



Hydration behavior of magnesium potassium phosphate cement and stability analysis of its hydration products through thermodynamic modeling

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ABSTRACT

Magnesium potassium phosphate cement (MKPC) is normally applied in civil engineering because of its short setting time and superior mechanical properties. This study investigates the hydration behavior and hydration products of MKPC influenced by molar ratio between magnesia and phosphate (M/P ratio) through thermodynamic method. Results show that the composition of ultimate hydration products are controlled by concentration of KH_2PO_4 and MgO , activity of water and pH value of solution. When M/P ratio is lower than 0.64, the hydration product is $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$; When M/P ratio is between 0.64 and 0.67, the hydration products are $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$. When M/P ratio is between 0.67 and 1.00, hydration products are $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$; When M/P ratio is higher than 1.00, the hydration product is $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ together with unreacted MgO . This study also investigated the effect of additives, namely $\text{B}(\text{OH})_3$, H_3PO_4 , K_2HPO_4 and KH_2PO_4 .

1. Introduction

Magnesium potassium phosphate cement (MKPC) belongs to magnesium phosphate cement (MPC) system, is one of the special cements which are widely applied in fast repair and rehabilitation of civil structures [1–3], stabilization of toxic matter [4–6], treatment of wastewater [7,8], and restorations of dental and bone [9–11]. Through solution acid-based reaction between dead burned magnesia and phosphate, the high strength chemically bonded ceramics possess characters of rapidly set, high impermeability and little shrinkage [12–14].

Before the invention of MKPC, ammonium dihydrogen phosphate (ADP) is normally used as phosphate ingredient to form magnesium ammonium phosphate cement (MAPC), with the main hydration product as magnesium ammonium phosphate hexahydrate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, MAP) [15]. MAPC possesses weaknesses of bad waterproof property, instability during processing and storage and releasing the odor of ammonium [15], which promote the invention of stable MPC. The application of MKPC is reported in dental and refractory area by Prosen in 1939 [16], and is popularized by the work of Wagh, Singh and other workers from Argonne National Laboratory about encapsulant for various nuclear wastes [17–20].

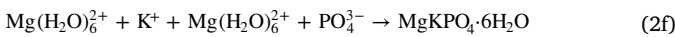
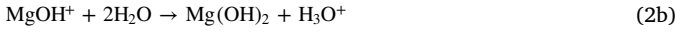
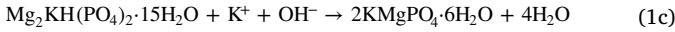
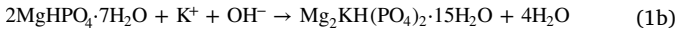
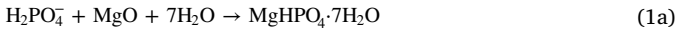
The mix proportion of MKPC has great influence on the composition of hydration products. The presence of magnesium potassium phosphate hexahydrate ($\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, MKP) is preferred because of its excellent mechanical properties. However, most studies in literature mainly focused on the experimental investigation of the influence of various factors on the mechanical properties, composition and stability of hydration products [21–23]. The experimental works indeed provide more phenomenon-based qualitative information; however, the intrinsic mechanism has to be disclosed via theoretical study. Currently few theoretical works have been done to give quantitative clues and reveal the underlying mechanisms [24,25]. Thermodynamic modeling could be a good theoretical method since it can demonstrate the theoretical composition of the hydration products.

Qiao and Chau [26–28] reported that $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, MKP can be detected from hardened MKPC paste, and recommended formation reaction of hydration products in Eqs. (1a)–(1d). Ding et al. [29–31] investigated the hydration process of MKPC using scanning electron microscopy (SEM), and stated that KH_2PO_4 would react with water firstly instead of MgO . The reactions took place in MKPC system are shown in Eqs. (2a)–(2f). Lahalle et al. [32,33] suggested that newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) as hydration product, was more stable than $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, and sometimes

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$Mg_3(PO_4)_2 \cdot 22H_2O$ can precipitate in the solution instead of MKP. The aforementioned hydration products have been identified from XRD test, however the formation and dissolution conditions of these hydration products still need further theoretical investigations [28,34–37].



It should be noted that the short setting time can limit its wide applications of MKPC. Therefore, researchers have investigated various retarders and additives and increase the setting time. Pirogov et al. [38] investigated the setting time and compressive strength of samples when K_2HPO_4 and K_3PO_4 are added into the MKPC system, and reported that the addition of K_2HPO_4 and K_3PO_4 lead to the increase of setting time and decrease of compressive strength at early time. Hall et al. [39] reported that Na_3PO_4 , boric acid, and borax can be applied as set-retarders. The mechanism of retarders is to reduce the intensity of the exothermic reactions during the initial setting and hardening stages. Lahalle et al. [32] indicated that boric acid doesn't slow down the initial dissolution of the reactants, but rather retards the precipitation of the products. Besides, boric acid tends to favor the formation of intermediate phases ($MgHPO_4 \cdot 3H_2O$ and $Mg_2KH(PO_4)_2 \cdot 15H_2O$) against that of K-struvite. These studies presented experimental results about the effect of some additives, however, the underlying mechanism and effect of these additives on composition and stability of hydration products still remains unclear.

Recently, thermodynamic modeling methods have been widely used in cement science. However, to the best of the authors' knowledge, there is not a thermodynamic database applicable for MKPC system. And the thermodynamic analysis has not been applied in analysis of stability of hydration products in MKPC system. Therefore, it is imperative to develop a database for MKPC and explore the properties of MKPC cement by thermodynamic modeling.

The framework of this study is as follows: firstly, there is a brief introduction about software and methodology, the database implemented in this study is proposed in this section. Afterwards, the validation of modeling is executed by anticipating pH value and ion concentration and comparing with literature results. Then, the effect of M/P ratio (For the sake of convenience, M/P ratio in the whole paper means molar ratio between magnesia and phosphates, rather than weight ratio.) on pH value, amount of hydration products and formation condition of hydration products, is explicitly presented in details. The volumes of hydration products influenced by M/P ratio and chemical reactions occurred in MKPC system are also summarized. Subsequently, the effect of some additives on composition and stability of hydration products are compared. Finally, this article ended with conclusions.

2. Thermodynamic modeling

2.1. Software and methodology

In this study, the thermodynamic modeling is carried out by using the geochemical specification code PHREEQC [40,41]. Pitzer model is employed to handle the conditions of high ion strength and complicate

ion interaction in MKPC solution. Voigt et al. [42] and Zhou et al. [43] found that Pitzer model can be used in the modeling of KH_2PO_4 and MgO system respectively, which provides preliminary work for MKPC systems. The Pitzer equation is given in Eq. (3a) [44].

$$\begin{aligned} \frac{1}{2} \sum_i m_i (\phi - 1) = & \frac{-A^\phi \cdot I^{3/2}}{\left(1 + b \cdot I^{1/2}\right)} \\ & + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \\ & + \sum_c \sum_c m_c m_c \phi^\phi + \sum_a \sum_a m_a m_a \phi^\phi \\ & + \sum_c \sum_c \sum_a m_c m_c m_a \psi_{cc'a} + \sum_c \sum_c \sum_a m_a m_a m_c \psi_{aa'c} \\ & + \sum_n \sum_a m_n m_a \lambda_{na} + \sum_n \sum_c m_n m_a \lambda_{nc} \\ & + \sum_n \sum_c \sum_a m_n m_c m_a \psi_{nca} \end{aligned} \quad (3a)$$

where A^ϕ : Debye–Hückel osmotic parameter, the theoretical expression is given in Eq. (3b). b : constant, 1.2, [$kg^{1/2} \cdot mol^{-1/2}$]. c : cation, a : anion, n : neutral species. \sum_c : the sum over all cations in the system; $\sum_c \sum_c$: denotes the sum over all the distinguishable pairs of dissimilar cations; analogous definitions apply to the anions. B , C , ϕ , ψ , λ and ζ are the combinations of experimental measured parameters.

$$A^\phi = \frac{1}{3} (2\pi N_0 \rho_w / 1000)^{1/2} (e^2 / \epsilon \kappa T)^{3/2} \quad (3b)$$

where ρ_w : density of water, $997.047 \text{ kg} \cdot \text{m}^{-3}$ at 25°C ; ϵ : dielectric constant of water, $78.36 \text{ [F} \cdot \text{m}^{-1}]$; κ : Boltzmann constant, $1.3806503 \times 10^{-23} \text{ [m}^2 \cdot \text{kg} \cdot \text{s}^{-2}]$; e : electron volt or charge of an electron, $1.602176565 \times 10^{-19} \text{ [C]}$; N_0 : Avogadro constant, $6.022 \times 10^{23} \text{ [mol}^{-1}]$. Therefore, $A^\phi = 0.39$ at 25°C and 0.1 MPa .

Calculations in this study are based on the assumption that the components in raw material, other than dead burnt magnesia and KDP, are not only inert in the MKPC reaction, but also stable in thermal analysis. The hydration condition in this study maintains at 25°C , 0.1 MPa [45].

2.2. Database

Thermodynamic data for MKPC system were all collected from critically reviewed literatures. Most of the data were collected from Pitzer [46] and MOC [43] database. The data were rewritten in the form recognized by PHREEQC. Potential hydration phases of MKPC include $MgHPO_4 \cdot 7H_2O$, $MgHPO_4 \cdot 3H_2O$, $Mg_2KH(PO_4)_2 \cdot 15H_2O$, $Mg_3(PO_4)_2 \cdot 8H_2O$, $Mg_3(PO_4)_2 \cdot 22H_2O$ and MKP based on the literature review [20,27,31,32,35]. Thermodynamic data for dead burnt magnesia are used in this study. Thermodynamic properties of other solid phases are shown in Table 1. Reactions included in MPC system are shown in Table 2.

2.3. Model verification

Ion concentrations and pH value of MKPC solution are compared with experimental results here to verify the accuracy of the database. Fig. 1 exhibits the activities of ions under different pH values with presence of $KMgPO_4 \cdot 6H_2O$. It can be found that the calculated ion activity agrees well with experimental results from Taylor et al. [13,58], which insured the accuracy of calculation for ion activity. Similarly, Fig. 2 presents the evolution of elements K, P and Mg with the hydration of magnesia. It can be found that with the hydration of MgO, the concentration of P and K decrease, the concentration of Mg increase at first, and then decrease. Calculation results have a good agreement with experimental results from Qiao et al. [56]. Fig. 3 displays the development of pH value in MKPC solution with the hydration of MgO. It can be easily found that the rise of pH value goes through several inflection points. When small amount of MgO is hydrated, measured pH

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