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Magnesium Phosphate Cements formulated with a low-grade MgO by-product: Physico-mechanical and durability aspects

J. Formosa [a,*], A.M. Lacasta [b], A. Navarro [c], R. del Valle-Zermeño [a], M. Niubó [a], J.R. Rosell [c], J.M. Chimenos [a]

[a] *Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain*
[b] *Departament de Física Aplicada, Universitat Politècnica de Catalunya, Av. Dr. Marañón 44-50, 08028 Barcelona, Spain*
[c] *Departament de Construccions Arquitectòniques II, Universitat Politècnica de Catalunya, Av. Dr. Marañón 44-50, 08028 Barcelona, Spain*

HIGHLIGHTS

- MPC formulated with LG-MgO by-product were selected from preliminary study.
- Evaluation as repairing mortar: adhesion and MOE tests.
- Durability studies evaluating the porosity and sorptivity prior and post-aging.
- MPCs formulated with LG-MgO by-product show good durability and repairing properties.

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ABSTRACT

Chemically Bonded Phosphate Ceramics (CBPCs) and, in particular, Magnesium Phosphate Cements (MPCs), show properties very adequate for using as repair mortar for concrete constructions. The obtainment of MPC using MgO-containing by-products as raw materials was proposed by the authors in previous works. There, formulations including boric acid as additive were optimized to obtain good mechanical properties and proper setting times. The current study aims to analyze the viability of the developed formulations to be used as repair mortar. Adhesion to concrete surfaces was evaluated, and in all cases good adhesion strength values were obtained. The durability tests, including freeze/thaw cycles and salts crystallization cycles, have shown an excellent behavior, especially the samples containing the higher amount of boric acid. These promising results indicate that MPC formulated with a low-cost MgO by-product can be an interesting alternative to other repair mortars. In addition to economic benefits in terms of cost of production, the use of by-products has a positive impact on environmental and sustainability aspects.

1. Introduction

Repairing materials for construction are a subject of increasing interest. The great number of existing concrete structures suppose a great potential demand of repairing material. Sometimes the reparation must be carried on a few years after the concrete structure has been completed. The possibility of using a good repairing material or system supposes an economic benefit instead of substituting the damage concrete. In this sense, it is of high interest to make improvements by developing new materials, reducing costs, and others aspects that have to be considered in the building and construction sector [1].

Nowadays, the most commonly used repairing materials are polymer mortars and ordinary Portland cement (OPC) mortars [2,3]. In general, the OPC mortars are used owing to their wide range of work and potential fields of application. However, the use of polymer mortars may cover other particular characteristics needed because of their higher adhesion to the substrate, lower shrinkage and permeability [4]. Nevertheless, polymer mortars have problems associated with the thermal behavior due to their glass transition temperature [5]. Moreover, most polymeric materials undergo degradation when exposed to UV radiation and aggressive chemicals [6]. The exposition range of temperature must also be taken into account in resins binders [7].

However, over the last few years, more specific cements have been developed; which could extend the range of work and their application in other fields of technology. Chemically Bonded Phosphate Ceramic (CBPC) is one of those new developed cements,

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* Corresponding author. Tel.: +34 934037244; fax: +34 934035438.
E-mail address: joanformosa@ub.edu (J. Formosa).

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and it is frequently used as stabilizing agents and/or encapsulation [8–12] of hazardous wastes, either radioactive or with a high potential of leaching [13]. Moreover, other studies have already highlighted their potential use as repairing materials [14–21].

The formation of CBPCs is an acid-base reaction. This reaction takes place between a cationic metal (basic) and an oxyanion (acid, mainly phosphate), as described in the following equation [22]:

$$MO_n + nH_3PO_4 \Longleftrightarrow M(HPO_4)_n + nH_2O \tag{1}$$

The chemical setting process for the formation of CBPC is controlled by the dissolution and hydrolysis of metal oxides. For this reason, not all cationic metal oxides are valid for the formation of this cement [22]. A high reactivity of metal oxide increases the speed of formation of the corresponding phosphates, generating precipitates but not forming coherent structures [22,23].

The formation of CBPC using MgO and KH_2PO_4 leads to the formation of K-struvite –$KMg(PO_4)\cdot6H_2O$–, one of the CBPCs with best properties for its use as high-performance cement [23]. These kind of cements are commonly named Magnesium Phosphate Cement (MPC) [24–35]. According to the above mentioned, the MgO dissolution rate is the main parameter to form correct structures. In this sense, a pre-calcination process allows to control reactivity and thus the setting time of MPC [36]. The use of a high purity MgO requires a previous calcination at 1300 °C in order to improve its dissolution rate [22]. Thus, besides the high cost of raw materials, the cost of the calcination process must been also taken into account. Therefore, the high cost of the raw materials for the K-struvite formulation is the main inconvenient for its potential use as a substitute of OPC in some specific applications. Moreover, the formation rate of MPC using a high purity MgO has been extensively studied and cited in the literature, concluding that it is possible to use a small percentage of boron compounds as setting time retardants [26,27,29–32,37–40]. Furthermore, this ceramic's formation is very fast and the mechanical properties are good, allowing considering it for its potential use as repairing material [18,30]. Generally, the moisture of old concrete and the curing conditions have a significant influence on the repairing quality, especially on the interfacial bond between repair material and old concrete [18,41]. It is generally agreed that properties such as strength, elastic modulus, drying shrinkage and permeability are critical to the success of repairing [42].

In order to overtake the economical limitation, the authors have studied the possibility of obtaining a MPC formulated with a low-grade magnesium oxide (LG-MgO) [43,44], which is obtained as a by-product from the calcination process of natural magnesite [45]. By this manner, the cost of the products could be substantially diminished, and the mortar obtained would be a competitive alternative, while enhancing sustainability criteria and recyclability. According to the above mentioned, from previous works carried out by the research group [44], the relationship between LG-MgO, monopotassium phosphate (MKP), water kneaded, and boric acid (HB) as additive was determined, with the aim of finding a cement with a formulation that allows an optimum performance with good mechanical properties and hardening time [44]. Subsequently, a range of optimal dosages employing LG-MgO as raw material was determined. The properties obtained in this previous study showed that it is possible to formulate cements with a desirable compressive strength and/or setting time by using Design of Experiments (DoE) in the range studied. These results confirmed their potential use as repair construction material. Thus, the aim of the present study is to verify that these optimal dosages can be used as repairing material for concrete, achieving to reinforce structures while guaranteeing strength, stability and durability. In other words, the MPC formulated with LG-MgO must possess good mechanical properties, good adhesion to the surface to be repaired, a correct Modulus of Elasticity (MOE) value as well as an acceptable setting time. This work improves the performance and applicability of the optimal formulation. During the evaluation as a repair mortar, other properties such as the durability were also assessed.

2. Experimental procedure

As aforementioned, the experimental procedure described below followed the preliminary studies carried out by the authors [44]. Taking into account the setting time, workability and compressive strength values at different curing times, some formulations from the preliminary study were selected to evaluate repairing properties.

2.1. Materials

Low-grade magnesium oxide (LG-MgO) was supplied by Magnesitas Navarras S.A. based in Navarra (Spain). This LG-MgO is derived from the calcination of natural magnesite in a rotary kiln at 1100 °C. It is a by-product collected as cyclone dust in the fabric filters from the air pollution control system. Around 100 kg of LG-MgO were taken from various stockpiles. The sample was previously homogenized, quartered to a 1/16 split and dried in an oven at 105 °C for 24 h in order to obtain a representative sub-sample of about 500 g for physical and chemical characterization. The physical–chemical characterization of LG-MgO consisted in an analysis and an elementary structural characterization with X-ray Diffraction (XRD) and X-ray Fluorescence (XRF), as well as determining the density, the particle size distribution (PSD) and the specific surface. The source of phosphate employed for this study was monopotassium phosphate (MKP), KH_2PO_4, food grade, which is commonly used as a fertilizer. The characterization of the physical–chemical properties of MKP consisted of XRD to determine the presence of crystalline phases, qualitative XRF to determine its purity, the PSD and density. Moreover, a boric acid, Optibor® technical grade (HB), H_3BO_3, supplied by Borax España, S.A. (Castellón, Spain), was also used as a setting time retardant. An exhaustive description of the raw materials was carried out in an earlier study [44] and therefore the present paper only shows significant and relevant information.

2.2. Magnesium Phosphate Cements formulation and preparation

For all the experimental trials the water to solid ratio (W/S) was fixed at 0.24. Then, the MPC was prepared as a mixture of the different solid reagents in weight and then the tap kneading water was added. Table 1 summarized the references, dosages, and the mechanical properties obtained in a previous study [44] for the selected formulations. HB percentage refers to the weight of the solid mixture of MKP and LG-MgO, and it is considered as an extra addition to the solid content (LG-MgO and MKP).

2.3. Testing procedures

Different test specimens were casted in order to perform the different experiments carried out in this study. In this sense, it is very important to study properties such as MOE, bond adhesion, etc. Thus, MOE and bond adhesion were evaluated with two different kind of experimental tests each. Moreover, it is remarkable the need of studying the durability of this kind of MPC. Subsequently, durability tests were also carried out. Porosity is fundamental for a construction material as it can exert an influence on durability; therefore the open porosity accessible to water was measured. Testing of water absorption coefficient (capillarity) was also carried out. This test takes into account the water that mainly penetrates into construction materials by absorption and most of the damages are related to its presence. Some alteration processes might increase the water absorption coefficient. This test is useful for assessing the extent of some types of MPC formulated with LG-MgO decay. Moreover, the deterioration of specimens was evaluated by determining open porosity, density and sorptivity before and after the durability tests, consisting of determining the frozen–thaw and salt resistance behavior.

The description of the testing and the specifications of the specimens are described below. It should be noted that each formulation was mixed in such a way that all the specimens arised from the same batch. Specimens were left in their corresponding moulds for 24 h in a curing chamber at a constant temperature of 20 °C and a relative humidity of 95% and the unmolded mortars were further allowed to cure in the same conditions at different ages before testing.

2.3.1. Determination of MOE

The MOE procedure followed the standard UNE-EN 12504-4 [46], in which ultrasonic impulse velocity is used. The test consists in measuring the velocity at which the ultrasonic impulses propagate through the sample. A transmitting and receiving device of ultrasound C368 made by Matest (55 kHz transceiver sensors) was used for testing the samples. The test was performed over the specimens at 1, 7 and 28 days. In all cases, the samples were left in the drying oven for 4 h at