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Effect of Calcined MgO-rich Byproduct from the Extraction of Li₂CO₃ on the Performance of Magnesium Phosphate Cement

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Abstract
Magnesium phosphate cement was prepared with an MgO-containing byproduct (EL-MgO) obtained through the extraction of Li₂CO₃ from salt lakes, and was used to replace dead burnt MgO in magnesium phosphate cement (MPC) formulations. The properties of EL-MgO after calcination at various temperatures were investigated. Changes in pH, alternating-current impedance, and hydration-heat-release rate were assessed. Surface area and reactivity decreased while the degree of crystallization increased with increasing calcination temperature, resulting in longer setting times. The compressive strength of MPC prepared with EL-MgO calcined at 1000 °C was 53.9 MPa after 1 day, which is high for quick-repair materials.

1. Introduction
Magnesium phosphate cement (MPC), a new type of cementitious binder, is produced by the acid-base reaction between dead burnt magnesia and phosphates (Abdelrazig et al. 1988). It is also referred to as “chemically bonded phosphate ceramic” because of its similarity to ceramic materials (Roy 1987). Given its fast rate of setting, high early strength, good fire resistance, and adhesive properties, MPC has been widely used for the rehabilitation of civil engineering structures (Seehra et al. 1993; Sarker 1990; Popovics et al. 1987; Yang et al. 2000; Postl et al. 2008). Moreover, MPC is also attractive for a broader range of applications including the stabilization of radioactive and toxic industrial wastes (Hall et al. 1999; Singh et al. 2006), bone defect repairs (Wang et al. 2013; Krüger et al. 2013), and the sealing of boreholes (Wang et al. 2013), among others.

The production of dead burnt magnesia used in MPC, obtained by calcining magnesite at around 1700 °C (Wu et al. 2008; Soudée et al. 2002), usually requires high amounts of energy. Furthermore, magnesite reserves are limited by region. About 25% of the world’s magnesite reserves are found in China (Wang et al. 2015) with the largest proportion concentrated in Liao Ning Province. In addition, MPC pastes prepared with dead burnt magnesia and phosphates have short setting times; consequently the use of retardants such as borax or boric acid is required (Hall, et al. 2001; Yang, et al. 2010). However, it has been suggested that the phenomena involved in the retardation process, such as the adsorption of B(OH)₃ on the surface of MgO grains, or the precipitation of a coating layer of lineberghite (Mg₃B₂(PO₄)₂(OH)₆·6H₂O) on the surface of cement grains, slow down their dissolution (Wagh et al. 1995). Therefore, because of the high energy consumption associated with the production of dead burnt MgO, local magnesite-reserve limitations, and the need for the addition of retardants, the cost of MPC remains high and limits its use in large-scale applications. In order to reduce the cost of MPC while concurrently valorizing waste, industrial waste, such as fly ash and slag, have been used to produce MPC (Li et al. 2013; Gardner et al. 2015). Asbestos-containing wastes have also been employed for preparing MPC (Viani et al. 2013). In addition, the use of a hard-burning low-grade MgO can reduce the cost of quick repairs of concrete structures (Formosa et al. 2012).

In recent years, huge amounts of byproducts containing both magnesium and boron, generated during the production of lithium carbonate (Li₂CO₃) extracted from salt lakes, has been produced in Qinghai Province, China. Without proper treatment and utilization, it is difficult to separate magnesium and boron impurities from Li₂CO₃, which hinders the production of pure Li₂CO₃, resulting in “magnesium pollution”. Therefore, finding resource-efficient applications for these byproducts is an urgent need. Considering that these byproducts contain large amounts of Mg(OH)₂; and some MgO, it can be used, after calcination, as a raw material in MPC and to help reduce the cost of MPC production. Calcination temperature has been shown to be important in determining the reactivity of MgO (Ibrahim et al. 2011; Yang et al. 2010). The crystallinity of MgO is also affected by the calcination temperature (Sasakia et al. 2014). A significant amount of research (Soudée et al. 2002 ) has focused on prolonging the setting time of MPC by increasing the calcination temperature. Soudée...
et al. (2000) found that the setting time is strongly affected by the deformation rate and the surface state of MgO powders. High calcination temperatures result in MgO surfaces with less defects and lower specific surface areas, in turn reducing the MgO reactivity and leading to longer setting times. Dong et al. (2016) also reported that increasing the calcination temperature decreased the hydration temperature and prolonged the setting time.

In this paper, EL-MgO calcined at various temperatures, and potassium dihydrogen phosphate (KH₂PO₄ or KDP), were used to prepare MPC. The effect of calcination temperature on the properties of EL-MgO and its setting time, compressive strength, and MPC hydration products were thoroughly investigated.

2. Material and methods

2.1 Materials

The composition before extraction of Li₂CO₃ are Li (5.0g/L), Mg (81.1g/L), B₂O₃ (7.45g/L) and SO₃ (18.01g/L). The chemical composition of the MgO-rich byproduct obtained from the extraction of Li₂CO₃ is listed in Table 1. The main elements present are magnesium and boron. Figure 1 shows the XRD spectrum of the byproduct before calcination. The major mineral phases observed include Mg(OH)₂ and Mg₃B₂O₆, with a minor MgO phases also present. Given that Mg(OH)₂ was found in the byproduct, its calcination at temperatures that achieve the decomposition of Mg(OH)₂ to MgO was required prior to its use in the preparation of MPC.

The decomposition temperature of Mg(OH)₂ was determined by thermogravimetric (TG) and differential thermal analyses (DTA). Figure 2 depicts the TG-DTA curves of the byproduct. An endothermic peak was found between 320°C and 400 °C, and the decomposition rate reached its maximum value at 364.3 °C. The weight-loss changes in the TG curve are due to the decomposition of Mg(OH)₂ and the evaporation of H₂O, as depicted in Eq. (1). The highest weight loss observed was 23.89%. Based on the TG-DTA results, we conclude that the calcination temperature needs to be higher than 800 °C in order to achieve complete decomposition of Mg(OH)₂.

\[
\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \tag{1}
\]

The raw material used in this study was a byproduct from the extraction process of Li₂CO₃ obtained from the Qing Hai Citic Guoan Technology Development Co., Ltd, Qing Hai, China. Figure 3 shows how the Li₂CO₃ from the salt lakes is processed, including the generation of the magnesium hydroxide byproduct. First, the saturated brine containing lithium metal is dried to form lithium magnesium chloride, followed by calcination to form lithium magnesium slag. A mother liquor and lithium magnesium slag are produced after washing and filtering the lithium-containing magnesium slag. After evaporation and concentration of the mother liquor, sodium carbonate is added to produce lithium carbonate. The maximum particle size of the solid byproduct generated in this manner ranges up to about 30 mm. Calcination and grinding by ball-milling are required in order to obtain active magnesia powder. The byproduct was then calcined at high temperatures in an electric furnace at a heating rate of 5 °C/min. Once the specified temperature was reached, the temperature remained unchanged for an hour and the cooling rate was 10k/s. The calcination temperatures investigated were 800°C, 900°C, 1000°C, and 1100 °C. After calcination, the byproduct was ground in a planetary ball mill (PM2L) at 45 rad/min for 5 min. The byproduct was put into the steel bottle and occupied 2/3 of the volume. After 5min, the powder was passed through a sieve with a diameter...
of 75 μm and the amount of residue after being sieving accounted less than 10% of the total (Wu 2014).

The final powder was then used in the preparation of MPC. In addition, chemical-grade potassium dihydrogen phosphate (KH₂PO₄ or KDP), provided by the Tianjin Hongyan Reagent Co., China, was also used throughout these experiments.

### 2.2 Specimen preparation

The molar ratio of MgO to KDP (M/K) was 4, and the water to cement ratio (w/c) was fixed at 0.25. For the preparation of MPC, the powder of KDP was milled, then was mixed with the powder of byproduct and a specific amount of water was added at last. The mixture was agitated by hand at a high speed for 60 s. The paste was then cast into 20 × 20 × 20 mm steel molds and cured at a temperature of 20 ± 3 °C and a relative humidity of 50 ± 5%. The reaction process of MgO, KDP and water was speculated by detecting the change of pH. Given that MPC has a short setting time, making it difficult to detect changes in pH over time, KH₂PO₄ was first dissolved in sufficient water to form a solution before addition of the calcined byproduct (the M/K and w/c ratios were 4 and 10, respectively).

The setting times of the MPC pastes containing EL-MgO calcined at various temperatures were measured by a Vicat apparatus at 20 ± 3 °C, according to ASTM standard C807-05. The compressive strengths of the cured MPC samples at different ages were measured using strength testing equipment with a maximum load of 300 kN and a loading rate of 2.4 kN/s.

The chemical and mineralogical compositions of EL-MgO were determined by X-ray fluorescence (XRF, Axios PW4400) and X-ray diffraction (XRD). The powder samples were prepared by crushing the specimens and passing the powder through a sieve with a screen aperture of 75 μm, and then were tested by X-ray diffraction (XRD, PANalytical XPROPert) with CuKa radiation (k = 0.15419 nm) and 30 kV of acceleration voltage condition over a 2θ range of 5–70°. The surfaces of the EL-MgO calcined at different temperatures and those of MPC samples cured in air for 1 h and 28 d were examined by scanning electron microscopy (SEM, Jeol JSM-5610LV).

Moreover, the composition of mineral phases was determined by the Rietveld method (Sglavo et al. 2011) using Topas 4.2 software. First, XRD spectrum was put into Topas 4.2 software and then full spectrum fitting method was used to perform qualitative analysis. The specific surface area of EL-MgO calcined at various temperatures was determined by the Brunauer-Emmett-Teller (BET) method. In order to evaluate the reactivity of EL-MgO, 5 g of magnesia powder was placed in 50 mL of 10.0 wt% citric acid solution with phenolphthalein. Reactivity was determined by the time required for the color of the solution to change from colorless to pink. The porosities and distributions of the MPC-sample pores cured in air for 28 d were determined by

![Fig. 3 Lithium carbonate production process and magnesium hydroxide byproduct generation.](image-url)
mercury intrusion porosimetry (MIP), using an automatic mercury porosimeter (Micromeritics Auto Pore IV 9500). MIP tests were performed on samples of approximately 1.5 cm³. A Pascal 440 mercury porosimeter with a maximum load capacity of 420 MPa was used. However, the maximum pressure was limited to 200 MPa in order to avoid cracks induced by the mercury pressure. The adopted mercury surface tension and contact angle between the mercury and the solid surface were 48.2 mN/m and 142°, respectively. The pore diameters related to the pressure applied were calculated with the Washburn equation (Washburn 1921). Samples were first dried at 40 °C for 24 h, and then vacuum-dried at 20 ± 2 °C for two weeks at 0.1 bar.

The pH changes of the MPC cement pastes were measured using a calibrated pH meter. According to the standard method described in GB/T12959-2008, the hydration-heat-release rates of the MPC samples at different hydration times were determined using a cement hydration heat meter (YT12659-16). The alternating-current (AC) impedance of each MPC mortar (with a 1:1 weight ratio of standard sand to MPC) was determined using a CH Instruments CHI604E electrochemical workstation with two 40 × 40 mm stainless-steel plate electrodes. The AC impedance frequency was set to a value higher than 10 kHz, where the AC impedance approaches the pore solution resistance (Hafiane et al. 2000). In addition, the AC amplitude and sample interval were set at 0.005 V and 10 s, respectively.

3. Results and discussion

3.1 Effect of calcination temperature on the properties of the MgO-rich byproduct

Table 2 shows the XRD spectra of EL-MgO after calcination at different temperatures. The main mineral phases present in EL-MgO are MgO and Mg₃B₂O₆. After calcination of the as-received byproduct, the diffraction peaks corresponding to Mg(OH)₂ disappeared giving rise to MgO peaks. This confirms that the reaction shown in Eq. [1] had taken place. Moreover, the contents of the crystal phases, as obtained by the Rietveld method using the TOPAS 4.2 software are shown in Table 2 (Sglovo et al. 2011). The MgO content was observed to increase after byproduct calcination, reaching a maximum value of 80.40% at a calcination temperature of 1100 °C. In contrast, the Mg(OH)₂ content was reduced to zero under these conditions. In addition, the Mg₃B₂O₆ content increased to about 18% after calcination. The crystallite dimensions of EL-MgO calcined at different temperatures were calculated according to the Scherrer equation.

\[
D = \frac{(K \times \lambda)}{(B \times \cos \theta)}
\]  

where \(D\) is the crystallite size, \(K\) is a shape constant and is 0.89 when \(B\) is the full width at half-maximum of the diffraction peak, and \(\theta\) is the Bragg angle.

The crystallite dimensions were found to increase with increasing calcination temperature. The calcination temperature has a substantial effect on the degree of crystallization of EL-MgO; increasing calcination temperature leads to more prominent crystallization.

SEM images of the byproduct calcined at different temperatures are shown in Fig. 5. Table 3 lists some characteristics of the byproduct after calcination at vari-

| Temperature/°C | MgO/% | Mg(OH)₂/% | Mg₃B₂O₆/% | NaCl/% | Crystallite dimensions /nm |
|----------------|-------|-----------|-----------|--------|---------------------------|
| Before calcinating | 5.91  | 79.84     | 10.94     | 3.31   | 24.02                     |
| 800             | 78.74 | 0         | 18.51     | 2.76   | 33.45                     |
| 900             | 80    | 0         | 18.77     | 1.23   | 42.94                     |
| 1000            | 80.36 | 0         | 18.34     | 1.30   | 50.03                     |
| 1100            | 80.40 | 0         | 18.22     | 1.38   | 52.58                     |

| Temperature/°C | BET surface area (m²/g) | Citric acid color changing time /S |
|----------------|-------------------------|-------------------------------------|
| Before calcinating | 13.21                | 60                                  |
| 800             | 9.71                    | 75                                  |
| 900             | 4.44                    | 400                                 |
| 1000            | 2.69                    | 660                                 |
| 1100            | 1.62                    | 1923                                |

Fig. 4 XRD spectra of the byproduct at different calcination temperatures.
ous temperatures. As seen in Fig. 5, particle agglomeration occurred when the calcination temperature was low. This is due to the high BET surface area of EL-MgO (Table 3). In addition, EL-MgO, with a high BET surface area and low degree of crystallization, exhibited more surface flaws that inevitably led to higher reactivity. This was verified by the times taken for the citric acid solutions to change color, as listed in Table 3.

Hence, we concluded that MPC performance could be tailored by controlling the hydration process.

3.2 Effect of the EL-MgO calcination temperature on MPC setting time

The setting time is a very important performance parameter of MPC pastes. Borax or boric acid is usually added to prolong the setting time. With the addition of 10 wt% borax (relative to Mg), setting times that meet the requirements for use on construction sites are achieved (Yang et al. 1999). In this study, through increasing calcination temperature and, as a consequence, improved degrees of EL-MgO crystallization, the MPC setting time was prolonged without the addition of borax. The effect of the EL-MgO calcination temperature on MPC setting time is presented in Table 4. The setting time was found to be extended with increasing calcination temperature. For instance, the setting time increased from 5 to 35 min as the EL-MgO calcination temperature increased from 800 to 1100 °C. Therefore,

Fig. 5 SEM images of the byproduct calcined at different temperatures. (a) 0 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1100 °C
the setting time of the MPC paste can be adjusted by changing the calcination temperature of EL-MgO.

3.3 Effect of the EL-MgO calcination temperature on MPC compressive strength

The compressive strength of MPC pastes prepared with EL-MgO calcined at different temperatures was measured at curing ages of 1 h, 1 d, 3 d, 7 d and 28 d (Fig. 6). Overall, the compressive strength of the MPC pastes increased with curing time. For example, the compressive strength of the MPC specimen prepared with EL-MgO calcined at 1000 °C and cured for 28 d was 64.6%, 29.4%, 15.0%, and 6.4% higher than that of specimens cured for 1 h, 1 d, 3 d, and 7 d, respectively. The early compressive strength was seen to first increase and then decreased with increasing EL-MgO calcination temperature. The MPC specimen prepared with EL-MgO calcined at 1000 °C had the highest compressive strength. It is worth noting that the compressive strength of MPC with EL-MgO calcined at 1000 °C was 26 MPa and 53.9 MPa after curing for 1 h and 1 d, respectively. The setting time was 22 min, which means that it had a similar performance to that of quick-repair materials used in traffic areas. In this paper, MPC prepared with EL-MgO calcined at a lower temperature (1000 °C) was comparable to that prepared with dead burnt magnesia calcined at 1700 °C, without the addition of borax. Hence, lower-cost MPC samples with high compressive strengths and good working performance were prepared using MgO-rich byproducts sourced through the extraction of Li₂CO₃ from salt lakes.

3.4 Effect of the EL-MgO calcination temperature on the hydration products and microstructure

Figure 6 displays the XRD spectra of MPC pastes prepared with EL-MgO calcined at different temperatures (from 800 to 1100 °C) hydrated for 1 h and 28 d, and the relative quantities of the various components determined from these spectra are listed in Table 5. The XRD spectra reveal that the main hydration product in MPC was MgKPO₄·6H₂O, along with MgO, Mg₃B₂O₆, and KDP phases were also found in the MPC paste. As seen in Table 5, the relative quantity of MgO in the 1 h-cured samples increased and that of MgKPO₄·6H₂O decreased with increasing EL-MgO calcination temperature. This is due to the rapid chemical reaction between the EL-MgO calcined at low temperatures and KDP, as well as the high degree of hydration. Hence, more of the MgO was consumed and more of the MgKPO₄·6H₂O phase was produced. However, high EL-MgO calcination temperatures led to slower chemical reactions and lower degrees of hydration. Although MPC prepared with EL-MgO calcined at 800 °C had the highest level of MgKPO₄·6H₂O (32.94%) after curing for 1 h, the compressive strength did not follow the same trend. This is because the rapid chemical reaction led to fast nucleation that hindered crystal growth,
as shown in Figs. 8a and 8b. In addition, the large porosity (see Fig. 10, below) also affected the compressive strength. It is worth noting that the KDP was present in large quantities when the EL-MgO calcination temperature was 800 °C after the MPC samples had been cured for 1 h. This is due to the fact that the degree of the hydration reaction between MPC and EL-MgO calcined at 800 °C was high and, therefore, the water in MPC was consumed in large quantities resulting in the precipitation of KDP. This, however, does not mean that precipitated KDP was not involved in the hydration reaction. The concentration of KDP in the liquid phase decreased as the hydration reaction continued. The precipitated KDP then dissolved and continued to participate in the hydration reaction; this was confirmed by the reduced relative concentrations of KDP in the MPC specimens cured for 28 d (Table 5).

Table 5 The relative quantities of the MPC pastes.

| Temperature/°C | Age  | MgO/wt% | MgKPO$_4$:6H$_2$O/wt% | Mg$_3$B$_2$O$_6$/wt% | KH$_2$PO$_4$/wt% |
|---------------|------|---------|------------------------|----------------------|-----------------|
| 800           | 1h   | 42.09   | 32.94                  | 18.73                | 6.24            |
|               | 28d  | 36.2    | 45.50                  | 18.30                | 0               |
| 900           | 1h   | 48.2    | 33.56                  | 18.24                | 0               |
|               | 28d  | 32.8    | 50.25                  | 16.95                | 0               |
| 1000          | 1h   | 51.58   | 30.40                  | 18.02                | 0               |
|               | 28d  | 30.07   | 55.00                  | 14.93                | 0               |
| 1100          | 1h   | 53.7    | 28.80                  | 17.50                | 0               |
|               | 28d  | 33.5    | 52.08                  | 14.42                | 0               |

Table 5 also reveals that the relative quantities of MgKPO$_4$:6H$_2$O and MgO increase and decrease, respectively, with the curing time. MPC prepared with EL-MgO calcined at 1000 °C had the highest relative quantity of MgKPO$_4$:6H$_2$O (55%) after curing for 28 d. This is consistent with our findings regarding the development of compressive strength.

SEM images of MPC prepared with EL-MgO calcined at various temperatures after curing for 1 h and 28 d are presented in Figs. 8 and 9 respectively. The hydration product (MgKPO$_4$:6H$_2$O) was detected by EDS. As seen in Fig. 8c, samples of MPC prepared with EL-MgO calcined at 1000 °C, and cured for 1 h exhibited

Fig. 8 SEM images of MPC prepared by EL-MgO calcined at various temperatures and cured for 1 h. (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C
bar-shaped hydration products, while the remaining products were mainly granular in shape. This is because EL-MgO calcined at low temperatures induces faster chemical reactions leading to rapid nucleation in the MPC. As a result, crystal growth was hindered. Calcination of EL-MgO at high temperatures results in lower EL-MgO reactivity, and therefore, chemical reactions and crystal nucleation rates in MPC were slow. As the reaction progressed, more products were produced as shown in Fig. 9. After curing for 28 d, the sizes of the hydration-product particles in the MPC prepared with EL-MgO calcined at 1000 °C became large. Some particles even turned into thin sheets or short bars. This growth can be beneficial for the development of strength.

3.5 Effect of EL-MgO calcination temperature on MPC porosity
The mechanical strength of MPC is linked to the content and microstructure of the hydration products, as well as its porosity and pore distribution. The pores in MPC mainly consist of pores in MgO particles, pores between MgO particles, pores between MgO particles and hydration products, and pores between hydration products. As shown in Fig. 10, the cumulative MPC porosity exhibits a downward trend with increasing EL-MgO calcination temperature. For example, the cumulative porosities of MPC prepared with EL-MgO calcined at 800 °C and 1100 °C were 17.03% and 5.7%, respectively, after 28 d. The degree of crystallization in EL-MgO increased and crystal defects were minimized when EL-MgO was calcined at high temperatures. The pores in the MgO parti-

![Fig. 9 SEM images of MPC prepared by EL-MgO calcined at various temperatures and cured for 28 d. (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C](image)

![Fig. 10 Cumulative porosities of MPC with EL-MgO calcined at various temperatures after hydration for 28 d. [D is the pore diameter (nm)]](image)
cles and the pores between EL-MgO particles also decreased. However, the cumulative porosity of the MPC prepared with EL-MgO calcined at 1000 °C was slightly lower than that of the material calcined at 1100 °C. This is due to a higher degree of hydration (Table 5) when EL-MgO was calcined at 1000 °C. It is consistent with the higher compressive strength of MPC prepared with EL-MgO calcined at 1000 °C. The higher degree of hydration limited the growth of pores between MgO particles and hydration products, and pores between hydration products.

### 3.6 Effect of EL-MgO calcination temperature on pH and MPC alternating-current impedance

\[
\begin{align*}
\text{KH}_2\text{PO}_4 & \rightarrow \text{K}^+ + 2\text{H}_2\text{PO}_4^- \quad (3a) \\
\text{H}_2\text{PO}_4^- & \rightarrow \text{H}^+ + \text{HPO}_4^{2-} \quad (3b) \\
\text{MgO} + \text{H}_2\text{O} & \rightarrow \text{MgOH}_{\text{surface}} + \text{OH}^- \quad (4) \\
\text{H}_2\text{PO}_4^- + \text{MgOH}_{\text{surface}} + \text{OH}^- & \rightarrow \text{Mg}^{2+} + \text{PO}_4^{3-} + \text{H}_2\text{O} \quad (5) \\
\text{Mg}^{2+} + \text{PO}_4^{3-} + \text{K}^+ & \rightarrow \text{MgKPO}_4.6\text{H}_2\text{O} \quad (6)
\end{align*}
\]

Figure 11 depicts pH as a function of time for the various MPC samples. The pH of the MPC tended to increase initially before stabilizing. After the addition of KH₂PO₄ into water, K⁺, H⁺, H₂PO₄⁻, and HPO₄²⁻ were rapidly released, as shown in Eqs. (3a) and (3b). When the calcined byproduct comes into contact with water, OH⁻ is released, according to Eq. (4). The concentration of OH⁻ increases following hydration of the MgO in the byproduct, resulting in a rapid increase in pH. As shown in Fig 12, the alternating-current impedance of MPC mortars prepared with EL-MgO calcined at 1000 °C and 1100 °C decreased slightly before 0.07 h. As seen in Fig. 11, pH increased faster during the early stage (< 1 h) and was inversely related to increases in the EL-MgO calcination temperature. This was due to the fact that EL-MgO calcined at low temperature is more reactive and has a high specific surface area, which helps promote rapid reactions between MgO and water. The pH of the MPC mortars prepared with EL-MgO calcined at 800 °C and 900 °C decreased slightly after curing for 1 h. On the other hand, a steady increase in pH was observed for MPC mortars prepared with EL-MgO calcined at 1000 °C and 1100 °C. The concentration of Mg²⁺ and PO₄³⁻ increased continuously as hydration progressed, in accordance with Eq. (5). Once the concentration of MgKPO₄.6H₂O reached supersaturation, precipitates formed according to Eq. (6). This reaction led to increases in the solid phase and decreases in the diffusion rate of water on the MgO particle surface. The reaction described in Eq. (4) then slows down and the OH⁻ release rate becomes slower than the H⁺ ionization rate. Therefore, the pH values drop slightly.

It is worth noting that it was difficult to detect the drop in alternating-current impedance during the early stage (< 0.1 h) for MPC mortars prepared with EL-MgO calcined at 800 and 900 °C. This is due to the fact that the hydration reaction involving EL-MgO calcined at 800 and 900 °C was so fast that reactions shown in Eqs. (4), (5), and (6) were all accelerated. Hence, the rapid formation of the hydration product (MgKPO₄.6H₂O) led to an increase in the alternating-current impedance. For the MPC mortar prepared with EL-MgO calcined at 800 °C, both the precipitation of K₂HPO₄ (as seen in Fig. 11) and the decreasing concentration of K⁺ and H₂PO₄⁻ in solution also contribute to the increase in alternating-current impedance. For the MPC mortar prepared with EL-MgO calcined at 800 °C, Mg²⁺ was more slowly released.
and consumed, and MgKPO₄·6H₂O supersaturation could not achieve in a short time as a consequence. Therefore, the alternating-current impedance increased slowly during the early stage (< 1 h), followed by a more rapid increase as the consumption of water and formation of precipitates progressed. The MPC mortar prepared with EL-MgO calcined at 1000 °C had the highest alternating-current impedance after curing for 1 h.

3.7 Effect of EL-MgO calcination temperature on MPC hydration heat

The heat-release-rate curves for the MPC pastes with EL-MgO calcined at various temperatures are presented in Fig. 13. The curves for the pastes with EL-MgO calcined at 1000°C and 1100 °C exhibit two prominent exothermic peaks, whereas the curves of MPC pastes prepared with EL-MgO calcined at 800 and 900 °C show only one exothermic peak.

With the constant dissolution of KH₂PO₄, the concentration of H₂PO₄⁻ in solution increased continuously, accelerating the reaction shown in Eq. (5) and, as a consequence, leading to an increase in the exothermic rate. When the H₂PO₄⁻ consumption rate is higher than its dissolution rate, the concentration of H₃PO₄ decreases in a decrease in the reaction rate. As the concentration of Mg²⁺ and PO₄³⁻ in the solution increase. When the supersaturation point is exceeded, hydration products (MgKPO₄·6H₂O) are formed accompanied by a release of heat.

However, the heat-release-rate curves for the MPC pastes prepared with EL-MgO calcined at 800 and 900 °C exhibit only one exothermic peak, mainly because the hydration reaction involving EL-MgO calcined at 800 and 900 °C is fast, i.e., Mg²⁺ is rapidly formed in solution, and Mg²⁺ supersaturation occurs in a short time. This process is accompanied by the formation of the hydrated product (MgKPO₄·6H₂O), whereas the crystal growth is poor due to rapid nucleation.

4. Conclusions

This study investigated the effect of EL-MgO calcination temperature on the setting time, mechanical strength, hydration phases, porosities, pH changes, alternating-current impedance, and hydration-heat release rates of MPC. The following conclusions are drawn:

(1) The byproduct generated after extracting Li₂CO₃ from salt lakes can be used to prepare high-early-strength MPC.

(2) The setting time and crystal morphology of MPC can be adjusted by controlling the calcination temperature of EL-MgO used for its preparation.

(3) The compressive strength initially increased and then decreased with increasing EL-MgO calcination temperature. The MPC specimen prepared with the byproduct calcined at 1000 °C had the highest compressive strength. When EL-MgO was calcined at 1000 °C, the setting time of the MPC paste was 22 min and the compressive strength reached 53.9 MPa after 1 d, which is relatively high for a quick-repair material.

(4) The calcination temperature of EL-MgO had a substantial impact on the hydration-heat-release rate of MPC. When EL-MgO was calcined at high temperatures of 1000 °C and 1100 °C, the heat-release-rate curves of the MPC pastes exhibited two prominent exothermic peaks. On the other hand, the heat-release-rate curves of MPC pastes prepared with EL-MgO calcined at the lower temperatures of 800 °C and 900 °C exhibited one exothermic peak. The first peak is believed to be associated with changes in the H₂PO₄⁻ concentration, while the second peak is associated with the formation of the crystalline product. When calcining of the byproduct was carried out 800 °C and 900 °C, nucleation in of MPC paste was so fast that crystal growth was not favored.

(5) Finally, it is not clear whether or not impurities (mainly Mg₃B₂O₆) influence crystal defects and the formation of MPC. This requires further study.

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References

Abdelrazig, B., Sharp, J. and El-Jazairi, B., (1988). “The chemical composition of mortars made from magnesium phosphate cement.” Cem. Concr. Res., 18(3), 415-425.

Dong, J. and Yu, H., (2016). “Effects of calcination temperature of boron-containing magnesium oxide raw materials on properties of magnesium phosphate cement as a biomaterial.” Wuhan Univ. Technol. Mater. Sci. Ed., 31(3), 671-676.
Formosa, J., Chimenos, J. M., Lacasta, A. M. and Niubó, M., (2012). “Interaction between low-grade magnesium oxide and boric acid in chemically bonded phosphate ceramics formulation.” Ceram. Int., 38(3), 2483-2493.

Gardner, L. J., Bernal, S. A., Walling, S. A., Corkhill, C. L., Provis, J. L. and Hyatt, N. C., (2015). “Characterization of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag.” Cem. Concr. Res., 74(3), 78-87.

Hafiane, Y., Simith, A. and Bonnet, J. P., (2000). “Electrical characterization of aluminous cement at early ages the 10 Hz-1 GHz frequency range.” Cem. Concr. Res., 30(7), 1057-1062.

Hall, D. A., Stevens, R. and Jazairi, B. E., (2001). “The effect of retarders on the microstructure and mechanical properties of magnesia–phosphate cement mortar.” Cem. Concr. Res., 31(3), 455-465.

Ibrahim, W. A., Sibak, H. A. and Abadir, M. F., (2011). “Preparation and characterization of chemically bonded phosphate ceramics (CBPC) for encapsulation of harmful waste.” Am. J. Sci., 7(1), 543-548.

Kräger, R., Seitz, J. M., Ewald, A. Bach, F. M. and Groll, J., (2013). “Strong and tough magnesium wire reinforced phosphate cement composites for load-bearing bone replacement.” J. Mech. Behav. Biomed. Mater., 20(2), 3644.

Li, Y. and Chen, B., (2013). “Factors that affect the properties of magnesium potassium phosphate cement.” Constr. Build. Mater., 47(3), 977-983.

Postl, W. and Bojar, H., (2008). “Struvite-(K), KMgPO4·6H2O, the potassium equivalent of struvite – a new mineral.” Eur. J. Mineral., 20(4), 629-633.

Popovics, S., Rajendran, N. and Penko, M., (1987). “Rapid hardening cements for repair of concrete.” ACI Mater. J., 84(1), 64-73.

Roy, D. M., (1987). “New strong cement materials: chemically bonded ceramics.” Science, 235, 651-658.

Sarker, A. K., (1990). “Phosphate cement-based fast-setting binders” Ceram. Bull., 69(2), 234-238.

Sasaki, K. and Moriyama, S., (2014). “Effect of calcination temperature for magnesite on interaction of MgO-rich phases with boric acid.” Ceram. Int., 40(1), 1651-1660.

Seehra, S. S., Gupta, S. and Kumar, S., (1993). “Rapid setting magnesium phosphate cement for quick repair of concrete pavements—characterization and durability aspects.” Cem. Concr. Res., 23(2), 254-266.

Sglovo, V., Genua, F. D., Conci, A., Ceccato, R. and Cavallini, R., (2011). “Influence of curing temperature on the evolution of magnesium oxychloride cement.” J. Mater. Sci., 46(20), 6726-6733.

Singh, D., Mandalika, V. R., Parulekar, S. J. and Wagh, A. S., (2006). “Magnesium potassium phosphate ceramic for Tc-99 immobilization.” J. Nucl. Mater., 348(3), 272-282.

Soudée, E. and Péra, J., (2002). “Influence of magnesia surface on the setting time of magnesia-phosphate cement.” Cem. Concr. Res., 32(1), 153-157.

Soudée, E. and Péra, J., (2000). “Mechanism of setting reaction in magnesia-phosphate cements.” Cem. Concr. Res., 30(2), 315-321.

Vianii, A. and Guaitier, A. F., (2014). “Preparation of magnesium phosphate cement by recycling the product of thermal transformation of asbestos containing wastes.” Cem. Concr. Res., 58(3), 56-66.

Wagh, A. S., Singh, D. and Jeong, S. Y., (1995). “Stabilization of hazardous ash waste with newbeyrite-rich chemically bonded magnesium phosphate ceramic.” United States: N. p., 1995. Web. doi:10.2172/510298, 35p.

Wang, L., Tai, P., Jia, C., Li, X., Li, P. and Xiong, X., (2015). “Magnesium contamination in soil at a magnesite mining region of Liaoning province, China.” Bull. Environ. Contam. Toxicol., 95(1), 90-96.

Wang, A., Zang, J., Li, J., Ma, A. and Liu, L., (2013). “Effect of liquid-to-solid ratios on the properties of magnesium phosphate chemically bonded ceramics.” Mater. Sci. Eng., 33(5), 2508-2512.

Washburn, E. W., (1921). “The dynamics of capillary flow.” Phys. Rev., 17, 273-283.

Wu, C., (2014). “Fundamental theory and civil engineering application of basic magnesium sulfate cement.” University of Chinese Academy of Sciences, 147-151.

Wu, F., Wei, J., Guo, H., Chen, H. F., Hong, H. and Liu, C., (2008) “Self-setting bioactive calcium-magnesium phosphate cement with high strength and degradability for bone regeneration.” Acta Biomater., 4(6), 1873-1884.

Yang, J. and Qian, C., (2010). “Effect of borax on hydration and hardening properties of magnesium and potassium phosphate cement pastes.” Wuhan Univ. Tech. Mater. Sci., 25(4), 613-618.

Yang, Q. B., Zhu, B. R., Zhang, S. Q. and Wu, X. L., (2000). “Properties and applications of magnesia-phosphate cement mortar for rapid repair of concrete.” Cem. Concr. Res., 30(11), 1807-1813.

Yang, Q. B. and Wu, X. L., (1999). “Factors influencing properties of phosphate cement-based binder for rapid repair of concrete.” Cem. Concr. Res., 29(1), 389-396.