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Reaction mechanism of magnesium potassium phosphate cement with high magnesium-to-phosphate ratio

Biwan Xu*, Barbara Lothenbach, Andreas Leemann, Frank Winnefeld

Laboratory for Concrete & Construction Chemistry, Swiss Federal Laboratories for Materials Science and Technology (Empa), 8600 Dübendorf, Switzerland

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ABSTRACT

Understanding reaction mechanisms of magnesium potassium phosphate (MKP) cement is of significant importance, as it is closely related to the optimum design of MKP cement-based materials. In this study, reaction mechanisms of MKP cements with a high magnesium-to-phosphate (Mg/PO_4) molar ratio of 8 were investigated at two different water-to-solid (w/s) ratios of 0.5 and 5. The experimental findings show that the use of this high Mg/PO_4 molar ratio suppresses the formation of potassium-free magnesium phosphate hydrates. K-struvite is mainly formed with probably more phosphate than the theoretical value. Moreover, the w/s ratio plays a crucial role on governing the reaction path of MKP cements. The lower w/s ratio (w/s = 0.5) leads to higher potassium concentration and pH value, thus suppressing the formation of intermediate product, $Mg_2KH(PO_4)_2{\cdot}15H_2O$, which is formed at the higher w/s = 5. However, it causes the formation of minor amount of brucite at 28 d, which coexists with K-struvite in the paste.

1. Introduction

Magnesium phosphate cements, also known as magnesium phosphate ceramics, are clinker-free cements that have strong chemical bonding and high mechanical strength through acid-base reactions between magnesia and phosphate acid (H_3PO_4) or soluble acid phosphates, such as ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium dihydrogen phosphate (NaH_2PO_4), or potassium dihydrogen phosphate (KH_2PO_4) [1–4]. Magnesium potassium phosphate (MKP) cement which uses KH_2PO_4 has been intensively studied in the past two decades [4–36]. Rehabilitations of infrastructure [4–10,13–15,19–23,30–34] and waste stabilization/solidifications [18,27–29] are the two main practical applications of MKP cement.

MKP cement is a ternary system consisting of magnesia, KH_2PO_4 and water. The principal hardening reaction of MKP cement is the following

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4{\cdot}6H_2O\ (\text{K-struvite}) \qquad (1)$$

As indicated in Eq. (1), magnesium potassium phosphate hexahydrate ($MgKPO_4{\cdot}6H_2O$), or K-struvite, is the principal reaction product that provides mechanical strength of MKP cement-based composites. However, the reaction path that leads to the final precipitation of K-struvite is much more complicated than represented by Eq. (1). Variations of the ratios among magnesia, KH_2PO_4 and water can lead to different reaction products depending on time [10,25,28], as well as changed material performance, such as setting time, mechanical strength, and volume stability [7,8,12–14,19,29,33]. Thus a number of mix proportions have been used for fabricating MKP cement-based composites in the past two decades. The ternary phase diagram of MgO-KH_2PO_4-H_2O in Fig. 1(a) shows the mix proportions of MKP cement systems reported in open literature [5–36]. As displayed in Fig. 1(a), the distribution of these mix proportions can be generally divided into two zones.

Zone 1 includes mix proportions with the magnesium-to-phosphate (Mg/PO_4) molar ratios ranging from 1 to 12 and high water-to-solid (w/s) mass ratios (w/s > 1). These mix proportions were employed for making MKP cement suspensions that mainly aimed to study the reaction mechanisms [10,25]. The mix proportions in zone 2 have the Mg/PO_4 molar ratio ranging from 1 to 14, but small w/s ratios which were mostly lower than the theoretical value (0.51) for producing K-struvite (Eq. (1)). Normally, they were adopted for fabricating MKP cement-based composites that aimed for potential practical applications [5–9,24,26,27,29–36]. Moreover, as displayed in Fig. 1(b), optimum Mg/PO_4 molar ratios for fabricating high strength MKP cement-based composites were in the range from 4 to 8 [7,8,19,33,34].

Understanding reaction mechanisms of MKP cement is of significant importance, as it is closely related to the optimum design of MKP cement-based composites. Wagh [3] proposed a three-step mechanism, which could be described as follows: (i) the first formation of aqueous $Mg(H_2O)_6{}^{2+}$, when magnesia is mixed with KH_2PO_4 solution; (ii) the

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* Corresponding author.
E-mail address: biwan.xu@empa.ch (B. Xu).

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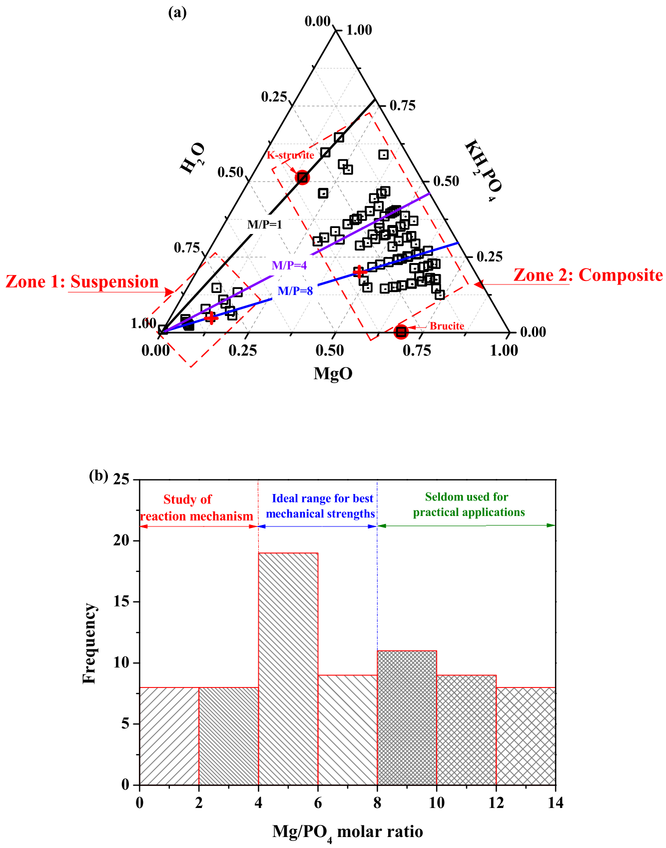

Fig. 1. (a) Reported mix proportions of MKP cements [5–36] in a ternary phase diagram; the areas of composite cements and of studies in diluted suspensions are indicated; the MKP cements with Mg/PO_4 molar ratio = 8 investigated in the present study are marked by crosses.
(b) Frequency distribution of the reported Mg/PO_4 molar ratios [5–36].

percolation and formation of K-struvite gel as the aqueous magnesium reacts with the released K^+ and PO_4^{3-} ions in solution; (iii) saturation and crystallization of K-struvite gel. Recently, the reactions involved in setting and hardening of MKP cement have been investigated in more detail. It was found that different solids formed consecutively before the precipitation of K-struvite [10,25,28]. As displayed in Fig. 2(a), Chau et al. [10] reported the formation of two intermediate reaction products, $MgHPO_4{\cdot}7H_2O$ (phosphorrösslerite) and $Mg_2KH(PO_4)_2{\cdot}15H_2O$, before precipitation of K-struvite in a MKP cement suspension with a Mg/PO_4 molar ratio of 4 and a w/s ratio of 10. In a highly diluted MKP cement suspension with a Mg/PO_4 molar ratio of 1 and a w/s ratio of 100, Lahalle et al. [25] observed $Mg_2KH(PO_4)_2{\cdot}15H_2O$ as the only intermediate reaction product, which was subsequently transformed to K-struvite and $Mg_3(PO_4)_2{\cdot}22H_2O$ (cattiite), as schematically demonstrated in Fig. 2(b). Rouzic et al. [28] studied the reaction evolution of a MKP cement paste with a Mg/PO_4 molar ratio of 1 and a low w/s ratio of 0.2 and found the intermediate reaction product, $MgHPO_4{\cdot}3H_2O$ (newberyite), before the formation of K-struvite. These studies suggest that the Mg/PO_4 ratio, the availability of water and the pH values [10,25,28] determine which hydrates precipitated during the reaction of MKP cement-based composites.

As discussed above, current studies of the reaction mechanism of MKP cement have been limited to those with low Mg/PO_4 molar ratios ($Mg/PO_4 \leq 4$) [10,25,28]. In practice, higher Mg/PO_4 molar ratios ($Mg/PO_4 > 4$) are more frequently used for making MKP cement-based composites, particularly those for infrastructural applications [5–10,13–15,19–23,30–34]. However, their reaction mechanism is still not fully explored. In this study, two MKP cement systems with a high Mg/PO_4 molar ratio of 8 and with two different w/s ratios of 0.5 and 5 were studied. Changes of the solid and liquid phase in these two systems during reaction were determined by various techniques.

2. Experimental

2.1. Materials and mix design

Dead-burnt magnesia, KH_2PO_4, and deionized water were used as raw materials. Chemical compositions of magnesia and KH_2PO_4 were determined by X-ray fluorescence (XRF) analysis, and are given in Table 1. Besides MgO, Mg_2SiO_4 and $CaMgSiO_4$ are present as minor phases in the magnesia. The mean particle size and BET surface area of the magnesia are 19.0 ± 0.3 μm and 0.55 ± 0.08 m^2/g, respectively.

The reactivity of the dead-burnt magnesia was evaluated by using the acetic acid method [19,37] at acid (1 M)-to-magnesia mass ratio of 5, where the reaction time until the suspension reaches a pH value of 7 is used as reactivity index (R_{MgO}) [19,37]. A higher R_{MgO} indicates low reactivity of magnesia powder. The measured R_{MgO} of the magnesia was 10 ± 1 min. Two MKP cement systems, a paste (w/s = 0.5) and a

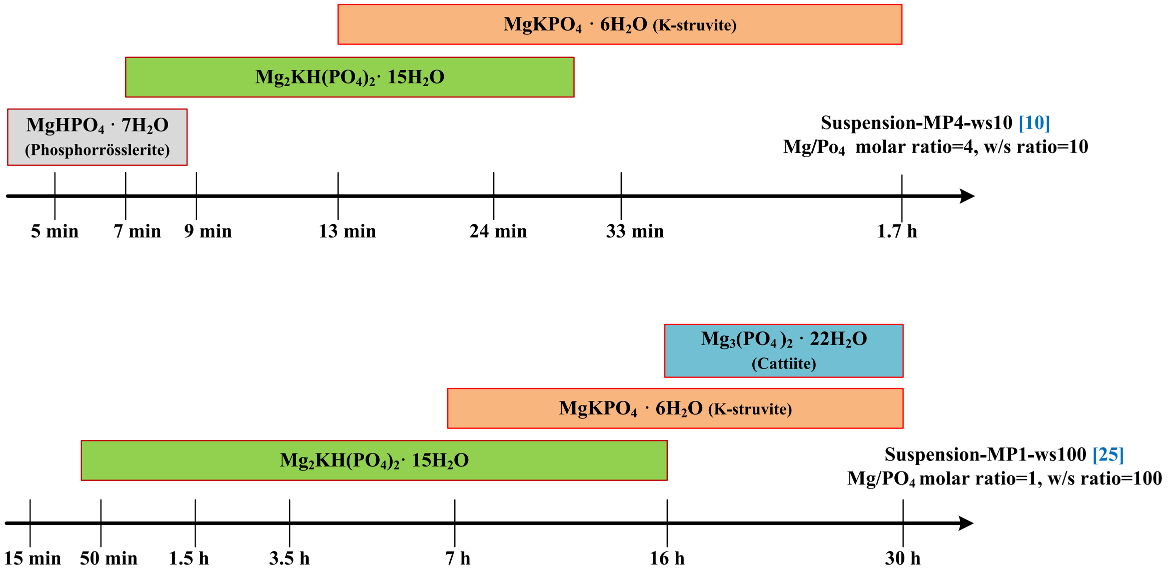

Fig. 2. Scheme of the reported hydration evolutions of MKP cement suspensions as described in [10,25].