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Experimental research on seawater erosion resistance of magnesium potassium phosphate cement pastes

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HIGHLIGHTS

- The resistance of magnesium potassium phosphate cement paste to seawater erosion are studied.
- The some macro properties were measured to evaluate its resistance to seawater erosion.
- The resistance mechanism to seawater erosion were characterized by microstructure observation.

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ABSTRACT

This paper aims to study the resistance of magnesium potassium phosphate cement (MKPC) paste to seawater erosion. MKPC paste specimens were prepared and their compressive strength, mass change, hydration temperature and water absorption were measured. The phase composition and microstructure were also analyzed. The results show that the initial hydration age of the reference sample M1 under natural curing condition has a significant effect on its compressive strength development in seawater. The residual ratios of the compressive strengths of M1(3d) and M1(28d), hydrated for 3 and 28 days, respectively, under natural curing condition, are 76.6% and 91.1% at 360-day seawater immersion age, respectively. This also indicates that early-age M1 has poor resistance to seawater erosion. Adding some limestone (LS) powders and silica fume (SF) can significantly improve the strength of early-age MKPC paste. The 3-day compressive strength of M2 with LS and SF is about 50% higher than that of M1. After immersion for 360 days in seawater, the residual ratios of the compressive strength of M2(3d) and M2 (28d) are both close to 93%. This implies that initial hydration age of M2 under natural curing condition has almost no effect on its compressive strength development in seawater. Compared with M1, M2 has higher resistance to seawater erosion, which is attributed to the higher hydration degree and more compact structure of M2. This paper might be useful for preparing MKPC-based materials that can meet the requirements of marine concrete.

1. Introduction

Hardened Portland cement paste has poor resistance to chloride ion diffusion and seawater erosion because of its porous structure. For this reason, the lifetime of marine concrete structure prepared by Portland cement is generally less than 30 years. Researchers are paying more attention on the technologies of preparing high performance marine concrete to improve the durability of marine concrete structure, such as improving the content of C3A and C4AF in Portland cement, adding water reducer and mineral admixtures in Portland cement concrete, etc. However, there is only limited improvement on the early strength, resistance to chloride ion diffusion and resistance to seawater erosion of Portland cement concrete, which is due to its inherent structural defects. Therefore, it is necessary to choose more suitable inorganic cementitious materials instead of Portland cement.

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 the final hydration products have typical properties of ceramics [1]. Compared with Portland cement, MPC has many advantages such as fast hardening, high early strength, strong adaptability to ambient temperature, good adhesion, small volume

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deformation, good compatibility with Portland cement-based materials, and high wear and frost resistance [1–5]. Therefore, in the end of last century, MPC-based materials has been used for repairing airport runway and municipal road engineering, which verifies its good durability [2]. In recent years, MPC has been used in civil engineering (concrete structure repair, corrosion-proof coating, fireproof coating, etc.), toxic waste solidification and biological filed, and some MPC products have entered the market [6].

Research on the resistance of MPC-based materials to seawater erosion is currently being carried out [5,7–9]. Zhen et al. [7] studied the erosion behavior of MPC mortar in sodium chloride solution and found that its ability to resist chloride ion penetration is better than that of Portland cement mortar. Jiang et al. [8] studied the early strength development and corrosion resistance to seawater of MPC mortar prepared by MPC and sea sand. Their results show that the MPC mortar at 180-day hydration age suffers almost no loss in strength, which proves its good resistance to seawater erosion. Li et al. [9] prepared MPC mortar samples with MPC, fly ash and quartz sand and immersed them in water, sodium chloride solution and sodium sulfate solution, respectively. Their results indicate that after immersion in sodium chloride and sodium sulfate solutions for one year, the strength loss of MPC mortar samples is less than 10%. Pei et al. [10] conducted a group of experiments on reinforced MPC concrete beams under accelerated corrosion conditions. According to the half-cell potential and galvanic current test results, MPC concrete beam has extra resistance to chloride induced corrosion. Note that in their study the hydration ages of MPC-based materials exceeded 28 days. There is currently little research on the resistance of MPC-based materials to seawater erosion at an early age. However, the ability to resist seawater erosion at an early age is required for materials used for quick repair applications.

Nevertheless, MPC-based materials have some disadvantages including fast setting, poor water stability and high cost, which limit their application. In our previous studies, composite retarder was used to solve the problems of fast setting and concentrated release of hydration heat of MKPC paste [11]. Some mineral admixtures such as fly ash, silica fume, limestone powders, alumina, metakaolin and sulphoaluminate have been used to improve the strength and water stability of MPC-based materials and decrease their cost [12–18]. The results demonstrate that adding a proper amount of mineral powders with Al, Si, Fe and Ca elements could improve the pore structure of hardened MPC-based materials, which further increase the compressive strength or water stability of the hardened MPC-based materials.

Seawater corrosion of concrete is mainly attributed to the degradation of compositions and structure of cement paste as well as the destruction of interface between cement and aggregates. In this study, only magnesium potassium phosphate cement (MKPC) pastes were prepared in order to exclude the influence of interface effects. The MKPC pastes were prepared with overburning MgO, potassium dihydrogen phosphate, composite retarder, silica fume, limestone powders and water according to existing research [12–18] and our previous research [11]. Further, the properties of MKPC pastes (hydrated for 3 days and 28 days, respectively) were studied under long-term seawater immersion conditions. This paper might provide useful information for preparing MKPC-based marine concretes and for later applications of MPC-based materials in marine repair works (especially the repair works of submerged concrete structures).

2. Materials and methods

2.1. Materials

The overburning MgO powders with specific surface area of 216 $m^2 \cdot kg^{-1}$ were obtained by grinding the electrical grade magnesia for 18 min in a small ball mill. The electrical grade magnesia was from Haicheng City (China) and produced by melting natural magnesite in electric arc furnace (over 1300 °C). Fig. 1 shows the particle size distribution of overburning MgO powders. The overburning MgO powders have an average particle diameter of 43.89 μm and a peak width of 71.32 μm. MgO particles with size less than 10 μm account for 7.52%. The oxide compositions of overburning MgO powders obtained by X-ray fluorescence (XRF) analysis are listed in Table 1, MgO content is higher than 90%, and the contents of CaO and SiO_2 are both higher than 3%.

The limestone (LS) powders were obtained by pulverizing natural limestone tailings. The particle size distribution of LS powders is shown in Fig. 1. The average particle size of LS powders is 63.98 μm, the peak width is 83.74 μm, and LS particles with size less than 10 μm account for 3.95%. The oxide compositions of the LS powders are shown in Table 1. The content of $CaCO_3$ (total contents of CaO and CO_2) is higher 80%, and the contents of MgO and SiO_2 are both higher 8%. The LS powders also contain a small amount of Al_2O_3 and Fe_2O_3. The specific surface area of silica fume (SF) is 22000 $m^2 \bullet kg^{-1}$. The particle size distribution of SF is shown in Fig. 1. The average particle size of SF is 0.49 μm, the peak width is 73.58 μm, and SF particles with size less than 1 μm account for more than 80%. The oxide compositions of the SF obtained by XRF analysis are listed in Table 1, showing the SiO_2 content is higher than 85%.

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 in the laboratory, which consists of borax, sodium phosphate dibasic dodecahydrate and inorganic chlorine salt.

2.2. MKPC pastes

In our previous study [11], composite retarder was used to solve the problems of fast setting of MKPC paste and concentrated release of hydration heat. The composite retarder was also used here for the same purpose. MKPC pastes were prepared with alkaline components (overburning MgO powders, SF and LS powders), acid component (KH_2PO_4), composite retarder (CR) and water. The mixing ratio is shown in Table 2. According to the study of Chau et al. [19] and our previous study [11], the optimal mass ratio of alkaline component to acid component was 3:1. In order to keep

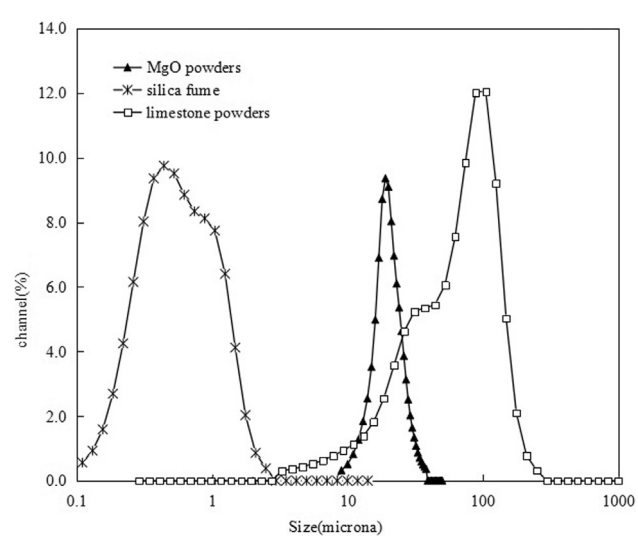

Fig. 1. The particle size distributions of MgO powders, silica fume and limestone powders.