Influence of magnesium-to-phosphate ratio and water-to-cement ratio on hydration and properties of magnesium potassium phosphate cements

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Abstract: Magnesium-to-phosphate (Mg/PO₄) and water-to-cement (w/c) ratios are important factors controlling hydration and properties of magnesium potassium phosphate (MKP) cements. This study investigated the influence of Mg/PO₄ molar ratios (2.7, 4 and 8) and w/c (0.25 and 5) on cement hydration, compressive strength and volume stability. Low w/c ratio slowed down cement hydration at lower Mg/PO₄ beyond 1 day, and prevented the precipitation of intermediate hydrates at higher Mg/PO₄. At lower Mg/PO₄ expansion and strength loss were observed with time due to the continuing hydration within the already hardened cement. Higher Mg/PO₄ resulted in faster hydration, higher strength, and in the precipitation of traces of brucite, which had no significant influence on the long-term volume stability and strength. Therefore, moderate Mg/PO₄ molar ratios between 4 and 8 depending on w/c ratio used are recommended for the production of MKP cements with robust performance.

Keywords: Magnesium potassium phosphate (MKP) cement; Magnesium-to-phosphate (Mg/PO₄) molar ratio; Water-to-cement (w/c) ratio; Hydration; Compressive strength.

1 Introduction

Magnesium phosphate cements (MPCs) are clinker-free cements, which harden through acid-base reaction between calcined magnesia (MgO) and phosphate acid or soluble acid phosphates in the presence of water [1]. Diammonium phosphate ((NH₄)₂HPO₄) [2, 3], monoammonium phosphate (NH₄H₂PO₄) [3-8], monopotassium phosphate (KH₂PO₄) [1, 3, 9-21] and monosodium phosphate (NaH₂PO₄) [22-24] are the typical acid phosphates for making MPCs. Compared with other acid phosphates, KH₂PO₄ has two prominent advantages that make the industrial application of magnesium potassium phosphate (MKP) cements more favorable. Generally, rapid reaction starts right after the contact of dry MPCs with water and releases significant amount of heat [1, 3, 11, 25, 26]. KH₂PO₄ has lower water solubility than NH₄H₂PO₄ and NaH₂PO₄; therefore, it slows down cement reaction and reduces heat release to some extent. Moreover, KH₂PO₄ avoids ammonium gas emission during cement setting and service life in contrast to ammonium phosphates. The advantages of MKP cements include fast setting [9, 26, 27], high early strength [9, 27-29], low shrinkage [9, 29, 30], and strong bonding with Portland cement concrete substrates [9, 10, 31, 32]. MKP cements have been used as rehabilitation materials [9, 31, 32], as stabilization/solidification agents for immobilizing wastes containing heavy metals [33-36], and been considered as potential binders for conditioning low-level nuclear wastes [3, 37-43]. Recent research involved also the use in medical technology due to their good biocompatibility and antibacterial properties [44, 45].

Traditionally, the following mass balance equation has been used to describe the principal hardening reaction of MKP cements:

As shown in Eq. (1) magnesium potassium phosphate hexahydrate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, K-struvite) is considered to be the stoichiometric reaction product of hydrated MKP cements and to provide mechanical properties [9, 10, 17]. However, recent studies [11-13, 20, 46] showed that the cement hydration paths could be more complicated, and largely affected by water-to-cement (w/c) ratio. Lahalle et al. [12, 13] compared the hydration paths of two MKP cement suspensions that had same Mg/PO_4 molar ratio of 1 and different w/c ratios of 1 and 100. It showed that the higher w/c ratio of 100 led to the first precipitation of the intermediate hydrate, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, and later co-precipitations of K-struvite and cattiiite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$) [13]. The decrease of w/c ratio to 1 increased the number of intermediate hydrates that were $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$), but limited the hydrates at later stage to only K-struvite [12]. A similar hydration path with the same intermediate hydrates and K-struvite as the only late hydrate was also reported by Chau et al. [46] in a MKP cement suspension with Mg/PO_4 molar ratio of 4 and w/c ratio of 10. Using Mg/PO_4 molar ratio of 1, Rouzic et al. [20] found at w/c ratio of 0.2 a different intermediate hydrate, newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), precipitating prior to the formation of K-struvite. Influence of w/c ratios at 0.5 and 5 on the hydration path of MKP cement with high Mg/PO_4 molar ratio of 8 was also reported by the authors of this study. It showed that the lower w/c ratio of 0.5 avoided the precipitation of intermediate hydrates, but caused the later co-precipitations of K-struvite and traces of brucite ($\text{Mg}(\text{OH})_2$) [11]. Based on those previous studies [11-13, 20, 46], it can be also indicated that Mg/PO_4 molar ratio in addition to w/c ratio is the other important factor controlling cement hydration path. However, systematic studies regarding this aspect are still rare in literature.

As demonstrated in Eq. (1), Mg/PO_4 molar ratio equal to 1 is adequate to generate K-struvite, and is expected to lead to good material performance. However, an excess of magnesia over

KH₂PO₄ has been proved to be more beneficial in practice [9, 14, 15, 18, 19, 21]. High Mg/PO₄ molar ratios (≥ 4) have been frequently used for preparing MKP cementitious materials aiming for rehabilitations [9, 18, 21]. On the contrary, low Mg/PO₄ molar ratios (< 4) have been more preferably used for waste immobilizations due to the low pH conditions [14, 15]. Excessive unreacted magnesia in MKP cementitious materials, especially those with high Mg/PO₄ molar ratios, normally raises the concern over brucite formation and the consequent detrimental volume expansion [12]. However, the formation of brucite and its effect on the long-term properties has not yet been investigated in open literature. In addition, efflorescence along with material volume expansion has been documented for some MKP cementitious materials with low Mg/PO₄ molar ratios [3, 19]. But the nature of efflorescence and the relevant impact on material performance, like strength and volume stability, are still not well explored yet.

To investigate the influence of Mg/PO₄ molar ratio and w/c on cement hydration and material properties, MKP cements were prepared in this study at various Mg/PO₄ molar ratios of 2.7, 4, and 8 and w/c ratios of 0.25 and 5. The evolution of the solid and liquid phase with time were determined at w/c ratios of 0.25 and 5; the changes in microstructure, compressive strength, and volume stability of the cement pastes only at w/c = 0.25.

2 Materials and methods

2.1 Materials and mix design

The raw materials were dead-burnt magnesia, KH₂PO₄, and deionized water as already detailed in [11]. The chemical compositions of magnesia and KH₂PO₄ were determined by X-ray fluorescence analysis, and are given in Table 1. The mineralogical compositions of the magnesia

determined by X-ray diffraction (XRD) showed the main phase of periclase (MgO) and minor phases of forsterite (Mg₂SiO₄) and monticellite (CaMgSiO₄). The mean particle size and BET surface area of the magnesia determined by laser particle size analyzer and nitrogen adsorption are $19.0 \pm 0.3 \mu\text{m}$ and $0.55 \pm 0.08 \text{ m}^2/\text{g}$, as reported in [11].

Table 1 Chemical composition of the raw materials reported in [11] *wt. %*

Materials	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	P ₂ O ₅	CO ₂ ^a	L.O.I. ^b
Magnesia	93.54	4.37	0.04	0.15	1.62	<0.02	<0.04	<0.007	<0.04	0.008	0.18	0.18
KH ₂ PO ₄	0.45	2.01	<0.30	0.07	<0.06	36.63	0.28	0.021	<0.024	40.44	-	20.94

^a: CO₂ content was calculated based on the total carbon content determined by combustion analysis.

^b: Loss on ignition.

MKP cement suspensions and pastes with various Mg/PO₄ molar ratios of 2.7, 4, and 8 were prepared at the w/c ratios of 5 and 0.25. The mix proportions are given in Table 2. It should be noted that the mix proportion of MP8-S and the corresponding results presented in the latter part of this work have already been reported in [11]. They are summarized partially here to better clarify the influence of Mg/PO₄ molar ratio on the cement hydration at the high w/c ratio of 5.

Table 2 Mix proportions of the MKP cement suspensions and pastes, and final setting time (t_{FS}) of the pastes

Sample	Mg/PO ₄	w/c	Cement		Water	t_{FS}^a
	molar ratio	mass ratio	Magnesia [g]	KH ₂ PO ₄ [g]	[g]	[min]
MP2.7-S	2.7	5	44.4	55.6	500	-
MP8-S ^b	8	5	70.1	29.9	500	-
MP2.7-P	2.7	0.25	44.4	55.6	25	11 ± 2
MP4-P	4	0.25	54.1	45.9	25	8 ± 1
MP8-P	8	0.25	70.1	29.9	25	5 ± 1

^a: The final setting time (t_{FS}) of the pastes was measured by Vicat needle test. The sample amount used was around 200 g. ^b: Data of MP8-S were taken from [11].

2.2 Methods

2.2.1 Electrical conductivity, pH and ion activity

The changes of electrical conductivity, pH and ion activity of potassium (K^+) and magnesium (Mg^{2+}) in hydrated cement suspensions were continuously measured by the experimental setup detailed in [11]. Before each measurement, the pH electrode (Mettler Toledo) was calibrated against pH buffer solutions at 4, 7, 9, and 12. The K-selective electrode (perfectION™ comb K Lemo) was calibrated against KH₂PO₄ standard solutions at 0.0044, 0.04, 0.22, 0.43, 0.48, and 0.77 M. Since the precipitation of magnesium phosphate hydrates on the electrode surface could affect the measured values of Mg-selective electrode (DX244-Mg), rather the measured mV raw data than absolute concentrations are present in this work. As specified in [11], the prepared cement suspension was stored in a vessel with a lid tightly locked to avoid possible carbonation and water

evaporation. Further water bath with a constant temperature of 20 °C was used to ensure stable thermal environment for the cement hydration. Magnesia and KH_2PO_4 were well dry-mixed before their addition to water. The cement suspension was continuously stirred with an overhead stirrer until the end of testing after 24 h. Data was automatically recorded at time steps of 1 min.

2.2.2 Ion concentrations

Solution of the cement suspensions was obtained through filtration using a nylon filter with a mesh size of 0.45 μm . One part of the solution was diluted by Milli-Q water and used for ion chromatography measurement (IC, Dionex, DP series ICS-3000), which determines the total concentrations of K, PO_4 and Mg. The other part of the solution was used for pH measurement. The pH meter (Meter 766) was calibrated against pH buffer at 4, 7, 9, and 12.

2.2.3 Isothermal calorimetry

Heat release of the hydrated cements was determined by isothermal conduction calorimetry (TA instruments, TAM Air) at 20 °C. According to the mix proportions given in Table 2, magnesia and KH_2PO_4 were weighted into an ampoule and well dry-mixed for 1 min. Deionized water that was proportioned to the dry mixture was stored in a syringe, and injected into the ampoule after the calorimeter reached thermal equilibrium. The internal mixing time for the cement suspensions and pastes was 2 min.

2.2.4 X-ray diffraction and thermogravimetric analyses

In order to determine the hydrate assemblages, hydration of the cement suspensions and the pastes was stopped at specific hydration times. The cement suspension after each specific hydration time was filtered with a Büchner funnel under vacuum. The remaining sample solids were soaked in isopropanol for around 15 min, filtered and washed with diethyl ether and filtered again to

remove the residual isopropanol in the solids. Finally the solid sample was further dried in oven at 40 °C for around 10 min to remove any residual organic solvents, and then stored in a sealed bottle. The paste samples at each specific hydration time were gently crushed and the same hydration stoppage protocol was applied. Before X-ray diffraction (XRD) and thermogravimetric analyses (TGA), the samples were further ground by hand to a grain size below 63 µm. XRD patterns were measured with a Panalytical X'pert Pro powder diffractometer equipped with CoK α radiation and X'Celerator detector in 2 θ -range of 5 - 90°. Thermogravimetric analysis (TGA) was carried out using Mettler Toledo TGA/SDTA 815e device from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.2.5 Mercury intrusion porosimetry and scanning electron microscopy

Pore size distribution of the pastes (MP2.7-P and MP8-P) after 1 and 28 days was characterized by mercury intrusion porosimetry (MIP, Thermo Finnigan Pascal 440 and 140). Cylindrical samples with diameter of around 35 mm and height of around 60 mm were cast, and subsequently cured in air at 70 % relative humidity (RH) and 20 °C. After curing for 1 and 28 days, sample slices with thickness of around 2 mm were cut from the center of the cylinders, and soaked in isopropanol for 2 days for water exchange. Afterwards, they were dried in an oven at 50 °C for 5 days. Finally these dry sample slices were fractured into small pieces for MIP analysis. Pore radius was calculated from the applied pressure by using Washburn's equation assuming a contact angle of 140° and a surface tension of mercury of 0.48 N/m [47].

Scanning electron microscopy (SEM) images of the efflorescence on the surface of MP2.7-P after 170 days were acquired by SEM (ESEM Quanta FEG 650). Small pieces taken from the paste cast surface were soaked in isopropanol for 1 week to remove the water, and further dried in oven

at 40 °C for 1 week. Afterwards, the dried samples were carbon coated (20 nm thickness), and used for SEM characterization. Furthermore, the microstructure and the hydrates of these two pastes were also characterized and analyzed by backscattered electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDS). Samples with the dimensions of $20 \times 20 \times 15 \text{ mm}^3$ were cut from the center of larger prisms with the dimensions of $20 \times 20 \times 100 \text{ mm}^3$. They were soaked in isopropanol for 1 week to remove the water, and further dried in an oven at 40 °C for 2 weeks. Afterwards, they were impregnated by using a low-viscosity epoxy resin, cut, polished and carbon coated (10 nm thickness). SEM was carried out under high vacuum mode ($3 - 4 \times 10^{-6} \text{ Pa}$) with an accelerating voltage of 10 - 12 kV and an emission current of 175 - 180 μA .

2.2.6 Volume stability

According to the paste mix proportions given in Table 2, prism samples with the dimensions of $20 \times 20 \times 100 \text{ mm}^3$ were cast and demoulded right after their final setting (see Table 2). Gauge alignments were glued to the ends of the prisms using an epoxy adhesive at 70 % RH and 20 °C. The first length reading was carried out by using a micro-meter comparator (ABSOLUTE, Mitutoyo) at 1 h after the deionized water was added to the dry mixture. Thereafter, the prepared samples were divided into three groups and stored at relative humidities of 50 %, 70 % and 90 %, respectively, at 20 °C. Sample lengths were periodically measured, and the relative length change over time was calculated. Each presented length change data was averaged from three individual samples.

2.2.7 Compressive strength

According to the paste mix proportions in Table 2, prisms with the dimensions of $20 \times 20 \times 100 \text{ mm}^3$ were prepared and demoulded right after their final setting (see Table 2). They were cured in air at 70 % RH and 20°C until the conduction of compressive strength test after 1, 3, 7, 28, 150 and 200 days. Three-point bending test was first carried out with a loading rate of 20 N/s and a span of 60 mm. Two prisms were measured for each paste after each curing age. Afterwards, the obtained four halves were used for the compressive strength measurement by applying a loading rate of 1 MPa/s and a contact surface area of $20 \times 20 \text{ mm}^2$.

3. Results and discussion

3.1 Cement suspensions at w/c ratio of 5

3.1.1 Isothermal calorimetry

The influence of Mg/PO_4 molar ratio on the heat generation of the cement suspensions is shown in Fig. 1. Both cement suspensions show an initial endothermic peak followed by two exothermic peaks. The lower Mg/PO_4 molar ratio of 2.7 leads to a larger endothermic peak, delayed and much smaller exothermic peaks, and consequently a lower cumulative heat up to 8 h. The higher endothermic heat of MP2.7-S is mostly attributed to its higher KH_2PO_4 content, which dissolves rapidly in water under consumption of heat. Meanwhile, the lower heat release rate and the lower cumulative heat reveal slower hydration kinetics and a possible different hydration of MP2.7-S compared to MP8-S.

Fig. 1 Heat flow and cumulative heat of the cement suspensions at the high w/c ratio of 5.

Both the heat flow and the cumulative heat are normalized to the weight of magnesia plus KH_2PO_4 , which is referred to as ‘cement’ in the unit of the Y-axis. Data of MP8-S were taken from [11].

3.1.2 Electrical conductivity and pH

The changes of the pH and the electrical conductivity with ongoing cement hydration are shown in Fig. 2. The changes of the pH values and the electrical conductivities of MP2.7-S and MP8-S occur before around 400 and 150 min, respectively. The longer time for MP2.7-S to reach its stable state confirms the slower heat development observed for the sample with the lower Mg/PO_4 molar ratio. Formation of magnesium phosphate hydrates and their phase transformations are highly pH dependent [48]. Therefore, the much lower pH of MP2.7-S before 400 min could indicate a different hydration path than for MP8-S. In addition to the pH results in Fig. 2(a), Fig. 2(b) shows that the lower Mg/PO_4 molar ratio of 2.7 leads to a significantly higher electrical conductivity over

time, indicating a higher concentration of ions in the cement suspension. The higher electrical conductivity of MP2.7-S can be explained by its higher portion of KH_2PO_4 in the cement, which is dissolved in the solution, and the slower hydration rate. Inflection points can be seen on the electrical conductivity curves, which occur at the same hydration time as the peaks of the pH curves in Fig. 2(a). They may indicate changes in phase dissolution/precipitation regime and the precipitations of different phases [11-13]. Therefore the much later appearance of these inflection points in MP2.7-S could indicate a different hydration path compared to MP8-S.

Fig. 2 Developments of: (a) pH and (b) electrical conductivity of the cement suspensions at the w/c ratio of 5. BP1= before the 1st peak; P1 = the 1st peak; AP1= after the 1st peak; P2 = the 2nd peak; AP2 = after the 2nd peak. Data of MP8-S were taken from [11].

3.1.3 Solid phases in suspension experiments

The changes of the solid phase assemblages in the cement suspensions with ongoing hydration were determined by XRD and TGA. The XRD patterns of MP2.7-S are shown in Fig. 3, and those of MP8-S have been detailed in [11]. As displayed in Fig. 3(a), only magnesia but no unreacted KH_2PO_4 are detected after 5 min (BP1) reaction of MP2.7-S, due to the complete dissolution of KH_2PO_4 in water at this high w/c ratio of 5. The XRD patterns after 5 (BP1) and 22 min (P1) are enlarged and presented in Fig. 3(b). A trace of phosphorrrösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$) is formed initially (5 min BP1) through the following equation (Eq. (2)):

256 After 22 min (P1), newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, and a trace of K-struvite
 257 are formed according to equations (Eq. (3) - (5)), along with the increase of the phosphorösslerite
 258 amount.

262 Phosphorösslerite and newberyite both disappear after 50 min (AP1), while the amounts of
 263 $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite increase. $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ has disappeared after 66 min
 264 (P2) while K-struvite continues to form. These XRD results illustrate the transformations between
 265 the different hydrates. Phosphorösslerite is very unstable [12, 48] and can be easily transformed
 266 to the thermodynamically more stable newberyite according to the following equation (Eq. (6)):

268 Most of the reactions (see Eqs. (2) - (4)) increase the pH as also visible in the measurements shown
 269 in Fig. 2(a), which eases the transformation of newberyite to K-struvite as indicated by the
 270 following equation (Eq. (7)):

272 The disappearance of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ after 66 min (P2) is due to its transformation to K-
 273 struvite through the following equation (Eq. (8)):

275 As shown in Eqs. (7) - (8), the continuous increase of K-struvite originates from the transformations
 276 from both newberyite and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$. These two reactions also consume hydroxide, as
 277 visible in the lowering of the pH after 66 minutes in the case of MP2.7-S shown in Fig. 2(a). In
 278 addition to these transformations, also the direct formation of K-struvite is possible according to
 279 Eq. (9):

281 This direct formation of K-struvite is the dominant reaction after more than 1 h as mirrored in the
 282 pH increase. K-struvite is the only hydrate detected after 66 min (P2) and until 24 h. Thus the
 283 hydrate formations and transformations shown in Eqs. (2) - (9) are mirrored in the pH and electrical
 284 conductivity changes as displayed in Fig. 2.

Fig. 3 XRD patterns of MP2.7-S: (a) Hydration after 5 min (BP1) and until 24 h; (b) Hydration after 5 min (BP1) and 22 min (P1). H = $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, M = MgO, N = $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, P = $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, S = $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

The XRD results are further confirmed by the TGA analyses. The TGA/DTG curves of MP2.7-S are displayed in Fig. 4 while those of MP8-S had been reported in [11]. The TGA curves in Fig. 4(a) show that the cement hydration proceeds very fast before 50 min (AP1), while afterwards it gradually slows down with only a small increase of the amount of bound water. The DTG curves below 210 °C are further detailed in Fig. 4(b). The small and broad DTG peak at around 60 °C after the first 5 min (BP1) could be assigned to phosphorösslerite based on the XRD result in Fig. 3(b) and the data recorded on pure phosphorösslerite reported in [48]. The changing composition during hydration is shown by the changes in the DTG peaks, which are assigned to phosphorösslerite, newberyite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite as shown in Fig. 4(b), confirming the XRD results in Fig. 3(a). TGA showed that a small amount of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is still present after 66 min (P2), showing its still incomplete transformation to K-struvite. Only after 185 min and longer, K-struvite as the only hydrate has its amount almost unchanged, suggesting the almost completion of hydration.

Compared with MP2.7-S, the evolution of the solid phase assemblages of MP8-S is much simpler [11]. $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is the only intermediate hydrate observed, and it is quickly and completely transformed to K-struvite after around 35 min. The obviously different hydration paths between MP2.7-S and MP8-S reveal the central role of the Mg/PO₄ molar ratio in the hydration mechanism.

Fig. 4 TGA/DTG curves of MP2.7-S after 5 min and until 24 h of hydration. H = $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, N = $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, P = $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, S = $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

3.1.4 Aqueous phase composition

The total concentrations of K, PO₄ and Mg and the activities of K⁺ and Mg²⁺ in the cement suspensions are shown in Fig. 5. The total concentrations of MP2.7-S are also provided in Table 3, as well as the calculated concentration decreases at different hydration stages. MP2.7-S has higher K, PO₄ and Mg concentrations than MP8-S at early hydration time due to the higher fraction of KH₂PO₄ in the MP2.7-S. This explains the higher electrical conductivity of MP2.7-S. With ongoing hydration, the concentrations decrease such that the phosphate concentrations after 185 min (AP2-1) are comparable in both systems, while K remains higher in the MP2.7-S. As detailed in Table 3, the concentration decreases of phosphate up to 22 min (P1) are much higher than the decrease of K, which agrees with the XRD and TGA results that show the formation of phosphorösslerite (see Eq. (2)), newberyite (see Eq. (3)), Mg₂KH(PO₄)₂·15H₂O (see Eq. (4)) but little K-struvite (see Eq. (5)) in this stage. At intermediate hydration times (between 22 min (P1) and 50 min (AP1)) the concentration decreases of K and phosphate are comparable since at this stage phosphorösslerite (see Eq. (6)) and newberyite (see Eq. (7)) are replaced by Mg₂KH(PO₄)₂·15H₂O (see Eq. (4)) and K-struvite (see Eq. (5)). In this period the strongest decrease of K, PO₄ and Mg concentrations are observed, which indicates the most intensive hydration.

Between 50 min (AP1) and 66 min (P2) K concentrations decrease more strongly than the phosphate concentrations due to the destabilization of Mg₂KH(PO₄)₂·15H₂O to K-struvite (see Eq. (8)). At later reaction times (between 66 min (P2) and 185 min (AP2-1)) K and phosphate have comparable concentration decreases. It agrees well with the XRD and TGA results, which show that the continuous formation of K-struvite (see Eqs. (5) or (9)) is the main reaction such that phosphate and K should be consumed to a similar extent.

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Fig. 5: (a) Total concentrations of K, PO₄ and Mg and electrical conductivity curves of the cement suspensions. Data for MP2.7-S connected by solid lines, data for MP8-S connected by dashed lines; (b) K⁺ and (c) Mg²⁺ activities measured by the selective electrodes in comparison to their total concentrations measured by IC. Data for MP8-S data were taken from [11].

Table 3 Concentrations in MP2.7-S and, in *italic*, the calculated concentration decreases at different hydration stages

Hydration time [min]	Total concentration [mM]							pH ^a	Time stage [min]	Total concentration decrease [mM]		
	Na	K	Mg	Ca	Si	PO ₄				K	Mg	PO ₄
22 [P1]	5	798	56	4	5	748	6.2	3 ^b -22		-21 ^c	- ^d	-71 ^c
50 [AP1]	6	269	6	0.8	5	175	7.3	22-50 [P1 to AP1]		-530	-50	-573
66 [P2]	6	138	4	0.5	5	93	7.8	50-66 [AP1 to P2]		-130	-2	-82
185 [AP2-1]	6	97	<0.002	0.3	4	51	10.6	66-185 [P2 to AP2-1]		-41	-4	-42

^a: The slight pH variations at 22, 50 and 66 min to those presented in Fig. 2(a) are within the error range. The higher pH at 185 min compared to that presented in Fig. 2(a) might be due to the unwell controlled temperature such that a slightly faster kinetics.

^b: Electrical conductivity of MP2.7-S reached its maximum after 3 min indicating a fast dissolution of KH_2PO_4 in the water. Both K and phosphate have the same maximum concentration of 819 mM.

^c: The concentration decreases between 3 and 22 min are calculated based on the assumption that K and phosphate have the same initial concentrations of 819 mM after 3 min.

^d: It is not possible to calculate the concentration decrease of Mg due to the unknown concentration after 3 min.

Fig. 5(b) & (c) compares the changes of K^+ and Mg^{2+} activities of the cement suspensions determined by ion selective electrodes with the total concentrations measured by IC. Fig. 5(b) shows a fair agreement between the K^+ activity and the total K concentration measured by IC. Due to the higher portion of KH_2PO_4 in cement, MP2.7-S has higher K concentrations and it takes longer time, more than 180 min, to reach the stable stage compared to MP8-S. This indicates slower hydration kinetics at lower Mg/ PO_4 molar ratio than at higher ratio, which confirms the observation in the solid phases. MP2.7-S shows higher Mg^{2+} activity and total Mg concentration during hydration than MP8-S.

3.1.5 Summary of cement suspension hydration at $w/c=5$

The hydration path of MP2.7-S is schematically illustrated in Fig. 6(a) based on the results obtained for the solid phase assemblages and the aqueous phase composition. The hydration path of MP8-S already reported in [11] is presented in Fig. 6(b) for comparison. The decrease of Mg/ PO_4

molar leads to lower pH values, slows down the cement hydration kinetics, and favors the formation of potassium-free magnesium phosphate hydrates, such as phosphorösslerite and newberyite. Moreover, the high w/c ratio of 5 facilitates the full transformation of the intermediate hydrates to K-struvite.

Fig. 6 Schematic hydration paths of the cement suspensions with the Mg/PO₄ molar ratios of: (a) 2.7 and (b) 8. The hydration path of MP8-S was taken from [11].

3.2 Paste at w/c ratio of 0.25

3.2.1 Isothermal calorimetry

The calorimetric results of the pastes at the w/c ratio of 0.25 are shown in Fig. 7. Comparing with the calorimetric results of the cement suspensions at the w/c ratio of 5 in Fig. 1, it can be observed that the decrease of the w/c ratio leads to the reduction of the endothermic heat observed during the first minutes of hydration, to an increase of the height of the exothermic peaks and a faster heat release rate. This indicates that the hydration kinetics is faster at the lower w/c ratio. Also in the paste experiments, the lower Mg/PO₄ molar ratio of 2.7 causes a delay of the 2nd exothermic peak and a longer continuation of heat evolution before the plateau in cumulative heat is reached indicating a slower hydration at the lower Mg/PO₄ molar ratio.

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410 3.2.2 Efflorescence

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Fig. 7 Heat flow and cumulative heat of the cement pastes at the w/c ratio of 0.25. Both the heat flow and cumulative heat are normalized to the weight of magnesia plus KH_2PO_4 , which is referred to as ‘cement’ in the unit of the Y-axis.

Efflorescence can be observed on the surfaces of the pastes with Mg/PO_4 molar ratio below 5 as reported previously [19]. In addition, expansion and cracking were observed at low Mg/PO_4 molar ratio [19]. In this work, efflorescence is also observed on the surfaces of the pastes with Mg/PO_4 molar ratios of 2.7 and 4 at all the investigated relative humidities of 50 %, 70 % and 90 %, while the paste with the highest Mg/PO_4 molar ratio of 8 does not show any efflorescence. The surface appearances of the paste specimens at 70 % RH are shown in Fig. 8 as an example.

Cast surfaces

Fig. 8 Specimen cast surfaces of the pastes with the Mg/PO₄ molar ratios of 2.7, 4, and 8 at 70 % RH and 20 °C.

Efflorescence product was collected from the cast surface of MP2.7-P after 7 days at 70 % RH and 20 °C, and analyzed by XRD and TGA. The XRD pattern displayed in Fig. 9(a) shows that the phases in the efflorescence are phosphorösslerite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, some unreacted KH_2PO_4 , as well as a phase with reflections at 2θ -values 11.75° , 14.22° , 16.68° , 26.01° , and 26.49° , which could not be identified. The TGA/DTG curves in Fig. 9(b) underline that $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and unreacted KH_2PO_4 are the two main phases in the efflorescence, along with the minor amount of phosphorösslerite. The weight loss and DTG peak due to the unidentified phase are not clearly visible as its quantity could be small or its weight loss overlapped with those of the defined phases.

Fig. 9 Efflorescence collected from the cast surface of MP2.7-P after 7 days at 70 % RH and 20 °C: (a) XRD; (b) TGA/DTG. H = $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, K = KH_2PO_4 , P = $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, * = Unidentified phase.

Furthermore, a representative SEM image of the efflorescence product on the surface of MP2.7-P after 170 days at 70 % RH and 20 °C is displayed in Fig. 10. Clusters of crystals with well-defined edges (e.g. 1#) or in large thin-plate shape (e.g. 2#) are observed inhomogeneously distributing on the surface, with fibril-like hydrates (e.g. 3#) beneath.

Fig. 10 Efflorescence product on the surface of MP2.7-P after 170 days at 70 % RH and 20 °C.

3.2.3 Volume stability

The volume stability of the pastes at different relative humidities was monitored by measuring the linear length change as shown in Fig. 11. The length changes of these MKP cement pastes are affected by the relative humidity and the Mg/PO₄ molar ratio. As displayed in Fig. 11(a) and (b), both MP2.7-P and MP4-P shrink first, and expand afterwards. The shrinkage is prolonged as the

Mg/PO₄ molar ratio is increased and only shrinkage is observed at all the investigated relative humidities for Mg/PO₄ = 8 (see Fig. 11(c)). In addition, the length changes are quite low at higher Mg/PO₄ such that the maximum shrinkage of MP8-P at 50 % RH after 390 days is only around 1.4 ‰, indicating high volume stability. In contrast, MP2.7-P shows severe expansion at all the investigated relative humidities. Visible damages, like longitudinal cracking at 50 % RH and significant deflection near the sample bottom surface at 90 % RH, are observed for MP2.7-P and shown in Fig. 11(a). These observations are in line with previous reports [19] that MKP cement pastes with low Mg/PO₄ molar ratio (< 5) were more likely to show expansion and cracking. The XRD and TGA results presented in the following section reveal that brucite is formed in MP8-P after 28 days and later. Normally, brucite formed in hardened Portland cement-based materials raises the concern over the deleterious expansion [12]. Fig. 11(c) shows that MP8-P shrinks only under all the investigated relative humidities and throughout whole periods, which indicates the amount of brucite formed in MP8-P does not lead to significant expansions.

Fig. 11 Length changes of the pastes with Mg/PO₄ molar ratios of 2.7, 4, and 8 at different relative humidities (50 %, 70 % and 90 %) and 20 °C. Note the strong variation in length change and thus the Y-axis scale.

3.2.4 Compressive strength

The compressive strength development of the pastes at 70 % RH and 20 °C is shown in Fig. 12. Generally, the increase of Mg/PO₄ molar ratio leads to higher strengths, particularly at later ages. The strength of MP2.7-P increases up to 7 days and decreases afterwards with the relative strength loss between 7 and 200 days of approximately 50 %. This strength loss could be related to the significant expansion in the hardened paste as shown in Fig. 11(a). A small strength decrease within the accuracy of the measurement is observed for MP4-P after 28 days, while the strength of MP8-P increases continuously. A strength increase of approximately 12 % occurs between 28 and 200 days, possibly indicating a continuation of hydration.

Fig. 12 Compressive strength of the pastes with Mg/PO₄ molar ratios of 2.7, 4 and 8 at 70 % RH and 20 °C.

3.2.5 Pore size distribution

Fig. 13 shows the MIP results of the pastes with the Mg/PO₄ molar ratios of 2.7 and 8 after 1 and 28 days curing at 70 % RH and 20 °C. The cumulative pore volume distributions are presented in Fig. 13(a). The increase of curing age leads to an increase of the total porosity of approximately 35 % for MP2.7-P, but to a reduction of approximately 24 % for MP8-P. This is consistent with the strength developments shown in Fig. 12. Moreover, the differential pore size distribution results in Fig. 13(b) show that the porosity increase of MP2.7-P is due to the higher amount of large pores (1 – 5 μm), although a small portion of fine pores (< 100 nm) is formed as well between 1 and 28 days. This change of the pore size distribution of MP2.7-P could be related to cracking due to the significant expansion in the hardened paste as shown in Fig. 11(a). On the contrary, the critical pore entry radius (r_{Critical}) of MP8-P after 28 days is shifted to a smaller size, along with a small

portion of fine pores (<100 nm) formed. It indicates that the microstructure of MP8-P becomes denser, which accounts for the continuous strength increase over time as demonstrated in Fig. 12.

Fig. 13: (a) Cumulative pore volume distribution of the pastes with the Mg/PO₄ molar ratios of 2.7 and 8 after 1 and 28 days at 70 % RH and 20 °C; (b) First derivatives of the results presented in (a).

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505 3.2.6 Solid phase assemblages

506 The XRD patterns of MP2.7-P are presented in Fig. 14(a). They show that a relevant amount
 507 of KH_2PO_4 is still present after 15 min when final setting is observed (see Table 2). Most KH_2PO_4
 508 is consumed after 2 h, although a small amount is present up to 28 days. K-struvite is the first
 509 hydrate detected after 2 h. It forms rapidly within the first day and slowly continues to form up to
 510 200 days. A trace of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is first observed after 5 h, its content increases until up
 511 to 1 day, and decreases thereafter due to its transformation to K-struvite (see Eq. (8)). However, a
 512 small amount of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is still present after 200 days. It should be noted that low
 513 quantities of hydrates, such as phosphorösslerite which is present in the efflorescence, might be
 514 difficult to observe by XRD. Fig. 14(b) & (c) display the XRD patterns of MP8-P. Due to its much
 515 faster hydration kinetics, K-struvite is already formed after the first 5 min while KH_2PO_4 is almost
 516 depleted. K-struvite is the only hydrate occurring except of traces of brucite observed after 28 days
 517 and later, as demonstrated in Fig. 14(c).

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Fig. 14 XRD patterns: (a) MP2.7-P; (b) MP8-P; (c) Enlarged 2θ-range of 21 - 23° of MP8-
ws0.25. B = $\text{Mg}(\text{OH})_2$, H = $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, K = KH_2PO_4 , M = MgO , S =
 $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

The TGA/DTG results of MP2.7-P and MP8-P are presented in Figs. 15 and 16. Fig. 15(a) shows that the total bound water in MP2.7-P continues to increase between 28 and 200 days. This is consistent with the XRD findings in Fig. 14 (a) that some cement hydration continues after 1 day and later. The DTG curves before and after 200 °C are enlarged in Fig. 15(b) & (c) to allow a closer look on the phase evolutions over time. The DTG data in Fig. 15(b) show that a small amount of hydrates, possibly $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite, is already formed after 15 min. The DTG data confirm the presence of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and its increasing content up to 1 day, and its subsequent destabilization to K-struvite. Phosphorösslerite, which was found in the efflorescence as minor component, could not be observed by TGA as well due to its probably small amount and the overlap of its main weight loss region with the one of K-struvite [48, 49]. Although newberyite is not detected by XRD, the DTG peak at around 155 °C suggests its presence, and the observed decreasing trend of this peak after 5 h indicates its subsequent transformation to K-struvite (see Eq. (7)).

The reaction of KH_2PO_4 over time could be followed through the DTG curves displayed in Fig. 15(c) confirming that KH_2PO_4 is not fully reacted even after 200 days, consistent with the continuous hydration observed up 200 days. On the basis of the TGA/DTG results shown in Fig. 15(a), (b) & (c), the amount of the main solid phases and the reaction degree of magnesia can be estimated [10, 16], as demonstrated in Fig. 16(a). It should be noted that the calculated K-struvite content might be somewhat affected by the presence $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and phosphorösslerite, since their main weight loss regions overlap with K-struvite, especially when their amounts are small [48, 49].

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Fig. 15: (a) TGA/DTG curves of MP2.7-P over time; (b) and (c) Enlarged range 20 – 200 °C and 200 – 500 °C. H = $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, K = KH_2PO_4 , N = $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, S = $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

As shown in Fig. 16 (a), the formation of the hydrates before 1 day leads to a decrease of the amounts of unreacted KH_2PO_4 and magnesia. At intermediate hydration times between 1 and 28 days little changes in the amount of MgO and KH_2PO_4 are observed indicating that the transformations of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and newberyite to K-struvite are the main reactions. Between 28 and 200 days, the decrease of the amount of unreacted KH_2PO_4 and magnesia and the corresponding increase of K-struvite indicates a continued hydration mainly governed by the formation of K-struvite.

Fig. 16 Estimated phase contents normalized to the anhydrous at 600 °C: (a) MP2.7-P; (b) MP8-P.

Fig. 17 presents the TGA/DTG curves of MP8-P during hydration. It becomes obvious from Fig. 17(a) & (b) that the weight loss is increasing significantly until 1 h, due to the formation of K-struvite. Beyond 1 h, the bound water increases only slightly up to 450 days. The enlarged DTG

curves in Fig. 17(c) show the formation of some brucite between 28 and 450 days, confirming the XRD finding in Fig. 14(c). As above the TGA/DTG results are used to estimate the contents of K-struvite, brucite and unreacted magnesia, which are presented in Fig. 16(b). K-struvite forms rapidly during the first hour, which corresponds to the decrease of magnesia. After 1 h, the formation of K-struvite is strongly slowed down, while little magnesia reaction is observed. The formation of a small amount of brucite between 28 and 450 days agrees with the very limited magnesia reaction observed. As can be seen in Fig. 11(c), the presence of this small amount of brucite has little impact on the volume stability of MP8-P. Its presence may contribute to the observed denser microstructure (see Fig. 13) and the consequent strength improvement after 28 days (see Fig. 12).

Fig. 17: (a) TGA/DTG curves of MP8-P over time; (b) and (c) Enlarged range 30 - 200 °C and 300 - 500 °C in (a). B = $\text{Mg}(\text{OH})_2$, S = $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$. Note that TGA up to 1000 °C showing no MgCO_3 presented in the paste after 28, 200, and 450 days.

3.2.7 SEM analyses

The microstructure and the composition of the hydrates are further studied by BSE and EDS on polished sections. Fig. 18 shows the BSE images of MP2.7-P after 170 days at 70 % RH and 20 °C. Fig. 18(a) shows that the formed hydrates surround the unreacted magnesia particles. Numerous micro-cracks propagate through the hydrates, and coarse pores are present. This could be correlated to the observed significant expansion of the hardened paste (see Fig. 11(a)), and agrees well with the highly increased porosity (see Fig. 13) and the strength loss after 28 days (see Fig. 12). The densities of the hydrates are apparently different as visible in the domains labelled “D” and “L” in Fig. 18(a). The domain D has a very dense and homogenous texture; while the domain L is more loosely packed, has a structured texture and micro-cracks with different orientations. Within the pores, hydrates with fan-like microstructure are observed, as shown in Fig. 18(b).

Fig. 18 Representative microstructures of MP2.7-P after 170 days at 70 % RH and 20 °C by BSE.

The compositions of the hydrates in the densely (D) and loosely (L) packed areas in Fig. 18(a) are shown in Fig. 19(a), and compared to the stoichiometric values of MgO, KH_2PO_4 , brucite, newberyite, phosphorösslerite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite. When comparing with the stoichiometric values of these phases, a small portion of the compositions in the densely packed area D fall in between $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite indicating a mixture of them. Most of the compositions have higher P/Mg and K/Mg ratios than $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite and show a trend towards KH_2PO_4 . In addition, unidentified non-stoichiometric (amorphous) hydrates could be present. The loosely packed domain L has higher K/Mg and P/Mg ratios. Average K/P ratios of the hydrates in the matrix (domains D and L) are calculated as 0.74 ± 0.06 and 0.89 ± 0.12 , respectively. The higher phosphate than K content in the hydrates is consistent with the lower phosphate concentration measured in the suspension of MP2.7-P (see Fig. 5 (a) and Table 3). The hydrates growing in the pores (domain F in Fig. 18(b)) contain calcium as shown in Fig. 19(b), and are compared to the stoichiometric values of $\text{CaK}_3\text{H}(\text{PO}_4)_2$. The average P/Ca, K/Ca

and Mg/Ca ratios are calculated as 2.96 ± 0.26 , 3.04 ± 0.2 and 0.14 ± 0.09 , respectively. The K/Ca ratio of 3 would be well consistent with the formation of $\text{CaK}_3\text{H}(\text{PO}_4)_2$ although the P/Ca ratio is higher than expected, which could be due to intermixing with some magnesium phosphate hydrates. The Ca originates from the reaction of monticellite (CaMgSiO_4), a minor phase in the raw magnesite. The formation of $\text{CaK}_3\text{H}(\text{PO}_4)_2$ is highly pH dependent and favored at around pH 11 (see Appendix). At the low Mg/ PO_4 molar ratio of 2.7 not only a surplus K^+ and HPO_4^{2-} in the pore solution is expected but also favorable pH conditions. The chemical reaction of $\text{CaK}_3\text{H}(\text{PO}_4)_2$ occurring in the pores can be expressed according to Eq. (10):

Fig. 19 EDS analysis of the hydrates in MP2.7-P after 170 days at 70 % RH and 20 °C: (a) Hydrates in the matrix (the domains D and L in Fig. 18(a)); (b) Hydrates growing into the pores (the domain F in Fig. 18(b))

The microstructure of MP8-P after 380 days at 70 % RH and 20 °C is shown in Fig. 20, together with the compositions obtained by EDS analyses. As displayed in Fig. 20(a), the Si-rich phases, forsterite (Mg_2SiO_4) and monticellite (MgCaSiO_4) impurities in the raw magnesia, are embedded in a K-struvite matrix. A summary of the EDS analyses is shown in Fig. 20(b). The data follow a linear trend indicating similar K/P ratios in all hydrates. The average K/P ratio is calculated as 0.76 ± 0.13 , which implies again higher phosphate content in the hydrates, and agrees well with the higher phosphate content observed for MP2.7-P in Fig. 19(a). As suggested by the XRD and TGA results in Figs. 14(b) and 17, K-struvite, brucite and MgO are the main solids present.

Fig. 20 MP8-P after 380 days at 70 % RH and 20 °C: (a) Representative microstructure by BSE; (b) EDS analyses of the hydrates in the matrix

3.2.7 Discussion of cement hydration and paste properties

Table 4 summarizes the densities and molar volumes of solid phases, relevant chemical reactions and the resulting volume changes. Hydrate formation leads to volume increases from 19 to 152 *vol.%* in the order: newberyite < phosphorösslerite $\approx$ K-struvite < $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ = brucite < $\text{CaK}_3\text{H}(\text{PO}_4)_2$. Also the transformation of newberyite to K-struvite causes around 72 *vol.%* volume increase, while the transformations of phosphorösslerite to newberyite and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ to K-struvite lead to volume decreases of 41 *vol.%* and 6 *vol.%*, respectively. This indicates that the continuous formation of hydrates and the hydrate transformations in the hardened cement matrix could have strong impact on the volume. With the phase contents (see Fig. 16) and the densities (see Table 4) present, the development of the individual solid phase volume as well as the total solid volume during hydration can be calculated, as shown in Fig. 21. MP2.7-P has a small decrease of the total solid volume during the first two hours, and a large increase thereafter. It agrees well with the measured length change of MP2.7-P presented in Fig. 11 (a), where shrinkage is observed within the first few hours, and expansion occurs later on. MP8-P has a volume increase during the first hour due to the fast hydration and the formation of K-struvite, and a minor change thereafter. Although the formation of brucite leads to 118 *vol.%* volume increase, it forms only in very small quantities in the paste (< 2 *wt.%* after 450 days), which seem to contribute to a denser pore structure (see Fig. 13) and strength increase (see Fig. 12).

Table 4 Molar volumes of solids, chemical reactions and resulting volume changes

Phase	Molar volume [cm^3/mol]	Reference
MgO	11.3	[48]
CaMgSiO_4 (Monticellite)	50.3	[50]
KH_2PO_4	58.2	[16]

672	Mg(OH) ₂ (Brucite)	24.6	[48]
673	MgHPO ₄ ·3H ₂ O (Newberyite)	82.9	[48]
674	MgHPO ₄ ·7H ₂ O (Phosphorösslerite)	141.6	[48]
675	Mg ₂ KH(PO ₄) ₂ ·15H ₂ O	303.2	[48]
676	MgKPO ₄ ·6H ₂ O (K-struvite)	142.5	[48]
677	CaK ₃ H(PO ₄) ₂	127.0	[51]
678	Chemical reactions	Volume changes [vol. %]	
679	Hydrate formation (<i>aqueous species plotted in italic</i>):		
680	MgO + KH ₂ PO ₄ + 7 <i>H₂O</i> → MgHPO ₄ ·7H ₂ O + K ⁺ + OH ⁻	104 (increase)	
681	MgO + KH ₂ PO ₄ + 3 <i>H₂O</i> → MgHPO ₄ ·3H ₂ O + K ⁺ + OH ⁻	19 (increase)	
682	2MgO + 2KH ₂ PO ₄ + 14 <i>H₂O</i> → Mg ₂ KH(PO ₄) ₂ ·15H ₂ O + K ⁺ + OH ⁻	118 (increase)	
683	MgO + KH ₂ PO ₄ + 5 <i>H₂O</i> → MgKPO ₄ · 6H ₂ O	105 (increase)	
684	CaMgSiO ₄ + 3K ⁺ + 2 <i>HPO₄²⁻</i> → CaK ₃ H(PO ₄) ₂ + OH ⁻ + Mg ²⁺ + SiO ₃ ²⁻	152 (increase)	
685	MgO + <i>H₂O</i> → Mg(OH) ₂	118 (increase)	
686	Hydrate transformation (<i>aqueous species plotted in italic</i>):		
687	MgHPO ₄ ·7H ₂ O → MgHPO ₄ ·3H ₂ O + 4 <i>H₂O</i>	41 (decrease)	
688	MgHPO ₄ ·3H ₂ O + K ⁺ + OH ⁻ + 2 <i>H₂O</i> → MgKPO ₄ ·6H ₂ O	72 (increase)	
689	Mg ₂ KH(PO ₄) ₂ ·15H ₂ O + K ⁺ + OH ⁻ → 2MgKPO ₄ ·6H ₂ O + 4 <i>H₂O</i>	6 (decrease)	

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691 Similar to the suspensions at the w/c ratio of 5, the increase of the Mg/PO₄ molar ratio from 2.7
692 to 8 suppresses the formation of intermediate hydrates, while traces of brucite are formed at later
693 age. The influence of the w/c ratio can be assessed by comparing the schematic hydration paths of
694 the cement suspensions (see Fig. 7) with the pastes (see Fig. 21). At the low Mg/PO₄ molar ratio
695 of 2.7, the formation of intermediate hydrates is observed at the low and high w/c ratios, but the

low w/c ratio slows down the hydration kinetics after the first day. At the high Mg/PO₄ molar ratio of 8, the formation Mg₂KH(PO₄)₂·15H₂O is suppressed at the low w/c and little influence of the w/c ratio on the hydration kinetics is observed.

Fig. 21 Estimated changes of phase volumes during hydration of: (a) MP2.7-P and (b) MP8-P. Note that the estimated phase volumes are normalized to anhydrous at 600 °C in TGA analyses.

703

704 4. Conclusions

705 This study investigated the influence of Mg/PO₄ molar ratio (2.7, 4, and 8) and w/c ratio (0.25
706 and 5) on the hydration and properties of MKP cements. The main findings are:

707 ■ Cement hydration

708 Low Mg/PO₄ molar ratios, i.e. ≤ 4 , leads to precipitations of intermediate hydrates, such as
709 newberyite, phosphorösslerite, and Mg₂KH(PO₄)₂·15H₂O. In addition, CaK₃H(PO₄)₂ precipitates
710 in the pores of the paste with low Mg/PO₄ of 2.7 due to the reaction between K⁺ and HPO₄²⁻ ions
711 in pore solution and the minor phase of CaMgSO₄ in magnesia. At low Mg/PO₄ molar ratio, the
712 decrease of w/c ratio slows down cement hydration beyond 1 day, but has little influence on the
713 precipitation of intermediate hydrates. At high Mg/PO₄ molar ratio fast hydration is observed both
714 at high and low w/c ratios. K struvite without any intermediate hydrates are formed at lower w/c,
715 however traces of brucite were present after 28 days and later without any detrimental impacts on
716 strength or volume stability.

717 ■ Efflorescence, volume stability and mechanical strength

718 Efflorescence is more likely to form on the surface of MKP cements with low Mg/PO₄ molar
719 ratios of ≤ 4 . Efflorescence can contain several phases such as Mg₂KH(PO₄)₂·15H₂O,
720 phosphorösslerite, unreacted KH₂PO₄, and an unidentified phase. Expansion and strength loss
721 occur together with efflorescence due to the continuing slow hydration in the already hardened
722 cement matrix which deteriorates the structure. The use of high Mg/PO₄ molar ratio e.g. 8 prevents
723 efflorescence, expansion and strength loss due to the acceleration of hydration kinetics.

724 This study reveals the important role of Mg/PO_4 and w/c ratios on cement hydration, volume
725 stability and strength. The obtained findings indicate that $\text{Mg}/\text{PO}_4 > 4$ prevents the formation of
726 intermediate hydrates and efflorescence, result in good short- and long-term mechanical properties.
727 Thus for the optimum design of MKP cements high Mg/PO_4 and low w/c are needed to ensure
728 robust performance and good long-term durability.

729

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737

Appendix

Fig. A1: Influence of pH on the formation of $\text{CaK}_3\text{H}(\text{PO}_4)_2$ at 20 °C. Same proportion of KH_2PO_4 : calcium acetate : water = 22 : 1 : 74 was used for all sample preparations. KOH was added to adjust the solution pH. $\Delta = \text{KH}_2\text{PO}_4$, $*$ = $\text{CaK}_3\text{H}(\text{PO}_4)_2$, $\times$ = $\text{CaKPO}_4 \cdot \text{H}_2\text{O}$.

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