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Magnesium potassium phosphate cement paste: Degree of reaction, porosity and pore structure

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ABSTRACT

Although magnesia–phosphate cements have been studied and applied in several fields for many years, the theoretical background on this kind of chemically bonded ceramics has not been sufficiently well established for the quantitative prediction of material properties. In this study, the stoichiometric factors of the chemical reaction in magnesium potassium phosphate cement (MKPC) paste are analyzed, and the degree of reaction of this cement is defined. Based on the stoichiometric factors and the degree of reaction, the porosity of MKPC paste, which is essential for predictions of both the mechanical and transport properties, is calculated. In addition, the pore structure is simulated by a newly developed computer model. The calculated porosities and the simulated pore structures are both found to be consistent with the results measured by mercury intrusion porosimetry (MIP).

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1. Introduction

Magnesia–phosphate cements (MPCs), or magnesium phosphate cements as sometimes referred to, are termed chemically bonded ceramics [1], as they are low-temperature high-strength materials formed by through-solution acid-based reaction between dead burnt magnesia and phosphate [2]. During decades of development, MPCs have been widely applied in many fields, such as the repair and rehabilitation of civil structures [3], stabilization of toxic matter and nuclear waste [4–7], treatment of waste water [8,9], and dental and bone restorations [10,11]. In civil engineering, MPCs are frequently used as repair materials for pavements and structures, as they set rapidly and produce high strength patches with low permeability, little drying shrinkage and good durability [3,12–16]. In early applications of MPCs in civil repair engineering, ammonium dihydrogen phosphate (ADP) was usually used as the phosphate component, with boric acid or borax compounds as the reaction retarder [3,13]. More strictly, the ADP-based MPC can be termed as magnesium ammonium phosphate cement (MAPC), as the main reaction product in the cement paste is magnesium ammonium phosphate (MAP) hexahydrate, with the formula $MgNH_4PO_4 \cdot 6H_2O$, which is a naturally existing crystal more commonly known as struvite [17]. However, as the byproduct of the reaction forming struvite, ammonium gas would generate an unpleasant odor, leading to attempts to replace ADP by potassium dihydrogen phosphate (KDP) [12,18–21]. As compared with ADP, KDP has smaller dissociation constant and lower solubility, which would lower the reaction rate to some extent, so that a retarder may not even be necessary, in some applications. The KDP-based MPC can be termed as magnesium potassium phosphate cement (MKPC), as the principal reaction product in the magnesia–KDP–water ternary system has been identified as magnesium potassium phosphate (MKP) hexahydrate, with the formula $MgKPO_4 \cdot 6H_2O$, which is more popularly known as struvite-(K). Struvite-(K) is isostructural with struvite [22], and has been found recently to be also a naturally existing mineral [23], which reflects its stability somewhat.

Most of the studies on MPCs focused directly on the engineering properties of the resulting paste or mortar, such as setting time, strength and durability, and attempted to obtain an optimized formula based on the raw materials available [3,4,12,14,15,18]. In recent years, some

Abbreviations: ADP, ammonium dihydrogen phosphate; COV, coefficient of variation; DTG, differential thermogravimetric analysis; H, water; KDP, potassium dihydrogen phosphate; KMP, potassium metaphosphate; M, magnesia; MAP, magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$; MAPC, magnesium ammonium phosphate cement; MIP, mercury intrusion porosimetry; MKP, magnesium potassium phosphate hexahydrate, $MgKPO_4 \cdot 6H_2O$; MKPC, magnesium potassium phosphate cement; MPC, magnesia–phosphate cement; REV, representative elementary volume; TGA, thermogravimetric analysis; XRD, X-ray diffraction; $L_{<200}$, weight loss below 200 °C; $L_{>200}$, weight loss above 200 °C; M/P, magnesia-to-phosphate molar ratio; M_i, molar mass of matter i, where i can be H, KDP, KMP, M, or MKP; m_{KDP}, initial weight of KDP before reaction; m_{KDP}^{un}, weight of unreacted KDP; $\tilde{m}M$, a mass parameter which is defined as $\tilde{m}M = MM \cdot M/P\eta M$; R_{600}, remaining weight of MKPC paste when heated to 600 °C; R_{KMP}, weight component of R_{600} due to KMP; R_M, weight component of R_{600} due to magnesia; v_H, volume of remaining bulk water in the REV; V_i, molar volume of matter i, where i can be H, KDP, M, or MKP; v_{IP}, volume of inner reaction products; v_j^i, initial volume of matter j in the REV, where j can be H, KDP, or M; v_j^r, reacted volume of matter j in the REV, where j can be KDP or M; v_{OP}, volume of outer reaction products; W/C, water-to-cement mass ratio; α_{KDP}, degree of reaction of KDP; α_M, degree of reaction of magnesia; γ, volume of reaction products formed when 1 unit volume of magnesia reacted; γ_H, volume of water consumed when 1 unit volume of magnesia reacted; η_M, purity of the dead burnt magnesia; ρ_i, density of matter i, where i can be H, KDP, M, or MKP; ϕ, porosity.

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researchers have begun to investigate the reaction mechanisms of MPCs [24–28]. However, theories that can be used to predict properties of MPC-based materials have not been established. Since MPCs have been considered as promising candidates for the partial replacement of Portland cement in construction and repair projects [21,29], it is imperative to develop such theories so that MPC-based materials can be designed in much the same way as Portland cement-based materials are designed, namely according to the properties of the raw materials and the desired performance. The present study aims to develop theories and methods as the basis of property prediction, and the scope is limited to MKPC since this seems to be more favored in recent research [4–7,12,30]. The stoichiometric factors of the chemical reaction in MKPC paste are first analyzed, and the degree of reaction of this cement is then defined through thermal analysis. Based on the stoichiometric factors and the degree of reaction, the porosity of MKPC paste, which is essential for predictions of both the mechanical and transport properties, is calculated. The pore structure is also simulated by a newly developed computer model. At last, the theory for porosity calculation and the model for pore structure simulation are validated by experimental results from mercury intrusion porosimetry (MIP) measurements.

2. Materials and experiments

Dead burnt magnesia powder (calcined at 1500 °C for 5 h) with a purity of 95.1%, powder KDP (chemical reagent) and deionized water were used as the raw materials for preparation of the MKPC paste. The chemical composition of the dead burnt magnesia is shown in Table 1. The milled magnesia and KDP powders were analyzed with a laser particle size analyzer, and the particle size distributions are shown in Fig. 1. In this study, pastes with the magnesia-to-phosphate molar ratios (*M*/*P*) of 4, 6, 8 and 12, and the water-to-cement mass ratio (*W*/*C*, where the cement contains magnesia and KDP) of 0.20 were prepared by mixing the raw materials according to the mix proportions. The mixing procedure involved firstly dry-mixing the powders for 1 min and then further mixing them with water for 3 min, in a vertical-axis planetary mixer. The mixed fresh pastes were cast into plastic tubes of diameter 2 cm and then sealed by plastic sheets. After 12 h, the specimens were demolded and sealed in airtight plastic bags.

At the ages of 3, 7 and 28 days, the specimens were taken out of the bags. Cylinders 2 cm long were cut from the specimens using a diamond saw, with the saw blade cooled by ethanol. Near-surface portions of each cylinder were removed, and the left central part was sawn into small cuboids with the smallest dimensions of 3–5 mm. The obtained cuboids were then vacuum-dried to constant weight. As recommended by Ma [31], such cuboids were used as samples for porosity measurements by MIP. In addition to the porosity, pore size distribution curves could also be obtained by MIP, based on the well-known Washburn equation in which theoretical parameters were chosen according to Ma [31]. A Micromeritics AutoPore IV 9500 was used for MIP measurements, and the maximum pressure that could be applied was 30,500 psi (210 MPa), which corresponds approximately to a minimum detectable pore diameter of 6 nm. Diamond [32] pointed out that MIP cannot provide valid estimates for pore size distributions of materials with complex pore structures, mainly due to the ink–bottle effect, and MIP results are valuable only to provide porosities and threshold pore diameters. However, as an easy and widely used method for pore structure characterization, MIP is still very useful in the comparative assessment of the pore structure and in providing physically or statistically meaningful parameters for developed models [31]. Recently, innovative schemes for MIP measurement have been developed to enable more accurate estimation of the pore size distribution [33,34], and intrusion curves from multi-cycle MIP measurements have been proposed as criteria for judging the reasonability of a pore size distribution deduced via other techniques [35,36]. In the present study, MIP measurements were conducted in two continuous intrusion–extrusion cycles. Pore size distribution curves deduced from the 1st intrusion were used for porosity determination and qualitative comparison of the pore structures, and the curves deduced from the 1st and 2nd intrusions were used for validating the computer model, by comparing them with the pore size distribution generated by the computer model.

Table 1
Chemical composition of the dead burnt magnesia (mass %).

MgO	SiO_2	CaO	Fe_2O_3	MnO
95.10	3.71	0.78	0.27	0.14

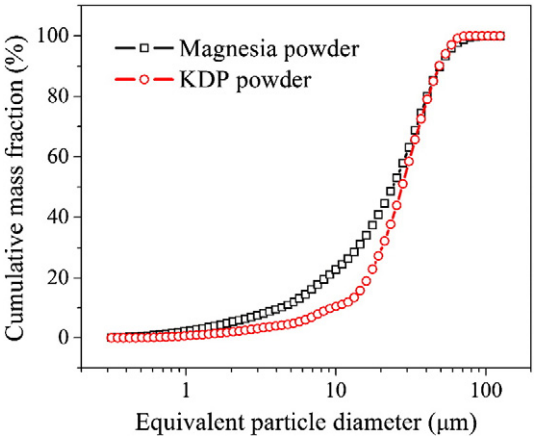

Fig. 1. Particle size distribution curves of magnesia and KDP powders.

The degree of reaction of MKPC was assessed by thermogravimetric analysis (TGA). To do so, dried cuboid samples as described above were crushed, pestled and sieved, and small particles ranging from 200 μm to 500 μm were collected as samples. In a thermal analysis, about 30 mg of a sample was put in an alumina top-opened crucible and heated from room temperature to 600 °C at a rate of 10 °C/min. The weight loss data was determined and recorded for further analysis. Nitrogen gas was chosen as the dynamic atmosphere, and corundum as the reference material.

3. From degree of reaction to porosity

The principal reaction in MAPC paste is the through-solution reaction between the dead burnt magnesia and the phosphate that produces struvite [26]. However, besides struvite, other minerals, such as $Mg_3(PO_4)_2 \cdot 4H_2O$ and $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$, can also be formed [13], which makes the quantitative analysis of this material more complicated. Contrarily, in the XRD (X-ray diffraction) patterns of MKPC paste reacted to some degree, all peaks other than the reactants correspond to MKP [6,12,25,29], and evidence of amorphous products is very weak. Therefore, assuming MKP to be the sole reaction product in MKPC will not introduce considerable error in the quantitative description of the microstructure. Another assumption in this study is that components other than magnesium oxide in the dead burnt magnesia are not only inert in the MKPC reaction but also stable in thermal analysis.

3.1. Stoichiometric factors

As frequently cited [6,18,29], the reaction in a MKPC paste can be written as

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O. \quad (1)$$

According to Eq. (1), 1 mol of magnesium oxide reacts with 1 mol of KDP and 5 mol of water, and produces 1 mol of MKP. The molar mass,

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