

HYDRATION BEHAVIOR OF MAGNESIUM AMMONIUM PHOSPHATE CEMENT AND STABILITY ANALYSIS OF ITS HYDRATION PRODUCTS THROUGH THERMODYNAMIC MODELING

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Abstract

Magnesium ammonium phosphate cement (MAPC) has been commonly applied in civil engineering. However, the analysis of hydration behavior and composition of solid assemblages still needs further exploration. From thermodynamic simulation, it is shown that the molar ratio between MgO and $\text{NH}_4\text{H}_2\text{PO}_4$ (M/P ratio) determines the final composition of hydration products. When M/P ratio is lower than 0.49, the solid assemblage is $(\text{NH}_4)_2\text{Mg}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; When M/P ratio is between 0.49 and 1.00, the solid assemblages are $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and unreacted MgO; When M/P ratio is higher than 1.00, the composition of solid assemblages is $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and unreacted MgO.

Keywords: MAPC, thermodynamic simulation, M/P molar ratio

1. INTRODUCTION

Magnesium phosphate cement (MPC) is a new kind of nonhydraulic cementitious material with ultra-fast setting, hardening and ultra-early strength, usually used for reinforcement of structure and quick repair stabilize/solidify deleterious waste, and treat wastewater [1-3]. MPC are formed through an acid-base reaction between dead-burned MgO and a soluble acid phosphate (typically an ammonium, potassium or sodium phosphate), forming a magnesium phosphate salt with cementitious properties [4].

Magnesium ammonium phosphate cement (MAPC), as one branch of MPC, was first patented by Prosen in 1936 as a binder materials to produce dental casting investment materials via mixing MgO with ammonium phosphate [5].

The performance of materials are intrinsically influenced by the assemblages of hydration products, so it is imperative to put efforts to the hydration products formed to further study the mechanism of cementitious materials. Various hydration products of MAPC have been found in the literature [6-10]. The predominant hydration product of MAPC is usually considered to be $\text{MgNH}_4\text{H}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite), while other phases such as

MgHPO₄·3H₂O (newberyite), (NH₄)₂Mg(PO₄)₂·4H₂O (schertelite), NH₄MgPO₄·H₂O (dittmarite), Mg₃(PO₄)₂·8H₂O (bobierrite) and (NH₄)₂Mg₃(PO₄)₄·8H₂O (hannayite), are perceived to be intermedia products [6-8].

Previous studies presented experimental results about the assemblage of hydration products, however, to the best of the authors' knowledge, the underlying mechanism for the composition and stability of hydration products remains unclear yet. In this study, thermodynamic calculation was conducted to investigate the mechanism behind.

2. THERMODYNAMIC MODEL

2.1 Model selection

Geochemical specification code PHREEQC is applied here to carry out the thermodynamic simulation of MAPC system. PHREEQC uses an ion-association model to calculate thermodynamic properties. PITZER model [11] is employed to handle the conditions of high ion strength and complicate ion interaction in MAPC solution. Ali et al. [12] and Zhou et al. [13] reported that PITZER model can be used in the modeling of NH₄H₂PO₄ and MgO system respectively, which provides preliminary work for MAPC systems. The PITZER equation is given in Eq. (1).

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

where A^ϕ : Debye–Hückel osmotic parameter, the theoretical expression is given in Eq. (2). b : constant, 1.2, [kg^{1/2}·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.

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

where ρ_w : density of water, 997.047 kg/m³ at 25 °C; ϵ : dielectric constant of water, 78.36 [F·m⁻¹]; κ : Boltzmann constant, 1.3806503 × 10⁻²³, [m²·kg·s⁻²]; e : electron volt or charge of an electron, 1.602176565 × 10⁻¹⁹, [C]; N_0 : Avogadro constant, 6.022 × 10²³ [mol⁻¹]. Therefore, $A^\phi = 0.39$ at 298 K and 0.1MPa.

2.2 Database construction

Thermodynamic data for MAPC system were all collected from critically reviewed literatures. Most of the data were collected from PITZER [11] and MOC [13] database. The data were rewritten in the form recognizable for PHREEQC. Based on the literature review, potential hydration phases of MAPC include, MgHPO₄·3H₂O, (NH₄)₂Mg(HPO₄)₂·4H₂O,

$\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Calculations in this study are based on the assumption that the components in raw material, other than dead burnt magnesia, are not inert in the MAPC reactions. The hydration condition in this study maintains at 25°C , 0.1MPa [14].

2.3 Verification

Ion concentrations and pH value of MAPC suspension are compared with experimental results here to verify the accuracy of the database. The analytical grade dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), net content >99.0%, magnesium oxide, net content >98% and deionized water were used. The $m(\text{NH}_4\text{H}_2\text{PO}_4)/m(\text{H}_2\text{O})$ is set to 0.024, while the molar ratio of MgO to $\text{NH}_4\text{H}_2\text{PO}_4$ (M/P) changes from 0 to 1 (in 0.1 increments). The prepared MAPC suspension was continuously stirred with an overhead stirrer and placed in a 25°C water bath until the end of testing. The pH data was automatically collected at time steps of 1 min. The measured equilibrium pH value of MAPC suspension is illustrated in Figure 1. Figure 2 exhibits that the calculated pH value and ion concentration of Mg^{2+} and PO_4^{3-} meet well with experimental results conducted in this paper and those from Ronteltap's work [15], which proves that the database used for simulation is reliable.

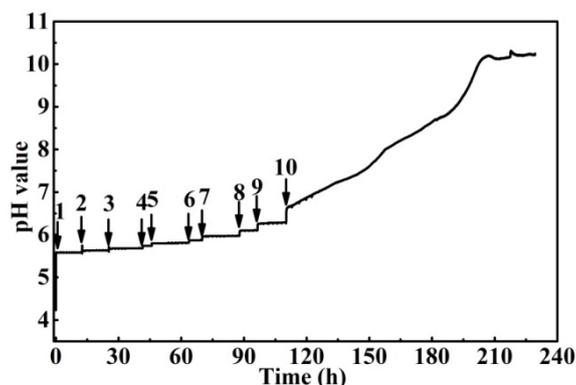


Figure 1: pH value of MAPC suspension with different M/P

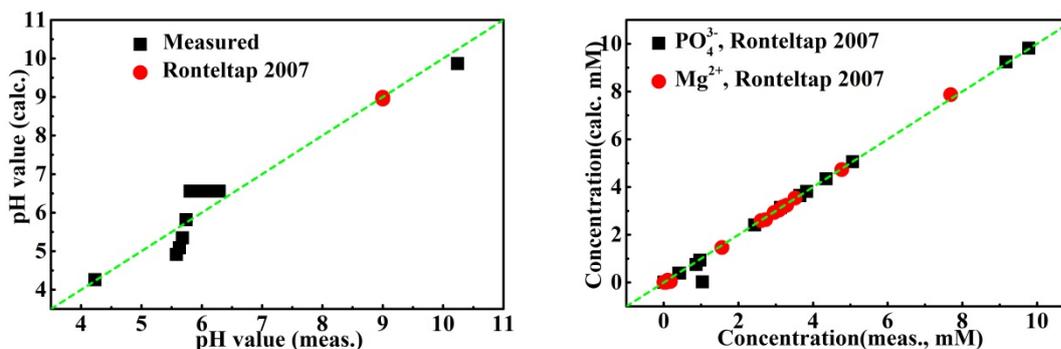


Figure 2: Comparison of measured and calculated pH values and concentration of Mg (Mg^{2+}) and P (PO_4^{3-}) of MAPC suspension.

3. MODELLING RESULTS AND DISCUSSION

Fig. 3 illustrates the assemblage of simulated hydration products and pH values of MAPC suspension with $n(\text{NH}_4\text{H}_2\text{PO}_4) = 0.21\text{mol}$, $m(\text{H}_2\text{O}) = 1\text{kg}$ and the $M/P(n(\text{MgO})/n(\text{NH}_4\text{H}_2\text{PO}_4))$ molar ratio changes from 0-4. As shown in Fig. 1, when

$\text{NH}_4\text{H}_2\text{PO}_4$ is added to deionized water, pH value drops from 7 to P0. The dissolution of MgO which releases Mg^{2+} to participate in consequent reaction accounts for the pH increase from P0 to P1. As M/P increases, $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitates from solution first, and the process can be described by Eq. (3). Compared with $\text{NH}_4\text{H}_2\text{PO}_4$, the amount of MgO added at first is relatively small not sufficient. The relatively excess $\text{NH}_4\text{H}_2\text{PO}_4$ reacts with MgO in terms of molar ratio 2:1 to form $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, as illustrated by Eq. (3). Whereafter, with the increase of M/P, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ starts to appear in hydration products, corresponding to the increase of pH from P2 to P3 (Eq. (4)). After that, the pH value remains unchanged (P3-P4). However, the amount of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is decreasing, and simultaneously $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ starts generating whose content continuously increases with the continued adding of MgO . This phenomenon can be explained through Eq. (5). The generated $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ reacts with MgO to form $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. This solid phase transformation process does not affect the pH value of investigated MAPC system. The increase of pH from P4 to P5 attributes to the transformation of generated $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. When M/P molar ratio is equal or greater than 1, the main and the only hydration product is struvite (Eq. (7)). It's worth noting that, the simulation results are the ideal results of a complete reaction in each step.

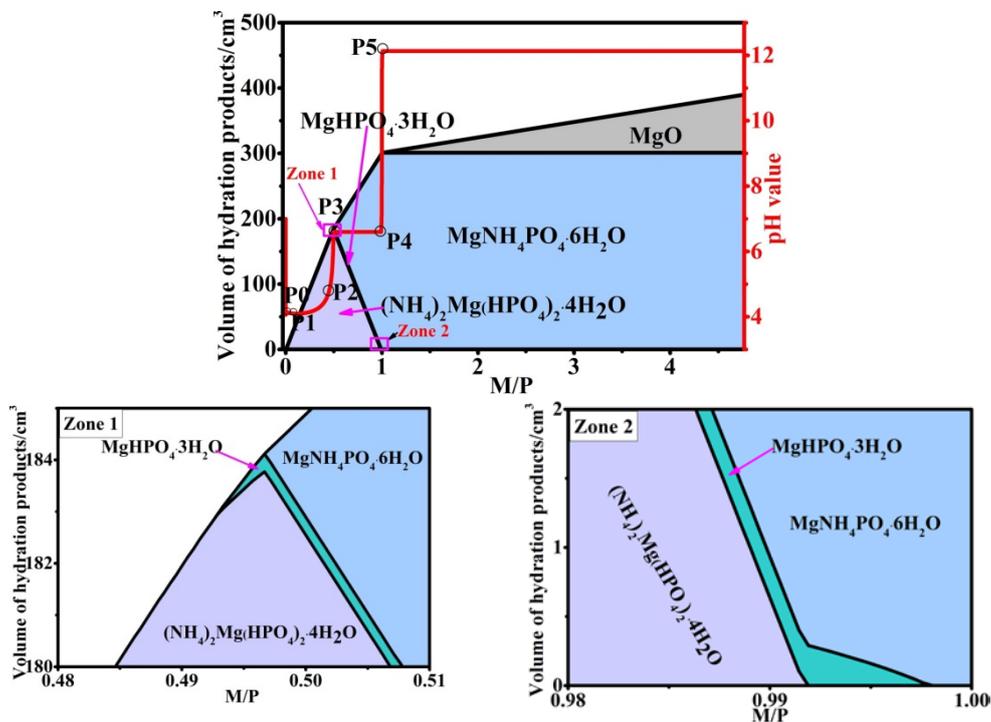
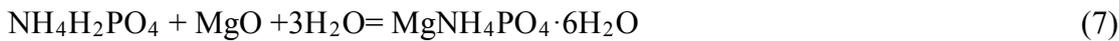
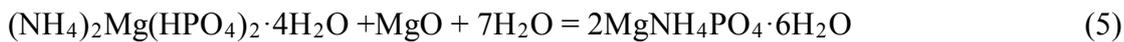


Figure 3: Assemblage of simulated hydration products and pH values of MAPC with different M/P or P/M values:(a): $n(\text{NH}_4\text{H}_2\text{PO}_4) = 2.1\text{mol}$, $m(\text{H}_2\text{O}) = 1\text{kg}$);(b): $n(\text{MgO}) = 10\text{mol}$, $m(\text{H}_2\text{O}) = 1\text{kg}$.

Fig.3 illustrates the evolution of hydration products with different M/P molar ratio. Following the order of precipitation, $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ can precipitate from solution at 25 °C, 0.1MPa in thermodynamic simulation, which have also been proved by XRD test in recent studies[8]. The precipitation and dissolution condition of hydration products are influenced by $\text{NH}_4\text{H}_2\text{PO}_4$ concentration and M/P ratio. From Fig. 3, it can be found that the formation areas and amount of these hydration products are determined by M/P ratio. When the concentration of ADP is specified, the amount of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ precipitated from solution increases firstly and then decreases with the increase of MgO. There is a maximal MgO content where maximum of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ can precipitate from the solution (M/P=0.49). The generation of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ shows similar trend with that of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ and the increase rate of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ amount is slower than that of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$. With the continue increase of MgO content (M/P>0.49), the amount of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ increases first and then maintain at a constant value. At the same time, the amount of $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ decreases with the increase of M/P. When M/P molar ratio exceeds 1.0, the content of unreacted MgO increases with the increase of M/P molar ratio.

Table 1: Influence of M/P ratio on composition of solid assemblages of MAPC system after hydration

M/P value	Hydration assemblage
<0.49	$(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$
0.49<M/P<1	$(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
M/P>1	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

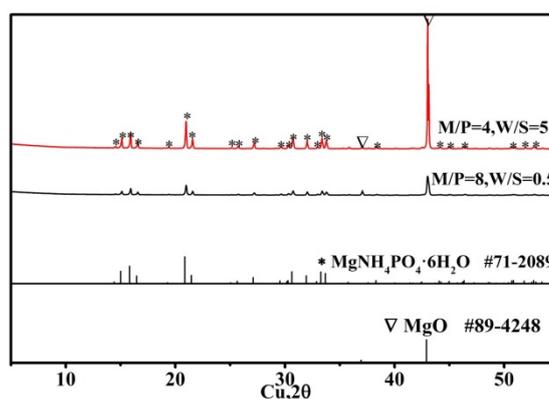


Figure 4: XRD analysis of MAPC system with M/P=8, W/S=0.5 and M/P=4, W/S=5

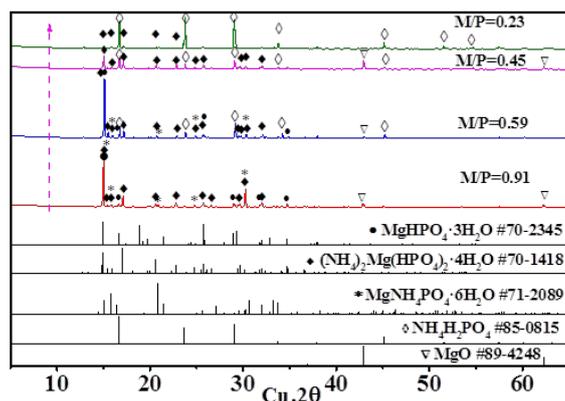


Figure 5: XRD analysis of MAPC system with $n(\text{H}_2\text{O})/n(\text{NH}_4\text{H}_2\text{PO}_4)=3.333$, $\text{P}/\text{M}=1.100, 1.692, 2.200, 4.400$

4. CONCLUSIONS

- In MAPC system, potential hydration products are $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and there are also unreacted MgO .
- The composition and stability of hydration products are determined by M/P ratio. When M/P ratio is lower than 0.49, the final hydration products is $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$. When M/P ratio is between 0.49 and 1.00, the final hydration products are $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. When M/P ratio is higher than 1.00, as intermediate phase, $(\text{NH}_4)_2\text{Mg}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ can precipitate from the solution at first, and dissolve into solution later, the final hydration products are $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and unreacted MgO .

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