Influence of the addition of grinding dust to a magnesium phosphate cement matrix

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ABSTRACT

Magnesium phosphate cement materials were prepared by reacting magnesium oxide with water-soluble phosphates such as mono-ammonium dihydrogen phosphate (ADP), which solidified at ambient temperature through the formation of hydrated phases in the material. Cylindrical specimens of magnesium phosphate cement were molded and varying amounts (0–40% weight) of grinding dust, waste generated in the clutch disc finishing process by grinding and polishing, were added to the ceramic matrices. The influence of the addition of grinding dust on the characteristics of the cement compositions was verified in terms of setting time, apparent porosity, density and leaching/solubilization tests. The setting time was analyzed according to NM 65 (the Vicat needle) and by indirect calorimetric measurements, the apparent porosity and density of the materials were analyzed by the water immersion method, based on the Archimedes principle. Using an Instron 5500R universal testing machine, various analyses were made to ascertain how the different waste contents in the compositions affected the mechanical strength (axial compression and tensile strength by diametral compression). The results obtained proved highly satisfactory for the application of this waste as an additive in magnesium phosphate mortars. The addition of grinding dust to the magnesium phosphate cement matrix did not affect the formation of new phases or the setting time to any appreciable extent, but an increase in grinding dust content led to an initial increase in strength up to a given limit (about 30% of waste).
They can be manufactured with the incorporation of pigment, and accept polymeric paint and coatings that adhere to various materials, particularly to steel, thus opening up a wide range of possibilities for combinations in metallic structures [6,7].

Phosphate cements possess mechanical and chemical properties that are superior to those of normal hydraulic (or Portland) cements in general, thanks to innovations in their processing and microstructural handling and to compositional modifications. The bonds in such chemically bonded phosphate ceramics (CBPCs) is a mixture of ionic, covalent and van der Waals bonds, with a predominance of ionic and covalent bonds; in traditional cement hydration products, van der Waals and hydrogen bonds predominate [8–10].

The reaction between magnesia and acid ammonium phosphate is very rapid and exothermic, and the materials cannot be practically used as such. Thus, the use of calcined or dead-burned magnesia is suggested. Today's commercial materials are formulated with many inexpensive inert materials such as sand, fly ash, etc. to control the rate of reaction or setting time while simultaneously providing high early compressive strength. Phosphate cements for commercial applications are generally based on reactions between a metallic oxide and an acid salt or derivative of phosphoric acid [8].

Immediately upon mixing the raw materials at ambient temperature, exothermic reactions occur and ammonium and magnesium phosphate phases are formed. These phases are hydrated and insoluble in water.

The main product of these reactions is a crystalline phase called struvite \((\text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O})\), which results from the following reaction:

\[
\text{MgO} + \text{NH}_4\text{H}_2\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \quad (1)
\]

Other phases such as dittmarite \((\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O})\), schertelite \([(\text{NH}_4\text{H})_2\text{Mg}_2\text{P}_2\text{O}_7\cdot4\text{H}_2\text{O})\], and stercorete \([\text{Na(NH}_4\text{H})_2\text{PO}_4 \cdot 4\text{H}_2\text{O})\) are ordinarily observed during hydration, while hanaite \([(\text{NH}_4\text{H})_2\text{Mg}_2\text{P}_2\text{O}_7\cdot8\text{H}_2\text{O})\], newberyite \([\text{MgHPO}_4 \cdot 3\text{H}_2\text{O})\] and other phosphate hydrates are found less frequently [11].

Struvite is a thermally stable phase in air up to a temperature of 55 °C, at which point it decomposes through the loss of \(\text{H}_2\text{O}\) and \(\text{NH}_3\) molecules from its structure, forming an amorphous composition that corresponds chemically to MgHPO\(_4\). In the presence of water at ambient temperature, this composition can be rehydrated, forming the original phase (struvite) and other amorphous and/or crystalline phases.

Struvite and dittmarite are chemically and structurally similar and the transformation of one into the other does not cause any microstructural damage to molded specimens. Dittmarite is the predominant phase when the reaction is fast, while struvite predominates when the reaction rate is slow [7].

\[
(\text{NH}_4)_2\text{Mg(HPO}_4\text{)}_2 \cdot 4\text{H}_2\text{O} + \text{MgO} + 7\text{H}_2\text{O} \rightarrow 2(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O} \quad (2)
\]

A recent study by Soudée and Péra [11] suggests a mechanism of formation of these materials, whereby, immediately following the addition of water to the mixture, the ADP goes into solution up to saturation while magnesia starts to be wetted. The drop in pH that occurs during this period leads to the dissociation of magnesia through an acid–base reaction. Crystallization of the hydrate phases begins when Mg\(^{2+}\) ions react with six molecules of water to form \(\text{Mg(H}_2\text{O)}_{6}^{2+}\) compounds. These compounds replace water molecules in the wetting process of magnesia. Their size prevents molecules in the wetting process of magnesia. Their size prevents


that the kinetics of these transformations is very similar to that of the conventional sol–gel process of ceramics fabrication. Fig. 1 gives a step-by-step illustration of the kinetics of CBPC formation.

- Dissolution of oxides and formation of gel by hydrolysis. When metal oxides are stirred into an acid solution, they dissolve slowly, releasing their own metal which contains cations and oxygen-containing anions (Fig. 1a – dissolution step). The cations react with water molecules and form positively charged "aquo-sols" by hydrolysis (Fig. 1b – hydration step). Dissolution and hydrolysis are the controlling steps in the formation of CBPCs.

- Acid–base reaction and formation of gel by condensation. Sols react with aqueous phosphate anions (Fig. 1c) to form hydrophosphate salts, while the protons and oxygen react to form water. The newly formed hydrophosphate salts make up a network of molecules in the aqueous solution, leading to the formation of a gel (Fig. 1d).

- Saturation and crystallization of the gel into a ceramic. As the reaction proceeds, this process introduces increasing amounts of reaction products into the gel, which is thus thickened. When sufficiently thick, the gel crystalizes around the unreacted core of each grain of the metal oxide, forming a well-connected crystal lattice that grows into a monolithic ceramic (Fig. 1e) [10].

The objective of this paper is to study the effectiveness of the magnesium phosphate cement matrix in encapsulating hazardous wastes without losing its characteristics of high performance. Thus, this new cementitious matrix may offer an alternative for the treatment of wastes that cannot be encapsulated in other cementitious matrices such as, for instance, Portland cement matrix.

2. Materials and methods

2.1. Materials

2.1.1. Magnesium oxide (MgO)

The present study used a commercial dead-burned magnesium oxide calcined at 1600 °C, with a MgO content of 88% to 93%. Dead-burned calcined magnesia is produced at temperatures above 1400 °C and is characterized by its low chemical reactivity and high resistance to basic slags. The magnesium oxide presented a specific surface area of 0.81 m\(^2\)/g, unitary mass of 1.34 kg/dm\(^3\) and specific gravity of 3.61 kg/dm\(^3\).

2.1.2. Ammonium dihydrogen phosphate (ADP)

The ammonium dihydrogen phosphate \((\text{NH}_4\text{H}_2\text{PO}_4),\) or ADP, reacts with magnesium oxide in the presence of water in an acid–base reaction.

The recent literature reports that the amount of hydrates decreases with the amount of \(\text{NH}_4\text{H}_2\text{PO}_4\) and, therefore, the strength of magnesium phosphate cement (MPC) theoretically decreases. From the proportions of MPC it can be calculated that the strength of MPC paste, provided the amount of phosphate hydrates is sufficient to surround the MgO grains thoroughly [12]. The ADP presented 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\(^3\).

2.1.3. Grinding dust

The automotive industry generates large and variable quantities of wastes. These include grinding dust, a hazardous waste (class I) generated in the clutch disc finishing process by grinding and polishing.

Table 1 presents the results of leaching and solubilization tests that classify the grinding dust as "hazardous" (class I). The main problem of this waste is its lead content, which is about eightfold higher than the maximum allowed in the leaching test according to the Brazilian NBR 10004 standard. Sodium, cyanides, phenols, sulfates and surfactants also show levels exceeding the maximum allowed in the solubilization test.

The material is particulate and quite complex due to its diverse constituents (metallic and polymeric fibers as well as fiberglass). This type of waste was used here. The scanning electron microphotographs exhibiting morphology of grinding dust is given in Fig. 2.
Grinding dust was supplied from ZF Sachs of Brazil factory, São Bernardo do Campo, Brazil. It had a surface area 1.32 m²/g, specific gravity 2.08 kg/dm³. Fig. 3 corresponds to the obtained diffraction spectrum that allows identifying the different hydroxides present.

2.1.4. Boric acid

Retardants have been found to increase the setting time and reduce the intensity of exothermic reactions during the initial setting and hardening stages. Therefore, chemical retardants are utilized in large-scale mixing operations [13]. Boric acid containing about 99.5% of H₃BO₃ was used in this study.

When boric acid containing MgO is mixed into a phosphate solution, lunebergite \[\text{Mg}_3\text{B}_2(\text{PO}_4)_2(\text{OH})_6\cdot6\text{H}_2\text{O}\] is formed around the MgO grains, preventing them from dissolving in the acid solution [10]. Subsequently, as the oxide powder is mixed into the acid solution, however, the coating itself dissolves and exposes the oxide particle surface to the acid solution, and magnesium oxide then starts dissolving into the solution [2].

2.1.5. Sodium tripolyphosphate (STPP)

The incorporation of sodium tripolyphosphate (Na₅P₃O₁₀), or simply STPP, into the magnesium phosphate mixture has a beneficial effect. The deflocculating characteristics of tripolyphosphate ions suggest that they may play a significant role in enabling improved compaction of the wet mix, reducing the porosity of the hardened material [8].

Moreover, Abdelrazig et al. [14] reported that the incorporation of STPP in mortars brought about an increase in compressive strength and a decrease in total and coarse pore volumes.

2.2. Methods

2.2.1. Dosage and molding of specimens

The raw materials were physicochemically characterized and the relation among the components was determined, in weight. The “reference proportion” used in the molding of the specimens was 1.0:0.75:0.10:0.30:0.50 (MgO: ADP: boric acid: STPP: H₂O). Cylindrical specimens (50 mm in diameter and 100 mm in length) of magnesium phosphate cement containing different amounts of grinding dust (0–40% in weight) were molded.

2.2.2. Setting time

The setting time was determined by the Vicat method, according to NM 65, and by indirect calorimetric measurements. Recent studies [14–16] have shown that the setting time of magnesium phosphate cements determined indirectly by calorimetry is correlated to the setting time measured by the Vicat needle; hence, the formation of hydrated phases in magnesium phosphate cements is an exothermic reaction.

As a further qualitative measure of the reaction rate, the setting time of the mortar was monitored using a Raytek laser pyrometer 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 \(T_{\text{max}}\) was attained, as illustrated in Fig. 4 [15].

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Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Solubilization</th>
<th>Leaching</th>
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<tbody>
<tr>
<td></td>
<td>Result (mg/L)</td>
<td>MVA* (mg/L)</td>
</tr>
<tr>
<td>Barium</td>
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<td>0.7</td>
</tr>
<tr>
<td>Cadmium</td>
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<td>0.005</td>
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<tr>
<td>Selenium</td>
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<td>0.01</td>
</tr>
<tr>
<td>Sodium</td>
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<td>Cyanide</td>
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<td>Phenols</td>
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<td>Fluorides</td>
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</tr>
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<td>Nitrates</td>
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</tr>
<tr>
<td>Sulfates</td>
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<td>250.0</td>
</tr>
<tr>
<td>Surfactants</td>
<td>0.5</td>
<td>0.5</td>
</tr>
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</table>

* = not required by the NBR 10004/2004 standard.
# = absence of a limit established by the NBR 10004/2004 standard.
* MVA = maximum value allowed by the NBR 10004/2004 standard.
Because the CBPC formation reaction is sufficiently exothermic, the amount of material directly affects in the reaction kinetics. During the calorimetric measurements, the compositions were molded in the same Vicat method mold, according to NM 65.

2.2.3. 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 h 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 below:

$$P_a = \frac{100 \times (M_u - M_s)}{M_u - M_i}$$  \hspace{1cm} (3)
$$D_a = \frac{\rho_L \times (M_u)}{M_i}$$  \hspace{1cm} (4)

The $\rho_L$ is the liquid density (in this case, the water, $\rho_L = 1.0 \text{ g/cm}^3$ at 25 °C).

2.2.4. X-ray diffraction (XRD)

The identification of the crystalline phases of a material by X-ray diffraction is based on the incidence of a monochromatic X-ray beam with an x wavelength, which is diffracted by periodically distributed planes of high atomic concentration in the sample, with destructive or constructive interferences occurring between the diffracted waves.

This technique was used to characterize the grinding dust and compositions (3, 7 and 28 days old), using a Rigaku Geigerflex ME 210GF2 diffractometer, with copper targets of 40 kV and 40 mA, and a monochromatic graphite filter system. A diffraction spectrum was obtained in the range of $2\theta$ 10°–80° at 2°/min. The phases in the samples were identified using DIFFRAC plus-EVA software, whose database follows the JCPDS system (Joint Committee on Power Diffraction Standards).

2.2.5. Mechanical strength

The values of axial compression and tensile strength under diametral compression correspond to the average of three values for each magnesium phosphate composition and mortar age (3, 7 and 28 days after molding), and were

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**Fig. 2.** SEM of grinding dust (scattered morphology).
obtained with an Instron 5500R universal testing machine and a load of 1.5 mm/min. The specimens that presented an error of more than 5% were excluded and replaced by others, following the procedure established by the Brazilian NBR 7222 standard (Mortar and concrete – Determination of the tensile strength of cylindrical specimens subjected to diametral compression – Test method).

2.2.6. Leaching/solubilization tests

The leaching/solubilization tests were carried out following the NBR 10.004 standard, which classifies wastes and materials as hazardous (class I) or non-hazardous (II-A non-inert, and II-B inert).

3. Results and discussion

3.1. Determination of setting time

The measured setting times indicated that the addition of this waste to the magnesium phosphate cement matrix considerably augmented the hardening reaction. The setting time measured by the Vicat needle method showed a reduction of about 33%, according to Fig. 5, due the high sodium content in the grinding dust. However, the addition of increasing amounts of waste hardly affected the setting time.

Fig. 5 shows that the setting time curve obtained by the Vicat needle is similar to the curve that represents the values of maximum temperature time ($t_2$), in the composition containing 10% of waste, which is congruent with the results observed by Hall [15]. Nonetheless, this similarity can only serve as a qualitative measure of the setting time, since there is no obvious correlation between the two methods used in this work and those used in previous studies [15,16].

Another behavior that was verified by the setting time analyzed by calorimetry was that the gradual addition of the waste to the phosphate matrix also gave rise to a gradual increase in the maximum temperature of reaction, as indicated in Fig. 6.

This behavior, which was attributed to parallel reactions between the phosphate and other metallic ions present in the waste, became more evident with increasing amounts of grinding dust. The high reaction temperature probably contributed to reduce the setting time, since large amounts of released heat accelerate the setting rate and the interval between the initial and final setting time is very short [11,17].

3.2. Apparent porosity and density

Porosity is detrimental to the strength of ceramic materials because it reduces the area of the transversal section where loads are applied, thus decreasing the loads the material can bear [18]. Hence, the apparent porosity is an important factor that affects the strength of these materials. Fig. 7 presents the results of apparent porosity.

An increase in waste content caused a gradual reduction in porosity. The unreacted water was eliminated during the time the sample remained in the furnace. Fig. 7 shows that the influence of loss of free water cannot be taken into consideration and that the process is influenced solely by the “filler effect”, with strong interactions between waste particles and matrix.

Fig. 7 also indicates that the results were practically the same, regardless of the age of the compositions (3, 7 or 28 days). This is
due to the fact that the material was sufficiently hydrated after 3 days and, consequently, the amount of unreacted water in the compositions (and lost in the furnace) was practically the same.

The density of the samples was then analyzed. As observed in the porosity analysis, the free water did not affect the results to any significant degree since the water was lost while the samples were being dried in the oven. The density initially decreased in the presence of the waste ($\rho_{\text{waste}} < \rho_{\text{mixture}}$). However, starting from 10% of waste content, the density increased as a function of the amount of waste added (filler effect). The results are shown in Fig. 8.

3.3. X-ray diffraction (XRD)

The 3, 7 and 28-day-old compositions were analyzed by X-ray diffraction. The X-ray spectra of the various compositions presented slight alterations, which did not suggest the formation of new phases in response to the addition of waste in the phosphate magnesium matrix.

As indicated in Fig. 9, the phases identified at the three ages were magnesium oxide (MgO), struvite ($\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$) and dittmarite ($\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$).

The only alterations shown in Fig. 9 are a reduction of the peak intensity corresponding to nonreacted MgO and a slight displacement of the diffractograms, which is more clearly depicted in Fig. 10. These results are not directly attributable to the addition of waste.

3.4. Mechanical strength

The initial mechanical strength of the magnesium phosphate cements with added grinding dust increased up to a limit (about 30%) with increasing waste content. This behavior held true for
both axial compressive strength and tensile strength by diametral compression, as illustrated in Figs. 11 and 12.

A similar behavior was reported by Zangh et al. [19], who observed an increase of 30% to 50% in the strength of composites containing fly ash, which reached a maximum at 50% and declined thereafter with the addition of 60% of waste.

This behavior can be attributed to a combination of two factors:

1. Reduction of the water/solids relation (w/s) due to a progressive increase of waste content, generating an increase in resistance [14,20], which can result from the increase in density of the compositions as a function of the increase in grinding dust content, due to better particle packing.

2. Interaction between the microcracks and the particles of the inorganic phase – elongated rods (waste). Microcracks normally begin in the matrix phase, and their propagation is obstructed or retarded by waste particles. These particles can inhibit the propagation of microcracks by deflecting their tips, forming bridges through the microcracked phase and absorbing energy and/or inducing a redistribution of stresses in regions adjacent to the tips of the microcracks [18,21].

The second aspect was aided by the fact that the specimens containing waste did not show catastrophic breaking, as occurs with traditional hydraulic cement mixtures such as Portland cement. The specimens continued bearing a large part of the load after breaking, giving the impression that the body was “stopped” by internal bridges (inorganic fraction – glass fibers – such as rod-like waste particles).

However, the addition of 40% of waste led to a reduction in the mechanical strength, because this amount of added waste affects the formation of CBPCs, negatively affecting the material’s structure (not percolating and/or packing interference). Although the values decrease, they are still higher than those of the mixture without the waste, mainly in terms of tensile strength by diametral compression.

It was also observed that the material was not completely stabilized after 28 days of analysis, as shown in Figs. 11 and 12. Additional tests were conducted at 90 days of age to verify the behavior of the composites, which yielded results similar to those reported by Abdelrazig et al. [14], who also observed constant mechanical strength between 28 and 90 days of age.

As can be seen from the results (see Fig. 13), there is no clear relationship between strength and apparent porosity. However, the “optimal” value of apparent porosity that satisfies the required strength is about 37%. Values above or below this level are associated with lower strengths.

3.5. Environmental performance analysis

After concluding the technical performance analysis, leaching and solubilization tests were carried out according to the NBR 10,004/2004 standard to analyze the environmental performance of the compounds produced.

Table 2 presents the results of the leaching and solubilization tests on the magnesium phosphate cement containing grinding dust.

As can be seen in Table 2, all the contents of the elements were approved in terms of leaching, classifying this material as class II (non-hazardous), according to the Brazilian NBR 10004/2004 standard. In the solubilization test, all the elements were approved for the composites containing 10% grinding dust, classifying these compounds as Class II-B (non-hazardous inert). The composites containing 20% and 30% of grinding dust were classified as Class II-A.
The analyses of the setting time, apparent porosity and density, mechanical strength and phase formation in a CBPC matrix using X-ray diffraction led to the following conclusions:

1. The addition of grinding dust to the magnesium phosphate cement matrix accelerated the hardening reaction, decreasing the setting time.
2. Successive additions of grinding dust to the magnesium phosphate cement matrix did not affect the setting time to any appreciable extent. Moreover, the gradual addition of waste also allowed for a gradual increase in maximum reaction temperature.
3. The calorimetric measurements only served as a qualitative analysis of the setting time.
4. The presence of grinding dust initially reduced the porosity of the magnesium phosphate matrix due to particle packing. However, in the early stages (first 24 hours), the porosity increased with the gradually increment of waste content. The gradual increment in waste content caused the density to increase, indicating that the grinding dust physically filled the voids.
5. The formation of new phases as a result of the presence of grinding dust in this matrix was not detected.
6. An increase in grinding dust content led to an initial increase in strength up to a given limit (about 30% of waste). At the age of 28 days the mechanical strength of these composites had not stabilized. Their full mechanical strength was only attained at the age of 90 days.
7. An increase in the porosity of the cementitious matrix caused a reduction of the mechanical strength, while an increase in the weight content of the grinding dust caused both porosity and setting time (hence, workability) to decrease. Therefore, the "optimal" grinding dust weight content that satisfies both strength and workability requirements was found to be 20%.
8. According to the leaching and solubilization tests, the magnesium phosphate cement matrix proved highly effective in encapsulating grinding dust, especially for a content of 10%, classified as "non-hazardous inert".

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