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Experimental and computational investigation of magnesium phosphate cement mortar

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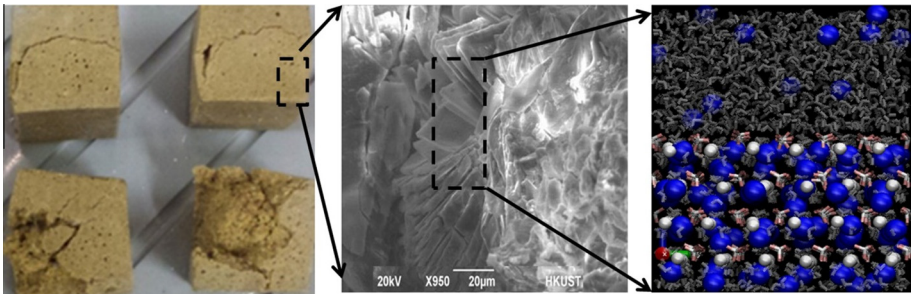
HIGHLIGHTS

- Increase of M/P ratio slows down the setting rate for MPC mortar.
- Increase of M/P ratio reduces the compressive strength of MKPC.
- The MNPC has optimum strength at M/P ratio 9.5.
- The properties of MPC are weakened after immersed in water solution.
- The unstable H-bonds and K—O bonds result in the hydrolytic weakening.

GRAPHICAL ABSTRACT

This figure studies the property of the MPC mortar at macro, micro and nano-level.



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ABSTRACT

For first time, an experimental and computational study has been conducted to investigate the properties of magnesium phosphate cement (MPC) mortar and its main hydration product struvite-K crystal that would account for the mechanical properties of these materials. Two types of MPC mortars, magnesium sodium phosphate cement (MNPC) and magnesium potassium phosphate cement (MKPC), were synthesized with magnesium to phosphate (M/P) ratio from 4 to 18 and water to solid ratio (w/s) from 0.16 to 0.2. Subsequently, the setting behavior, compressive strength and water resistance of MNPC and MKPC were investigated to study the influence of M/P and w/s ratios. An increase of M/P ratio can slow down the setting rate for both MPC mortar, and MNPC shows faster setting performance, as compared with MKPC. With increasing M/P ratio, the mechanical properties of MKPC mortar are gradually weakened, while the strength for MNPC mortar is first improved and then degrades, with the optimum value at M/P ratio of 9.5. Additionally, the saturated MPC mortars, immersed in water solution, are significantly weakened, showing poor water resistance. Micro-characterizations including X-ray diffraction and scanning electron microscopy of the MPC mortar reveal that MKPC mortars have good crystallization of struvite-K, with the morphology of plate packing at early hydration stage and the MNP hydrates show amorphous phase. Furthermore, molecular dynamics was conducted to study the structure, dynamics and mechanical properties of the main hydrated phase in MKPC cement, struvite-K crystal. The hydrolytic weakening effect of water molecules and failure mechanism have been unraveled that the H-bonds and K—Os connections lose the chemical stability due to water attacking and tensile loading, which explains the severe failure of MPC mortar observed in the water resistant experiments.

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1. Introduction

Magnesium phosphate cements (MPC), a type of chemically bonded ceramic, are produced by through-solution acid-based reaction between phosphate and dead burnt magnesia [1]. Due to the high strength at early stage, fast hydration process and the fire resistant properties, the MPCs have a wide range of applications in the rehabilitation of civil structures [23], stabilization of toxic matters and nuclear wastes [3], biomedical materials design [18]. In civil engineering, MPCs are frequently used to repair the pavements and concrete structures, as they produce high strength patches with low permeability and little shrinkage in very short setting time, and also have good binding ability with damaged structures. Hydration mechanism for the MPCs has been investigated for many years and is mainly based on the principal reaction [15], which can be written as:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$$

The major hydration product $MgKPO_4{\cdot}6H_2O$, termed as magnesium potassium phosphate hexa-hydrate (MKP), grows around the surface of magnesia and plays essential role in the development of the cohesion strength for the MPCs [16]. Interestingly, the hydration product MKP is also a natural crystal that is called as the struvite-K [22]. The microstructure of the struvite-K determines the mechanical and transport properties of MPC, which closely related to the durability of the material. Studying on the structure and properties of struvite can provide molecular understanding of the MPCs systems fundamentally, which guides for the high performance cement design. The engineering properties of the MPC cement, such as setting time, strength and durability, have been investigated obtain an optimized formula for the mix proportion of the raw materials [28,27]. Currently, the hydration mechanism and the microstructure of the MPCs materials have been investigated. In this respect, the relation between pore structure and hydration degree has been developed [17]. However, due to the experimental limitation, such as the material purity and the instrument accuracy, the properties of the struvite-K at molecular level have been seldom investigated. Computational method, such as molecular dynamics (MD), can help to explain the experimental findings and provide molecular insights on the structural and dynamic properties of MPC materials.

In this paper, an experimental and computational study has been conducted to investigate the properties of MPC mortar and its main hydration product struvite-K crystal. Two types of MPC mortars, magnesium sodium phosphate cement (MNPC) and magnesium potassium phosphate cement (MKPC), were first synthesized with magnesium to phosphate (M/P) ratio from 4 to 18 and water to solid ratio (w/s) from 0.16 to 0.2. Subsequently, the setting behavior, compressive strength and water resistance of MNPC and MKPC were investigated to study the influence of M/P ratio and water influence. X-ray diffraction and scanning electron microscopy was employed to characterize the microstructure of MPC cement. Finally, molecular dynamics was conducted to further explore the mechanism of the mechanical behavior and water resistant ability of the main hydration product in the MPC cement.

2. Methodology

2.1. Experimental method

2.1.1. Raw materials and mixture proportion

In this work, to prepare the MPC mortar, the raw materials include the dead-burnt magnesia (MgO) powder, potassium di-hydrogen phosphate (KDP) powder or sodium di-hydrogen phosphate (NDP), borax, tap water and sand. The MgO powder used was obtained by calcining a light-burnt magnesia powder at 1200 °C for 5 h. The KDP, NDP and borax powder were supplied by Guangzhou Chemical Reagent Factory, Guangdong, China. Chemical compositions of the dead-burnt magnesia powders were characterized by X-ray fluorescence spectrometry, and are given in Table 1. Both the dead-burnt magnesia powder and KDP powder or NDP powder were mechanically ground, and then passed through a sieve with a screen aperture of 150 μm. The sand also passed through a sieve with 2.35 mm. Mix proportions of the prepared MKPC and MNPC mortar are given in Table 2. As listed in the table, an M/P molar ratio ranging from 4 to 18, a water/powder ratio of 0.20 and a sand/powder (s/p) ratio of 1 were selected for the sample preparation. It should be pointed out here that the mentioned powder includes the dead-burnt magnesia, KDP powders or NDP powders and the borax. Additionally, to slow down the setting rate, 5% of borax powder was introduced to the solid reactants.

Table 1
The chemical composition characterization for dead-burnt MgO.

MgO	SiO_2	P_2O_5	CaO	MnO	Fe_2O_3
93.37	2.90	0.36	2.18	0.20	1.00

Table 2
Mixture portion for the MPC mortar.

M/P ratio	MgO (g)	KDP or NDP (g)	Borax (g)	Sand (g)	Water (g)	Water/powder
18	1147.5	202.5	67.5	1350	283	0.2
12.7	1000	250	62.5	1250	262.5	0.2
9.5	937.5	312.5	62.5	1250	262.5	0.2
7.4	875	375	62.5	1250	262.5	0.2
5.9	812.5	437.5	62.5	1250	262.5	0.2
4.8	750	500	62.5	1250	262.5	0.2

2.1.2. Properties evaluation

For each mixture, Vicat needle from ASTM standard C807-05 was utilized to determine the setting time. Prism specimens of $40 \times 40 \times 40\ mm^3$ were cast for strength measurement and were demoulded, then being cured in the condition of a temperature of 20 ± 1 °C and a relative humidity of 50 ± 5%. Compressive strength was carried out at 3, 7 and 28 days by an automatic concrete compression machine (ADS2000, unit test) with a loading rate of 3 kN per second.

The phase analysis was carried out by a PANalytical X'pert PRO-MPD diffractometer using Cu-Ka (wavelength = 1.54056 Å, 40 mA, 40 kV) radiation as the source with a step size of 0.05°. The morphology of MNDP and MKDP mortar were observed by scanning electron microscopy (SEM, JSM-6300F).

2.2. Computational method

2.2.1. Molecular model and force field

The simulation of crystal structure is based on struvite-K determined by Postl and Bojar [22]. In this simulation, the ClayFF force field [7] has been employed to describe the atomic potential between Mg, O, K, P and H atoms. The ClayFF, derived from the quantum mechanics, is an effective force field in modeling the structures and thermodynamic of oxide and hydroxide materials [14,6]. The force field parameters can be found in the reference [7,2].

MD simulation for the struvite-K crystal was conducted by using Lammps [21], a large scale molecule modeling package. The simulation follows two steps: the simulation systems are all relaxed at temperature 300 K for running 300 ps for the whole system to reach equilibrium, and then 10,000 ps NVT running continues after the equilibrium. Every 0.1 ps, the configuration information was sampled and therefore, equilibrium dynamic trajectories involving 100,000 atomic configurations were analyzed. This large samples can guarantee the statistically stability for data analysis.

2.2.2. Uniaxial tension test

The super-cell, obtained by periodically extending of original struvite-K model, undergoes uniaxial tension in *x*, *y*, *z* directions. The super-cells consist of 8400 atoms with the size of $4.1 \times 4.3 \times 4.4$ nm. The large simulation number gives statistical reliability for the failure simulation. In order to explore failure mechanism of struvite, the stress-strain relation and the change of molecular structure are investigated in the loading process. The supercell of struvite model was subjected to uniaxial tensile loading through gradual elongation with constant strain rate at 0.008/ps. NPT-ensemble MD simulation method for the tensile process has been widely utilized to study the fracture behavior of silica glass [10], calcium silicate hydrate [12] and other inorganic materials.