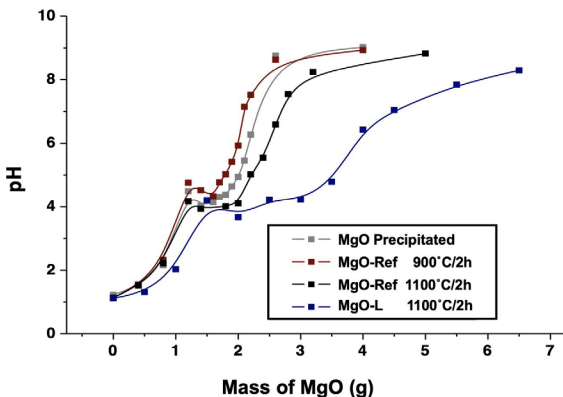
**Figure 2.** (A) Linear firing shrinkage (LFS) and (B) linear firing shrinkage rate (LFS<sub>R</sub>) for MgO calcined with and without the presence of Additive L, as a function of temperature.

The solubility of the MgO powder in a phosphate solution was evaluated using the method proposed by Singh et al.<sup>27</sup>, based on pH measurements, as shown in Figure 3. Notably, MgO powders containing the L additive calcined at 1100 °C for 2 h showed significantly lower solubility than MgO powders calcined without the additive. This behavior is due to its low specific surface area, high crystallinity, and large average particle size relative to the additive-free MgO powder.

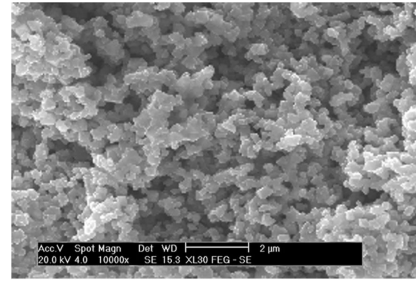
Figure 4 shows micrographs of MgO powders calcined at 1100 °C for 2 h without additives (Figure 5A) and in the presence of additive L (Figure 5B). The MgO powders calcined in the presence of the additive have larger particle sizes than their counterparts in an advanced stage of sintering and exhibited well-defined contours. The presence of a liquid phase was also observed in the contours between the particles. This allowed the increase in the average size of the particles and crystallinity, which correspond with the results presented above. However, the calcination of MgO without an additive occurred via solid state, owing to the high purity of the raw material used (oxide obtained via precipitation) and the refractory characteristic of MgO. Therefore, there is a direct relationship between the initial setting time and average particle size.

The particle size distribution curves (Figure 5) show that MgO powders calcined in the presence of additive L have a higher average particle size compared with powders calcined without additives, as observed in the micrographs presented in Figure 4. Notably, MgO calcined with L additive also showed a wider particle size distribution than that observed in precipitated MgO (without calcination) and MgO calcined without additives. Despite providing a longer setting time, a higher mass percentage of coarse grains in the additive powders can result in a higher tendency of exudation for cements prepared with these powders.

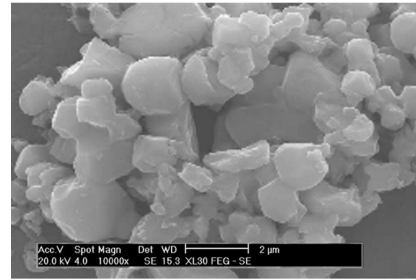
From Figure 6, MgO powders calcined with additive L present higher intensities of diffraction peaks compared with MgO powders calcined without the presence of an additive. This phenomenon is associated with differences in crystallinity and crystallite sizes of these powders, as the presence of liquid phases at high temperatures intensifies the diffusion mechanisms of magnesium oxide and, consequently, the diffraction peaks for MgO powders.



**Figure 3.** Variation of the solution pH as a function of the MgO contents obtained under different conditions.

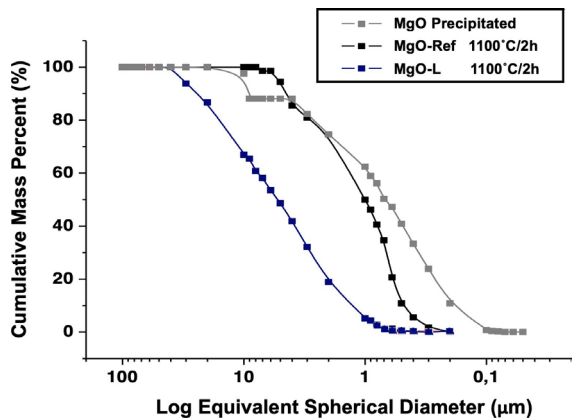


(A)

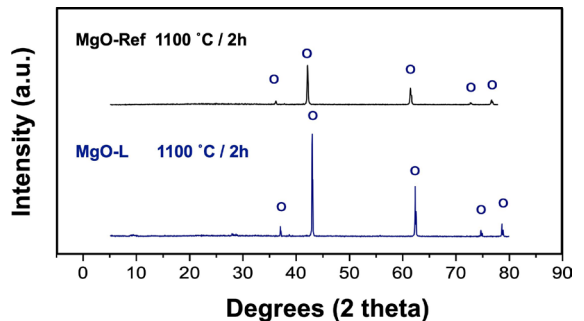


(B)

**Figure 4.** Morphology of MgO powders calcined at 1100 °C/2h (A) without additives and (B) in the presence of additive L, obtained using a scanning electron microscope, SEM (SE detector).



**Figure 5.** Particle size distribution of MgO powders without calcination (precipitated) and calcined at 1100 °C, with and without the presence of additives.



**Figure 6.** X-ray diffractograms of MgO powders calcined without and with additive L, at 1100 °C/2h (° MgO).

The presence of secondary phases was not observed; that is, if present, these phases would be in concentrations below the 1% detection limit of the equipment. This observation is significant, as these secondary phases could compromise the properties of MPC.

### 3.2. Characterization of MPCs containing MgO calcined in the presence of additives

Figure 7 shows the temperature evolution curves of the MPCs produced with MgO powders calcined without additives and with different additives as a function of time. These additives were introduced at a molar concentration of 0.5%, dry-mixed, and subsequently calcined at 1100 °C for 2 h. The presence of additives proved to be satisfactory, as many compositions showed lower maximum reaction temperatures and/or a delay in higher temperature peak, indicating a longer setting time. Such behavior was expected, as the increase in the setting time decreases the speed (rate) of the exothermic reactions in the cement.

The type of additive has a significant influence on the reactivity of the powders, with the resulting cements presenting reaction times (an indirect measurement of setting time) reasonably longer than those observed in cement produced with MgO calcined without additives. It is considered that the increase in the reaction time is a consequence of the higher degree of crystallinity (Figures 4 and 6), the larger average particle size (Figures 4 and 5), and the lower surface area (Table 2) of the additive powders, which contribute to the lower solubility of these powders (Figure 3).

Figure 8 shows comparative X-ray diffractograms of cement pastes prepared using MgO powders calcined with and without additive L. The pastes produced with MgO calcined in the presence of additive L did not show the formation of the dittmarite  $[\text{Mg}(\text{NH}_4)(\text{PO}_4)\cdot\text{H}_2\text{O}]$  phase, as the larger surface area of its particles results in a lower reactivity; that is, it allows more time for the development and formation of the hydrated phases in this cement (i.e., slower reaction).

From the FTIR spectrum (Figure 9), the presence of additives in the calcination of MgO led to an increase in the intensity of the peak associated with the vibrations of angular deformation in the  $\delta$  plane (P-OH) of the phosphate groups ( $1195\text{ cm}^{-1}$ ). There was also an increase in the intensity of the peaks corresponding to the internal stretching vibrations of the  $\text{H}_2\text{O}$  molecules of the cement ( $3625\text{ cm}^{-1}$ ) and the vibrations of angular deformation  $\nu_4$  of the  $\text{NH}_4^+$  groups ( $1505\text{ cm}^{-1}$ ). This indicates the higher crystallinity of the hydrated phases of cement pastes produced using doped MgO. These results agree with those presented in Figure 9, that is, samples with additives have a lower concentration of poorly hydrated phases compared with those without the additives.

The apparent porosity ( $P_A$ ) and density ( $D_A$ ) of MPC pastes vary depending on the type of additive used in the calcination of MgO (Table 3). That is, considering the formulation adopted in this research ( $\text{H}_2\text{O}/\text{MgO}$  ratio = 0.60 and boric acid content = 15%), the addition of different additives to magnesium oxide during its calcination considerably reduces porosity and increases the density of the pastes, compared with pastes containing calcined MgO without additives.

Notably, the pastes produced with MgO powders doped with additive L showed the best results, with porosity approximately 9 times (881%) lower and density approximately 38% higher than the pastes produced with MgO calcined without additives.

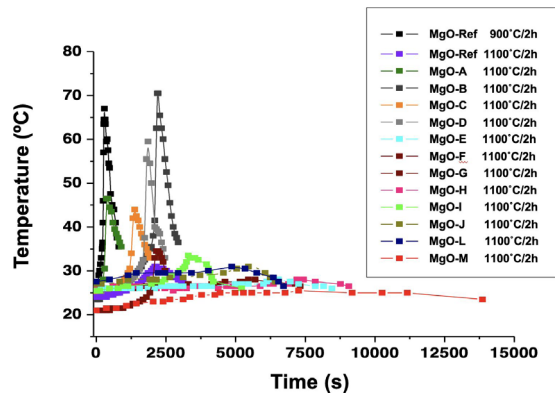


Figure 7. Reaction temperature of cement pastes produced with MgO powders calcined at 1100 °C/2h, in the presence of different inorganic additives as a function of time.

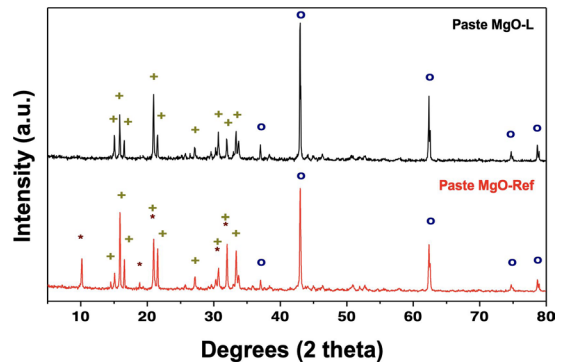


Figure 8. X-ray diffractograms of magnesium phosphate cement pastes prepared using MgO powders calcined with and without additive L ( $^+$  struvite;  $^*$  dittmarite;  $^\circ$  MgO).

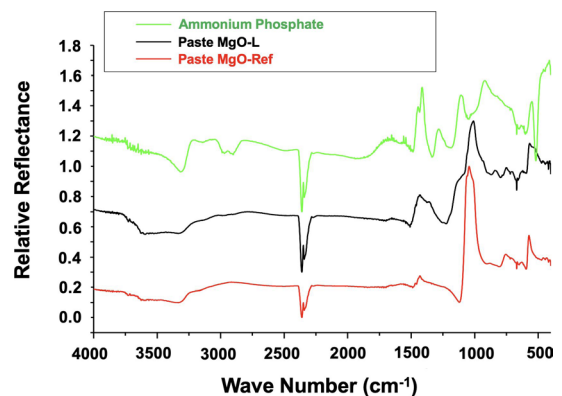


Figure 9. FTIR spectrum of magnesium phosphate cement pastes prepared from MgO powders calcined at 1100 °C, with and without the presence of additive L.

According to Figure 10, the presence of additives in the calcination of MgO enables the reduction of the open porosity of the MPCs produced, and it reduces the open porosity more effectively than the increase in the calcination temperature of the MgO powders (or the addition of higher concentrations of retardant). The reduced surface area (reactivity) and consequent increase in the setting time lead to the formation of more crystallized and denser phases of struvite  $[\text{Mg}(\text{NH}_4)(\text{PO}_4)\cdot 6\text{H}_2\text{O}]$ , to the detriment of dittmarite  $[\text{Mg}(\text{NH}_4)(\text{PO}_4)\cdot \text{H}_2\text{O}]$  formation<sup>28,29</sup>, resulting in a significant increase in the mechanical strength of this material (Table 4).

The axial compressive strength of cement pastes produced using the MgO calcined with the additive L is approximately nine times higher than the strength observed in reference cement pastes. Therefore, the presence of additives significantly improved the general properties of these cements.

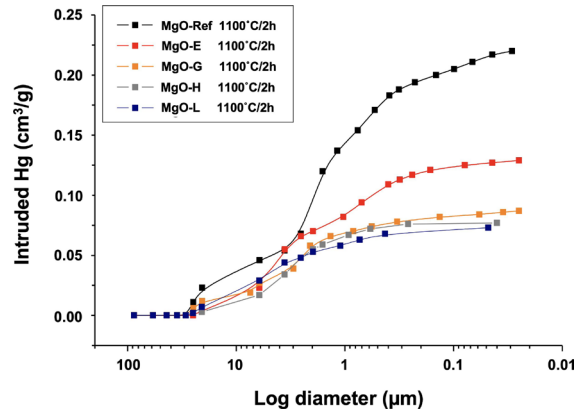
An important concern to be highlighted is that the additive L, which provided the best results, has Pb in its composition. There is a tendency nowadays to avoid lead in materials because its toxicity. But, the concentration of additive L is very low (0.5 mol%) and, as this additive is composed of  $\text{Na}_2\text{O}\text{-PbO}\text{-SiO}_2\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ , the Pb content is only 0.12 mol%. In addition, Pb is combined as PbO, being insoluble in water.

#### 4. Conclusions

From an analysis of the results obtained at the experimental conditions adopted for this work, the following can be concluded:

- The presence of inorganic additives during the calcination of MgO significantly reduced the BET surface area of the calcined MgO powders, regardless of the type of additive used.
- The presence of additive L ( $\text{Na}_2\text{O}\text{-PbO}\text{-SiO}_2\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ) in the calcination of MgO resulted in powders with better performances (lower BET surface area, higher degree of crystallinity and larger crystallite size) compared to other samples investigated in this study.
- The increase in the setting time is a consequence of the higher degree of crystallinity, larger average particle size, wider particle size distribution, and lower BET surface area.
- Reduced surface area of the MgO powders calcined with additives at 900 °C and 1100 °C was about 5 times and 5.7 times lower, respectively, than MgO powders calcined without additives (traditional method), which also contributed to its lower solubility.
- The presence of liquid phases at high temperatures intensifies the diffusion of MgO.
- For doped MgO samples, at approximately 800 °C, a rapid increase in the  $\text{LFS}_r$  is observed owing to the formation of liquid phases that aid the sintering mechanisms. For samples calcined without additives, the sintering mechanisms were activated only at approximately 950 °C.
- Inorganic additivation in MgO calcination reduces the open porosity (approximately 5 times lower) of MPCs more effectively than merely increasing the calcination temperature of MgO powders or adding higher concentrations of retardant.

- The lower surface area (less reactivity) and consequent increase in the setting time leads to the formation of more crystallized and denser struvite phases to the detriment of dittmarite formation, resulting in a significant increase in the mechanical strength (approximately 9 times higher).
- The inorganic additivation procedure in the calcination of MgO is a technically viable alternative to improve the properties of MPCs and reduce calcination costs.



**Figure 10.** Pore size distribution, obtained via mercury intrusion porosimetry (MIP), of magnesium phosphate cement pastes produced with MgO doped and with 15 wt.% retardant (boric acid).

**Table 3.** Apparent porosity ( $P_A$ ) and apparent density ( $D_A$ ) of cements produced from MgO powders with different additives calcined at 1100 °C/2h.

Paste	$P_A$ (%)	$D_A$ (g/cm <sup>3</sup> )
Paste MgO-Ref (without additives)	11.28	1.45
Paste MgO-A	9.87	1.48
Paste MgO-B	4.50	1.63
Paste MgO-C	2.58	1.76
Paste MgO-D	2.42	1.82
Paste MgO-E	2.34	2.03
Paste MgO-F	3.50	1.86
Paste MgO-G	2.24	2.09
Paste MgO-H	2.27	2.07
Paste MgO-I	3.38	1.91
Paste MgO-L	1.88	2.00

**Table 4.** Axial compressive strength of cement pastes produced with and without MgO calcined with the additive L at 1100 °C/2h,  $\text{H}_2\text{O}/\text{MgO}$  ratio equal to 0.60 and boric acid content equal to 15%.

Paste	Axial compressive strength (MPa)
Paste MgO-Ref (without additives)	$3.40 \pm 0.40$
Paste MgO-L	$30.11 \pm 3.11$

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