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The effect of seawater curing on properties of magnesium potassium phosphate cement

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HIGHLIGHTS

- The effect of seawater curing on properties of MKPC paste was studied.
- The physical and mechanical properties of MKPC paste were investigated in seawater curing condition.
- The seawater corrosion resistance of MKPC paste early was evaluated.
- Sea water corrosion resistance mechanism of MKPC paste was characterized.

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ABSTRACT

This paper investigated the effect of early seawater curing on properties of magnesium potassium phosphate cement (MKPC) paste. First, the MKPC paste was prepared by mixing overburning MgO powders, KH_2PO_4, the composite retarder (CR) and water in a certain proportion. Then, we measured the compressive strength, drying shrinkage deformation, and mass change of it under different curing conditions. The results were as follows. For MKPC paste specimens under seawater curing condition, the hydration ages before they were soaked in seawater had a significant effect on their compressive strength, drying shrinkage and mass increase. For MKPC paste specimens cured in seawater after 3-day natural curing, their 28-day and 60-day compressive strengths were 112.8% and 105.4% of those of MKPC paste specimens with same hydration ages under natural curing condition, respectively. In addition, the 60-day shrinkage strain of them (0.82×10^{-4}) was significantly less than that of MKPC paste specimens with the same hydration age under natural curing condition (5.14×10^{-4}). Moreover, they had higher mass increase ratio (1.23%). These were due to higher production, higher degree of crystallinity and less defects of MKP crystals, and more perfect pore size distribution in MKPC specimens soaked in seawater after 3-day natural curing.

1. Introduction

Marine construction attracts more and more attention. Currently, Portland cement concrete is much used for it. However, the Portland cement paste has poor resistance to chloride ion penetration and seawater because of its porous structure. To enhance the resistance to chloride ion penetration and seawater of Portland cement-based materials, some methods are adopted such as increasing contents of C_3A and C_4AF and adding mineral admixtures [1,2]. However, the early strength and resistance to chloride ion penetration of these materials cannot be improved significantly. Therefore, inorganic cementitious materials with better properties instead of them are more and more often used for marine construction.

Magnesium phosphate cement (MPC) is a type of inorganic cementitious material in which phosphate binder phases are formed by neutralization reaction. MPC pastes react, set and harden at room temperature, which is similar to the hardening process of Portland cement, and final hydration products have typical properties of ceramics [3]. Two types of MPCs are commonly used, one is the magnesium ammonium phosphate cement (MAPC) and the other is the magnesium potassium phosphate cement (MKPC). They use the ammonium dihydrogen phosphate (ADP) and the potassium dihydrogen phosphate (KDP) as the phosphate

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component, respectively. In addition, the main reaction products for producing them are magnesium ammonium phosphate (MAP) hexahydrate and magnesium potassium phosphate (MKP) hexahydrate, respectively. The main reactions for producing MAPC and MKPC can be expressed as follows [3,4]:

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

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

Main hydration products of MPC system, $MgNH_4PO_4{\cdot}6H_2O$ and $MgKPO_4{\cdot}6H_2O$ (struvite and K-struvite), attribute to the gel property of MPC system, and remain stable over a wide range of pH (7–11) [5,6]. The hardened MPC pastes consist of unreacted overburning MgO particles and phosphate hydrates, which are combined by ionic bond to form network structure. The compact structure of hardened MPC paste is similar to that of the ceramic [7,8]. Compared with the hardened Portland cement paste in which there is high content of $Ca(OH)_2$, main hydrates C-S-H depending on alkaline environment and porous structure, the hardened MPC pastes have better resistance to chloride ion penetration and slats [1,2]. The previous studies [9–12] have proved that MKPC-based materials had high resistance to chloride ion penetration and seawater.

Compared with MAPC, MKPC does not generate unpleasant odor when reacting with water and the reaction rate is easier to control since KDP has smaller dissociation constant and lower solubility than ADP [1]. The chemical reaction shown by Eq. (2) occurs under the condition that MgO and KDP dissolve and react with each other in solution. Struvite-K ($MgKPO_4{\cdot}6H_2O$) is formed during the reaction, which is isostructural to struvite ($NH_4MgPO_4{\cdot}6H_2O$) [6] and is a type of naturally cementitious material. The advantages of MKPC above make MKPC-based materials to be focus on more. Currently, problems limiting the application of MKPC-based materials are fast setting and the concentrated release of hydration heat. The composite retarder can be used to solve these problems [13–15]. Furthermore, Paceagiu et al. [16] demonstrated that curing conditions, such as temperature, humidity and solution, had significant influences on the properties of MPC-based materials. However, there are almost no the related results about the effect of seawater curing on the properties of MPC system in previous studies. In order to provide insights into the effect of seawater curing on properties of MKPC paste, we prepared MKPC paste specimens with composite retarder, and soaked them in seawater after they were cured under natural condition for different periods. Then, their physical and mechanics properties were measured. Besides, their phase components and microstructure were also analyzed.

2. Materials and methods

2.1. Materials

The electrical grade magnesia was from Haicheng, Liaoning province, China. It was prepared by melting natural magnesite in electric arc furnace (above 1500 °C). The mean diameter of the electrical grade magnesia particle was 420–640 μm, and MgO, CaO and SiO_2 contents in it were 96.8%, 1.33% and 0.92%, respectively. In addition, we prepared the overburning MgO powders by grinding the magnesia for 30 min by a ball mill, and their specific surface area was 225 $m^2{\cdot}kg^{-1}$. SEM analysis of the overburning MgO powders indicates that MgO grains had shapes of irregular polygons. Industrial grade potassium dihydrogen phosphate (KH_2PO_4), columnar crystal with grain size of 80/177–100/147 (mesh/μm), was from Georgia legislature Chemical Company (Lianyungang, Jiangsu province, China). The composite retarder was made by the laboratory, which consists of borax, sodium phosphate dibasic dodecahydrate and inorganic chlorine salt.

MKPC paste was prepared by mixing overburning MgO powders, KH_2PO_4, the composite retarder (CR) and water. According to previous experimental results [15], the mass ratio of magnesia to phosphate salt was set at 3. The content of composite retarder was 10 wt.% of dry MKPC. The mass ratio of water to solid (W/S) was 0.11. The flow value of fresh MKPC paste was about 140 mm, and its initial setting time was 54 min because of the effect of protective film, cooling effect and pH adjustment caused by addition of composite retarder [13,15].

In this study, the seawater with the salinity of 31–34‰ and a pH of 8.14–8.76 was taken from the Huanghai Sea near Dafeng port (Jiangsu Province, China).

2.2. Experimental methods

The fluidity and setting time of fresh MKPC paste were measured at ambient temperature (25 °C). The fluidity of fresh MKPC paste was determined by the flow table test according to ASTM C1437-2007, and the initial setting time of it was measured by Vicar according to ASTM C191a-2001. According to ASTM C 109/C 109M-2001, fresh MKPC paste was cast into 30 mm cubic molds and conserved in an indoor environment (ambient temperature of 20 ± 5 °C and relative humidity ranging from 50% to 70%). Then, MKPC paste specimens were unloaded after five hours and cured under four kinds of conditions (A, B, C and D), respectively, until the time of test. A: being cured in indoor environment (ambient temperature of 20 ± 5 °C and relative humidity ranging from 50% to 70%) (specimens: M60d); B: being cured in seawater at 20 ± 5 °C after 5-h hydration age in indoor environment (specimens: M5h); C: being cured in seawater at 20 ± 5 °C after 3-day hydration age in indoor environment (specimens: M3d); D: being cured in seawater at 20 ± 5 °C after 28-day hydration age in indoor environment (specimens: M28d).

MKPC specimens (four cubic specimens) cured in seawater for three days were taken out, and their surfaces were wiped with wet cloth. Then, the specimens were weighed, and their respective weight was taken as the initial mass of the saturated-surface-dry specimen (M0). Then, these specimens continued to be cured in seawater. Finally, the MKPC specimens were taken out and weighed (Mt) when specified soaking age was reached. The mass change ratio was calculated according to the formula (Mt—M0)/M0 (the average weight of four cubic specimens was used with an accuracy of 0.1%). The compressive strengths of MKPC specimens were measured by WED-300 electronic universal testing machine with a loading rate in the range of 0.5–1.0 MPa/min, and the average values were used with an accuracy of 0.1 MPa. It should be noted that the surface of MKPC specimens soaked in seawater must be wiped with wet cloth before the compressive strength was tested. The compressive strength of MKPC specimen soaked in seawater until specified hydration age (t) was divided by that of MKPC specimen cured under condition A with same hydration age and then the residual rate of compressive strength (R_t) was obtained. In addition, MKPC paste bar specimens with the size of 25 × 25 × 285 mm were used for the drying shrinkage test according to the modified British Standard method BS ISO 1920-8 (2009). The length of MKPC paste specimens after 5-h hydration age, which was as the initial length of specimens (L_0), was measured by a large diameter micrometer, and the testing direction of specimens was marked. The specimen length (L_t) after t-d hydration ages (such as 7/24, 1, 3, 7, 15, 28 and 60 days) was measured. Then, the linear deformation (ε_t) was calculated as follows:

$$\varepsilon_t = (L_t - L_0)/250 \quad (3)$$