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Experimental study of phosphate salts influencing properties of magnesium phosphate cement

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HIGHLIGHTS

- The effect of sodium triphosphate on the thermodynamic property and setting time for magnesium phosphate were studied.
- The exothermic and mechanical properties for MPC prepared with different types of phosphate salts were investigated.
- Hydration products for MPC system are analyzed by using X-ray diffraction and scanning electron microscopy.

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ABSTRACT

Magnesium phosphate cement (MPC) was prepared with dead burned magnesia oxide and phosphate salts, such as ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and potassium dihydrogen phosphate (KH_2PO_4). The properties of MPC prepared with varied phosphate salts were of much difference. In this paper the exothermia kinetics, mechanical properties and phase compositions of MPC prepared by mixing MgO with either ammonium dihydrogen phosphate or potassium dihydrogen phosphate, or a combination of both were studied. Besides, the effects of sodium triphosphate ($Na_5P_3O_{10}$) on the microstructure and mechanical properties of MPC were also investigated. The results revealed that MPC prepared with ammonium dihydrogen phosphate exhibited substantially higher early strength and hydration temperature than that of magnesium potassium phosphate, while the later demonstrated better strength development. The strength of MPC prepared with equivalent mixture of ammonium dihydrogen phosphate and potassium dihydrogen phosphate was higher than that of MPC containing magnesium ammonium phosphate or magnesium potassium phosphate only. Moreover, the testing presented that the addition of sodium triphosphate improved the mechanical properties of MPC significantly. It also prolongs the setting time. Finally, the reaction products and their micro-morphology of MPC paste were examined and analyzed by X-ray diffraction (XRD) and Scanning Electronic Microscopic (SEM).

1. Introduction

Magnesium phosphate cements was a kind of chemically bonded phosphate ceramics which were first discovered and developed as dental cement in the late 19th century. Since then, several ceramic cements have been developed and used in different clinical applications due to their similarly mineral phase with bone and properties that are relevant to biomedical applications [1–3]. Magnesium phosphate based cement was discovered by Prosen [4] as materials for casting alloys during 1939–1940. At early time, the MPCs were prepared by mixing magnesium oxide and acid phosphates. Due to the high solubility of phosphoric acid, however, the setting reaction was very fierce thus allow very short time for clinical applications. Following researches were mainly focus on finding the proper way to decrease the setting time. Phosphate salts, such as ammonium dihydrogen phosphate (ADP, $NH_4H_2PO_4$), potassium dihydrogen phosphate (PDP, KH_2PO_4) and sodium dihydrogen phosphate (SDP, NaH_2PO_4), were found an effective replacement of the phosphoric acid to reduce the reaction rate in the compound [5,6].

Starting in 1970, magnesium phosphate ceramics have been investigated as structural materials, which were mainly used as fast setting repair material. More recently, a wide range of applications of MPC were developed in civil engineering. These include uses of: light magnesium cement foamed material [7], wastes stabilized and solidified [8,9] and recycling of construction or industry waste, such as fly ash and mineral wastes [10]. MPC have excellent mechanical properties, such as high early strength, ability to set and harden at temperatures as low as −20 °C, high bonding strength and very good durability, including chemical attack resistance, deicer scaling resistance and permeation resistance [11].

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However, compared to silicophosphate cements, they also have some drawbacks, such as poor water resistance and highly exothermic setting reaction. Those properties limit their use to a more wide range applications.

Compared to acid phosphate, ADP was seemly to be a more desirable raw material used in forming MPC, for the high early strength obtained during setting and hardening and the relative slow reaction rate. However, the main problem of magnesium ammonium phosphate cement was that the reaction releases a large amount of ammonia which restricts it to outdoor applications. Therefore, attempts have been made to seek a more effective phosphate salt to replace ADP. Though, exhibited a low solubility, PDP was reported a promising candidate of ADP in preparing MPC because of no ammonia volatilization. It is also a weak acid which indicated that the reaction would not be too rapid [12–14]. Although there are of much difference between ADP and PDP on the properties for MPC, little has been reported on this subject.

Previous research showed that the properties especially setting time and mechanical properties for MPC were affected by w/c ratio, casting temperature, M/P ratio and the addition of retarder [11,15]. Although, the use of retarders such as borax may elongate the setting time. The excessive use of borax also results in a decrease of the strength [16]. Hence, to select the proper additions and the optimal compound of MPC might be a more economical way to control the setting time and improve mechanical properties at the same time.

Sodium tripolyphosphate (STP, $Na_5P_3O_{10}$) is commonly used in the making of refractory castables and employed as a dispersing agent in ceramics processing [17]. Besides, it can be used as a source of alkalinity to control the pH value of interstitial solution [18]. As an addition in MPC system, however, STP was still rarely reported.

In the present work, the effect of either ADP or PDP on the exothermia kinetics and mechanical properties were systematic studied. Besides, to evaluate the effect of STP on the properties of MPC, the experiment of exothermy and mechanism were performed in the present work. Finally, the morphology of the phase for MPC prepared with STP was examined by using SEM.

2. Experimental details

2.1. Materials

The magnesium phosphate cement (MPC) was prepared from a mixture of magnesium oxide (MgO), acidic phosphate, fly ash, borax ($Na_2B_4O_7{\cdot}10H_2O$) and sodium tripolyphosphate (STP, $Na_5P_3O_{10}$) in various proportions. Dead burned magnesium oxide powder employed in the present study with a SSA in 230,000 m^2/g, calcined at 1500 °C for 6 h and with an averaged particle size of about 20 μm, was obtained from ATK flame retardant materials company of Jiangsu. The ammonium dihydrogen phosphate, potassium dihydrogen phosphate and borax used in the current research was industrial grade which were provided by Fine Chemical Plant of Wujiang, Jiangsu province. Sodium tripolyphosphate employed was an analytic grade chemical. The sand used was standard sand according to Chinese standard (GB178-77) for cement strength test. The details chemical composition of MgO and fly ash was provided in Table 1.

2.2. Test methods

In order to investigate the effects of sodium tripolyphosphate and the weight ratio of ADP to PDP on the properties of MPC mortar, MPC mixtures prepared were divided to three series: series (M1) the weight ratio of ADP to PDP was controlled with the value of 1:0, 1:2, 1:1, 2:1 and 0:1, respectively; and series (M2) compared with series M1, the STP was added into the compounds which have the same ADP to PDP ratio with M1; and series (M3) the contents of sodium tripolyphosphate varied from 0.5%, 1.0%, 1.5% 2.0% and 2.5%. In all series, a MgO to phosphate salts mol ratio of 5:1, the water to solid ratio of 0.1 and the fly ash to MgO weight ratio of 0.4 were employed. The mixing proportions are listed in Table 2.

Table 1
Chemical compositions of magnesia and fly ash.

Raw material	Mass fraction of the sample (%)									
	MgO	Al_2O_3	SiO_2	P_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	SO_3	Loss
Magnesia	89.51	2.35	4.91	0.11	1.44	1.16	–	–	–	–
Fly ash	1.8	25.8	54.9	–	8.7	6.9	0.3	0.1	0.6	0.2

The temperature evolution during setting for MPC mortar was recorded by an automatic recorder. The sample was cast in an insulted 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 was determined using a modified Vicat needle according to ASTM standard C807-05.

The compressive strength and flexure strength of hardened MPC were measured using the MTS servo hydraulic testing machine at a speed of 50 N s^{-1}. The specimens were cast in the molds of 40 × 40 × 40 mm cube for measuring compressive strength and 40 × 40 × 160 mm for measuring flexure strength. Strength of samples at 1 h, 3 h, 1, 7 and 28 days were tested. The setting reaction was stopped by immersing the samples in ethanol for 3 h and drying them at 40 °C for 2 days.

The reaction product of MPC were analyzed by X-ray diffraction (XRD, D8 ADVANCE) with a scanning rate of 0.5° 2θ/min. Indexing of the peaks was carried out by means of cards JCPDS No. 79-1107 for PDP (KH_2PO_4), JCPDS No. 89-7746 for MgO, JCPDS No. 77-2303 for struvite ($MgNH_4PO_4{\cdot}6H_2O$), and JCPDS No. 35-0812 for MKP ($MgKPO_4{\cdot}6H_2O$). Besides, the microstructure and morphology of the reactants was observed by scanning electron microscopy (SEM, NOVA NanoSEM 230).

3. Results and discussion

3.1. Setting time and temperature variation of MPC mortar

The effect of the ADP to PDP weight ratio on the setting time of MPC samples were shown in Fig. 1. The samples prepared with ADP alone exhibited the lowest setting time of about 13 min among all of the specimens. The setting time was prolonged with the increasing amount of PDP in phosphate compound. Samples prepared with PDP alone show the longest setting time of about 17.2 min which was 4.2 min longer than that of the samples prepared with ADP alone which is important in terms of rapid setting material. The various setting time obtained between different types of phosphate salts was probably due to their different solubilities. The solubilities (mol/100 g H_2O) of ADP and PDP are 0.2484 and 0.147, respectively [19]. Namely, ADP has a solubility that is higher than PDP which is responsible for the faster reaction of ADP–MPC.

Fig. 2 illustrates the effect of sodium tripolyphosphate (STP) on the setting time of MPC mortar. As is clearly revealed in Fig. 2 that increasing the amount of STP resulted in an extension of the initial hardening period. The setting time of samples containing STP at a level of 2.5% in mass increased from 12.7 min to 16.9 min. A slightly drop of this increase trend was appeared when the addition of STP was surpassed 1.5%. In the previous study, it is founded that high level of STP in the compounds may resulted in a loss of walkability. Thus, the addition of STP was within 2.5%. Although attempts to investigate the retard mechanism had been made [20], it is still difficult to elucidate the mechanism of it. In a related study, Ltifi et al. [21] reported that sodium tripolyphosphate have a similarly delay effect on Portland cement. This might be that the addition of sodium tripolyphosphate caused the absorption of phosphate ions on the surface of cement grains and block the dissolution of the phase, as Mounir Ltifi suggested. This explanation was very similar to the retard mechanism of borax which was reported by many researchers [22,23]. However, little attention has been paid to that the STP dissolution also causes the rise in pH [24]. And the rise of pH may elongate the dissolution of metal oxide grains which leads to a decrease of setting time [16], as supposed.

The effect of the type of phosphate salts and the content of borax on the exothermic reaction for the MPC mortar was shown in Fig. 3. For the samples prepared without the addition of borax, the maximum temperature reached within 8 min. It is also demonstrated that the mortar prepared with ADP alone the exothermic peak