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Tests on magnesium potassium phosphate composite mortars with different water-to-binder ratios and molar ratios of magnesium-to-phosphate

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HIGHLIGHTS

- We provide lots of test data for magnesium potassium phosphate composites (MKPC).
- We found that the molar ratio of MgO-KH_2PO_4 for the highest strength depends on *W/B*.
- For practical application of MKPC, adequate molar ratio and *W/B* are recommended.
- Compressive strength development of MKPC mortars is formulated.

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ABSTRACT

The objective of the present study is to examine the effect of the water-to-binder ratio (*W/B*) and the molar ratio (M_{mp}) of magnesium-to-phosphate on the fluid characteristics, compressive strength development, and pH variation of magnesium potassium phosphate composite (MKPC) mortars. A total of 25 mortar mixes were prepared, with the *W/B* varying from 20% to 40% and M_{mp} varying from 3.4 to 30.4. Using the present test data, the compressive strength development of MKPC mortars was empirically formulated, which reflects rapid strength gain. Considering practical qualifications, including a relatively good 28-day compressive strength above 30 MPa, delayed setting time, and a near-neutral pH not exceeding 9.4, it can be recommended that the M_{mp} and *W/B* be chosen to be below 5.1 and above 25%, respectively, in the MKPC system. With a decrease in the M_{mp} value, the peak intensities for struvite-k increased slightly, whereas the peak intensities for unreacted MgO were considerably weakened as the M_{mp} value fell below 5.1. The total porosity of the MKPC pastes was governed by the macro-capillary pores, implying that the 28-day compressive strength is inversely proportional to the macro-capillaries.

1. Introduction

With the gradual increase in the promotion of ecological environments for buildings and infra-structure, low-pH cementitious materials have been encouraged for producing vegetation restoration concrete and self-purifying bacteria concrete [1,2]. Low-pH cementitious materials are commonly addressed from different approaches depending on the type of source material, such as calcium silicate, calcium aluminate, or magnesium-phosphate composites (MPCs) [3]. MPC, in particular, has become one of the hot topics in civil engineering materials due to its advantageous properties, including near-neutral pH, rapid setting, low water demand, low drying shrinkage, high-strength gain at an early age, good durability, and high bonding strength [4–6]. The near-neutral pH and good durability allow MPCs to be recognized as a special cementitious material applicable for vegetation resources such as artificial soils and lightweight aggregate particles for soil protections.

MPCs are commonly known as low-temperature high-strength materials derived by through-solution acid-based reaction between dead burned magnesia and phosphate [7]. Considering the enhanced mechanical strength of MPCs, magnesium ammonium phosphate composites (MAPCs) and magnesium potassium phosphate composites (MKPCs) are the most widely found type of cementitious materials in engineering practice and experimental research programs. The main reaction product in the MAPC, magnesium ammonium phosphate hexahydrate, releases a certain

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amount of ammonia in gaseous form during the reaction, which leads to environmental pollution [8]. As a result, MKPCs have been attracting more attention in practical applications. However, MKPC pastes usually set within 10 min under a lower water-to-binder ratio (*W/B*), which causes rapid workability loss of the mortar or concrete. Furthermore, the effect of the *W/B* on the setting time and mechanical strength gain of MKPC pastes depends significantly on the molar ratio of magnesium oxide (MgO) to phosphate. Insufficient experimental data on these characteristics are reckoned to be one of the obstacles for practical applications of MKPCs.

The present study prepared 25 MKPC mortars to explore the optimum molar ratio (M_{mp}) of MgO-to-potassium phosphate in terms of the delayed setting time and enhanced compressive strength gain. The cementitious materials were prepared by mixing calcined MgO with potassium dihydrogen phosphate (KH_2PO_4). The compressive strength development of MKPC mortars were formulated by regression analysis of the test data. The variation in the pH values of the MKPC mortars was measured at different ages. The hydration products and microstructural pore distribution of the MKPC pastes were traced using X-ray diffraction (XRD) and mercury intrusion porosimetry (MIP), respectively.

2. Experimental details

2.1. Materials

The MKPCs were prepared from a mixture of magnesia (MgO) powder (with a purity of 95% as given in Table 1, which was calcined under 1500 °C for 6 h), potassium dihydrogen phosphate (KH_2PO_4), and boric acid (H_3BO_3), which is used to retard the setting time of mortar specimens. The specific surface area and density of the MgO powder were 2600 cm^2/g and 3.50 g/cm^3, respectively. The maximum particle size of the KH_2PO_4 and H_3BO_3, which were of an industrial grade, was 700 μm and 2 μm, respectively, and their purity was greater than 98% and 95%, respectively. Sand satisfying the ISO requirements for fine aggregates was used in a saturated surface dry condition for producing the MKPC mortar specimens. The density, grading, and maximum size of the sand particles were 2.6 g/cm^3, 2.93, and 2 mm, respectively. Portable water was used for the mixing water.

2.2. Specimens and mixture proportions

A total of 25 MKPC mortar mixtures were prepared, as given in Table 2. The *W/B* varied from 20% to 40% in increments of 5%. At each *W/B*, the M_{mp} ranged between 3.4 and 30.4, which corresponded to MgO: KH_2PO_4 = 9:1 to 5:5 by weight. Hence, the mortar specimens given in Table 2 were identified using the selected parameters of *W/B* and M_{mp}. For example, specimen 2-30.4 indicates a mortar produced with a *W/B* = 20% and M_{mp} = 30.4. For all of the mortar mixes, the sand-to-binder ratio (*S/B*) by weight was fixed at 2.0, and H_3BO_3 was added as 4% of the binder weight.

2.3. Casting, curing and testing procedure

The powdered materials, consisting of MgO, KH_2PO_4, and H_3BO_3, were dry-mixed in a mixer pan for 3 min with sand, and then water was added and mixed in for another 1 min. After testing for the initial flow and viscosity, each mix was poured into various steel molds to measure the compressive strength development and pH variation at different ages. Immediately after casting, all specimens were cured at a constant temperature and relative humidity of 21 ± 2 °C and 60 ± 5%, respectively, until testing at the specified age. All steel molds were removed at an age of 3 h.

The initial flow was measured in accordance with ASTM C124 [9], using a cone-shaped mold having a total height of 50 mm, a bottom diameter of 100 mm and a top diameter of 70 mm. To determine the setting behavior against the elapse of time, penetration resistance testing was conducted in accordance with ASTM C403/C403M [9]. Viscosity was recorded from rheological measurements of MKPC pastes produced at the same *W/B* as the mortar specimens. To create uniform conditions for each paste, the samples were loaded into a coaxial cylinder with a height of 85 mm and then cured at the constant temperature of 20 ± 1 °C. To structurally break down the pastes, rotors were spun within the cylinder at the constant velocity of 100 rpm for a period of 60 s. The rheological measurements were completed between 10 and 13 min following the initial contact of the cement with water. The measurements of compressive strength were started with demolding. Hence, the compressive strength gain with age was measured at 3 h, 12 h, and 1, 3, 7, and 28 days. The compressive strength testing, using cubes with 50 mm sides, was conducted in accordance with ASTM C109. To measure the pH values according to the test procedure specified in ASTM D4972, samples were crushed and the powder, with a particle size of less than 2 mm, was suspended in distilled water with a solid–to–liquid ratio of 1.0. A pH-meter was used to determine the pH value in the supernatant fluid using two different electrodes. The pH values were measured at an age of 1, 3, 7, and 28 days.

To evaluate the effect of test parameters on the hydration products, and the microstructural pore characteristics of the mixed MKPC systems, XRD and MIP analyses were carried out on the pastes at an age of 28 days. The XRD patterns were recorded on a Philips X'pert pro-MRD spectrometer using Cu K_α Radiation with a scanning rate of 4.2 °/min from 7° to 70° (2θ). To determine the pore size distribution, mercury intrusion porosimetry was used on oven-dried paste samples under a pressure of 200 MPa.

3. Test results and discussions

3.1. Initial flow

As commonly observed for cement mortars, a lower initial flow was obtained for the MKPC mortars with a lower *W/B*, as shown in Fig. 1 and Table 3. All the mortars with a *W/B* below 25% showed no workability, revealing an extremely poor mixing condition with a flocculation phenomenon. Furthermore, the flow measurement was impracticable for mortars with a *W/B* of 20%. The most important factor affecting the workability of mortars is the water content of the mix [10]. For the unit weight mixture method for mortars, a lower *W/B* results in a lower water content in the mix, as given in Table 2. Hence, a *W/B* of less than 25% can result in the lack of mixing water for the MKPC mortars. The flow of MKPC mortars was also slightly affected by the M_{mp}. The flow of MKPC mortars tended to increase with the increase in M_{mp} up to 7.9, beyond which the flow gradually decreased. This increasing rate of the flow up to M_{mp} of 7.9 was more prominent for mortars with a higher *W/B*. For example, when M_{mp} increased from 3.4 to 7.9, the initial flow increased by 8.7% and 14.7% for the mortars with *W/B* of 30% and 40%, respectively. The decreasing rate of the flow beyond M_{mp} of 7.9 was insignificantly affected by *W/B*.

3.2. Viscosity

The viscosity of MKPC pastes increased with the increase in M_{mp} and the decrease in *W/B*, showing a higher increasing rate for

Table 1
Chemical composition of magnesia (% by mass).

MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	P_2O_5
95.50	0.16	1.73	1.63	0.81	0.17