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Experimental research on magnesium phosphate cements containing alumina

Ning Liu, Bing Chen *

Department of Civil Engineering, Shanghai Jiaotong University, Shanghai 200240, PR China

HIGHLIGHTS

- Novel magnesium aluminum phosphate cements were prepared in the present work.
- The substitutions of magnesia by alumina can improve properties of MPC greatly.
- The mechanism of affections of alumina on properties of MPC was analyzed.
- A structure model for magnesia alumina phosphate geopolymer was developed.

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ABSTRACT

The main concern of the present work is to understand the effects of the addition of alumina on the properties of magnesium phosphate cement with respect to changes in temperature, mechanical properties, porosity and microstructure of hydration products. Experimental results demonstrated that the presence of alumina could reduce the intensity of exothermic reactions, as well as prolonged the setting time. Also, a significant increase in compressive strength was observed during all hardening stages after the substitution of magnesia by alumina. However, the effectiveness of alumina was limited by its solubility. Successive addition of alumina caused a cumulative increase in water requirement as indicated by a gradual loss in workability. Furthermore, the addition of alumina led to a reduction in porosity, and left a finely porous structure. Finally, the hydration products were examined through the techniques of thermogravimetric (DTA-TG), Scanning Electronic Microscopic-Energy Dispersive Spectrometer (SEM-EDs) and mercury intrusion porosimetry (MIP). These experimental results provided detailed information to improve basic understanding of magnesium phosphate cement blended with alumina and the structures of hydration products.

1. Introduction

Magnesium phosphate cements (MPCs), formed by through-solution acid-based reaction between dead burnt magnesia and phosphate salts, were first discovered and developed as dental cement in the late 19th century [1–3]. Formed at an ambient temperature and exhibiting property like ceramics, MPCs are also termed chemically bonded phosphate ceramics [4]. In 1970, MPCs were adopted as rapid repair materials in civil engineering [5]. During decades of development, MPCs have been employed in many fields such as in the uses of: stabilized and solidified, light magnesium phosphate cement foamed material, dental or bone restorations, repair and rehabilitation of structure, and 3D powder printing materials [6–12]. MPCs have several advantages over conventional Portland cement such as rapid setting time, high early strength, good bonding with Portland cement, little drying shrinkage, and good resistance to abrasion [13–16]. These superior properties endow MPCs with the potential to be widely used in engineering structures.

Earlier, MPCs featuring a “two part” system, consisting of dead burnt magnesia and soluble ammonium dihydrogen orthophosphate (ADP; $NH_4H_2PO_4$) were developed as fast repair materials for concrete pavements [17]. However, the reaction was too fast to allow enough time for operation. Subsequently, a “three part” MPCs system based on magnesium and ADP were prepared with the addition of retarders [18]. The uses of sodium triphosphate (STP), boric acid (H_3BO_3) or borax ($Na_2B_4O_7{\cdot}10H_2O$) as retarders have been reported in the literature [19–21]. Particularly, borax has been widely used in academic study and commercial formation due to its easy storage and effectiveness.

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* Corresponding author.
E-mail address: hntchen@sjtu.edu.cn (B. Chen).

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Allan and Asgar [22] identified the main reaction product of ADP-based MPCs as magnesium ammonium phosphate hexahydrate, with the molecular formula $MgNH_4PO_4{\cdot}6H_2O$, also known as naturally mineral struvite. The overall reaction scheme for forming ADP-based MPCs was described as [23]:

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (1)$$

The setting reaction releases a large amount of ammonia gas which restricts it to outdoor application, leading to attempts to replace ADP with other phosphates, such as potassium dihydrogen phosphate (KDP) and sodium dihydrogen phosphate (SDP) [24,25]. Subsequent study showed that the replacement of ADP by KDP not only avoided generation of the unpleasant gas but also led to a reduction in exothermic reaction rate as well as the curing time [26]. Therefore, in some applications of KDP-based MPCs, a retarder may not even be necessary. Recently [16], it was recognized that KDP-based MPC exhibited lower early strength than ADP-based MPC, although KDP-MPC was superior in strength development. By substituting ADP with 50% KDP, the mix showed the highest performance in mechanical strength. In the KDP-MPC system, magnesium potassium phosphate hexahydrate (MKP, $MgKPO{\cdot}6H_2O$) is the main product, and is also known as struvite-(K) or MKP, which is isostructural with struvite. The overall setting reaction can be written as [27]:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \quad (2)$$

A review of the literature of MPCs indicated that the most attention were paid to finding proper ways to control the setting time and optimizing the formula based on the raw materials [28–31]. As far as the authors were concerned, the effects of metal oxides, a part of the “three part” MPCs system, on the properties of MPCs have not been well studied. In fact, metal oxides such as calcium oxide, magnesium oxide, zinc oxide, aluminum oxide and iron oxide are candidates for forming phosphate cements [32,33]. These metal oxides are abundant in earth’s crust and easily available. Compared with magnesium oxide, zinc oxide and calcium oxide have higher solubility, hence may not be suitable for the use in civil engineering. In contrast, alumina which has lower solubility, is reasonably suitable for forming phosphate cement without the process of sintering, which is a necessary process of magnesia for the preparation of MPCs aiming to control the exothermic reaction [4].

Alumina is one of the most abundant metal oxides on earth. Its abundant and inexpensive characteristics make it a promising candidate to totally or partially replace the magnesium for forming phosphate cements. However, phosphate cement only based on alumina and phosphates is difficult to form because the solubility of alumina is somewhat too low in water. Fortunately, this solubility can be increased by a mild thermal environment [34]. Therefore, it is supposed that the partial replacement of magnesia by alumina would lead to the acceleration in solubility of alumina to some extent. The present study mainly concerns the effects of the partial replacement of magnesia by alumina on the properties of MPC pastes, with a particular emphasis on the pore structure and strength development of MPC pastes. The reaction products were subsequently analyzed using techniques of DTA-TG, SEM-EDs and MIP.

2. Materials and experiments

2.1. Materials

Magnesium phosphate cement pastes was prepared from a mixture of magnesium oxide (MgO), aluminum oxide (Al_2O_3), acidic phosphate (ADP, KDP), and borax in various proportions. Dead burnt magnesium oxide powder employed in the present study with a specific surface area (SSA) in 230 m^2/kg and an averaged particle size of about 20 μm was calcined at 1500 °C for 6 h, and obtained from ATK flame retardant materials company of Jiangsu, China. Neutral Alumina with a SSA in 270 m^2/kg was purchased from Sinopharm Chemical Reagent Co., Ltd. The ammonium dihydrogen phosphate, potassium dihydrogen phosphate and borax used in the current research were of industrial grade and were provided by Fine Chemical Plant of Wujiang, Jiangsu province, China. The chemical characteristics of the raw materials are listed in Table 1.

2.2. Test methods

In the current study, MPC pastes with phosphates to the metal oxide (magnesium and aluminum oxide) mass ratio (m_p/m_o) of 0.55, the borax to metal oxide mass ratio (m_B/m_o) of 0.04 and water to binder mass ratios (m_{water}/m_{binder}) of 0.14, 0.15 and 0.16 were prepared by mixing the raw materials in light of the mix proportions. The water content was adjusted to obtain the same workability of each paste. Flowing table test (standard UNE-EN 1015-3) were tested to evaluate the workability of MPC mortar and the flow were keep as 250 mm. The m_{ADP} to m_{KDP} mass ratio (m_{ADP}/m_{KDP}) of 1:1 was applied according to the early experimental results [16]. An aluminum oxide to metal oxide mass ratios of 0, 0.05, 0.1, 0.2 and 0.4 were employed to study the effects of different aluminum oxide contents on the properties of MPCs. The mixing proportions are listed in Table 2.

For the paste samples preparation, powders were first weighed and mixed according to the mixing proportions (Table 2). After dry-mixing the powders for 1 min in a vertical-axis planetary mixer, water was added into the mixer, and mixed for 3 min. The mixed fresh pastes were cast into the molds. Temperature evolutions of MPC pastes during setting were recorded by an automatic recorder. The sample was cast in an insulated container, the volume of which is 64 cm^3. All of the specimens were tested in the same environment (Temperature 12 ± 2 °C, Humidity of 60 ± 5%). For each mixture, the setting time were determined by using a modified Vicat needle according to ASTM standard C807-05.

Compressive strength of hardened MPCs was measured by using the MTS servo hydraulic testing machine at a speed of 1 mm/min. The specimens were cast in the molds of 40 × 40 × 40 mm cube

Table 1
Characteristics of raw materials.

Component	Characteristics
Magnesium oxide (MgO)	90% MgO, 5.0% SiO_2, 1.5% CaO
Aluminum oxide[a] (Al_2O_3)	Analytically grade, >99% Al_2O_3
ADP ($NH_4H_2PO_4$)	Industrial grade, >98% ADP
KDP (KH_2PO4)	Industrial grade, >98% KDP
Borax ($Na_2B_4O_7{\cdot}10H_2O$)	Industrial grade, >97% borax

[a] Aluminum oxide used in the present study is neutral aluminum oxide.

Table 2
Mixing proportions of MPC pastes.

Batch	m_o/m_p[a]	m_a/m_o	m_{ADP}/m_{KDP}	m_B/m_o	m_{water}/m_{binder}
M1	55:100	0:100	1:1	4:100	1.4:10
M2	55:100	5:100	1:1	4:100	1.4:10
M3	55:100	10:100	1:1	4:100	1.4:10
M4	55:100	20:100	1:1	4:100	1.5:10
M5	55:100	40:100	1:1	4:100	1.6:10[b]

[a] Abbreviations: m_o, mass of metal oxide ($MgO + Al_2O_3$); m_p, mass of phosphates (ADP + KDP); m_a, mass of Al_2O_3; m_B, mass of borax.

[b] The adjustments of m_{water}/m_{binder} ratio was a result of the obtainment of the same workability.