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Cement and Concrete Research

Discussion

Discussion of the paper "Characterisation of magnesium potassium phosphate cement blended with fly ash and ground granulated blast furnace slag" by L.J. Gardner et al.

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ABSTRACT

A recently published paper authored by Gardner et al. [Characterisation of magnesium potassium phosphate cement blended with fly ash and ground granulated blast furnace slag, Cem. Concr. Res. 74 (2015) 78–87] is discussed. This work is of great significance in understanding the reaction mechanism of magnesium potassium phosphate cement blended with supplementary cementitious materials. However, several points in this work need to be further discussed, as shown in this discussion, including the mix proportion, paste morphology, mechanism of the synergy between MKPC and fly ash/ground granulated blast furnace slag.

1. Introduction

In a recent paper, Gardner et al. [1] presented an experimental study on the synergetic effect between magnesium potassium phosphate cement (MKPC) and fly ash (FA)/ground granulated blast furnace slag (GGBFS), in terms of compressive strength, phase composition, morphology and the synergy mechanisms. It was reported that the incorporation of FA and GGBFS could increase the compressive strength of MKPC pastes. Struvite-K was identified as the main reaction product (or binder phase) in either MKPC paste or FA/MKPC and GGBFS/MKPC pastes. In addition, an amorphous orthophosphate phase, although not identified, was proven to be present in the blended pastes and was believed to contribute to the increased compressive strength. Evidence that the glassy aluminosilicate phase in FA and GGBFS can be partially dissolved under the near-neutral conditions of MKPC paste, and evidence of the potential formation of a potassium-aluminosilicate phase, were also presented in the light of microstructure characterization and nuclear magnetic resonance (NMR) analysis. This work is of great significance in understanding the mechanism of the synergetic effect between MKPC and the supplementary cementitious materials. However, there are several points that need further discussion, involving the mix proportion used in this study, the morphology of the MKPC-based pastes, and the FA/MKPC and GGBFS/MKPC synergy mechanisms.

2. Mix proportion

To prepare MKPC-based pastes, an MgO-to-KH_2PO_4 molar ratio (m/p) of 1.7 and a water-to-solids mass ratio (w/s) of 0.24 were adopted, and the amounts of retarder, FA and GGBFS in the pastes were calculated based on given weight ratios to the sum of weights of MgO, KH_2PO_4 and water. The m/p of 1.7 adopted in the experiments is relatively low. Note that in civil engineering applications, the m/p of MKPC based materials is normally much higher than that. Typical m/p values can range from 4 to 16 [2–5]. On the one hand, with a low m/p, a considerable portion of KH_2PO_4 will be remained in the paste with a typically adopted w/s in the range of 0.13–0.32 [2–6]. Since KH_2PO_4 is a soluble phase, too much residual KH_2PO_4 will lead to a poor water resistance of the resultant material, apart from aesthetic issues due to leaching. On the other hand, it has been reported that when w/s equaled 0.2, an optimal m/p of 6 appeared to give the highest compressive strength, the lowest porosity as well as the lowest permeability [6]. And there seems to be a trend that the optimal m/p increases following the decrease of w/s [2–8]. In the case of w/s = 0.24, the optimal m/p should be around 5. The adopted m/p of 1.7 could be much lower than the optimal value for the purpose of performance optimization.

The authors didn't clearly state where the material would be used, but according to their previous work [9], perhaps they were targeting on the encapsulation of radioactive waste. This application requires low permeability, large amount of hydration products (binder phase), and as little as possible water remained. Pursuing more binder phase for
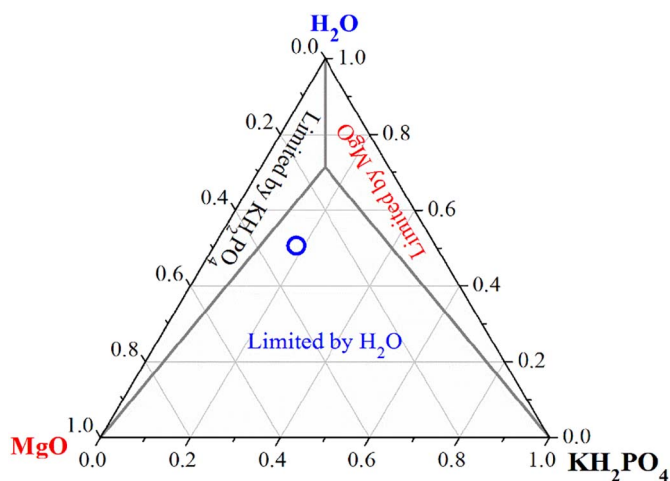

Fig. 1. Triangular phase diagram of the MgO-KH$_2$PO$_4$-H$_2$O ternary system (molar ratio). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

sorption of radionuclides was perhaps one of the reasons why a low m/p of 1.7 was adopted. The authors should have also realized the potential problems that remained KH$_2$PO$_4$ could result in, as they claimed that the adopted m/p of 1.7 was "in excess of the stoichiometric proportions to ensure the conversion of all phosphate to struvite-K". However, it is impossible that KH$_2$PO$_4$ is consumed out in the reaction of forming struvite-K with a relatively low w/s of 0.24 used in the work under discussion.

It is well-known that the chemical reaction in an MgO-KH$_2$PO$_4$-H$_2$O ternary system can be written as

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \qquad (1)$$
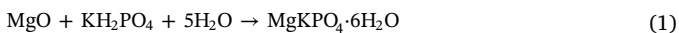
The reaction formula shows clearly that the stoichiometric

proportions of MgO:KH$_2$PO$_4$:H$_2$O read 1:1:5. When proportions of one or two reactants of the three are comparatively lower than the theoretical values, the reaction will be limited by its/their availability. The potential limits have been clearly shown in Fig. 1, the triangular phase diagram of the MgO-KH$_2$PO$_4$-H$_2$O ternary system (molar ratio). The mix proportion of the MKPC paste (m/p = 1.7, w/s = 0.24) used in the work under discussion is marked by a blue circle in Fig. 1. It can be seen that the chemical reaction in this paste should be limited by the availability of water. That is to say, KH$_2$PO$_4$ cannot be completely converted into struvite-K, but an unreacted portion should be remained in the paste. Even though FA and GGBFA have a potential to consume phosphate, and even though the effective water/(MgO + KH$_2$PO$_4$) ratio equals 0.41 in the FA/MKPC and GGBFS/MKPC pastes, KH$_2$PO$_4$ is not completely converted as proven by the NMR spectra (Fig. 8 in the article under discussion). Through a calculation based on the stoichiometry, to completely convert the KH$_2$PO$_4$, a much higher w/s (~0.44) is needed. If the w/s of 0.24 is to be kept, a higher m/p (~5.9) can make sure the complete conversion of KH$_2$PO$_4$, which can also potentially result in a much higher compressive strength and much better water resistance and durability.

3. Morphology

The article under discussion includes backscattered electron (BSE) images of the FA/MKPC and GGBFS/MKPC pastes, which show that the struvite-K particles appear with a laminar habit in polished sections and to be highly "cracked" due to "dehydration under vacuum" for analysis. However, in our view, this morphology could be formed in the growing process of struvite-K particles, rather than due to dehydration-induced cracking.

The authors didn't put a BSE image of the reference MKPC paste in the article under discussion. A BSE image of a MKPC paste with the same m/p and w/s as the one used in the study under discussion is shown in Fig. 2, with the corresponding elemental maps. This image shows the same characteristics as those described by the authors.
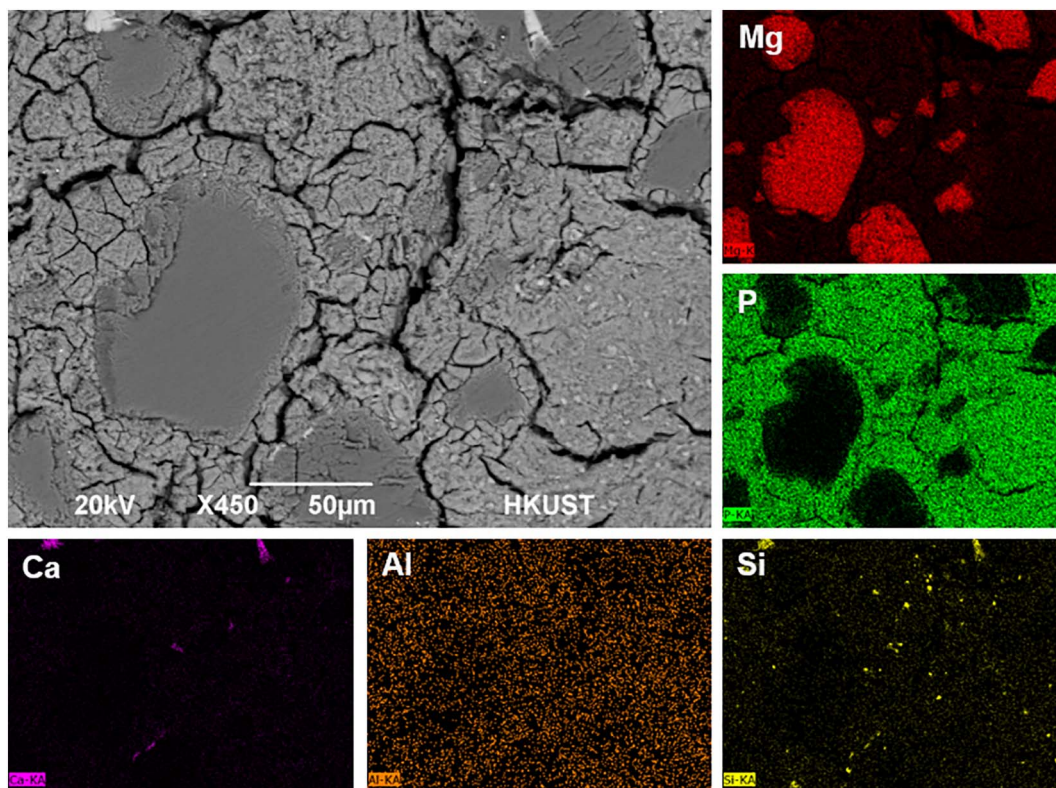

Fig. 2. Backscattered electron micrograph and elemental maps of hardened MKPC paste (m/p = 1.7, w/s = 0.24) after 28 days of curing.