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Effect of $MgO/NH_4H_2PO_4$ Ratio on the Properties of Magnesium Phosphate Cements

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Magnesium phosphate cements (MPCs) are formed when an aqueous solution of ammonium dihydrogen phosphate (ADP, $NH_4H_2PO_4$) and magnesium oxide (MgO) react in the presence of other aggregates for filling or reinforcement (e.g., fibers, waste, and sand). Therefore, understanding how the MgO/ADP ratio influences phase formation to produce cementitious matrices with better performance is essential. MgO dissolved in an acid solution undergoes numerous transformations because of which different opinions exist regarding the mechanisms by which the setting reactions and formation of hydrated phases occurs in MPCs. In this study, the effect of different MgO/ADP ratios on the properties of MPCs was evaluated regarding phase formation using X-ray diffraction, setting time, and pore size distribution. Increased ADP concentration was found to increase the concentration of hydrated phases, however, this increases the pore content while decreasing the apparent density of MPCs. Compared with compositions with lower MgO/ADP ratios, the composition with the highest MgO/ADP ratio required higher setting time due to the lower concentration of hydrated phases.

Keywords: *Chemically bonded phosphate ceramics, cement, magnesium phosphate,* $NH_4H_2PO_4$.

1. Introduction

Chemically bonded phosphate ceramics (CBPCs) are formed from the reaction between metal cations and water-soluble phosphates. Some of these phosphates usually employed are H_3PO_4[1], $(NH_4)_2HPO_4$[2], $Al(H_2PO_4)_3$[3], $NH_4H_2PO_4$[4], and KH_2PO_4[5].

Péra and Ambroise[6] stated that the mechanical strength developed in this cement after 3 hours is comparable to the resistance developed in the Portland cement after 28 days. In addition, they observed no decrease in strength when the CBPC specimens were subjected to alternating cycles of immersion in water and drying at 50 °C for a period of 28 days. However, the same is not true for Portland cement tested under the same conditions.

Hall and Stevens[7] reported the production of magnesium phosphate cement (MPC) mortars with a compressive strength of 60 MPa and apparent density of 2.10 g/cm^3, after 7 days of moist curing. Furthermore, Yang and Wu[8] reported that cements with compressive strengths of 83 MPa were obtained with the same cure duration without the addition of fibers or any other reinforcing aggregate to the cement matrix. It is known that high performance concretes may have mechanical compressive strength greater than 60 MPa; however, they are relatively heavy materials with densities usually greater than 2.40 g/cm^3, processed under special curing conditions with high compaction energy[9].

Thus, low weight and high mechanical strength make these cements a potential material for insulation walls or fireproof partitions in the presence of other aggregates for filling or reinforcement[10].

These cements generally have superior properties than the Portland cements, including a higher hardness and a greater impermeability to water at a lower density. However, they cannot be considered as a substitute, mainly because of the higher cost, which has limited their use in small niche markets, such as rapid repair of damaged structures and treatment of waste[11,12].

Sant'Anna and Morelli[13] reported that the amount of principal reactants have a great influence on the crystalline phases to be formed after the reaction. These are directly related to the mechanical resistance of CBPC. The quantity of principal reactants also influences the physical characteristics of the material, such as apparent porosity and bulk density.

Several authors[4,13,14] have studied the effect of magnesium oxide (MgO) contents on the mechanical strength of MPCs. They observed that as the amount of MgO increases, the mechanical strength to compression ratio increases. They suggested that the non-solubilized MgO particles play an important role, acting as a skeleton in the cement structure. Therefore, compositions with a high concentration of MgO present greater mechanical resistance. Yang and Wu[8] further emphasized that the mechanical strength of unreacted MgO grains is much higher than that of the formed hydrated phases. However, the authors stated that hydrated phases concentration should be high enough to bind the MgO grains together.

Ammonium dihydrogen phosphate (ADP) ($NH_4H_2PO_4$) reacts with MgO in the presence of water in an acid–base

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reaction. Recent literature reports that the amount of hydrates decreases with an increase in the amount of $NH_4H_2PO_4$. Therefore, theoretically, the strength of the MPC decreases. The strength of MgO grains is much higher than that of the phosphate hydrates. Therefore, the decrease in the amount of ADP increases the strength of the MPC paste, provided the amount of phosphate hydrates is sufficient to surround the MgO grains thoroughly[15,16].

A crystalline phase called struvite ($NH_4MgPO_4.6H_2O$) is the main product of these reactions. Other phases, such as dittmarite ($NH_4MgPO_4.H_2O$), schertelite [$(NH_4)_2MgH_2(PO_4)_24H_2O$], and stercorite [$Na(NH_4)HPO_4.4H_2O$] are generally observed during the hydration reaction, while compounds, such as hanaite [$(NH_4)_2Mg_3(HPO_4)_48H_2O$], newberyite [$MgHPO_4.3H_2O$], and other phosphate hydrates are found less frequently[7,12]. Struvite ($NH_4MgPO_4.6H_2O$) is thermally stable in air, although at a temperature of 55°C, it loses the H_2O and NH_3 molecules from its structure and decomposes, forming an amorphous phase represented chemically as $MgHPO_4$. This phase can be hydrated again in the presence of water at ambient temperature, forming the original phase (struvite), and other amorphous and/or crystalline phases[17].

The type of phase formed after rehydration depends primarily on the amount of ammonia remaining in its structure. The recrystallization from struvite ($NH_4MgPO_4.6H_2O$) occurs only with the availability of NH_3 molecules in the compound. Struvite is more stable in water than in air as the excess water prevents the loss of NH_3 molecules[17].

The final microstructure of MPCs is mainly formed by the struvite crystals present around the remaining magnesium grains; this develops an interconnected cementitious network that adheres both to these grains and to the other constituents (inert materials) present in the cement matrix[18].

Recent works have evaluated the effect of boric acid content[19] and microwave calcination of MgO[20,21] on the properties and durability[22] of MPCs. Therefore, the objective of this work is to evaluate the effect of different $MgO/NH_4H_2PO_4$ ratios on the formation reactions (setting time and phases formed), of microstructure and the porosity of these materials, as consolidated dosage method is not available for the MPC matrices.

2. Materials and Methods

2.1 Materials

Raw materials with commercial purity were used in this study, although raw materials of high purity were used when necessary to aid in the analysis of phase formation. The main materials used include MgO, ADP, and boric acid (setting time retarder).

2.1.1 MgO

The MgO (basic component) was required to be calcined due to its high surface area. The MgO was calcined using a Termolab BL 260/03 oven, with a heating rate of 10°C/min. Then, two distinct temperatures were selected (900 and 1100 °C) and the dwell time was fixed at 2 hours for this work.

The densities and specific surface areas of MgO powders precipitated (without calcination) and calcined at different temperatures are shown in Table 1.

Table 1. Density and specific surface area of MgO powders precipitated (without calcination) and calcined at different temperatures.

MgO	Density (g/cm^3)	Specific Surface Area (m^2/g)
Precipitated (without calcination)	2.79	46.02
Calcined at 900 °C / 2 h	3.34	24.68
Calcined at 1100 °C / 2 h	3.53	7.87

A gradual increase in the density and a decrease in the surface area of the calcined MgO powder was observed, as the calcination temperature increased, with the density approaching the theoretical value of 3.58 g/cm^3. It was also observed that an increase in the calcination temperature led to a decrease in the specific surface area values; consequently, a high reactivity of the non-calcined (precipitated) powder was observed.

2.1.2 ADP

ADP ($NH_4H_2PO_4$) reacts with MgO in the presence of water in an acid–base reaction. ADP is the source of phosphate anions in that reaction; it releases a small amount of ammonia into the atmosphere during the reaction. Therefore, a higher amount of ADP is associated with higher strength of MPC paste, provided the amount of phosphate hydrates is sufficient to surround the MgO grains thoroughly[13]. The ADP used had a surface area of 0.68 m^2/g, unitary mass of 0.79 kg/dm^3, and specific gravity of 1.87 kg/dm^3; It was provided by LabSynth.

2.1.3 Boric acid (H_3BO_3)

The retardants have been found to increase the setting time and reduce the intensity of the exothermic reactions during the initial setting and hardening stages. They delay the setting time reactions, improve the workability conditions and give necessary time for the reactions to occur and effectively form phosphates[9]. Therefore, chemical retardants are utilized in large-scale mixing operations. Commercial boric acid containing approximately 98% H_3BO_3 was used in this study.

2.2 Methods

2.2.1 Materials characterization

The materials were characterized by X-ray diffraction (XRD) (Rigaku Geigerflex ME 210GF2 Diffractometer, configured with CuKα radiation, 40 kV of voltage, 100 mA of current, 10-80º 2θ scanning, and 4º/min of scanning speed), X-ray fluorescence (Philips PW1480 X-ray Fluorescence Spectrometer), and scanning electron microscopy (Philips SEM, model XL 30 FEG, gold coating). Relevant physical parameters, such as the particle size distribution (Horiba sedentary model CP5000), mercury intrusion porosimetry (MIP) (Porosizer 9320, Micromeritics), specific surface area estimation by BET method (using a Micrometrics Gemini 2370 V1.02 equipment), and specific gravity (Helium Pycnometer Accupyc 1330 V2.01 from Micrometrics) were determined.

2.2.2 Mixing and molding of compositions

After the calcination of MgO, five different compositions with different $MgO/NH_4H_2PO_4$ ratio, in mass, were prepared, as shown in Table 2. The amount of retardant (boric acid)

Table 2. Compositions used to evaluate the effect of $MgO/NH_4H_2PO_4$ ratio in magnesium phosphate cement compositions.

Composition	MgO (%, in mass)	ADP (%, in mass)	MgO/ADP Ratio	Boric Acid (%, in mass) **	H_2O (%)***
C_01	70	30	2.33	15	60
C_02	65	35	1.86		
C_03	60	40	1.50		
C_04	55	45	1.22		
S *	26	74	0,35	---	---

* Stoichiometric composition for the formation of 100% struvite is composed by 26% MgO and 74% ADP, in mass. ** % in relation to the mass of MgO (calcined at 900 ºC/2h and 1100 ºC / 2 h); *** % relative to the mass of MgO + $NH_4H_2PO_4$

added was 15% of the total mass of MgO, based on the studies of Yang and Wu[8]. The amount of retardant varied for each composition, as these compositions had different concentrations of MgO.

The conformation of the test specimens was performed by mixing the three primary materials (MgO, $NH_4H_2PO_4$, and boric acid) for one minute at room temperature. A mass of excellent moldability was obtained from this mixture, which was poured into cubic forms ($3 \times 3 \times 3$ cm^3) on a vibratory table. However, the specimens used for the measurement compression resistance were poured into cylindrical molds (ø 25 mm × 50 mm).

2.2.3 Composition characterization

The indirect measurements of setting time were performed as proposed by Hall et al.[23] and Ribeiro and Morelli[24] to characterize the compositions. In addition, the compositions were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (Philips SEM, model XL 30 FEG, gold coating), MIP, and apparent porosity.

The measurement of setting time should be performed using the Vicat apparatus according to the Brazilian standard NBR NM 65:2013 ("Portland Cement - Determination of Setting Time"). However, recent studies[12,18,25] have shown that for MPCs, setting time can be indirectly determined using calorimetry assay. These authors observed a direct relationship between the results obtained by using calorimetric measurements and using the Vicat apparatus. As the formation of the hydrated phases in cement is an exothermic reaction, the temperature measurements during hardening result in an indirect data, which can provide comparative values of setting time, as shown in Figure 1. In this work, a Raytec MT infrared pyrometer was used to perform such measurements.

This technique was of fundamental importance for the accomplishment of this work, as it allowed the evaluation for the extent of interference of the studied variables in the setting times of the cements, which is an extremely important property that must be increased when dealing with MPCs.

The phases of the cement were identified by XRD in experiments using the Rigaku Geigerflex ME 210GF2 Diffractometer, copper targets of 40 kV and 40 mA, and a monochromatic graphite filter system. A diffraction spectrum was obtained having a range of 2θ 5-75º at 2º/min. The phases in the samples were identified using DIFFRAC plus-EVA software, whose database follows the joint committee on power diffraction standards (JCPDS) system.

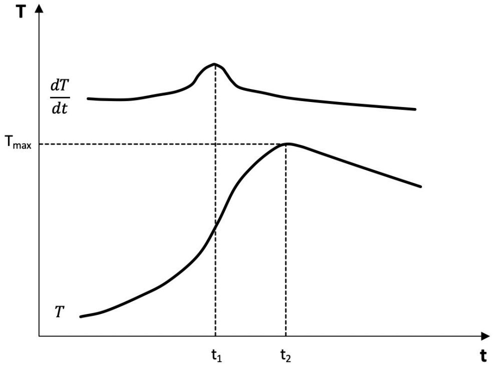


Figure 1. Schematic illustration of indirect measurement of setting time by calorimetry[12,17].

3. Results and Discussion

3.1 Phases Formation

The X-ray diffractograms of MPCs prepared from MgO powders calcined at 1100 °C/2 h with different $MgO/NH_4H_2PO_4$ (ADP) proportions by mass, are shown in Figure 2.

It can be observed that, independent of the composition, the two main phases found in the diffractogram are MgO and $NH_4MgPO_4.6H_2O$, also known as struvite. An unreacted ADP peak was not detected, and this raw material was considered completely solubilized in the aqueous solution in the presence of the other constituents of the cement. In the compositions with the lowest $MgO/NH_4H_2PO_4$ ratio (C_03 and C_04), the $NH_4MgPO_4.H_2O$ phase (dittmarite) also appeared; its concentration increased with the increase in ADP. Ribeiro[12] reported that dittmarite is an intermediate phase of struvite, formed in samples with low setting times. This occurred in situations where the struvite did not find sufficient time to form completely before the hardening of the cement.

The compositions C_03 and C_04 presented higher concentrations of hydrated phases when compared to the first two compositions, as observed from the intensity analysis of the diffraction peaks. The availability of both phosphates and MgO is required for the formation of these phases. MgO is available to be solubilized even for the C_04 composition, as shown in Figure 3; this explains the higher proportion of hydrated phases present in the compositions C_03 and C_04. The level is even higher for composition C_S (Figure 3), in

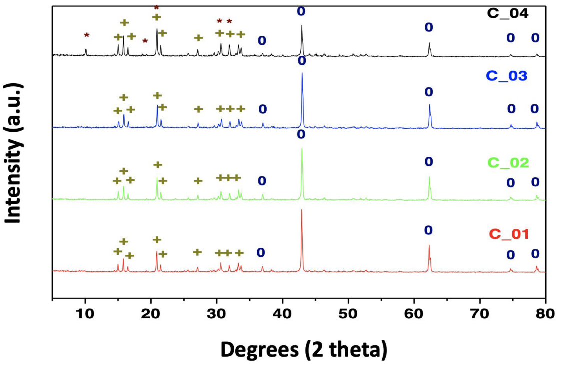


Figure 2. X-ray diffractograms of CBPC compositions prepared from MgO powders calcined at 1100 °C / 2 h, with different MgO/$NH_4H_2PO_4$ ratio, in mass. (Phases: $^+$ struvite; * dittmarite; ^{o} MgO).

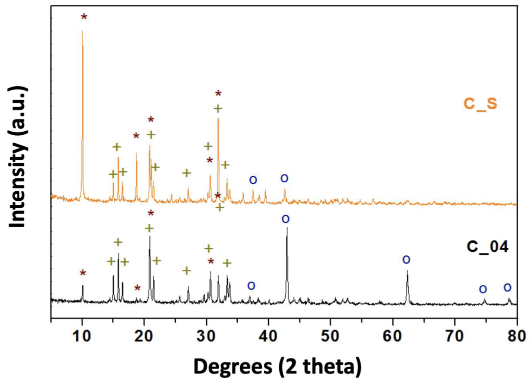


Figure 3. X-ray diffractograms of compositions C_S and C_04 prepared from MgO powders calcined at 1100 °C / 2 h, with different MgO/$NH_4H_2PO_4$ ratios, by mass. (Phases: $^+$ struvite; * dittmarite; ^{o} MgO).

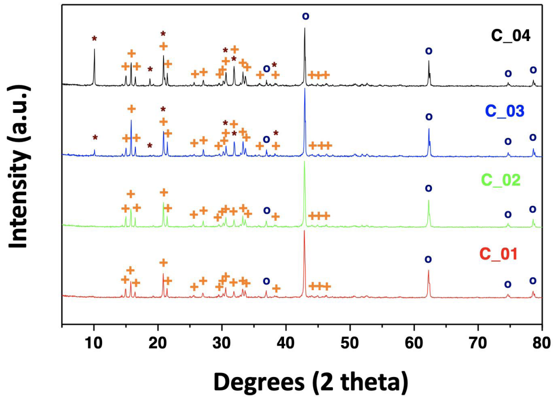


Figure 4. X-ray diffractograms of CBPC compositions prepared from MgO powders calcined at 900 °C / 2 h, with different MgO/$NH_4H_2PO_4$ ratios, by mass. (Phases: $^+$ struvite; * dittmarite; o MgO).

which the MgO/ADP ratio is much lower than the compositions shown in Figure 2. As expected, the concentration of dittmarite ($NH_4MgPO_4.H_2O$) in composition C_S is higher than in the other compositions.

The use of calcined MgO powders at a low temperature (900 °C/2 h) in the preparation of MPCs led to an increase in the intensity of dittmarite ($NH_4MgPO_4.H_2O$) peaks, as shown in Figure 4. This implies that decreasing the calcination temperature would also favor the formation of this hydrated phase for the detriment of struvite. This pattern is associated with the availability of less time for the development of hydration and microstructural reactions in cements employing calcined MgO at low temperatures (short setting times). As previously mentioned, there would not be sufficient time for the complete formation of struvite under these conditions, which would increase the concentration of dittmarite.

The calcination temperature did not significantly influence the formation of the hydrated phases for compositions C_01 and C_02, most likely due to the absence of a sufficient quantity of ADP to enable the hydration reactions of the cement. In Figure 5, there are no significant differences in the X-ray diffractograms for composition C_01 prepared from calcined MgO powders at different temperatures.

Given the low concentration of ADP in these compositions, it is readily complexed by the Mg^{+2} ions present in solution, regardless of the degree of calcination of MgO. As time passes and ions cease to be available due to ADP solubilization, the formation of new hydrated phases ceases, as shown in Figure 6. The same behavior also applies to composition C_02.

The presence of water and byproducts of ADP solubilization (phosphate and ammonium ions) was observed in composition C_04 (Figure 7) due to the high concentration of phosphate. The decrease in MgO concentration over time could be linked to the consumption of this oxide and the formation of new hydrated phases, specifically struvite. Such behavior is in accordance with that proposed by Sarkar[17], who verified that compositions with high concentrations of MgO lacked available NH_4^+ ions for the formation of new hydrated phases. This is due to the low quantity of ADP added and the high loss of released ammonia during the setting reactions of this cement.

The infrared (IR) spectroscopy results of the cements prepared from MgO powders calcined at 1100 °C/2 h, after aging for 30 days are shown in Figure 8. The analyzed portion was concentrated in the upper part of the samples. The IR spectrum of ammonium phosphate was included as a comparison parameter.

For MPC, the sum of the internal stretching vibrations of the H_2O molecules of the cement in the region between 3650 and 3100 cm^{-1} correspond to the internal stretching vibrations of its NH_4^+ groups (lower wavelength). There is a band around 1660 cm^{-1} related to the deformation vibrations of the H_2O molecules, in addition to the vibrations associated with the NH_4^+ groups. All these peaks were observed to become increasingly clear as the amount of ADP in the cement increased, indicating the formation of hydrated phases.

As expected, the 1485 cm^{-1} peak for the angular deformation vibrations ν_4 of the NH_4^+ groups are clearer in the spectra of cement with higher concentrations of ADP. It is also noted that there is an overlap of the peaks at 1175 and 1045 cm^{-1}, in the form of a rather wide band in the spectra of these cement, which can be attributed to the angular strain vibrations in the δ plane (P-OH) of the phosphate groups and the internal vibrations of stretching ν_3 of PO_4^{-3} ions, respectively. Finally, in addition to the 590 and 510 cm^{-1} peaks associated with the angular deformation vibrations ν_2 and ν_4 of the same PO_4^{-3} groups, there is a strong band between 900 and 780 cm^{-1} due to the overlapping of the peaks related to the ammonia-water bonds (higher wavelength), and due to the deformation of the water molecules present in the structure.

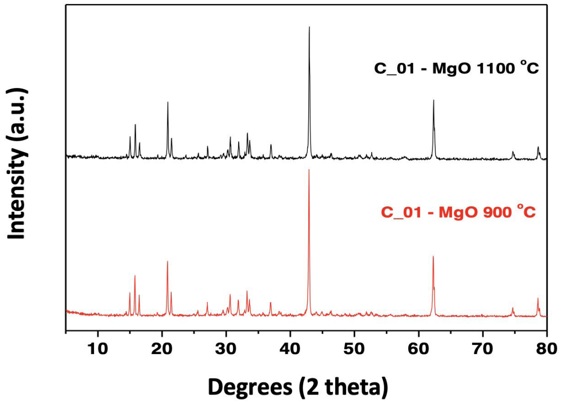


Figure 5. X-ray diffractograms of composition C_01, prepared from MgO powders calcined at 900 °C/2 h and 1100 °C / 2 h.

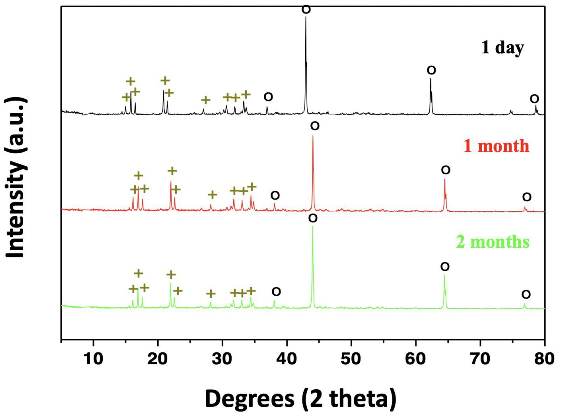


Figure 6. X-ray diffractograms of composition C_01, prepared from MgO powders calcined at 1100 °C / 2 h, with different ages, after setting (Phases: + struvite; * dittmarite; o MgO).

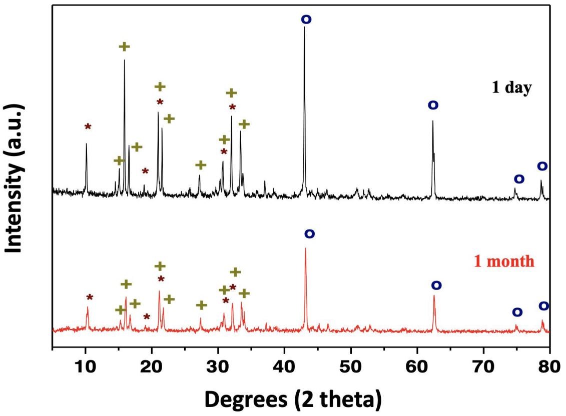


Figure 7. X-ray diffractograms of composition C_04, prepared from MgO powders calcined at 1100 °C / 2 h, with different ages, after setting (Phases: + struvite; * dittmarite; o MgO).

The IR spectra on the surface of these same samples are shown in Figure 9; it is possible to observe a strong difference between these spectra and those shown in Figure 8. The explanation can be attributed to the presence of a large quantity of MgO aggregates. If the cement is not properly mixed prior to its setting, these aggregates tend toward sedimentation, leaving the top of the cement rich in phosphate and ammonium ions in a process known as exudation. The extent of this process is greater for samples with smaller amounts of MgO. This occurs, because the viscosity of the cement paste decreases with decrease in the concentration of this oxide, which intensifies the sedimentation process. Moreover, a large amount of water remains adsorbed on the MgO particles, this amount is related to its surface area. Thus, compositions with higher concentrations of ADP (C_02 and C_03) present strong sedimentation, with their IV spectra close to those of ammonium phosphate.

In this way, the mixing and homogenization process is beneficial for two reasons: i) it hinders the formation of agglomerates and avoids the stratification of the aggregates in the cement, ii) it favors the formation of new hydrated phases and the consumption of MgO, as verified by Singh *et al.*[26].

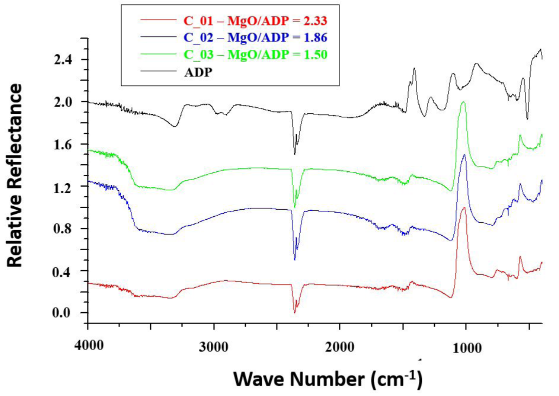


Figure 8. FTIR spectra of the lower region of the magnesium phosphate cements prepared from MgO powders calcined at 1100 °C / 2 h and with different $MgO/NH_4H_2PO_4$ ratios, by mass.

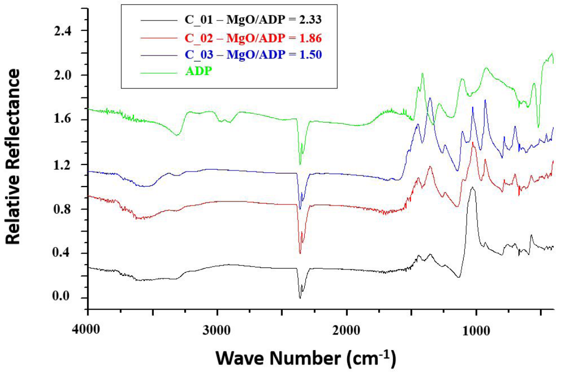


Figure 9. FTIR spectra of the surface region of the magnesium phosphate cements prepared from MgO powders calcined at 1100 °C / 2 h and with different $MgO/NH_4H_2PO_4$ ratios, by mass.

3.2 Apparent Density and Pore Size Distribution

The apparent density results of the cement prepared from the MgO powders calcined at 900 °C/2 h, are shown in Figure 10.

The increase in ADP concentration favored an increase in the concentration of the hydrated phases, which consumes much of the water mixed in their formation, as shown in Figure 1. This explains the alterations found in the density values of compositions C_03 and C_04 until the water content reaches around 60%. Successive increases in water concentration eventually generates pores that decrease the apparent density of these cement. This caused a decrease in bulk density with increase in quantity of mixed water, for all compositions. In compositions C_01 and C_02 this decrease occurred early on, i.e. at a low volume of added mixing water, as there is only a small quantity of ADP to be consumed in these compositions.

The compositions with lower concentrations of MgO and higher concentrations of hydrated phases (C_03 and C_04) showed lower bulk density or low water content. Thus, contrary to the expectations, the quantity of hydrated phases seems to have little impact on the densification of the MPC; however, it seems to be more associated with the packing of the MgO particles. This can be a problem when working with MgO powders with a high surface area and strong agglomeration.

The pore size distribution results of these samples, obtained by MIP applied to MPC, prepared from MgO powders calcined at both 900 °C/2 h and 1100 °C/2 h, are shown in Figure 11. It is noted that the compositions prepared from these powders exhibit similar distributions in the sizes of their pores, and the volume of penetrated Hg is same for all compositions, in accordance with the porosity results with 60%water contents.

In Figure 11b, it can be observed that the increase of the calcination temperature caused an increase in the average pore diameter, compared to the results shown in Figure 11a. Such behavior is a consequence of the smaller surface area of the MgO calcined at 1100 °C, which led to a larger quantity of free water, unused in the cement hydration processes, lodging around the remaining MgO particles. This unreacted water leaves pores of high average size, after being evaporated, after the setting time. Pores larger than these, above 30 µm, are present only in samples of cement prepared from MgO powders calcined at 900 °C. Such pores may be associated with deficiencies in the mixing and homogenization processes of these cement. Effectively, the lower the calcination temperature of MgO, the greater its surface area, and the greater the difficulty of mixing, which makes homogenization difficult.

By comparing Figures 11a and 11b, it is observed that compositions C_01 and C_02 when composed of MgO calcined at lower temperatures (900 °C, Figure 11a) showing the lower pore volume; however, when they are composed of MgO calcined at higher temperatures (1100 °C, Figure 11b) they show the highest pore volume. There is a low concentration of ADP available in these cement for the formation of hydrated phases. When the surface area of the MgO powder particles is reduced (higher calcination temperatures), the excess water present in these cement samples is higher than that observed in compositions C_03 and C_04, as less water is consumed to form the hydrated phases.

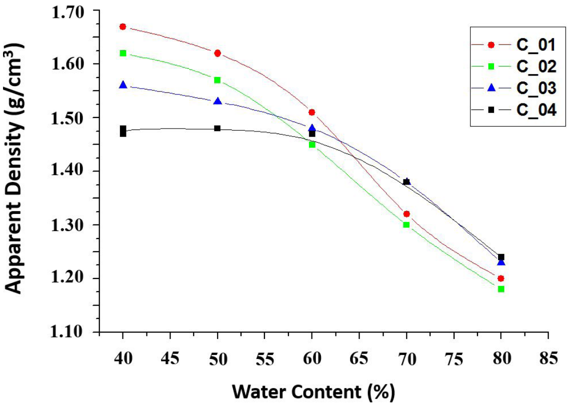


Figure 10. Apparent Density of the magnesium phosphate cements prepared from MgO powders calcined at 900 °C / 2 h and with different MgO/$NH_4H_2PO_4$ ratios, by mass.

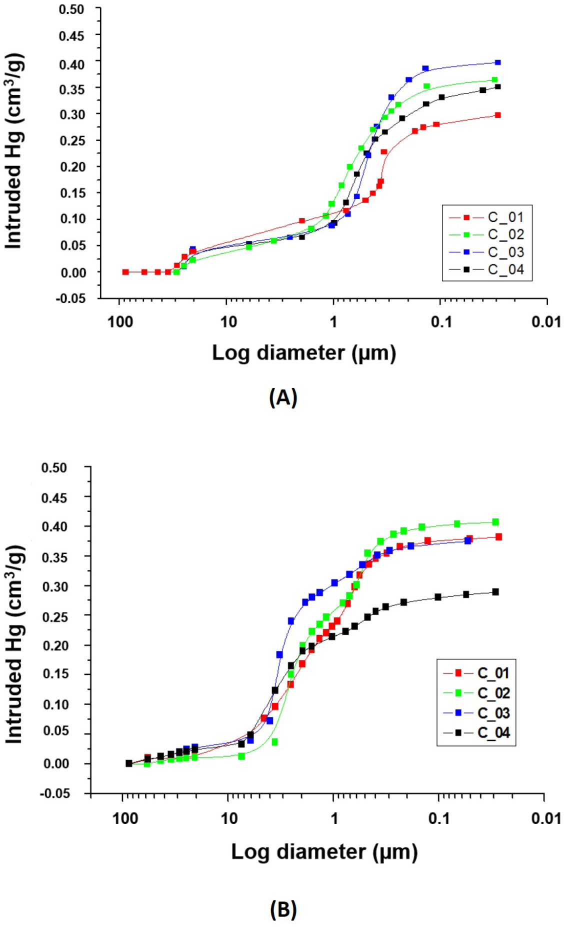


Figure 11. Pore size distributions of the magnesium phosphate cements prepared from MgO powders calcined at (A) 900 °C / 2 h and (B) 1100 °C / 2 h, with different MgO/$NH_4H_2PO_4$ ratios, by mass, with a water content of 60%.

3.3 Setting Time

The setting time measurements of the MPC compositions, obtained indirectly by pyrometry assays, in accordance with recent studies[12,24,25] are shown in Figures 12 and 13. The formation reaction of the hydrated phases of these cement is highly exothermic; thus, the measurement of the temperature variation during the setting time results in indirect data for obtaining the comparative values of setting time, with a reliable correlation with the results traditionally obtained by the Vicat method[24,25].

The setting time taken in the Hall et al.[23] studies, measured using the Vicat apparatus, coincides with the time of intense heat release in a sample of acid-base cement, evaluated using DSC assay. If measured by an infrared pyrometer, it would be the time for the rapid increase in temperature on the surface of the cement, just after the point of inflection of the curves[12,24,25]. This is verified in Figure 12.

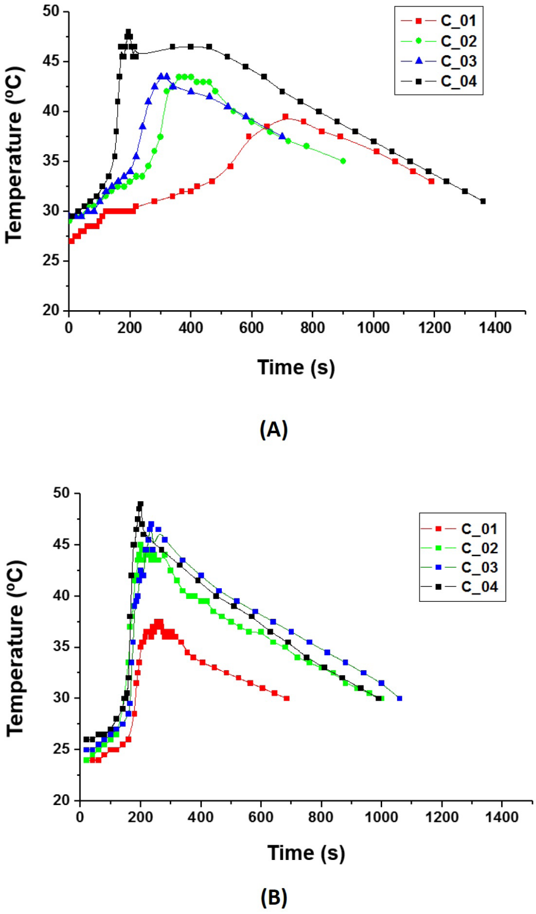
It is observed that the compositions with the highest MgO/ADP ratio are those that experienced the lowest temperatures during their setting. This is due to the lower concentration of their hydrated phases compared to the observed concentration in compositions with a lower MgO/ADP ratio.

The use of MgO powders calcined at higher temperatures (1100 °C/2 h), led to a shift of the curves to the right, independent of the composition, i.e., a more rapid setting time for these cement. This is due to the lower surface area of these powders (Table 1), which has lower solubility, exhibiting lower kinetics of formation of the hydrated phases (i.e., heat is released more slowly).

In addition, more relevant increase in the setting time occurred for the compositions with a higher MgO/$NH_4H_2PO_4$ ratio (C_01). According to Yang and Wu[8], such behavior could not occur as the setting time of the MPC is directly related to the ratio of boric acid to MgO. The reason is that, two or more formulations will present the same setting time if they have the same ratio of boric acid to MgO, independent of the composition (C_01 or C_04), and with all other variables (such as water volume and specific surface area of MgO powders) kept constant. This is a direct consequence of the effect of boric acid on the MgO particles, such as acting as a MgO particle coating, retarding their solubilization, the formation of the hydrated phases, and consequently, the cement setting time. Boric acid does not have this effect on ADP.

The behavior was the same as that reported above, with the curves very close to each other for samples containing MgO powders calcined at 900 °C/2 h (Figure 12a). This did not occur for post-calcined samples at 1100 °C/2 h (Figure 12b). This might be due to the presence of excess retardants for the cement with MgO powders calcined at 1100 °C/2 h. As observed, the increase in the calcination temperature contributed to the decrease of the specific surface area, so a smaller amount of retardant would be required to act as a coating for MgO particles. However, a higher retardant concentration was added for the C_01 to C_04 composition to maintain the same ratio of boric acid to MgO. A considerable difference in setting time and temperature peak was observed as the retardant was in excess (Figure 12b).

By comparing Figures 12 and 13, it was observed that the addition of higher amounts of retardant (higher boric acid/MgO ratio) increased the difference between the compositions' temperatures, leading to a behavior similar to that of the powders calcined at 1100 °C/2 h (Figure 12b). This change in behavior ratifies the effect of the excess retardants for the modification of the mechanism proposed by Yang and Wu[8].



(A)

(B)

Figure 12. Temperature measured by pyrometry as a function of the time after mixing, of the magnesium phosphate cements prepared from MgO powders calcined at (A) 900 °C / 2 h and (B) 1100 °C / 2 h, with different MgO/$NH_4H_2PO_4$ ratios and with a boric acid/MgO ratio of 15%.

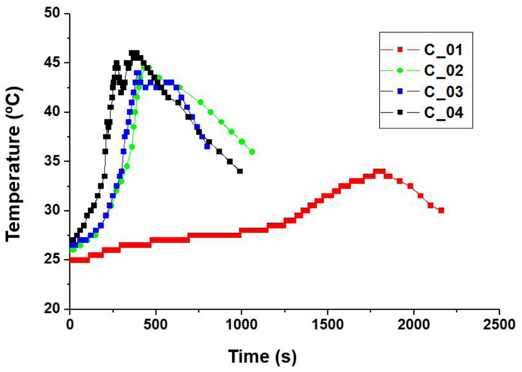


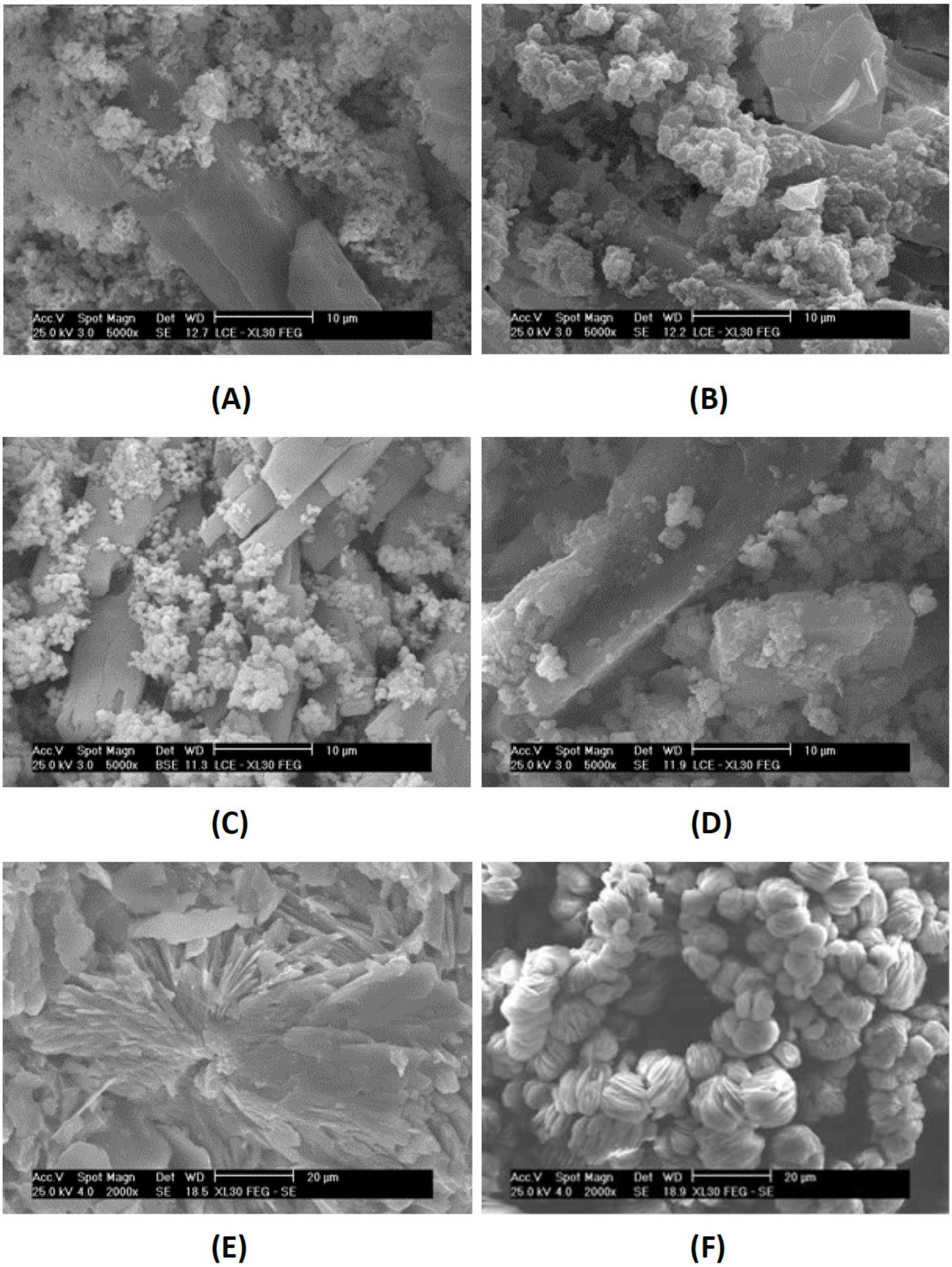
Figure 13. Temperature measured by pyrometry as a function of the time after mixing, of the magnesium phosphate cements prepared from MgO powders calcined at (A) 900 °C / 2 h, with different MgO/ $NH_4H_2PO_4$ ratios and with boric acid/MgO ratio equal to 40%.

3.4 Microstructure

The micrographs of different CBPC compositions, prepared from the powders calcined at 1100 °C/2 h, are shown in Figure 14.

It is observed that regardless of the composition, the microstructure of the MPC is formed by MgO particles dispersed around acicular crystals of struvite. Note that the struvite crystals are greater than the MgO aggregates. These crystals are arranged in different orientations, without proper packaging; they sort out the aggregates of MgO, due to which the hydrated phases compromise packaging of the MPC. The presence of dittmarite ($NH_4MgPO_4.H_2O$) was observed in the compositions C_03 and C_04, and crystallization did not occur in the form of needles.

From the analysis of these micrographs, it is observed that pores sized between 1 and 4 μm, observed by the pore size distribution curves (Figure 11), occur between the MgO aggregates and struvite ($NH_4MgPO_4.6H_2O$) crystals.



(A) **(B)** **(C)** **(D)** **(E)** **(F)**

Figure 14. Microstructure of the magnesium phosphate cements prepared from MgO powders calcined at 1100 °C / 2 h. (A) C_01; (B) C_02; (C) C_03; (D) C_04; (E) struvite in composition C_S; (F) dittmarite in composition C_04.

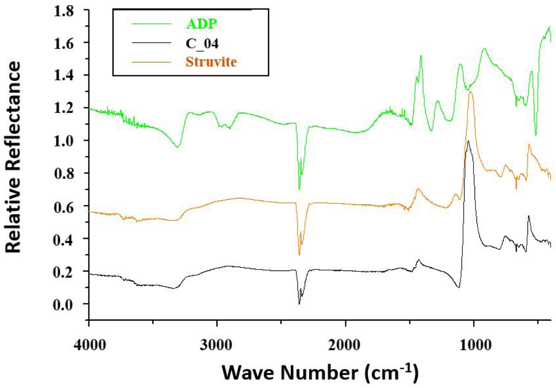


Figure 15. FTIR spectra of ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP) compositions C_S and C_04 prepared from MgO powders calcined at 1100 ° C / 2 h.

The pore size is related to the excess water not used in the hydration reactions that remains in the mixture and the low packing density of struvite ($NH_4MgPO_4.6H_2O$). The family of smaller pores, between 0.4 and 0.7 µm, is made up of pores located within the agglomerates and aggregates of the unreacted MgO particles.

There are differences in the geometry of the struvite ($NH_4MgPO_4.6H_2O$) crystals of C_S composition with respect to other compositions. The changes were detected in the intensity of the diffraction peaks of the hydrated phases, with no additional hydrated phase present apart from struvite ($NH_4MgPO_4.6H_2O$) and dittmarite ($NH_4MgPO_4.H_2O$), as depicted in the X-ray diffractograms presented in Figure 3. Although these phases are present to a greater extent in C_S, the differences in crystallinity in the two compositions cannot be easily visualized, as seen in Figure 3. Nevertheless, Figure 15 shows that consequent differences in geometry and crystallinity were detected in the IR spectrum for these two compositions. The peak in the C_S composition occurs at 1195 cm^{-1}, which refers to the angular strain vibrations in the plane δ (P-OH) of the phosphate groups, and the angular deformation vibrations, ν_4, of the ammonium groups. This peak is even sharper than in the C_04 composition, indicating that differences exist even when the hydrated phases are the same.

From the densification point of view, C_S presented very low bulk density (0.98 g/cm^3) and high-water absorption (42.88%) compared to other compositions, such as the C_04 composition prepared from MgO powders calcined at 1100 °C, which had an apparent density of 1.52 g/cm^3 and water absorption of 6.57%.

Sant'Anna and Morelli[13] observed that the mechanical strength of MPC was also increased, as the MgO concentration of their compositions increased. This behavior was attributed to the remaining MgO particles which played a supporting role ("skeleton") within the formed structure, similar to the effect of silica on a ceramic triaxial (silica - clay - fluxing material). This explains why the C_S cement composition exhibits low mechanical strength. The high-water absorption and the low apparent density are due to the presence of excess hydrated phases for which the compaction is difficult.

4. Conclusions

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

- In the compositions with a lower MgO/$NH_4H_2PO_4$ ratio, the formation of the $NH_4MgPO_4.H_2O$ phase (dittmarite) occurs, and the concentration increases as the quantity of added ADP increases.
- The reduction of the calcination temperature of MgO favors the formation of dittmarite ($NH_4MgPO_4.H_2O$) to the detriment of the struvite ($NH_4MgPO_4.6H_2O$), due to the availability of less time for the hydration and microstructural development (faster setting) reactions, which is not a factor in compositions with low quantities of ADP.
- The compositions with a low ADP concentration are complexed by Mg^{+2} ions present in solution, regardless of the degree of calcination of MgO. There is no formation of new hydrated phases as there are no other ions coming from the solubilization of the available ADP.
- The increase in the ADP concentration favors the increase in the concentration of the hydrated phases, which consume a large part of the mixed water in their formation. However, successive increase in water concentration generates pores and decreases the apparent density of these cement.
- The compositions containing calcined MgO at higher temperatures have higher average pore diameters, which results in more free water that does not participate in the hydration of the cement.
- The compositions with the highest MgO/ADP ratio showed higher setting times and lower temperatures during picking, due to the lower concentration of their hydrated phases compared to the concentration observed in compositions with lower MgO/ADP ratios.
- Regardless of the composition, the use of calcined MgO powders at higher temperatures results in an increase in the setting time of these cement, due to the lower surface area of these powders, which have lower kinetics of formation of the hydrated phases due to their lower solubility.
- The increase in the setting time occurs significantly for the compositions with a higher MgO/ADP ratio.
- The setting time for MPC is directly related to the boric acid/MgO rate, i.e., two or more formulations will have the same setting time if they have the same boric acid/MgO rate independent of the composition and with all other variables kept constant.
- The results by using CBPC compositions with high concentrations of ADP (such as composition C_S) are not attractive, reinforcing the need for optimizing the properties of the cement, maximizing its setting time, and decreasing the calcination temperature of the MgO used.

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