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Hydration mechanism of wollastonite-blended magnesium potassium phosphate cements

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ABSTRACT

Magnesium potassium phosphate (MKP) cement has been mainly used as rapid repair materials in the field of civil engineering and as immobilization material for heavy metals and low-level nuclear wastes in the field of waste management. The addition of wollastonite as a supplementary material in MKP cement can improve the cement properties such as efflorescence resistance, heat resistance, flexural and compressive strengths. However, the role of wollastonite in MKP cements is yet not well understood. This study explores the hydration mechanisms of wollastonite-blended MKP cements considering the impact of the key factors such as magnesium-to-phosphate (Mg/PO_4) molar ratio and water-to-solid (w/s) ratio through experimental approaches and thermodynamic modelling. The experimental results show a higher wollastonite reaction in MKP cements with a lower Mg/PO_4 molar ratio. Less magnesia reacted establishes a lower pH value, which is favorable for the reaction of wollastonite. The hydration of wollastonite does not lead to the formation of crystalline hydrates, but to the precipitation of amorphous hydroxyapatite and magnesium silicate hydrate (M-S-H) as suggested by both experimental and thermodynamic findings. Those phases largely contribute to higher flexural and compressive strengths of the MKP cements at later ages.

KEYWORDS: *Magnesium potassium phosphate cement; Wollastonite; Hydration mechanism; Thermodynamic modelling.*

1. Introduction

Magnesium potassium phosphate (MKP) cement is an alternative to Portland cement. Generally, the main hardening mechanism of MKP cement can be described through the following equation, giving K-struvite ($MgKPO_4\cdot 6H_2O$) as main hydration product.

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4\cdot 6H_2O \quad (1)$$

Wollastonite ($CaSiO_3$) is an inosilicate mineral and has been used in cementitious materials for decades (Low and Beaudoin (1992)). The use of wollastonite in MKP cements can improve cement properties such as efflorescence resistance (Xu et al. (2020)), heat resistance (Gao et al. (2016)), flexural and compressive strengths (Xu et al. (2020, 2021)); however, the role of wollastonite in MKP cements is not yet well understood. This study explores the hydration mechanisms of wollastonite-blended MKP cements considering the key factors of magnesium-to-phosphate (Mg/PO_4) molar ratio and water-to-solid (w/s) ratio through experimental approaches and thermodynamic modelling.

2. Experimental

Dead-burnt magnesia (MgO), monopotassium dihydrogen phosphate (KH_2PO_4) and wollastonite were used as starting materials (Xu et al. (2020, 2021)). The MKP cements were prepared at Mg/PO_4 molar ratios of 2.7 and 4, w/s ratios of 0.25, 0.5, and 5, and with wollastonite at the levels of 0, 35%, and 40%, by weight of the binder (sum of magnesia, KH_2PO_4 and wollastonite). The samples were cured at 20 °C and 70% relative humidity (RH). Flexural and compressive strengths were determined on two prisms with the dimension 20 mm × 20 mm × 100 mm. The solid phase assemblages of the hydrated pastes were determined by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The pH development in MKP cement suspensions was monitored in-situ for 24 h. The sample preparation and test protocols were detailed in (Xu et al. (2019)). Thermodynamic modelling was carried out using the geochemical GEMS-PSI software, coupled with the thermodynamic data for magnesium potassium phosphates (Lothenbach et al. (2019)).

3. Results and discussion

3.1 Flexural and compressive strength of pastes

As displayed in **Fig. 1**, the MKP cements without wollastonite show better strengths at the higher Mg/PO_4 molar ratio of 4. The strength reduction at lower Mg/PO_4 molar ratio of 2.7 over time could be attributed to the unreacted KH_2PO_4, formation of intermediate hydrates, and thus to potential expansion and micro-cracking (Xu et al. (2019)). The use of wollastonite greatly improves the strengths, especially at later ages. Furthermore, the wollastonite-blended MKP cements demonstrate higher strengths at the lower Mg/PO_4 molar ratio of 2.7, in contrast to the plain MKP cements without wollastonite.

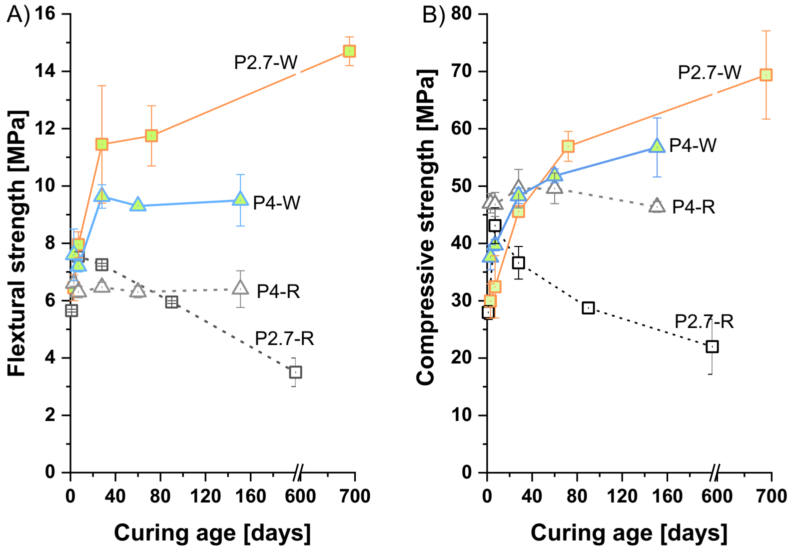

Fig. 1 A) Flexural strength, B) compressive strength of the MKP cement pastes at w/s ratio of 0.25 without (P2.7-R and P4-R) / with wollastonite (P2.7-W and P4-W). The number in the sample names refers to the molar Mg/PO_4 ratio. Note that the wollastonite levels in the samples P2.7-W and P4-W are 40% and 35%, respectively.

3.2 Hydration kinetics

The pH-development of the suspensions share two common characteristic maxima (P1, P2) as labelled in **Fig. 2**. Compared with the plain MKP cement suspensions, the use of wollastonite extends the plateau after the peak P2 to later reaction time, especially for the lower Mg/PO_4 molar ratio of 2.7, indicating the slowed-down MgO reaction. Further, the pH values of the wollastonite-blended MKP cement suspensions after 24 h are reduced by around 1.2 units, which can be attributed to the lower portion of MKP cement used in the blend and to partial chemical reaction of wollastonite.

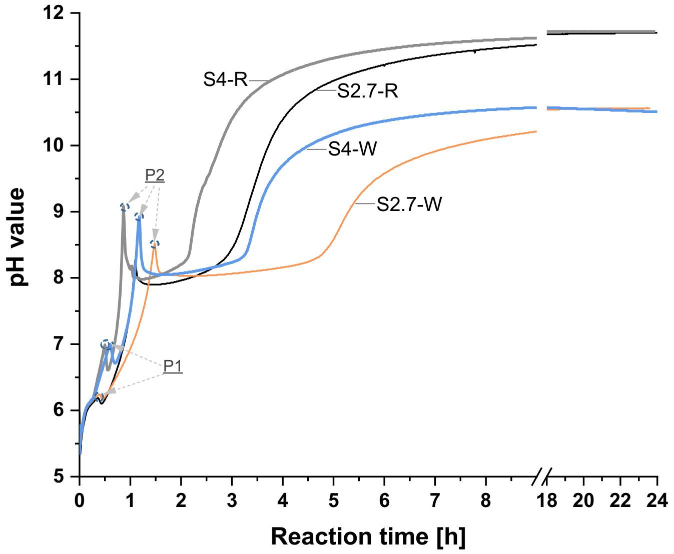

Fig. 2 The pH development curves of the MKP cement suspensions at w/s ratio of 5 without (S2.7-R and S4-R) / with wollastonite (S2.7-W and S4-W). Note that the wollastonite levels in the samples S2.7-W and S4-W are 40% and 35%, respectively.

3.3 Phase assemblage

The effect of the Mg/PO4 molar ratio on the hydrate assemblages of wollastonite-blended MKP cements is predicted as given in **Fig. 3**. At lower Mg/PO4 molar ratios, hydrates such as newberyite ($MgHPO_4 \cdot 3H_2O$), brushite ($CaHPO_4 \cdot 2H_2O$), $CaK_3H(PO_4)_2$ are more likely to form due to the lower pH. The increase of the Mg/PO4 molar ratio increases the pH, thus favoring precipitation of hydrates such as K-struvite, calcium hydroxyapatite (HAP), magnesium silicate hydrate (M-S-H), and even traces of brucite.

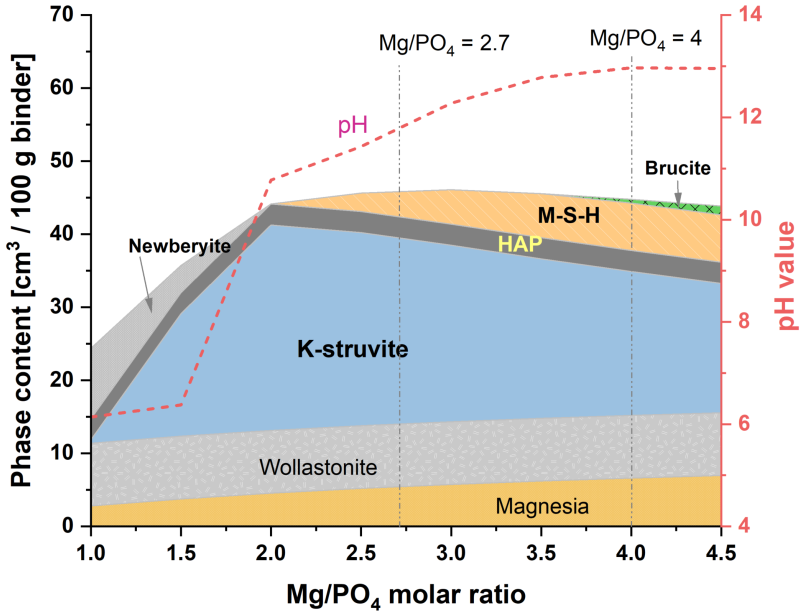

Fig. 3 Phase assemblages of wollastonite-blended MKP cement pastes as predicted by thermodynamic modelling, considering Mg/PO4 molar ratios from 1 to 4.5, a w/s ratio of 0.5, a wollastonite level of 35% (by weight of binder), and reaction degrees of magnesia and wollastonite of 0.35 and 0.30, respectively.

Consistent with the modelling results, the XRD and TGA results given in **Fig. 4** confirm K-struvite as the main hydrate in wollastonite-blended MKP cements; however, no additional crystalline hydrate was determined by XRD in both pastes. The further hydrates predicted by thermodynamic modelling such as HAP and M-S-H may exist in ill-crystalline or amorphous forms as evidenced by energy-disperse microanalyses in (Xu et al. (2020, 2021)). The potential presence of some M-S-H is also mirrored in the slightly increased water loss between 300 to 600°C. In addition, the TGA data of the sample P2.7-W* shows a small weight loss at around 700 °C, indicating the formation of a small amount of calcite.

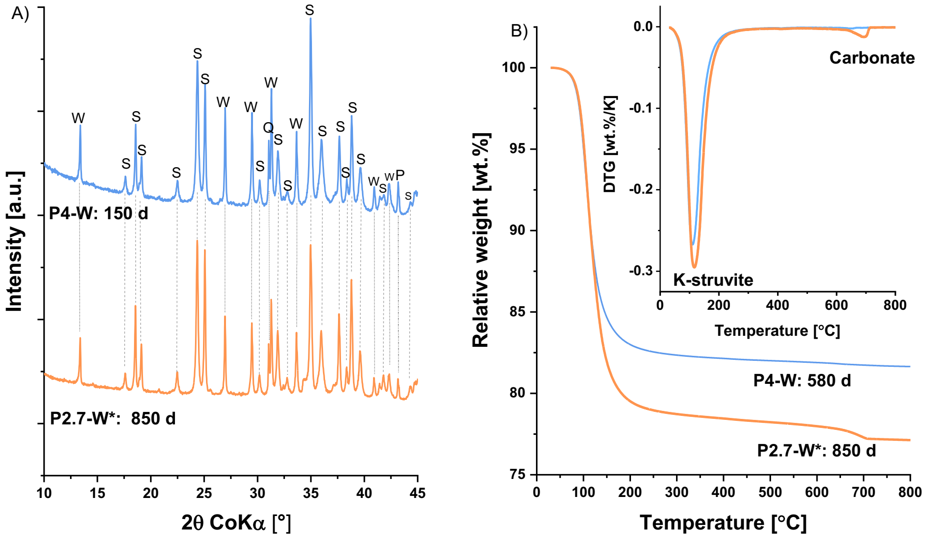

Fig. 4 A) XRD patterns and B) TGA/DTG curves of the wollastonite-blended MKP cement pastes at Mg/PO_4 molar ratios of 2.7 and 4. Note that the samples P2.7-W* and P4-W were prepared at w/s ratio of 0.5 and 0.25. The wollastonite levels in the samples P2.7-W* and P4-W were 40% and 35%, respectively. S = K-struvite ($MgKPO_4 \cdot 6H_2O$), Q = quartz (SiO_2), W = wollastonite-*2M* ($CaSiO_3$).

3. Conclusions

Wollastonite can be used as an effective supplementary cementitious material in MKP cements, which can not only help to lower the CO_2 emissions by replacing a part of the dead-burnt magnesia, but also improves cement performance. This study explored the influence of wollastonite on mechanical strength and hydration of MKP cements at different Mg/PO_4 molar ratios through experimental approaches and via thermodynamic modelling. The experimental findings show that wollastonite can well improve strengths of MKP cements at later age, in particular at lower Mg/PO_4 molar ratios. Wollastonite reacts more at lower Mg/PO_4 molar ratios, and forms ill-crystalline or amorphous phases, such as calcium hydroxyapatite (HAP) and magnesium silicate hydrate (M-S-H) as suggested by thermodynamic modelling.

Acknowledgements

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