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Materials Letters

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Modeling magnesia-phosphate cement paste at the micro-scale



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ARTICLE INFO

Article history:

Received 9 January 2014

Accepted 22 March 2014

Available online 29 March 2014

Keywords:

Ceramics

Microstructure

Simulation and modeling

Magnesia-phosphate cement

Pore size distribution

ABSTRACT

In this paper, a computer model is established to simulate the microstructure of magnesia-phosphate cement paste at the micro-scale. The chemical reaction in the paste is analyzed first, based on which the microstructure is modeled through interacted growing and eroding spherical particles representing the solid phases. The pore structure of the simulated paste is characterized by a closing operation based algorithm. It is found that the simulated pore size distribution curves are consistent with corresponding experimental results.

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1. Introduction

Magnesia-phosphate cements (MPCs), which are also known as chemically bonded ceramics [1], have been widely utilized in rehabilitation of civil structures [2], stabilization of toxic matters and nuclear wastes [3,4], biomedical applications [5,6], etc. However, most of the studies on MPCs focused on directly the engineering properties, and attempted to obtain an optimized formula based on the locally available raw materials [2,3,7–9]. To the authors' knowledge, there are few methods that can predict the properties of MPC-based materials. The present study aims to develop a numerical model to simulate the microstructure of MPC paste, especially the pore structure, as it determines both mechanical and transport properties of the material. The MPC using KDP (potassium dihydrogen phosphate) as the phosphate component is focused on in this study, since it seems to be more favored in recent years compared with other types of MPCs [2–4]. This type of MPC is termed MKPC, as the principal reaction product in magnesia-KDP-water ternary system has been identified as MKP (magnesium potassium phosphate hexahydrate). The numerical simulation is achieved by interacted spheres representing the solid phases, based on voxel operation, and validated by MIP (mercury intrusion porosimetry) results.

2. Materials and experiments

Two MKPC pastes, with the *M/P* (magnesia-to-phosphate molar ratio) of 4 and 12, and the *W/C* (water-to-cement mass ratio) of

0.2, were made from dead burnt magnesia powder (calcined under 1500 °C for 5 h) with the purity of 95.1%, powder KDP (chemical reagent) and deionized water. As characterized by a laser particle size analyzer, the mean particle diameters of the milled magnesia and KDP powders are 26.9 μm and 31.2 μm, respectively. The particle size distribution curves are given in Supplementary materials. For specimen preparation, powders were first weighted and dry-mixed, and then mixed with water. The fresh paste was cast into a plastic tube and sealed by a plastic sheet. After 12 h, the specimen was de-molded and sealed in an airtight bag. At a specific age, the central portion of the specimen was sawed into small cuboids, and vacuum-dried to constant weight. The resulting dried samples were used for MIP measurements, according to the details recommended by Ma [10].

3. Algorithm

The principal reaction in the MKPC paste can be written as [7]:

$$\text{MgO} + \text{KH}_2\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot 6\text{H}_2\text{O} \quad (1)$$

The molar mass, molar volume and density of the four substances involved in Eq. (1) are listed in Table 1, in which M, KDP, H and MKP denote MgO, KH₂PO₄, H₂O and MgKPO₄ · 6H₂O, respectively.

In the reaction between MPC and water, phosphate is dissolved continuously in water, and the reaction occurs on the wetted surface of magnesia particles. The reaction products grow around the magnesia particles and connect with each other, developing the cementitious matrix [11]. This reaction mechanism is employed to direct the numerical simulation of the microstructure of MKPC paste.

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Table 1
Properties of the 4 substances involved in MKPC reaction.

Items	M	KDP	H	MKP
Molar mass M_i (g/mol)	40.30	136.09	18.02	266.47
Molar volume V_i (cm ³ /mol)	11.25	58.21	18.02	143.03
Density ρ_i (g/cm ³)	3.58	2.34	1	1.86

When MKPC in a paste reacts with water to a specific degree, the microstructure of the paste is determined by the degree of reaction of the magnesia, α_M , and the degree of reaction of the KDP, α_{KDP} . α_M and α_{KDP} can be related to each other as:

$$\alpha_M = \frac{\alpha_{KDP} \eta_M}{M/P} \quad (2)$$

where η_M denotes the purity of the magnesia. Given the W/C and M/P of a MKPC paste, the initial volumes of magnesia, KDP and water in a specific volume of paste, e.g. in a REV (representative elementary volume), can be easily obtained as v_M^i , v_{KDP}^i and v_H^i , respectively. To achieve the status defined by α_M and α_{KDP} , the volume of KDP that should be eroded or dissolved into the water for reaction is

$$v_{e,KDP} = v_{KDP}^i \alpha_{KDP} \quad (3)$$

and the volume of magnesia reacted is

$$v_{r,M} = v_M^i \alpha_M \quad (4)$$

As the reaction products grow around magnesia particles, the volume originally occupied by the reacted magnesia will be replaced by MKP. This part of the reaction products are defined as inner products, since they form inside the original surface of the magnesia particles, and the volume is denoted by v_{IP} . Obviously,

$$v_{IP} = v_{r,M} \quad (5)$$

According to Eq. (1) and Table 1, when magnesium oxide is transformed into MKP, the volume is enlarged by a factor of $\gamma = V_{MKP}/V_M = 12.71$. The reaction products other than inner products are defined as outer products, and the volume can be calculated as:

$$v_{OP} = (\gamma - 1)v_{r,M} \quad (6)$$

Chemically speaking, inner and outer products have no difference, they are just distinguished from each other by locations for the sake of numerical simulation. In addition, when one volume of magnesium oxide is reacted, the volume of water consumed in the reaction is $\gamma_H = 5V_H/V_M = 8.01$. Thus, the volume of bulk water remaining in the system can be calculated as

$$v_H = v_H^i - \gamma_H v_{r,M} \quad (7)$$

The unreacted MKPC paste is simulated by randomly distributing spheres representing magnesia and KDP particles in a cubic REV ($100 \times 100 \times 100 \mu\text{m}^3$) with periodic boundary conditions, according to the particle size distributions, M/P and W/C . The particle size distributions in the simulation system copy the real ones obtained through measurements, just particles smaller than $1 \mu\text{m}$ and those larger than $50 \mu\text{m}$ are cut off for saving the computational cost. Then, the REV is discretized into $500 \times 500 \times 500$ voxels. The consumption of reactants and the formation of reaction products are both processed through voxel operation, so that their real-time volumes can be easily computed by counting the corresponding voxels. Input α_M and α_{KDP} , the microstructure of the MKPC paste can be simulated by several steps as shown in Fig. 1. First, KDP particles, which are spherical assemblies of KDP voxels in the simulation system, are eroded inwards from their surfaces to simulate the dissolution. The erosion is conducted on all KDP particles layer by layer (each 1 voxel thick), until the volume of

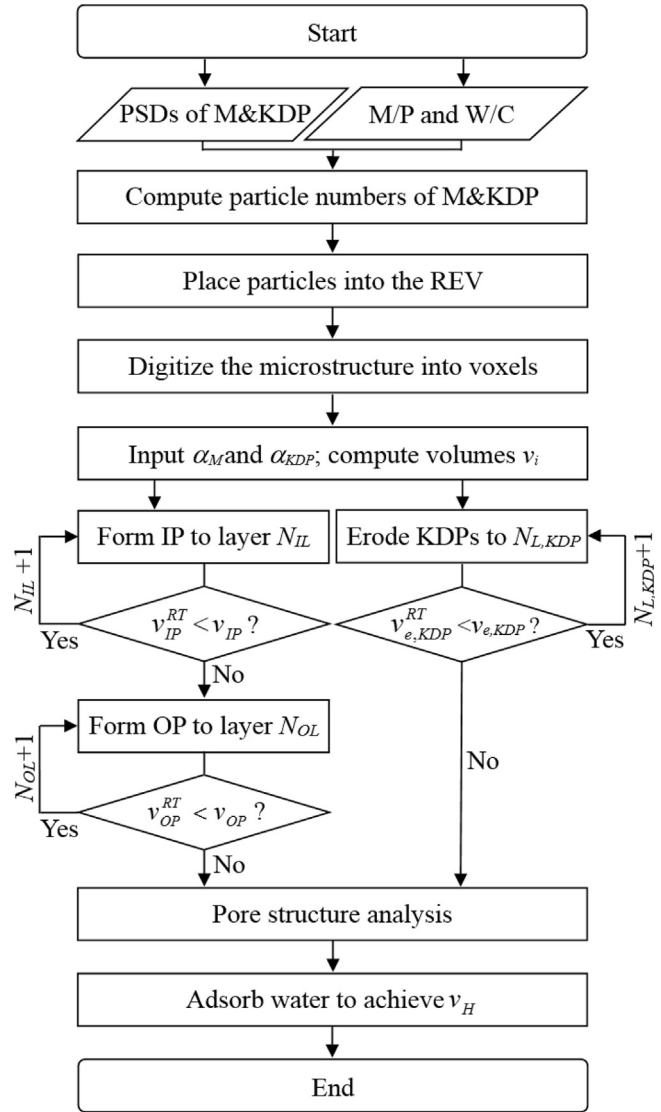


Fig. 1. Flowchart of the microstructure simulation of MKPC paste.

eroded KDP achieves the value calculated from Eq. (3). Simultaneously, all magnesia particles are processed in a similar manner, but the eroded magnesia voxels are immediately transformed into inner products. This operation stops once the volume of inner products can fulfill the value calculated from Eqs. (4) and (5). In the following step, from the original boundaries of the magnesia particles, outer products voxels are formed outwards, layer by layer, until v_{OP} calculated from Eq. (6) is achieved. When growing outer products, layers get in contact with each other, only free surfaces that are still exposed to the open space are allowed to grow further in their outer-pointing normal directions. To this step, the solid skeleton of the paste has been formed. The open space left in the REV represents the pore phases, including remaining bulk water, and voids formed due to the fact that the volume of the reaction products is smaller than that of the reactants. The pore structure is analyzed by a closing operation-based algorithm. This algorithm considers the REV as 500 digital images with 500×500 pixels each, in any of the three (x -, y -, and z -) directions. Each image is processed by the closing operation as illustrated in detail in Supplementary materials. In the output file, each pore voxel is assigned to a cylindrical pore with a specific diameter and 1 voxel high. After the algorithm is applied in all the three directions, each pore voxel will have three open

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