Thermodynamic data for magnesium (potassium) phosphates

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Abstract:

Magnesium potassium phosphate (MKP) cements show fast setting and high early strength. MKP cements harden in the presence of water due to the reaction of potassium dihydrogen phosphate (KH_2PO_4) with magnesia (MgO) resulting in the formation of mainly K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$). Other hydrates, newberyite, phosphorösslerite, cattite and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ are formed as intermediate phases during hydration. This paper presents a consistent thermodynamic database for magnesium phosphate hydrates based on solubility measurements for newberyite, phosphorösslerite, farringtonite, $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, bobierite, cattite, K-struvite, $\text{KMgPO}_4 \cdot \text{H}_2\text{O}$, and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ carried at different temperature. It was found that the formation of the different hydrates is strongly influenced by pH. Newberyite, phosphorösslerite and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ are intermediate phases, which form at low pH as typical at very early hydration times. As pH rises, bobierite and cattite may be stabilised, while at high pH K-struvite forms. The phases formed are also strongly influenced by the temperature.

Keywords: Magnesium phosphate cement, thermodynamic data, solubility, temperature

1. Introduction

Magnesium potassium phosphate (MKP) cement hardens in the presence of water through the reaction between potassium dihydrogen phosphate (KH_2PO_4) and magnesia (MgO). Compared to Portland cement, MKP cement has different advantages such as fast setting (Qiao et al., 2010; Wagh, 2004), high early strength (Qiao et al., 2010; Xu et al., 2017), strong bonding with concrete substrate (Qiao et al., 2010; Xu et al., 2015), low pH (Wagh, 2004; Walling and Provis, 2016), and good bio-compatibility (Wang et al., 2013) such that MKP cement is used as rehabilitation materials (Ding and Li, 2005; Lee et al., 2017; Qiao et al., 2010; Wagh, 2004; Xu et al., 2017; Xu et al., 2015), as solidification/stabilization agent for low-level nuclear wastes and other wastes containing heavy metals (Buj et al., 2009; Buj et al., 2010; Wagh, 2004; Walling and Provis, 2016), and as bio-material (Wang et al., 2013).

The main reaction of hydrating MKP cement can be described as $\text{MgO} + \text{KH}_2\text{PO}_4 + 5\text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite). Thus magnesium potassium hexahydrate ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, K-struvite) is the main hydrate formed providing mechanical strength. However, different experimental studies (Chau et al., 2012; Lahalle et al., 2016; Le Rouzic et al., 2017a) showed that a number of other hydrates, such as $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) (Le Rouzic et al., 2017a), $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ (phosphorösslerite) (Chau et al., 2012), $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (bobierrite), $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ (cattiite) (Lahalle et al., 2016), and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (Chau et al., 2012; Lahalle et al., 2016) are formed as well during hydration. The kind of the hydrates formed is influenced by the availability of water, magnesium, phosphate, potassium ions and pH value. (Le Rouzic et al., 2017b) reported that K-struvite in MKP cement pastes with water-to-cement (w/c) ratio of 0.2 had a needle-like shape at a magnesium-to-phosphate (Mg/PO_4) molar ratio of 1, but that it had a platelet-like shape at $\text{Mg}/\text{PO}_4 = 5$. The type of hydrate formed and its morphology are crucial for the cement properties, such as efflorescence, strength and volume stability.

Although MKP cement is a simple quaternary system of $\text{MgO}-\text{KH}_2\text{PO}_4-\text{H}_2\text{O}$, its optimum design is still challenging due to the insufficient understanding of the reaction mechanisms. Mg/PO_4 molar ratio and w/c ratio are the two important factors controlling pH of the cement system, reaction path (Chau et al., 2012; Lahalle et al., 2016; Le Rouzic et al., 2017a; Xu et al., 2018a), microstructure (Le Rouzic et

al., 2017b; Ma et al., 2014a; Ma et al., 2014b; Xu et al., 2015), and thus performance (Le Rouzic et al., 2017b; Lee et al., 2017; Ma et al., 2014b; Qiao et al., 2010; Xu et al., 2017; Xu et al., 2015). A low Mg/PO₄ molar ratio (<4) MKP cement is preferably used as waste solidification agent (Buj et al., 2009; Buj et al., 2010; Gardner et al., 2015a; Gardner et al., 2015b; Lahalle et al., 2016; Le Rouzic et al., 2017b; Walling and Provis, 2016), as a lower Mg/PO₄ molar ratios decrease pH values, which is favourable for immobilizing metallic wastes (Coumes et al., 2014; Covill et al., 2011; Gardner et al., 2015b; Walling and Provis, 2016) such as aluminium, magnesium, and uranium containing nuclear wastes. However, some MKP cement-based materials with low Mg/PO₄ molar ratio showed problems such as efflorescence, strength decrease at later ages and expansion due to the formation of intermediate phases (Chau et al., 2012; Le Rouzic et al., 2017a; Le Rouzic et al., 2017b; Xu et al., 2019). A high Mg/PO₄ molar ratio (≥ 4) has been more frequently used for producing MKP cement-based materials for infrastructure applications (Lee et al., 2017; Li et al., 2017; Ma and Xu, 2017; Qiao et al., 2010; Xu et al., 2018a; Xu et al., 2018b; Xu et al., 2017; Xu et al., 2019; Xu et al., 2015; Yue et al., 2014). Optimum Mg/PO₄ molar ratio that contributes to high mechanical strength was reported to be in the range of 4 – 8 (Ma and Xu, 2017; Xu et al., 2019), depending on the exact w/c ratio used. The use of high Mg/PO₄ molar ratio simplifies the reaction path such that no or very little intermediate hydrates were formed (Chau et al., 2012; Lahalle et al., 2016; Le Rouzic et al., 2017a; Le Rouzic et al., 2017b; Xu et al., 2018a; Xu et al., 2019). Furthermore, the cement reaction path is affected by the w/c ratio. The formation of intermediate hydrates was observed at a high w/c of 5; at a low w/c of 0.5 and below their formation was avoided (Xu et al., 2018a; Xu et al., 2019). Currently the understanding of the reaction mechanism of hydrating MKP cement system is still insufficient, which makes optimising material design difficult and material performance over time hard to predict. Therefore, instruments to efficiently and accurately investigate the complexity of hydrating MKP cement are of great importance.

Thermodynamic models have been developed over the past decades to better understand and investigate hydrating cements and have been applied successfully to different cements such as Portland cement (Lothenbach and Winnefeld, 2006), blended Portland cement (Lothenbach et al., 2008; Lothenbach et al., 2011), calcium sulfoaluminate cement (Winnefeld and Lothenbach, 2010), or alkali-activated cement (Ben Haha et al., 2011). The reliability of such model predictions relies on the accuracy

and completeness of the underlying thermodynamic database. While during the last past two decades, significant effort has been made to complete thermodynamic data for calcium, silicon and aluminium based cements (Dilnesa et al., 2014; Lothenbach et al., 2019; Lothenbach et al., 2008; Lothenbach et al., 2012; Lothenbach and Winnefeld, 2006; Matschei et al., 2007; Myers et al., 2015; Nied et al., 2016), much less effort had been focussed on magnesium phosphate cements. Only limited measured thermodynamic data are available for some magnesium phosphate hydrates: newberyite, cattite, K-struvite and bobierrite (Babić-Ivančić et al., 2006; Racz and Soper, 1968; Taylor et al., 1963a; Taylor et al., 1963b), while for other phosphate hydrates, such as $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, no measured solubility data have been published. Thermodynamic data for magnesium phosphates have also been estimated from the free energy and enthalpy of the oxides (Chau et al., 2012; La Iglesia, 2009; Zhang et al., 2017), a procedure which can lead to accurate estimations in some cases, but can deviate in the order of several 10 of kJ/mol to the data derived from solubility measurements (Lothenbach et al., 2017), which makes predictions of solubility and relative stability based on such data difficult. This lack of a complete and reliable thermodynamic database for magnesium (potassium) phosphate hydrates prevents the efficient use of thermodynamic models to predict the effect of varying cement composition, temperature and time in such systems. Thus, the present paper builds a consistent thermodynamic database for magnesium phosphate hydrates based on solubility measurements for newberyite, phosphorösslerite, $\text{KMgPO}_4 \cdot \text{H}_2\text{O}$, K-struvite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, farringtonite ($\text{Mg}_3(\text{PO}_4)_2$), $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, bobierrite, and cattite, carried out at different temperatures and a critical review of existing thermodynamic data and solubility measurements from literature. Finally the derived thermodynamic data are used to model the effect of Mg/PO₄ ratio, of the water to cement ratio, of pH values and of temperature on the stable phases.

2. Materials and methods

2.1 Materials

All the starting materials used in this study were magnesia (MgO , 97%, Emsure[®]), magnesium chloride (MgCl_2 , $\geq 98\%$, Sigma[®]), magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.5-

102.0%, Esure[®]), magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99.5\%$, Emsure[®]), potassium dihydrogen phosphate (KH_2PO_4 , 99.5-100.5%, Sigma-Aldrich[®]), potassium phosphate dibasic trihydrate [$\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.0\%$, Sigma-Aldrich[®]], potassium hydroxide (KOH , $\geq 85\%$, Honeywell-Fluka[®]), sodium phosphate dibasic dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 98.5-101%, Sigma-Aldrich[®]), and calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%, Sigma-Aldrich[®]).

Magnesium phosphate hydrates were precipitated in solution as detailed in Table 1-1; after different equilibration times the suspensions were filtrated as detailed below and the composition of the solid and liquid phase was investigated. A fraction of the dried solids was re-dissolved in Milli-Q water and equilibrated at different temperatures and times, as summarised in Table 1-2. In order to further study the influence of several important factors, such as pH, Mg/PO_4 molar ratio, water-to-solid (w/s) ratio and temperature on the formation of magnesium phosphate hydrates, three systems of MgCl_2 - KH_2PO_4 - H_2O , MgO - KH_2PO_4 - H_2O and MgSO_4 - KH_2PO_4 - H_2O were prepared as listed in Table 1-3.

Table 1: Materials and mix proportions used to prepare magnesium phosphate solids (in [g/100 g solution]).

1: Synthesis of pure magnesium phosphate hydrates										
Name	composition	MgCl ₂	Mg(ac) ₂ ^a	Mg-sulf ^a --- [g/100g solution]	NaH ₂ PO ₄ ^a ---	KH ₂ PO ₄ ---	KOH [mM]	Ca-nit. ^a [g]	Temp. [°C]	Time
New ^b	MgHPO ₄ ·7H ₂ O	0.48	-	-	-	0.68	50	-	20	60 d
Phos	MgHPO ₄ ·3H ₂ O	-	14.39	-	-	8.40	-	-	20	5, 30min, 1h, 1d
K-str	MgKPO ₄ ·6H ₂ O	5.00	-	-	-	25.00	^c	-	20	14 d
H15	Mg ₂ KH(PO ₄) ₂ ·15H ₂ O	-	-	2.91	-	2.69 ^d	-	-	20	28 d
MO4 ^e	Mg ₃ (PO ₄) ₂ ·4H ₂ O	-	-	0.55	0.53	-	-	-	90	2.5 h
Bob	Mg ₃ (PO ₄) ₂ ·8H ₂ O	-	-	0.54	0.55	-	-	0.0054	90	2.5 h
Cat_5	Mg ₃ (PO ₄) ₂ ·22H ₂ O	-	-	0.66	0.64	-	-	-	5	50, 140 d
Cat_40 ^f	Mg ₃ (PO ₄) ₂ ·22H ₂ O	-	-	0.66	0.64	-	-	-	5/40	30d

2: Dissolution and equilibration of magnesium phosphate hydrates at different temperature and time					
Name	Composition		Weight [g/100g MilliQ water]	Temperature [°C]	Time [d]
K-str	K-struvite	MgKPO ₄ ·6H ₂ O	1.00	20, 40, 80	30
Bob	Bobierite	Mg ₃ (PO ₄) ₂ ·8H ₂ O	1.00	20, 40, 80	14
Cat	Cattiite	Mg ₃ (PO ₄) ₂ ·22H ₂ O	0.19	20, 40, 80	30
Cat_D	Cattiite dried ^g	Mg ₃ (PO ₄) ₂	0.50	20, 40, 80	30

3: Influence of pH, Mg/PO ₄ molar ratio, w/s on the formation of magnesium phosphate hydrates										
Name	Mg/PO ₄ [mol/mol]	w/s [g/g]	K conc. [mM]	KH ₂ PO ₄ added in	MgO [g/100g solution]	MgCl ₂	MgSO ₄ ·7H ₂ O ^h [mM]	KOH [mM]	Temp. [°C]	Time [d]

a): Variation pH, samples with chloride and KOH

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1_43	1.0	43	150	1.36	-	0.952	-	50	20	60
1_86L ^a	1.0	86	110	0.68	-	0.476	-	50	20	60, 120
1_86M	1.0	86	124	0.68	-	0.476	-	74	20	60
1_86H	1.0	86	150	0.68	-	0.476	-	100	20	60, 750
b): Mg/PO₄: Variation Mg/PO₄ at low and high w/s										
05_5	0.5	5	1.282	17.44	2.56	-	-	-	20	75, 480
05_10	0.5	10	0.641	8.72	1.28	-	-	-	20	75, 480
05_64	0.5	64	0.100	1.36	0.20	-	-	-	20	60, 750
	0.5	64	0.100	1.36	0.20	-	-	-	5, 50, 80	30
06_62	0.6	62	0.100	1.36	0.24	-	-	-	20	60
07_61	0.7	61	0.100	1.36	0.28	-	-	-	20	60, 480
08_5	0.8	5	1.190	16.19	3.81	-	-	-	20	75
08_10	0.8	10	0.595	8.10	1.91	-	-	-	20	75
08_59	0.8	59	0.100	1.36	0.32	-	-	-	20	60
1_5	1.0	5	1.136	15.46	4.54	-	-	-	20	75, 480
1_10	1.0	10	0.568	7.73	2.27	-	-	-	20	75, 480
1_57	1.0	57	0.100	1.36	0.40	-	-	-	20	60, 750
	1.0	57	0.100	1.36	0.40	-	-	-	5, 50	30, 360
	1.0	57	0.100	1.36	0.40	-	-	-	80	30
1.5_51	1.5	51	0.100	1.36	0.60	-	-	-	20	60, 480
c): w/s: Variation w/s prepared from magnesium sulfate										
1_7S	1.0	6.8	>800	6.8	-	-	12.32	*	20	30
1_10S	1.0	10	249.8	3.4	-	-	6.16	-	20	760
1_15S	1.0	15	>400	3.4	-	-	6.17	*	20	30
1_76S	1.0	76	>100	0.68	-	-	1.25	*	20	30
1.3-10S ^c	1.3	10	381.72	4.36 ^c	-	-	6.16	-	20	760

^a Mg(ac)₂: Mg(CH₃COO)₂·4H₂O; Mg-sulf: MgSO₄·7H₂O; NaH₂PO₄: NaH₂PO₄·12H₂O. ^b New and 1_86L have identical starting compositions. ^c Amount of KOH was not recorded. ^d K₂HPO₄·3H₂O. ^e Filtered solution was not analysed by IC; ^f

Cat_5 suspension directly re-equilibrated at 40°C without filtration, washing or drying; ^g Mg₃(PO₄)₂ was obtained by calcinating cattite at 300°C for 4 h. ^h H₂O in MgSO₄·7H₂O considered as water to calculate w/s.

2.2 Methods

After equilibration, the solid and liquid phases in each sample mixture were separated by vacuum filtration through 0.45 µm Nylon filters. The obtained solids were first rinsed by Milli-Q water, then soaked in isopropanol for 10 min to remove the remaining liquid, filtered again and rinsed with diethyl ether to remove residual isopropanol following the procedure outlined in (Snellings et al., 2018; Winnefeld et al., 2016). The solids were further dried in an oven at 40 °C for 5 min to evaporate any remaining organic solvents; the applied relatively mild drying procedure together with a rapid analysis of the solids generally within a day, allowed to stabilise also the water rich hydrates phosphorösslerite (MgHPO₄·7H₂O), Mg₂KH(PO₄)₂·15H₂O and cattite (Mg₃(PO₄)₂·22H₂O). The mineralogical composition of the solid samples was determined by X-ray diffraction (XRD, PANalytical X'Pert Pro) in a θ - θ configuration using CoK α radiation. A summary of the XRD references patterns used is summarised in the Supplementary Material.

Thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA 851e with a heating rate of 10 °C/min from 30 to 600 °C and N₂ as protective gas. Fourier transformation infrared spectroscopy (FT-IR) spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer in a wavenumber range from 4000 to 300 cm⁻¹. Raman spectra were acquired using a Raman Bruker Senterra microscope equipped with a Peltier-cooled CCD detector and operated with the software Opus 6.5. Scanning electron microscopy (SEM, ESM Quanta FEG 650) was done in high vacuum mode with an accelerating voltage of 10-15 kV and a spot size of 2.5-4. The powder samples were applied to carbon tape first, and coated with 20 nm carbon.

The filtered liquid was separated into two parts. The pH measurements were carried out immediately after filtration on a part of the filtered liquid using a Knick pH meter (pH-Meter 766) with a Knick SE100 electrode. The pH electrode was calibrated with pH buffers (4, 7, 9 and 12) before measurement. The second part of the filtered liquid was diluted by Milli-Q water for ion chromatography (IC) analysis. Concentrations of magnesium, potassium, calcium, sodium, phosphate, chloride and sulfate were quantified using a Dionex DP series ICS-3000 ion chromatograph. Standards from 0.1 to 50 mg/L were used.

2.3 Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS (Kulik et al., 2013; Wagner et al., 2012). GEMS is a broad-purpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk composition. Thermodynamic data for aqueous species, as well as for many solids, were taken from the GEMS-PSI thermodynamic database (Thoenen et al., 2014; Thoenen and Kulik, 2003). The constants given in the original PSI thermodynamic database (Thoenen et al., 2014) have been converted into standard molar Gibbs energies and merged with the slop98.dat database as documented in (Johnson et al., 1992). For aqueous species, this dataset includes the HKF (Helgeson-Kirkham-Flowers) equation of state which is used to calculate temperature and pressure corrections up to 1000°C and 5 kbar.

The measured concentrations in the solution were used to calculate ion activity and solubility products for the different magnesium phosphate hydrates. The solubility of the different solids, if

present, can be calculated from the same measured solution composition; in a system with Mg, K, phosphate and water the maximum number of solids that thermodynamically can be in equilibrium is limited to 3 solid phases by the Gibbs phase rule. In general, all measured data where the solid was observed, were used to calculate solubility products. The activity of a species i , $\{i\}$, was calculated with GEMS from the measured concentrations considering the formation of aqueous complexes by $\{i\} = \gamma_i \cdot m_i$, where γ_i is the activity coefficient and m_i the concentration in mol/kg H₂O. The activity coefficients of the aqueous species γ were computed with the built-in extended Debye-Hückel equation with common ion-size parameter a_i of 3.67 Å for KOH solutions and common third parameter b_y , according to Eq. (1)

$$\log \gamma_i = \frac{-A_y z_i^2 \sqrt{I}}{1 + B_y a_i \sqrt{I}} + b_y I \quad (1)$$

where z_i denotes the charge of species i , I the effective molar ionic strength, b_y is a semi-empirical parameter (~ 0.123 for KOH electrolyte at 25°C), and A_y and B_y are P,T-dependent coefficients. This activity correction is applicable up to approx. 1 M ionic strength (Merkel and Planer-Friederich, 2008). Thus experimental data with an ionic strength above 1 M were not considered for the calculation of solubility products.

The thermodynamic data for solids at temperatures other than 25°C were calculated using the temperature dependence of the apparent Gibbs free energy of formation from element $\Delta_a G^\circ$ according to Eq.(2):

$$\begin{aligned} \Delta_a G_T^\circ &= \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) - \int_{T_0}^T \int_{T_0}^T \frac{C_p^\circ}{T} dT dT \\ &= \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) - a_0 \left(T \ln \frac{T}{T_0} - T + T_0 \right) - 0.5 a_1 (T - T_0)^2 - a_2 \frac{(T - T_0)^2}{2T \cdot T_0^2} - a_3 \frac{2(\sqrt{T} - \sqrt{T_0})^2}{\sqrt{T_0}} \end{aligned} \quad (2)$$

where a_0 , a_1 , a_2 , and a_3 are the empirical coefficients of the heat capacity equation $C_p^\circ = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{-0.5}$ and T_0 is the reference temperature (298.15 K). The apparent Gibbs free energy of formation $\Delta_a G_{T_0}^\circ$ refers to the free energies of the elements at 298 K. The above calculation is built into the GEMS-PSI code. A more detailed description of the derivation of the dependence of temperature of the Gibbs

energy is given in the online documentation of GEMS, in (Kulik, 2002) or in (Anderson and Crerar, 1993).

Where no measured entropy or heat capacity data were available, they were estimated from structurally similar magnesium phosphates following the procedure outlined in (Helgeson et al., 1978). The entropy of a phase A was calculated from the entropy of the solids B and C assuming $\Delta S_r = 0$ considering the molar volume according to Eq. 62 in (Helgeson et al., 1978): $S_A = (S_B + S_C) \cdot (V_B^\circ + V_C^\circ + V_A^\circ) / 2 \cdot (V_B^\circ + V_C^\circ)$. The C_p was calculated directly from the heat capacity assuming $\Delta C_{p,r} = 0$ following Eq. 78 in (Helgeson et al., 1978).

The standard PSI/Nagra thermodynamic database in GEMS (Thoenen et al., 2014; Thoenen and Kulik, 2003) contains data for the deprotonation of phosphoric acid and pyrophosphoric acid (see Supplementary Material), but no data to account for the complex formation of alkali and earth alkali ions with aqueous phosphate species. Thus the aqueous data were completed with data for aqueous phosphate complexes, where possible from experimental data, and else with data from the comprehensive review of (Turner et al., 1981) as compiled in Table S.1 in the Supplementary Material).

3. Solubility of magnesium (potassium) phosphate phases

The analysis of the equilibrated solutions at 20°C as well as XRD, TGA, FT-IR, Raman and SEM observations of newberyite, K-struvite, $Mg_2KH(PO_4)_2 \cdot 15H_2O$, cattite, bobierrite and $Mg_3(PO_4)_2 \cdot 4H_2O$ are presented. Details on the preparation methods are summarised in Table 1, the measured data under different conditions and equilibration times are summarized in Table 2. The results are discussed in detail in the following sections.

Table 2: Measured concentrations, pH values and calculated ion activity products for the different magnesium phosphate solid precipitated from oversaturation at 20°C. Ion activity products (IAP) for those solids, which were observed in the dried samples are plotted, in bold; only those IAP have been used to calculate solubility products.

pH*	Mg	K	P	acetate	Phos	New	MO4	Cat	15	K-str	solids**
			--- [mM] ---								observed
<i>Precipitation pure phases</i>											
<i>Phosphorösslerite</i>											

5 min	5.12	269	564	258	1230	-17.06	-17.00	-25.29	-25.55	-29.48	-12.28	Phos
30 min	5.14	267	551	221	1230	-17.09	-17.03	-25.27	-25.53	-29.51	-12.29	Phos
1 h	5.01	220	603	302	nd	-17.16	-17.11	-25.77	-26.02	-29.73	-12.44	Phos, <i>New</i>
1 d	4.96	152	584	209	nd	-17.45	-17.41 ***	-26.63	-26.85	-30.40	-12.83	<i>New</i>

	pH*	Mg	K	P	Cl	New	MO4	Cat	15	K-str	solids**
			--- [mM] ---			---ion activity-product---					observed
<i>Newberyite</i>											
New	6.6	15.4	84	12.7	98	-17.69	-24.55	-24.58	-30.00	-12.30	<i>New</i>
<i>K-Struvite</i>											
K-Str* ^v	8.2	1.6	2023	830	725	-18.47	-25.19	-25.60	-29.04	-10.27	<i>K-str</i>
<i>Variation pH, samples with chloride and KOH</i>											
1_43	5.0	74.3	121	60.3	185	-17.93	-27.70	-27.76	-31.97	-13.99	<i>New</i>
1_43	5.0	74.3	124	60.8	187	-17.94	-27.74	-27.80	-31.98	-14.00	<i>New</i>
1_86L ^v											
60 d	6.6	15.4	84	12.7	96	-17.70	-24.64	-24.67	-30.07	-12.34	<i>New</i>
120 d	5.4	28.3	67	31.7	94	-18.02	-27.33	-27.35	-31.94	-13.90	<i>New</i>
1_86M ^v	7.1	13.6	107	21.7	101	-17.40	-23.13	-23.16	-28.85	-11.43	<i>New, MO4</i>
1_86M ^v	7.4	8.1	108	14.6	101	-17.67	-23.31	-23.34	-29.10	-11.41	<i>New, MO4</i>
1_86H ^v											
60 d	8.3	3.4	112	12.5	99	-18.00	-22.41	-22.44	-28.78	-10.76	<i>MO4, K-str</i>
60 d	8.3	3.4	110	12.4	100	-17.99	-22.41	-22.44	-28.79	-10.77	<i>MO4, K-str</i>
750 d	8.6	0.92	125	15.0	108	-18.52	-23.54	-23.57	-29.51	-10.98	<i>MO4, K-str, UP1</i>
<i>Mg/PO₄: Variation Mg/PO₄ at high w/s;</i>											
05_64 ^v											
60 d	7.3	8.7	87	61.1	<0.1	-17.29	-22.83	-22.85	-28.47	-11.17	<i>Cat, 15, New</i>
60 d	7.2	9.2	87	68.2	<0.1	-17.28	-23.09	-23.11	-28.59	-11.30	<i>Cat, 15, New</i>
750 d	8.3	1.84	101	56.2	<0.1	-17.95	-22.87	-22.89	-28.72	-10.76	<i>New, 15, Cat</i>
06_62	7.8	4.11	83	52.6	<0.1	-17.59	-22.92	-22.93	-28.67	-11.07	<i>Cat, 15, New</i>
07_61 ^v											
60 d	7.7	4.52	72	46.6	<0.1	-17.55	-22.91	-22.92	-28.71	-11.16	<i>Cat, 15, New</i>
480 d	8.2	2.03	77	44.0	<0.1	-17.89	-22.84	-22.85	-28.80	-10.91	<i>K-str, New, UP1</i>
08_59 ^v	8.4	2.7	60	35.5	<0.1	-17.75	-22.12	-22.14	-28.51	-10.75	<i>K-str, Cat, 15</i>
08_59 ^v	8.3	3.4	77	46.0	<0.1	-17.67	-22.00	-22.01	-28.29	-10.60	<i>K-str, Cat, 15</i>
1_57 ^v :											
60 d	8.5	3.0	53	35.6	<0.1	-17.70	-21.65	-21.67	-28.30	-10.59	<i>K-str</i>
60 d	8.5	3.0	61	35.7	<0.1	-17.71	-21.71	-21.72	-28.28	-10.56	<i>K-str</i>
750 d	10.9	0.090	13.0	4.2	<0.1	-19.93	-22.92	-22.92	-30.91	-10.97	<i>Cat, K-str</i>
1.5_51 ^v :											
60 d	11.8	0.035	13.4	2.8	<0.1	21.12	-24.41	-24.42	-32.39	-11.26	<i>K-str, brucite</i>
480 d	12.0	0.029	20.6	4.3	<0.1	-21.40	-24.88	-24.88	-32.57	-11.17	<i>K-str, brucite</i>
<i>Mg/PO₄: Variation Mg/PO₄ at low w/s</i>											
05_5 ^v											
75 d* ^v :	7.5	15.7	1149	781		-17.48	-23.65	-23.70	-27.88	-10.22	<i>New, 15</i>
480 d* ^v :	7.5	9.8	1210	738		-17.67	-24.19	-24.44	-28.12	-10.37	<i>New, K-str, 15</i>
05_10 ^v :											
75 d	7.4	7.2	578	389		-17.66	-24.32	-24.44	-28.54	-10.79	<i>New, 15</i>
480 d	7.5	4.5	621	367		-17.85	-24.67	-24.79	-28.73	-10.84	<i>New, 15</i>
08_5	7.6	8.8	623	447		-17.61	-23.73	-23.88	-28.20	-10.48	<i>New, 15, K-str</i>
08_10	7.9	4.6	348	215		-17.74	-23.34	-23.40	-28.29	-10.50	<i>15, K-str</i>
1_5 ^v											
75 d	8.6	1.9	292	173		-18.08	-23.04	-23.10	-28.39	-10.27	<i>Cat, K-str</i>
480d	8.5	0.74	232	126		-18.45	-24.15	-24.19	-29.21	-10.75	<i>K-str</i>
1_10 ^v											
75 d	8.2	2.7	200	122		-17.87	-23.09	-23.13	-28.48	-10.58	<i>15, Cat, K-str</i>
480 d	8.6	0.80	151	83		-18.35	-23.74	-23.74	-29.17	-10.81	<i>K-str</i>

w/s: Variation water/solid prepared from magnesium sulfate

	pH*	Mg	K	P	SO ₄	New	MO4	Cat	15	K-str	solids**
			---	[mM]	---	---ion activity-product---					observed
1_8S	7.7	19.2	778	24.0	510	-17.97	-23.37	-23.50	-28.70	-10.63	K-str, Cat, 15
1_10S	7.8	13.1	432	16.1	234	-18.09	-23.55	-23.62	-29.02	-10.91	New, 15
1_16S	7.5	20.4	392	23.6	266	-17.74	-23.23	-23.30	-28.67	-10.89	K-str, Cat, 15
1_78S	7.5	12.1	99	14.2	58	-17.70	-23.16	-23.18	-29.11	-11.39	New, MO4
1.3_10S	7.4	19.9	478	21.2	260	-17.87	-23.72	-23.81	-28.93	11.04	15, New
						Phos	New	MO4	Cat	15	K-str
						--- solubility product ---					
Mean log K_{so} at 20°C^{v*}						-17.10^{v**}	-17.73	-22.99	-22.97	-28.85^{v***}	-10.70
Standard deviation						±0.16	±0.45	±1.16	±0.92	±0.42	±0.59

* pH measured at room temperature and corrected to 20°C. ** Phos: Phosphorösslerite (MgHPO₄·7H₂O); New: Newberyite (MgHPO₄·3H₂O); MO4: Magnesium orthophosphate tetrahydrate (Mg₃(PO₄)₂·4H₂O); Cat: Cattiite (Mg₃(PO₄)₂·22H₂O); K-str: K-struvite (MgKPO₄·6H₂O); 15: Mg₂KH(PO₄)₂·15H₂O; UP1: unidentified phase(s) observed in the presence of K with main reflections at 9.8° and 11.0° 2θ CoKα (d values = 10.4Å and 9.4Å), see text; *** not yet in equilibrium; solubility product not used.; ^v calculated ion activity products not considered for mean value as high ionic strength (>1 M) outside the validity of the activity correction used; plotted in italic.; ^v several samples prepared; ^{v*} Mean of IAP calculated at 20°C for those samples, where the solid has been observed (IAP plotted in bold) including samples at 20°C from Table 5; ^{v**} Mean of short-term samples (5 minutes to 1 hour); ^{v***} Mean of long-term samples (450-760 days: 1_10S, 1.3_10S, 05_10, 05_64).

3.1 Phosphorösslerite (MgHPO₄·7H₂O) and newberyite (MgHPO₄·3H₂O)

At very short equilibration times of up to 1 hour, at low pH values and in the presence of high initial magnesium concentrations the occurrence of phosphorösslerite (MgHPO₄·7H₂O) is observed as summarised in Table 2 and shown in the Figure S.2 i(Supplementary Material). Phosphorösslerite is destabilised after 1 hour and longer to newberyite (MgHPO₄·3H₂O).

The total weight loss observed by TGA of 52.4 wt.% for phosphorösslerite corresponds well to the theoretical weight loss of 51.2 wt.% expected for the water loss of MgHPO₄·7H₂O. The TGA data in Figure S.2 (Supplementary Material) show also that phosphorösslerite loses the first five water molecules between 40 and 120°C indicating that these water molecules are only loosely bound, while the last two, more strongly bound water molecules are lost between 120 and 200°C. The sample equilibrated for 1 day, where only newberyite is present, shows a lower total weight loss of 30.6 wt.% between 120 and 250°C. XRD data (Street and Whitaker, 1973) have shown that most of the water in the structure of phosphorösslerite is loosely bound to Mg²⁺ without sharing of water between the different Mg(H₂O)₆ units forming open water channels comparable to K-struvite. This water is thus released at low temperatures during heating, similar as e.g. the water in the channels of the ettringite structure (Lothenbach et al., 2016).

Phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$) has a monoclinic structure (space group $C2/c$ (Street and Whitaker, 1973)) and contains more water than newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), which has the same magnesium to phosphate ratio but an orthorhombic structure (space group $Pbca$) (Abbona et al., 1979; Bartl et al., 1983; Sutor, 1967). In agreement with the only transient observation of phosphorösslerite (Figure S.2 in Supplementary Material), the formation of phosphorösslerite is reported only during the first hours of hydration of MKP cements (Chau et al., 2012; Lahalle et al., 2018; Lahalle et al., 2016). Others authors observed only newberyite but no phosphorösslerite (Le Rouzic, 2014; Le Rouzic et al., 2017a; Le Rouzic et al., 2017b; Xu et al., 2019). It has been reported that phosphorösslerite can be transformed into newberyite during storage of samples before analysis (Lahalle et al., 2018), which would explain its infrequent observation in the literature indicating that phosphorösslerite might have been present more often than reported.

At pH values below 7 and at equilibration times of 1 day and longer, the formation of newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) is observed as summarised in Table 2. At pH values between 7 to 8.3, newberyite is present together with magnesium orthophosphate tetrahydrate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$: MO4), while above pH 8.3 newberyite is absent. The formation of newberyite at low pH values and its destabilisation at higher pH values agrees with the observations by (Le Rouzic et al., 2017a) in hydrating MKP cements.

The XRD data of newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) are reported in Figure S.3 (Supplementary Material) and agree well with the literature data (Abbona et al., 1979; Bartl et al., 1983; Sutor, 1967). Refinement of the structure indicated that the H_2O groups are bound to the magnesium ion (Abbona et al., 1979; Bartl et al., 1983; Sutor, 1967). The obtained TGA shown in Supplementary Material indicate a total weight loss of 30.6 wt.% between 120 and 250°C, consistent with the expected weight loss of 31.0 wt.% due to the loss of the 3 water molecules per formula unit. The main water loss at well above 100°C indicates a stronger water retention, consistent with the binding of the water groups to magnesium derived from XRD. A further gradual mass loss of 5.6 wt.% occurs above 250°C, which is attributed to the weight loss of the OH group associated with the phosphate ion as newberyite decomposes to MgHPO_4 and eventually to monoclinic β -magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) upon further heating (Frost et al., 2011b).

The FTIR and Raman spectra of newberyite in Table S.3 and Figure S.2 (Supplementary Material) show H-O-H stretching vibrations between 3200 and 3550 cm^{-1} , i.e. at relatively high wavenumber consistent with the association of water with the magnesium. H-O-H bending vibrations are observed at 1640 and 1650 cm^{-1} as summarised in Table S.3 (Supplementary Material). HPO_4 stretching vibrations are observed at $\approx 880 \text{ cm}^{-1}$ and PO_4 stretching vibrations between 980 and 1270 cm^{-1} . Further PO_4 bending vibrations are observed at 392, 500 and 603 cm^{-1} (FTIR) and 395, 497 and 519 cm^{-1} (Raman), in agreement with the observations of (Frost et al., 2011a; Frost et al., 2005) for newberyite. The SEM picture (Figure S.3A in Supplementary Material) shows that newberyite precipitates as angular particles.

To verify whether any dehydration of phosphorösslerite to newberyite could have occurred during the drying of the later-age samples before analysis, a sample was analysed still wet directly after filtration. Both in wet and dry samples only newberyite was observed by XRD, indicating no systematic changes during the drying and (short) storage time before analysis. A newberyite sample was dried for 2 hours at 300°C to investigate the solids present after dehydration in TGA; an amorphous solid with a broad XRD signal at $32^\circ 2\theta$ $\text{CoK}\alpha$ (d value = 3.2Å) was observed, which could be MgHPO_4 or a precursor of $\beta\text{-Mg}_2\text{P}_2\text{O}_7$ as observed by (Frost et al., 2011b) after further heating.

The samples where newberyite or phosphorösslerite were the dominant phases, had pH values between 5 to 8 and magnesium and phosphate concentrations between 10 to 300 mM (Table 2). The magnesium and phosphate concentrations in equilibrium with newberyite decreased with increasing pH values. Based on the measured concentrations, ion activity products (IAP) for phosphorösslerite and newberyite at 20 °C have been calculated (Table 2) using the thermodynamic software GEMS employing the data for aqueous species compiled in Table S.1 (Supplementary Material) as detailed in section 2.3 “Thermodynamic modelling”.

A solubility product $\log K_{\text{SO}}$ of -17.73 ± 0.44 for newberyite was derived from all measured data equilibrated for 30 days and longer from the measured data at 20°C (Table 2) at different pH values and in the presence of potassium, chloride or sulfate as also shown in Figure 1A. Newberyite was also observed at 40°C and 50°C (Table 3). At 40°C a $\log K_{\text{SO}}$ of -18.1 and at 50°C a $\log K_{\text{SO}}$ of -18.2 was calculated, indicating a slight stabilisation of newberyite at increasing temperatures.

Figure 1: A) Solubility products for newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{H}^+ + \text{PO}_4^{3-} + 3\text{H}_2\text{O}$) calculated from experimental data reported from 20 to 38°C in literature (Belopolsky et al., 1950; Holt et al., 1954; Lobanov, 2018; Lobanov et al., 2013; Racz and Soper, 1968; Tabor and Hastings, 1943; Taylor et al., 1963a; Taylor et al., 1963b; Verbeeck et al., 1984; Webber and Racz, 1970) and from this study as a function of pH, B) Solubility products for newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{H}^+ + \text{PO}_4^{3-} + 3\text{H}_2\text{O}$) and phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{H}^+ + \text{PO}_4^{3-} + 7\text{H}_2\text{O}$) as a function of temperature. The lines indicate the solubility calculated from the thermodynamic data compiled in Table 4.

Table 3: Measured concentrations, pH values and calculated ion activity products for magnesium phosphate solids investigated at different temperatures. Ion activity products for those solids, which were observed in the samples, are plotted in bold; only those IAP have been used to calculate solubility products.

	pH*	Mg	Na --- [mM] ---	P ---	SO ₄	K	New ---ion activity-product---	MO4	Cat	Bob	K-str	solids** observed
<i>Precipitation: magnesium orthophosphate, prepared from MgSO₄ and Na₂HPO₄ or K₂HPO₄</i>												
5°C												
Cat_5												
50 d	7.3	19.4	35.2	13.1	28.1		-17.50	-22.72	-22.73			Cat
140 d	7.7	16.4	35.7	12.3	31.9		-17.56	-22.11	-22.12			Cat, New
20°C												
H15	7.3	7.06	0.3	10.36	29.9	47.9	-17.95	-24.23	-24.24	-24.24	-12.14	New, Bob
40°C												
Cat_40	6.1	15.8	35.9	9.3	28.4		-18.12	-26.52	-26.52			New,
MO4												
90°C												
MO4				not analysed								MO4

	pH*	Mg	Na --- [mM] ---	P ---	SO ₄	Ca	New ---ion activity-product---	MO4	Cat	Bob	K-str	solids** observed
<i>Precipitation: Bobierite, prepared from MgSO₄, Na₂HPO₄, and Ca(NO₃)₂·4H₂O</i>												
90°C												
Bob1	4.5	22.5	40.5	18.0	35.4	0.4	-19.45	-32.55	-32.55	-32.55		Bob
Bob2	4.8	14.3	33.3	12.5	27.5	0.3	-19.37	-31.77	-31.77	-31.77		Bob

	pH*	Mg	K --- [mM] ---	P ---	Na	New ---ion activity-product---	MO4	Cat	Bob	K-str	solids** observed
<i>Dissolution of pre-synthesized magnesium phosphate***</i>											
20°C											
Cat_5	9.8	0.30	<0.01	0.28	0.001	-19.66	-22.44	-23.44	-23.44	-	Cat
Cat_D	10.8	0.51	<0.01	0.037	-	-20.51	-22.89	-22.89	-22.89	-	Cat
Bob	9.0	0.19	<0.01	0.18	0.016	-20.01	-25.76	-25.76	-25.76		Bob
K_St	11.0	0.062	9.54	4.84	-	-20.14	-23.43	-23.43	-23.43	-11.22	K-str, Cat
40°C											
Cat_5	7.4	0.67	<0.01	0.63	0.001	-19.11	-26.68	-26.68	-26.68	-	Bob
Cat_D	8.6	0.64	<0.01	0.56	-	-19.08	-24.28	-24.28	-24.28	-	Cat, UP2
Bob	8.0	0.18	<0.01	0.21	0.004	-19.39	-26.36	-26.36	-26.36		Bob
K_St	10.5	0.051	18.2	9.31	-	-20.44	-25.65	-25.65	-25.64	-11.78	K-str, 1* ^v
80°C											
Cat_5	6.1	0.54	0.06	0.78	-	-19.96	-31.20	-31.20	-31.20	-18.10	MO4
Cat_D	7.2	0.22	<0.01	0.21	-	-20.18	-29.75	-29.75	-29.75	-	MO4
Bob	6.6	0.18	<0.01	0.21	0.004	-20.47	-31.54	-31.54	-31.54	-	Bob
K_St	10.1	0.016	31.3	13.2	-	-22.01	-31.16	-31.16	-31.16	-13.62	Bob, UP1

	pH*	Mg	K	P	New	MO4	Cat	15	K-str	solids**
			--- [mM] ---		---	ion activity-product---				observed
<i>Precipitation: Variation Mg/PO₄ at high w/s</i>										
5°C										
05_64	7.4	7.9	77	67.9	-17.30	-22.67	-22.69	-28.49	-11.17	15, Cat,
1_57										
30 d	9.9	0.27	29	16.6	-18.80	-21.88	-21.88	-29.34	-10.54	K-str, 15, Cat
360 d	9.4	0.46	39	21.2	-18.53	-22.09	-22.10	-29.16	-10.62	Cat, K-str, 15
50°C										
05_64	6.2	3.2	89	64.1	-18.17	-27.40	-27.41	-31.33	-13.15	New, MO4, UP1
1_57										
30 d	10.1	0.13	59	31.0	-20.12	-25.75	-25.76	-31.54	-11.41	K-str, 1 ^{*v} , UP1
360 d	10.6	0.03	72	32.6	-21.16	-27.95	-27.97	-33.09	-11.92	K-str, 1 ^{*v} , MO4, UP1
80°C										
05_64	5.4	0.70	89	66.4	-19.56	-32.59	-32.61	-34.96	-15.38	MO4, UP1
1_57	9.8	<0.04 ^v	79	39.5	<-21.4	<-30.1	<-30.1	<-34.4	<-13	MO4, UP1

* pH measured at room temperature and corrected to 5, 20, 40, 50, 80 or 90°C. ** Phos: Phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$); New: Newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$); 1: $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$; MO4: Magnesium orthophosphate tetrahydrate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$); Bob: Bobierite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$); Cat: Cattiite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$); K-str: K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$); 15: $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$; UP1: unidentified phase(s) observed in the presence of K with main reflections at 9.8° and 11.0° 2θ CoK α (d values = 10.4Å and 9.4Å), see text. UP2: unidentified phase(s) 2 with main reflection at 7.1° 2θ CoK α (d value = 14.4Å) observed in the cattiite sample only. *** Na and sulfate concentrations were in all cases below the detection limit of 0.004 (Na) and 0.001 (sulfate) mM. ^v $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$; its presence is also deduced from the decrease in K concentrations. ^v ion activity product not used as Mg concentrations below the detection limit; plotted in italics.

Solubility products for newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) have also been reported in a number of papers at 25°C to 80°C as summarised in Table 4. The reported solubility products at 25°C ranged from -17.8 to -18.2. Most solubility data for newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) reported in literature are based on the measurements of (Racz and Soper, 1968; Taylor et al., 1963a; Taylor et al., 1963b). As in the older papers either the formation of MgHPO_4^0 and pyrophosphate complexes were neglected or a stronger complex formation constant of MgHPO_4^0 was used ($\log K_{\text{MgHPO}_4^0} = 15.23$ for $\text{H}^+ + \text{PO}_4^{3-} + \text{Mg}^{2+} \rightleftharpoons \text{MgHPO}_4^0$) than in the present work: $\log K_{\text{MgHPO}_4^0} = 14.80$), all solubility data were recalculated as far as possible and compiled in the 2nd half of Table 4. The recalculation of the data of (Taylor et al., 1963a; Taylor et al., 1963b) and (Racz and Soper, 1968) using the data for aqueous species compiled in the Supplementary Material resulted in $\log K_{\text{SO}} = -17.99$ and -18.03 as shown in Figure 1. Also from the data measured by (Belopolsky et al., 1950; Holt et al., 1954; Lobanov, 2018; Lobanov et al., 2013; Tabor and Hastings, 1943; Verbeeck et al., 1984) comparable solubility products were obtained. These values calculated directly from the experimental data agree well with the $K_{\text{SO}} = -17.89$ fitted by (Babić-Ivančić et al., 2006) using the same complex formation constant of $\log K_{\text{MgHPO}_4^0} = 14.80$ for MgHPO_4^0 as in the present work. From all these data a weighted mean value of -17.93 ± 0.23 at 25°C was derived (see Table 4).

The solubility of newberyite was also calculated as a function of temperature based on the selected entropy and heat capacity values according to equation (2). As no measured heat capacity and entropy are available, they were estimated from the entropy and heat capacity data of K-struvite using $\Delta S_r = \Delta C_p = 0$ for the reaction $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite) $-1/2 \text{ K}_2\text{O} - 2 1/2 \text{ H}_2\text{O}_{\text{structural}} \rightleftharpoons \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ as detailed in Table 4. Despite the insecurity introduced by using estimated entropy and heat capacity data, the solubilities of newberyite and phosphorösslerite calculated as a function of temperature agree well with the trends in the available measured data (Figure 1B) and indicate some stabilisation at higher

temperature in the case of newberyite, while phosphorösslerite is expected to become somewhat less unstable at lower temperature.

Table 4: Compilation of thermodynamic data for newberyite and phosphorösslerite reported in the literature and determined in the present paper.

Species	$\log K_{so}^{\circ}$ ^a	$\Delta_f G^{\circ}$ [kJ/mol]	$\Delta_f H^{\circ}$ [kJ/mol]	S° [J/mol/K]	C_p° [J/mol/K]	Vol [cm ³ /mol]	Reference ^b
Newberyite: $MgHPO_4 \cdot 3H_2O \rightleftharpoons Mg^{2+} + H^+ + PO_4^{3-} + 3 H_2O$							
38°C	-16.8						(Tabor and Hastings, 1943)
38°C	-17.3						(Holt et al., 1954)
25°C	-18.17						(Taylor et al., 1963a; Taylor et al., 1963b)
25°C	-18.18						(Racz and Soper, 1968)
25°C	-18.17						(Smith and Martell, 1976)
25°C	-18.18						(Webber and Racz, 1970)
25°C	-18.18	-2288.9					(Vieillard and Tardy, 1984)
25°C	-18.13						(Verbeeck et al., 1984)
25°C		-2278.1					(La Iglesia, 2009)
25°C	-18.2						(Lobanov et al., 2013)
35°C	-18.3						(Lobanov et al., 2013)
45°C	-18.4						(Lobanov et al., 2013)
25°C	-18.23						(Bennett et al., 2017)
25°C	-18.15	-2278.1	-2608.0			82.9	(Zhang et al., 2017)
calculated, 25°C	-17.8±3.0 ^c						ts (Belopolsky et al., 1950)
calculated, 80°C	-18.4±1.8 ^c						ts (Belopolsky et al., 1950)
reported, 25°C	-17.89±0.5						(Babić-Ivančić et al., 2006)
calculated, 38°C	-17.83±0.5						ts (Tabor and Hastings, 1943)
calculated, 38°C	-17.92±0.5						ts (Holt et al., 1954)
calculated, 25°C	-17.99±0.63						ts (Taylor et al., 1963a; Taylor et al., 1963b)
calculated, 25°C	-18.03±0.5						ts (Racz and Soper, 1968)
calculated, 25°C	-18.02±0.5						ts (Webber and Racz, 1970)
calculated, 25°C	-18.07±0.5						ts (Verbeeck et al., 1984)
calculated, 5°C ^d	-17.80±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 12°C ^d	-17.65±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 20°C	-17.89±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 25°C	-18.11±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 35°C	-18.27±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 45°C	-18.45±1.0						ts (Lobanov, 2018; Lobanov et al., 2013)
measured 5°C	-17.56±1.0						this study
measured 20°C	-17.73±0.45						this study
measured 40°C	-18.12±1.0						this study
measured 50°C	-18.17±1.0						this study
weighted mean at 25°C	-17.93±0.23	-2286.5	-2600.6	195.9^e	182.6^e	82.2	this study
Phosphorösslerite: $MgHPO_4 \cdot 7H_2O \rightleftharpoons Mg^{2+} + H^+ + PO_4^{3-} + 7 H_2O$							

25°C		-3234.46	-3804.98				(Chau et al., 2012)
25°C		-3234.46	-3804.98		122.4		(Zhang et al., 2017)
5°C	-18.0 ^f						(Lobanov et al., 2013)
12°C	-17.8 ^f						(Lobanov et al., 2013)
calculated, 5°C	-17.80±1.0 ^f						ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 12°C	-17.65±1.0 ^f						ts (Lobanov, 2018; Lobanov et al., 2013)
measured 20°C	-17.10±0.16						this study
extrapolated to 25°C	-17.01±0.25	-3230.0	-3772.3	361.8^g	342.8^g	141.6	this study

^a solubility products refer to reactions formulated with H⁺, Mg²⁺, PO₄³⁻ and H₂O; ^b ts: calculated in this study using experimental data from the reference indicated; ^c no pH values were reported, resulting in a considerable variation in the calculated solubility products. ^d from partial destabilization of phosphorösslerite. ^e obtained from $\Delta_r S^\circ = \Delta_r C_p^\circ = 0$ for the isocoulombic reaction: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite) $-\frac{1}{2} \text{K}_2\text{O} - 2\frac{1}{2} \text{H}_2\text{O}_{\text{structural}} \rightleftharpoons \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite). Properties of H₂O_{structural} ($S^\circ = 40.2$, $V^\circ = 13.7$ and $C_p^\circ = 40.0$) from (Helgeson et al., 1978) were used. ^f measured after 4 days, partial destabilization to newberyite observed. ^g obtained from $\Delta_r S^\circ = \Delta_r C_p^\circ = 0$ for the isocoulombic reaction: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite) $-\frac{1}{2} \text{K}_2\text{O} + 1\frac{1}{2} \text{H}_2\text{O}_{\text{structural}} \rightleftharpoons \text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ (phosphorösslerite); to estimate the effect of water in the solid, H₂O_{structural} ($S^\circ = 40.2$, $V^\circ = 13.7$ and $C_p^\circ = 40.0$) from (Helgeson et al., 1978) was used.

For phosphorösslerite a mean ion activity product of -17.10±0.16 at 20°C was derived from the concentrations measured after 5, 40 and 60 minutes as summarised in Table 2. After 1 day, where newberyite was observed, a clearly lower ion activity product of -17.45 was obtained. In none of the other experiments any phosphorösslerite had been observed. The only other measured solubility products for phosphorösslerite available have been determined at 5 and 12 °C using pre-synthesised phosphorösslerite and an equilibration time of 4 days. These solubility products are with -18.0 and -17.8 ((Lobanov et al., 2013), see Table 4) somewhat more negative than the data measured here; this could be related to the observed partial destabilization of phosphorösslerite in those experiments to newberyite and cattite during the 4 days of those experiments. From the measured solubility products at 20°C and the calculated entropy and heat capacity data as given in Table 4, a solubility product of -17.1±0.3 at 25°C was derived according to Eq. (2).

In Figure 1 the solubility product calculated for phosphorösslerite is compared with solubility products derived for newberyite from literature data and own measurements, as discussed below. As phosphorösslerite has been observed as intermediate phase only before newberyite formation, phosphorösslerite can be expected to be less stable than newberyite, i.e. phosphorösslerite should have a less negative solubility product for the reaction $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} + \text{Mg}^{2+} + 7\text{H}_2\text{O}^0$ than

newberyite. The observed less negative solubility product of phosphorösslerite confirms the instability of phosphorösslerite towards newberyite and is consistent with the presence of phosphorösslerite at early reaction times only (see Table 2).

The complete set of thermodynamic data selected for newberyite, phosphorösslerite and other solid phases relevant for MKP systems is summarised in Table 5.

Table 5: Standard thermodynamic properties of magnesium, phosphate and potassium containing solids and structural water at 25 °C and 1 bar.

Species	log K ^{° a}	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/mol/K]	C_p° [J/mol/K]	Vol [cm ³ /mol]	Ref ^b
Brucite Mg(OH) ₂	16.84	-832.23	-923.27	63.14	77.28	24.6 (Thoenen et al., 2014)	
Periclase MgO		-569.38	-601.66	26.95	37.8	11.3 (Thoenen et al., 2014)	
K ₂ O		-322.40	-363.17	94.14	84.09	40.4 (Helgeson et al., 1978)	
structural water				40.14	40.04	13.70 (Helgeson et al., 1978)	
Newberyite MgHPO ₄ ·3H ₂ O	-17.93	-2286.5	-2600.6	195.9	182.6	82.2	ts
Phosphorösslerite							
MgHPO ₄ ·7H ₂ O	-17.01	-3230.0	-3772.8	361.8	342.8	141.6	ts
K-struvite MgKPO ₄ ·6H ₂ O	-10.96	-3240.8	-3717.3	350.1	324.8	142.5	ts
MgKPO ₄ ·H ₂ O	-10.95	-2054.8	-2245.8	141.3	124.6	66.1	ts
Mg ₂ KH(PO ₄) ₂ ·15H ₂ O	-28.67	-6949.1	-8086.7	781.6	747.6	303.2	ts
Farringtonite Mg ₃ (PO ₄) ₂	-22.41	-3527.2	-3769.1	189.2	213.5	95.2	ts
Mg ₃ (PO ₄) ₂ ·4H ₂ O	-23.50	-4482.1	-4864.9	650.0	373.6	140.7	ts
Bobierite Mg ₃ (PO ₄) ₂ ·8H ₂ O	-25.30	-5441.1	-6056.5	801.4	533.8	191.1	ts
Cattiite Mg ₃ (PO ₄) ₂ ·22H ₂ O	-23.03	-8748.7	-10265.1	1046.6	1003.6	401.9	ts

^a solubility products refer to reactions formulated with H⁺, K⁺, Mg²⁺, PO₄³⁻ and H₂O; ^b ts: calculated in this study;

3.2 K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) and $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$

At pH values above 8 or at K concentrations >30 mM the formation of K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) is observed. K-struvite was synthesised from KH_2PO_4 and MgCl_2 as shown in Figure 2; the obtained pattern (Figure 2A) agrees with the pattern reported by (Graeser et al., 2008). K-struvite crystallizes in the orthorhombic crystal system, space group $\text{Pm}21\text{n}$ (Graeser et al., 2008; Mathew and Schroeder, 1979); the water in the structure of K-struvite is loosely bound to Mg^{2+} without sharing of water between the different $\text{Mg}(\text{H}_2\text{O})_6$ forming open water channels (Graeser et al., 2008), comparable to the structure of phosphorösslerite. The presence of loosely bound water is confirmed by the mass loss of K-struvite at slightly above 100°C observed in the TGA data (Figure 2B); the measured weight loss of 41.1 wt.% agrees well with theoretical weight loss of 40.5 wt.% upon complete dewatering: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O} \Rightarrow \text{MgKPO}_4 + 6\text{H}_2\text{O}$. In addition, experiments on cements have shown that K-struvite destabilises to $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at 50°C .

The FTIR spectra in Figure 2C shows broad H-O-H vibrations at around 1590 , 2330 and 2870 cm^{-1} ; again the broad signals and low wavenumbers are consistent with poorly ordered water. Signals of PO_4 stretching vibrations are observed at around 982 cm^{-1} (FTIR) and 946 and 1077 cm^{-1} (Raman) (Frost et al., 2005; Mácová and Viani, 2017; Stefov et al., 2004). Further PO_4 bending vibration is observed at around 562 cm^{-1} (IR). The signals at around 431 , 452 cm^{-1} (FTIR) and 431 and 470 cm^{-1} (Raman) could be either due to PO_4 bending vibrations and/or Mg-O stretching (Frost et al., 2005; Mácová and Viani, 2017; Stefov et al., 2004). The Raman spectra bands at around 153 , 231 , and 302 cm^{-1} are due to Mg-O stretching vibrations (Frost et al., 2005; Mácová and Viani, 2017; Stefov et al., 2004). The SEM picture in Figure 2D) shows that K-struvite crystallises as triangular platelets. The shape of precipitated K-struvite can vary depending on the synthesis conditions; in low Mg/ PO_4 cements rather needle-like or acicular K-struvite is observed (Chau et al., 2011; Le Rouzic et al., 2017b).

D) K-struvite

E) Mg₂KH(PO₄)₂·15H₂O

Figure 2: A) XRD patterns of K-struvite and Mg₂KH(PO₄)₂·15H₂O (sample 05_64: 5 °C). C: Mg₃(PO₄)₂·22H₂O; S: MgKPO₄·6H₂O; 15: Mg₂KH(PO₄)₂·15H₂O; B) TGA/DTG curves; C)

FTIR/Raman curves; D) SEM image of K-struvite synthesized at 20 °C; E) SEM image of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ synthesized at 5 °C for 30 d. Details on the synthesis procedures of K-str and 05_64: 5 °C are given in Table 1-1 and 1-3.

Some thermodynamic data for K-struvite have been reported in the literature as compiled in Table 6. (Bennett et al., 2017; Frank, 2013; Taylor et al., 1963a; Yang et al., 2019) have determined solubility products in the range of $K_{\text{SO}} = -10.6$ to -11.0 at 25°C from measurements between pH 8 and 12. (Luff and Reed, 1980) determined heat capacity, entropy and enthalpy of K-struvite (Table 6) and derived based on these data a much lower solubility of -11.7 .

Our experiments compiled in Table 2 and Table 3 resulted in a log K_{SO} of -10.77 ± 0.55 at 20°C; the consideration of only long-term data (360 days and longer) and the under-saturation experiment (Table 3) gave a slightly lower, but statistically not significantly different, value of -10.98 ± 0.42 . Together with the solubility products recalculated from data of (Bennett et al., 2017; Frank, 2013; Taylor et al., 1963a) and the data compiled in Table 3, a log K_{SO} of -11.0 ± 0.3 at 25°C was derived (see Table 6). The enthalpy of -3717 kJ/mol, calculated from the Gibbs free energy obtained from the solubility product and the entropy determined by (Luff and Reed, 1980) is comparable to the reported enthalpy of -3722 ± 21 kJ/mol (Luff and Reed, 1980) and the -3724 kJ/mol and -3729 kJ/mol estimated by (Vieillard and Tardy, 1984) and (La Iglesia, 2009).

The entropy and heat capacity data measured by (Luff and Reed, 1980) result in only small changes in the solubility of K-struvite with temperature, which agrees well with the measured trends shown in Figure 3. The limited solubility variation with temperature is similar to newberyite and to struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), which also shows only a weak dependence of its solubility on temperature (Aage et al., 1997).

At 50 and 80°C less or no K-struvite was observed by XRD and TGA than at 20°C, although the potassium concentrations were reduced, consistent with the (partial) formation of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$. Thus, K-struvite can be expected to be more stable than $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ below 25°C; at 50°C and above rather the formation of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ can be expected (Table 3).

Figure 3: A) Calculated solubility products for K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{K}^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$) from experimental data reported in literature at 20°C (this study) and 25°C (Bennett et al., 2017; Frank, 2013; Taylor et al., 1963a; Yang et al., 2019) as a function of pH and B) calculated solubility products of K-struvite and MgKPO_4 as a function of temperature. The solid line indicates the K-struvite solubility calculated from the thermodynamic data compiled in Table 5 and Table 6; the dashed line gives the calculated solubility product of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$, i.e. dehydrated K-struvite.

Table 6: Compilation of thermodynamic data for K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$), $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ reported in the literature and determined in the present paper.

Species	$\log K^\circ$ ^a	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	S° [J/mol/K]	C_p° [J/mol/K]	Vol [cm ³ /mol]	Reference ^b
$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{K}^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$							

25°C	-10.62						(Taylor et al., 1963a)
25°C	-11.68		-3722±21	350.1	324.8		(Luff and Reed, 1980)
25°C	-10.84						(Frank, 2013)
25°C	-10.63	-3241	-3724.3	330			(Vieillard and Tardy, 1984)
25°C		-3257.2	-3729.3				(La Iglesia, 2009)
25°C		-3241	-3724.3				(Chau et al., 2012)
25°C	-10.62	-3241	-3724.3		156.5		(Zhang et al., 2017)
10°C	-11.07						(Bennett et al., 2017)
25°C	-11.00						(Bennett et al., 2017)
36°C	-10.90						(Bennett et al., 2017)
25°C	-10.87						(Yang et al., 2019)

calculated, 25°C	-10.98±0.5						ts (Taylor et al., 1963a)
calculated, 25°C	-11.08±0.95						ts (Frank, 2013)
calculated 10°C	-11.07±0.7						ts (Bennett et al., 2017)
calculated 25°C	-11.00±0.7						ts (Bennett et al., 2017)
calculated 36°C	-11.01±0.7						ts (Bennett et al., 2017)
measured 5°C	-10.58±1.0						this study
measured 20°C	-10.77±0.55						this study
measured 40°C	-11.78±2.0						this study
measured 50°C	-11.67±1.5						this study
weighted mean at							
25°C	-10.96±0.31	-3240.8	-3717.3	350.1	324.8	142.5	this study

measured 40°C	-11.78±1.5						this study
measured 50°C	-11.66±1.5						this study
derived mean at							
25°C	-10.95±1.50	-2054.8	-2245.8	141.3 ^c	124.6 ^c	66.1	this study

25°C		-6969.9	-8142.3				(Chau et al., 2012)
25°C	-29.54	-6969.9	-8142.3		293.0		(Zhang et al., 2017)

measured 5°C	-28.99±1.43						this study
measured 20°C							
450-760 days	-28.85±0.42						this study
weighted mean at							
25°C	-28.67±0.60	-6949.1	-8086.7	781.6 ^d	747.6 ^d	303.2	this study

^a solubility products refer to reactions formulated with H^+ , Mg^{2+} , PO_4^{3-} and H_2O ; ^b ts: calculated in this study using experimental data from the reference indicated; ^c $\Delta_r S^\circ = \Delta_r C_p^\circ = 0$ for the isocoulombic reaction:

3.3 $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$

At pH values between 7.0 and 8.5 the formation of another water-rich magnesium phosphate, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, was observed. The formation of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ occurred together with cattite at lower pH values (see Table 2); at pH values above 8 or at K concentrations > 30 mM together with K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$). At 20°C , $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was only present at higher PO_4 concentrations (≥ 24 mM); at lower concentrations magnesium orthophosphate tetrahydrate ($\text{Mg}_3(\text{PO}_4)_2$) formed instead. $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ precipitated as the main phase at 5°C , while it was present as minor phase only at 20°C and completely absent at higher temperatures, indicating a strong destabilisation of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ with increasing temperature.

The TGA data in Figure S.3B (Supplementary Material) of the sample obtained at 5°C indicated a main water loss of the loosely bound water between 50 to 200°C with a total weight loss 45.9 wt.%, i.e. slightly lower than the theoretical mass loss of 49.2 wt.%; the observed 45.9 wt.%, would correspond rather to 14 instead of 15 water per formula unit. XRD studies have indicated that the water and potassium in the structure of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ are present in channels (Takagi et al., 1982) consistent with the water loss at low temperatures. The water in the structure of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is loosely bound to Mg^{2+} without sharing of water between the different $\text{Mg}(\text{H}_2\text{O})_6$ as in the case of K-struvite and phosphorösslerite. Also its chemical composition lies between phosphorösslerite and K-struvite, although the crystal system of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (anorthic, space group P-1, density $1.81 \text{ cm}^3/\text{g}$ (Takagi et al., 1982)) is different to those of K-struvite (orthorhombic, space group Pm21n (Graeser et al., 2008)) or phosphorösslerite (monoclinic, space group C2/c (Street and Whitaker, 1973)).

The FTIR spectra in Figure S.3C (Supplementary Material) show H-O-H vibrations at around 1637, 2356 and 3009 cm^{-1} (IR) due to the presence of poorly ordered water similar to K-struvite and consistent with the high water loss at low temperature observed by TGA. As in the case of K-struvite, PO_4 stretching vibrations are observed at around 1017 cm^{-1} (FTIR) and 941, 998 and 1030 cm^{-1} (Raman) (Koleva et al., 2017; Koleva et al., 2015; Pecovska-Gjorgjevich et al., 2018; Stefov et al., 2017). Further PO_4 bending vibration is observed at 544 cm^{-1} (FTIR) and 560 cm^{-1} (Raman) (Koleva et al., 2017; Koleva et al., 2015; Pecovska-Gjorgjevich et al., 2018; Stefov et al., 2017). The signals at around 389 and 420 cm^{-1} (FTIR) and 268 and 410 cm^{-1} (Raman) could be due to bending vibrations of PO_4 or Mg-O

stretching vibrations (Koleva et al., 2017; Koleva et al., 2015; Pecovska-Gjorgjevich et al., 2018; Stefov et al., 2017). The SEM picture in Figure 2 shows that $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ crystallises as rectangular platelets.

The formation of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ has been observed in the experiments shown here as well as at early reaction times in MKP cements hydrating at ambient temperature (Chau et al., 2012; Lahalle et al., 2018; Lahalle et al., 2016; Xu et al., 2018a; Xu et al., 2019), however, its solubility had not yet been determined experimentally. Recently its thermodynamic properties have been estimated by (Chau et al., 2012) assuming that the $\Delta_r G = \Delta_r H = 0$ from the oxides, from which a log K of -29.5 had been suggested by (Zhang et al., 2017) as indicated in Table 6. The experimental data collected in Table 2 and Figure 4 indicate a somewhat less negative solubility product in the range -28.2 to -29.0 for $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ at 20°C; the four long-term measurements (480 and 760 days) result in a mean solubility of -28.85; those data were selected. The solubility of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ increases with temperature (Figure 4) such that $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is stabilised at lower temperature and not expected to be observed above ambient temperatures, in agreement with the absence in any of the experiments above 20°C and its presence as intermediate phase only during the hydration of MKP cements (Chau et al., 2012; Lahalle et al., 2018; Lahalle et al., 2016; Xu et al., 2018a; Xu et al., 2019). As an intermediate phase between newberyite and K-struvite, in the long-term $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is only stable if its solubility product is comparable or more negative than the cumulative solubility product of newberyite and K-struvite ($\log K_{\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}} + \log K_{\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}} = \log K_{\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}} \sim -28.8$). The comparable solubility suggests that $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ can be stable at 20°C in the long-term and is stabilised at temperatures below 20°C, which agrees with the long-term experiments in Table 2 (samples 05_64, 05_10, 05_5, 1_10S and 1.3_10S) at pH values 7.2 to 8.5 (Figure 4A). Thus $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is formed at intermediate pH values and preferentially at lower temperatures; at higher temperatures it will destabilise to newberyite or K-struvite. Its stability is expected to be limited to intermediate pH values also at lower temperatures. In agreement with the solubility trends plotted in Figure 4, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is observed at 5 and 20°C (Table 2, Table 3) even after long equilibration times, but never at 50 or 80 °C, where instead K-struvite or magnesium orthophosphate tetrahydrate ($\text{Mg}_3(\text{PO}_4)_2$) have been formed.

Figure 4: Solubility products for $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O} \rightleftharpoons 2\text{Mg}^{2+} + \text{K}^+ + \text{H}^+ + 2\text{PO}_4^{3-} + 15\text{H}_2\text{O}$ calculated from experimental data measured in this study. A) at 20°C as a function of pH and B) the data at 5 and 20°C as a function of temperature. The solid line indicates the solubility of calculated $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ from the thermodynamic data compiled in Table 5, the dotted line shows for comparison the sum of the solubility of newberyite and K-struvite.

3.4 Magnesium orthophosphates

At intermediate pH values the formation of magnesium orthophosphate tetrahydrate (MO4: $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) or cattite (MO22: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$) was observed in the present study, while bobierite (MO8: $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) was formed only in the presence of some calcium or potassium as detailed in Table 3. Although these minerals have - with exception of the water content - the same

chemical composition, their crystal systems are different. Cattiite has an anortic systems (space group P-1) (Catti et al., 1981; Schroeder et al., 1978), bobierrite crystallizes in the monoclinic crystal system (space group C2/c) (Takagi et al., 1986), while magnesium orthophosphates tetrahydrate has an orthorhombic structure (Kongshaug et al., 2001). The spectra of the synthesized phase-pure samples are summarised in Figure S.4 (Supplementary Material). The measured total weight losses during TGA are with 21.9 wt.% for MO4, 35.7 wt.% for MO8 and 59.2 wt.% for MO22 comparable to the theoretical weight losses of 21.5, 35.4 and 60.1 wt.%, respectively.

Cattiite (MO22) shows the main weight loss at around 100°C indicating loosely bound water similar to phosphorösslerite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and K-struvite, while MO8 loses its water at 200°C. MO4 loses its 4 water in two steps, at 200 °C and at 330°C. The water in the structure of cattiite (M22) is loosely bound to Mg^{2+} without sharing of water between the different $\text{Mg}(\text{H}_2\text{O})_6$, comparable to K-struvite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and phosphorösslerite. Also the FTIR signal of MO22 in Figure S.4C (Supplementary Material) shows, similar to K-struvite, a very broad signal due to H-O-H stretching vibrations between 2200 and 3000 cm^{-1} . The main signals of PO_4 stretching vibrations is observed at around 980, 1057, 1160 cm^{-1} (FTIR) and 936, 1005 cm^{-1} (Raman) similar to the main signals of K-struvite (Frost et al., 2005; Mácová and Viani, 2017; Stefov et al., 2004) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ (Koleva et al., 2017; Koleva et al., 2015; Pecovska-Gjorgjevich et al., 2018; Stefov et al., 2017). Further PO_4 bending vibrations are observed at around 553 cm^{-1} (FTIR) and 558 cm^{-1} (Raman). The signals at 390 cm^{-1} (FTIR) and 436 cm^{-1} (Raman) could be due to PO_4 bending vibration and/or Mg-O stretching vibration. The Raman signals at 131, 218 and 285 cm^{-1} could be assigned to Mg-O stretching vibrations.

The FTIR and Raman spectra in Figure S.4C (Supplementary Material) show little intensity for the vibrations associated with water for MO4, more for bobierrite and cattiite. The narrower band at 3051 cm^{-1} for MO8 shows a higher degree of ordering of the bound water than for cattiite, consistent with the different temperatures due to water loss observed by TGA. Both MO8 and MO4 show several PO_4 stretching vibrations at around 950 to 1080 cm^{-1} for MO8, and between 940 and 1165 cm^{-1} for MO4 as detailed in Table S.3 (Supplementary Material). The FTIR showed much broader bands for cattiite indicating less ordering than for bobierrite or MO4, while no such differences in the band broadness was observed for the Raman bands.

The SEM images (Figure S.4 E-G in Supplementary Material) show for MO4 and cattite rectangular shapes, while bobierrite precipitates as small platelets.

(Racz and Soper, 1968) reported solubility data for the anhydrous magnesium orthophosphate: farringtonite (MO: $\text{Mg}_3(\text{PO}_4)_2$) equilibrated for 1 day in water. Recalculations of their experimental data using the aqueous dataset compiled in Table S.1 (Supplementary Material), resulted in $\log K_{\text{SO}} = -22.41 \pm 0.30$ as shown in Figure 5B and Table 7. The derived solubility could be more negative than the actual solubility of farringtonite as the formation of amorphous magnesium phosphate hydrates or of a hydrated surface layer during the experiments cannot be excluded although XRD indicated the presence of farringtonite only. Heat capacity and entropy data measured by (Oeting and McDonald, 1963) complete the thermodynamic dataset for farringtonite, as summarised in Table 7. Based on the entropy and Gibbs free energy an enthalpy of -3769 kJ/mol was calculated, which is within the range of the experimentally determined enthalpy of $-3780 \pm 11 \text{ kJ/mol}$ (Oeting and McDonald, 1963).

Table 7: Compilation of thermodynamic data for magnesium orthophosphates (farringtonite, magnesium orthophosphates tetrahydrate, bobierrite and cattite) reported in the literature and determined in the present paper.

Species	$\log K_{\text{SO}}^{\circ \text{ a}}$	$\Delta_f G^{\circ}$ [kJ/mol]	$\Delta_f H^{\circ}$ [kJ/mol]	S° [J/mol/K]	C_p° [J/mol/K]	Vol [cm ³ /mol]	Reference ^b
Farringtonite (magnesium orthophosphate): $\text{Mg}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Mg}^{2+} + 2\text{PO}_4^{3-}$							
25°C			-3780±11	189.2±1	213.5±1		(Oeting and McDonald, 1963)
25°C	-23.28						(Racz and Soper, 1968)
25°C	-23.28						(Smith and Martell, 1976)
25°C	-23.3	-3538.8					(Vieillard and Tardy, 1984)
25°C		-3538.0	-3780.0	189.2	213.5		(Lodders, 1999)
25°C		-3522.5	-3801.9				(La Iglesia, 2009)
calculated, 25°C	-22.41±0.30						ts (Racz and Soper, 1968)
25°C	-22.41±0.30	-3527.2	-3769.1	189.2	213.5	95.2	this study
Magnesium orthophosphate tetrahydrate, MO4: $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 4\text{H}_2\text{O}$							
38°C, MO4 ^c	-27.27						(Holt et al., 1954)
calculated ^c , 38°C	-25.09±0.80						ts (Holt et al., 1954)
calculated, 85°C	-30.26±1.5						ts (Lobanov, 2018; Lobanov et al., 2013)

measured 20°C	-22.99±1.16							this study
measured 40°C	-26.52±1.5							this study
measured 50°C	-27.67±1.7							this study
measured 80°C	-31.18±1.5							this study
weighted mean at 25°C	-23.50±1.8	-4482.1	-4864.9	650^d	373.6^e	140.7		this study

Bobierite: $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$

25°C	-25.20							(Taylor et al., 1963a; Taylor et al., 1963b)
25°C	-25.22	-5450.5						(Vieillard and Tardy, 1984)
25°C		-5435.3						(La Iglesia, 2009)
35°C	-26.0							(Lobanov et al., 2013)
45°C	-27.0							(Lobanov et al., 2013)
55°C	-27.6							(Lobanov et al., 2013)
25°C	-25.47							(Bennett et al., 2017)
25°C	-25.19	-5458.1	-6199.4			223.1		(Zhang et al., 2017)

calculated, 25°C	-24.50±0.85							ts (Taylor et al., 1963a; Taylor et al., 1963b)
calculated, 20°C	-24.44±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 35°C	-26.07±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 45°C	-27.00±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 55°C	-27.16±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 65°C	-30.82±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 75°C	-29.91±1.5							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 36°C	-24.81±0.79							ts (Bennett et al., 2017)
measured 20°C	-25.00±4.61							this study
measured 40°C	-26.23±1.69							this study
measured 80°C	-31.35±1.15							this study
measured 90°C	-32.16±2.39							this study
weighted mean at 25°C	-25.30±1.0	-5441.1	-6056.5	801.4^f	533.8^f	191.1		this study

Cattiite: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 22\text{H}_2\text{O}$

25°C	-23.12							(Taylor et al., 1963a; Taylor et al., 1963b)
25°C	-23.70							(Racz and Soper, 1968)
25°C	-23.12	-8751.8						(Vieillard and Tardy, 1984)
25°C		-8782.6						(La Iglesia, 2009)
5°C	-24.0							(Lobanov et al., 2013)
12°C	-23.7							(Lobanov et al., 2013)
20°C	-23.4							(Lobanov et al., 2013)
25°C	-23.22							(Bennett et al., 2017)
25°C	-23.10	-8751.8	-3780.70			399.8		(Zhang et al., 2017)

calculated, 25°C	-23.03±1.18							ts (Taylor et al., 1963a; Taylor et al., 1963b)
calculated, 25°C	-22.90±1.00							ts (Racz and Soper, 1968)
calculated, 5°C	-23.94±1.50							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 12°C	-23.75±1.50							ts (Lobanov, 2018; Lobanov et al., 2013)
calculated, 20°C	-23.35±1.50							ts (Lobanov, 2018; Lobanov et al., 2013)
measured 5°C	-22.30±1.08							this study
measured 20°C	-22.97±0.92							this study
measured 40°C	-24.28±1.50							this study

weighted mean at

25°C	-23.03±0.56	-8748.7	-10265.1	1046.6^g	1003.6^g	401.9	this study
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^a solubility products refer to reactions formulated with H⁺, Mg²⁺, PO₄³⁻ and H₂O; ^b ts: calculated in this study using experimental data from the reference indicated; ^c not specified which solid had precipitated (Holt et al., 1954) in the paper; formation of MO4 assumed in the present study; ^d S° = 650 J/mol/K fitted to describe the observed decrease of solubility with temperature, see Figure 5. ^e C_p° obtained from Δ_rC_p° = 0 for isocoulombic reaction: Mg₃(PO₄)₂ + 4 H₂O_{structural} ⇌ Mg₃(PO₄)₂·4H₂O (MO4) using H₂O_{structural} (S° = 40.2, V° = 13.7 and C_p° = 40.0) from (Helgeson et al., 1978); ^f Δ_rS° = Δ_rC_p° = 0 for isocoulombic reaction: Mg₃(PO₄)₂·4H₂O + 4H₂O_{structural} ⇌ Mg₃(PO₄)₂·8H₂O (bobierrite); ^g Δ_rS° = Δ_rC_p° = 0 for the isocoulombic reaction: 2*MgKPO₄·6H₂O + MgO – K₂O + 10H₂O_{structural} ⇌ Mg₃(PO₄)₂·22H₂O (cattiite); K-struvite used due to its structural similarity with cattiite.

Both the formation of MO4 and cattiite (MO22) was observed at 20°C as reported in Table 2. The conditions under which preferentially MO4 or MO22 nucleate at 20°C remain presently unclear. However, experiments carried out at different temperatures (Table 3) showed that at 5°C only cattiite was observed to form, while at 40°C and above MO4 formed instead. This indicates a stabilisation of cattiite at low temperature, a comparable stability of cattiite and MO4 at 20°C, while above MO4 is more stable. The experiments showed also that the solubility measured for MO4 (see Table 2 and Table 3) decreased from -23.0 at 20°C to -31.2 at 80°C for log K_{SO} as shown in Figure 5C. From these data a solubility product -23.5 was derived for 25°C, while the decrease of its solubility with temperature was well described with an entropy value of 650±200 J/mol/K. This entropy is higher than entropy value (339 J/mol/K) estimated from farringtonite and structural water, which did not well describe the decrease in solubility with temperature. Solubility products for magnesium orthophosphate tetrahydrate (MO4) have not yet been explicitly been reported in the literature. However, Holt et al. (Holt et al., 1954) reported the formation of an unspecified magnesium orthophosphate at 38°C (possibly MO4) and (Lobanov, 2018; Lobanov et al., 2013) observed at 85°C in samples containing dittmarite and bobierrite the destabilisation of bobierrite to MO4. The solubility products derived from those measurements are in line with the calculated solubility of MO4 in this paper as shown in Figure 5C.

For cattiite a solubility product of -22.97 at 20°C has been derived from the measured data, a solubility comparable to MO4 at this temperature, explaining the observation of both, MO4 and MO22, at the experiments carried out at 20°C. At 5°C a slightly higher solubility was measured for MO22,

while at 40°C, cattite was destabilised in one of the samples (Cat_5), while a somewhat lower solubility was obtained from the other sample (Cat_D), where also an unidentified phase had been observed with a main reflection at $7.1^\circ 2\theta$ CoK α (d value = 14.4Å) in XRD. The data measured in this paper for cattite compare well with the solubility product of log K_{SO} of -22.9 to -23.0 at 25°C obtained from literature data (Racz and Soper, 1968; Taylor et al., 1963a; Taylor et al., 1963b) as shown in Figure 5C; these data showed no significant variation with temperature. The thermodynamic dataset selected in Table 7 for cattite describes the measured solubility adequately as illustrated in Figure 5C. The different temperature behaviour of the MO4 and MO22 is consistent with the presence of MO22 at low temperatures and of MO4 at higher temperatures as summarised in Table 2 and Table 3.

The formation of bobierrite was observed only in the presence of potassium or calcium at 20°C to 90°C (see the experiments Bob1, Bob2, and MO4 in Table 1 and Table 3). In the absence of calcium or potassium, MO4 formed instead even at 90°C. However, once formed, bobierrite remained stable in the temperature range 20 to 90 °C as observed in the re-dissolution experiments using pre-synthesised bobierrite reported in Table 3. Similarly, (Bennett et al., 2017) has observed the formation of bobierrite in samples containing potassium, (Lobanov, 2018; Lobanov et al., 2013) in the presence of ammonium, while (Taylor et al., 1963a) reported the destabilisation of cattite to the more stable bobierrite at 25°C within a week in the presence of ammonium. (Racz and Soper, 1968) observed in the presence of sodium only MO22 but no bobierrite formation. Together these data seem to indicate that bobierrite is stable at ambient and higher temperatures, but that its formation is kinetically hindered and that the presence of K, ammonium or Ca seems to ease bobierrite nucleation, due to reasons unknown.

In this study bobierrite solubility was measured from the dissolution of bobierrite synthesized at 90°C. The data are summarised in Table 7 and Figure 5 and show a strong decrease of its solubility with temperature, a trend which is mirrored in the solubility products calculated from the data of (Lobanov, 2018; Lobanov et al., 2013). From the data reported in Table 7, a log K_{SO} = -25.3 at 25°C was derived for bobierrite; its decrease with temperature is again well described by the entropy of 801 J/mol/K estimated from MO4 and structural water. The solubility of bobierrite ($Mg_3(PO_4)_2 \cdot 8H_2O$) has also been measured by (Taylor et al., 1963a; Taylor et al., 1963b) at 25°C, where bobierrite had formed in solutions

originally equilibrated with cattite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$), indicating a higher stability of bobierrite than of cattite. In fact, the data plotted in Figure 5B and C indicate that bobierrite is more stable than cattite and MO4 in the temperature range of 10°C to approximately 90°C, which agrees with the destabilisation of cattite to bobierrite observed by (Taylor et al., 1963a; Taylor et al., 1963b) at 25°C. At temperatures above 90°C MO4 is predicted to be slightly more stable than bobierrite; the difference however, is small in agreement with the observations of both MO4 and MO8 at 80 and 90°C.

Figure 5: Calculated solubility products for magnesium orthophosphates (farringtonite: MO, magnesium orthophosphates tetrahydrate: MO4, bobbierite: MO8 and cattite: MO22; $\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + x\text{H}_2\text{O}$) A) at 20-25°C as a function of pH, and B, C) as a function of temperature. Recalculated using measured concentrations from this study (Bennett et al., 2017; Holt et al., 1954; Lobanov, 2018; Lobanov et al., 2013; Racz and Soper, 1968; Taylor et al., 1963a; Taylor et al., 1963b) as a function of temperature. The lines indicate the solubility calculated from the thermodynamic data summarized in Table 5.

The solubility trends plotted in Figure 5B and C indicate that the formation of cattite is more probable at low temperature, bobbierite at intermediate temperatures, while magnesium orthophosphate tetrahydrate can be expected above 90°C. The comparable stability of MO4 ($\log K_{so} = -23.0$) and cattite ($\log K_{so} = -23.0$) at 20°C leads to the formation of both solids at this temperature, while at lower temperature cattite is more stable and MO4 at higher temperature. Bobbierite formation is kinetically

hindered in the absence of potassium, ammonium or calcium, in particular at lower temperatures, although bobierite is thermodynamically the most stable magnesium orthophosphate at ambient temperature.

4 Application of thermodynamic data to hydrated MKP cements

Based on the thermodynamic data established above and compiled in Table 5, the effect of Mg/PO₄, water to solid ratio, pH, and temperature on the stable hydrates and pore solution composition is calculated and compared to the experimental results in the following section.

4.1 Effect of pH on aqueous and solid phase composition

The effect of pH on the hydrates formed and the solution composition was studied on solids prepared from MgCl₂ and KH₂PO₄, as the presence of chlorides allowed studying also low pH values. Thermodynamic modelling using the data compiled in Table 5 indicates that below a pH value of 7.8 only newberyite (MgHPO₄·3H₂O) is expected to form as shown in Figure 6. In this range a pH increase is accompanied by a parallel decrease of both magnesium and phosphate concentrations as only one phase, MgHPO₄·3H₂O, is calculated to precipitate. Between pH 7.8 to 9.1, magnesium orthophosphates are predicted to precipitate, at pH values above 8.0 K-struvite replaces newberyite and brucite occurs at pH above 10.5. The general trends of the measured concentrations and the sequence at which the solids occur agree generally well with the experimental observations as shown in Figure 6C. The only significant difference is that experimentally magnesium orthophosphate were observed at lower pH values (7.1 and 7.4) than predicted (pH 7.8). However, even a small variation of the solubility products by ±0.2 log units (see Figure 6) lowered that to pH 7.4, illustrating the sensitivity of the systems to the thermodynamic data derived. Whether the formation of magnesium orthophosphate tetrahydrate (Mg₃(PO₄)₂·4H₂O) or cattite (Mg₃(PO₄)₂·22H₂O) was allowed, led to no significant differences in the aqueous concentrations; the variations were well within the uncertainty of at least 0.2 log units in experimental solubility products as shown in Figure 6. The calculations indicated, however, rather the formation of Mg₃(PO₄)₂·22H₂O, which has a slightly higher stability at 20°C, than of Mg₃(PO₄)₂·4H₂O.

$\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was calculated to be absent in agreement with the experiments, but was only little undersaturated (0.05 log units) between pH 7.5 to 8.1.

Figure 6: A) Aqueous concentrations as a function of pH in solutions with 50 mM Mg, 50 mM phosphate, 100 mM chloride and increasing amounts of potassium hydroxide at 20°C: solid lines: calculated concentrations (darker lines: MO 22, lighter lines: MO4 (MO22 formation suppressed); dotted and dashed lines: variation of solubility products by ± 0.2 log units; symbols: measured values from Table 2. The formation of bobierite has been suppressed in the calculations as its formation at 20°C is kinetically hindered. * This experiment contained 200 mM K and Cl. B) Calculated amount of solid phases; the shadowed areas indicate the pH of the samples shown. C) XRD of samples 1_43, 1_86L, 1_86M and 1_86H after 60 and 750 days (Solid lines: 60 days; dashed (red) line: 750 days). N: $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$; 4: $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; S: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$; * unidentified phase(s) (UP1).

The formation of newberyite at low pH values and its destabilisation at higher pH values agrees with the observations of (Le Rouzic et al., 2017a), who observed in solutions containing 800 mM chloride the formation of newberyite at pH 5 to 7 and of K-struvite at pH 7 and 8.

The sequence of stabilisation with pH (newberyite at low pH values, $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ or $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ at intermediate pH values and K-struvite at high pH values and high K concentrations) corresponds to the sequence of phases formed during the reaction of magnesium potassium phosphate cements (Chau et al., 2012; Le Rouzic et al., 2017a; Xu et al., 2018a; Xu et al., 2019). The early reaction of magnesium phosphate cements starts at pH values below 6, i.e. under conditions where newberyite can be expected to form, whose formation is in fact observed during the first minutes of the reaction of magnesium phosphate cements (Chau et al., 2012; Le Rouzic et al., 2017a; Xu et al., 2019). After 5 to 10 minutes, the formation of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was observed in systems with high water to solid ratios (suspensions) (Chau et al., 2012; Le Rouzic et al., 2017a; Xu et al., 2018a; Xu et al., 2019), at intermediate pH values of 7 to 8. The further reaction of magnesium phosphate cements is accompanied by a further pH rise where K-struvite is the main hydrate formed.

4.2 Effect of the magnesium to phosphate molar ratio

Figure 7A illustrates how the increase of the Mg/PO₄ affects the composition of the aqueous phase; potassium, phosphate and magnesium concentrations decrease at higher Mg/PO₄, while hydroxide concentrations and thus the pH values increase strongly. The magnesium to phosphate ratio influences also the hydrates formed as shown in Figure 7B. At Mg/PO₄ < 0.5 the formation of newberyite only ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) is predicted, between Mg/PO₄ 0.5 to 0.7 catiite plus K-struvite (or possibly $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$) are calculated, while at higher Mg/PO₄ K-struvite plus minor amounts of catiite

and brucite are calculated. The experimental observations in Figure 7C show the same trends. At $\text{Mg}/\text{PO}_4 = 0.7$, the presence of $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was observed at intermediate times (60 days; Table 2), which was destabilised to K-struvite, some newberyite and unidentified phase(s) after long hydration times. At $\text{Mg}/\text{PO}_4 = 1$, cattite and K-struvite were observed after 750 days, but no or only very low amounts of cattite were present after 60 days. The main difference was observed at high $\text{Mg}/\text{PO}_4 = 1.5$, where no cattite was observed experimentally but only K-struvite and some brucite.

A comparison of Figure 6 and Figure 7 shows that an increase of the Mg/PO_4 and of pH have a comparable effect on the hydrates and the composition of the solution; Mg and phosphate concentrations decrease and K-struvite instead of newberyite is formed. The same sequence from low to high Mg/PO_4 , from low to high pH and from newberyite to K-struvite is also observed during the reaction of MKP cements (Lahalle et al., 2018; Lahalle et al., 2016; Le Rouzic et al., 2017a; Le Rouzic et al., 2017b; Xu et al., 2019). The dissolution of KH_2PO_4 in MKP cements occurs very fast within less than a minute, while reaction of MgO is slower and only partial, such that a hydrating MKP cement has initially a very low Mg/PO_4 , which increases with time. This slow reaction of MgO leads initially to low pH values and a low availability of magnesium, resulting in the formation of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, which react to K-struvite only with time (Chau et al., 2012; Lahalle et al., 2018; Lahalle et al., 2016; Le Rouzic et al., 2017a; Le Rouzic et al., 2017b; Xu et al., 2018a; Xu et al., 2019).

Figure 7: A) Aqueous concentrations as a function of the total Mg/PO_4 at high water to solid ratios in solutions with 100 mM potassium and phosphate and 50 to 150 mM magnesium at 20°C : solid lines: calculated concentrations; dotted and dashed lines: variation of solubility products by ± 0.2 log units; symbols: measured values; full symbols: Samples 0.5_64, 0.7_61, 1_57 and 1.5_51 after 480 or 750 days; empty symbols: Samples 0.5_64, 0.6_62, 0.7_61, 0.8_59, 1_57 and 1.5_51 after 60 day. The formation of bobierite has been suppressed in the calculations as its formation at 20°C was kinetically hindered. B) Calculated amount of solid phases; the shadowed areas indicate the composition of the samples shown. C) XRD of samples 0.5_64 (750 days), 0.7_61 (480 days), 1_57 (750 days) and 1.5_51 (480 days). C: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$; N: $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$; S: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$; 15: $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$. *: unidentified phase(s): UP1.

4.3 Effect of the water to solid ratio

In addition to pH and the Mg/PO_4 ratio also the water to solid ratio plays an important role and affects the aqueous and solid phase composition as shown in Figure 8 for samples with Mg/PO_4 ratio = 1. K-struvite is calculated to be stable at all water solid ratios investigated; its content is calculated to decrease at high water to solid ratios. An increase of water to solid ratio lowers the potassium, magnesium and phosphate concentrations, while the pH increases. The lowering of the K-concentrations stabilises cattite, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, at higher w/s leading to a stronger decrease of magnesium and phosphate concentrations than of K and thus to higher pH values. At very low water to solids ratio the

presence of a low amount of either newberyite or $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ is calculated. The measured concentrations after long reaction times (solid symbols) agree well with the calculated trends as shown in Figure 8A, while the measured data after 60 days (empty symbols) show higher potassium, phosphate and magnesium concentrations, due to slow reaction of the MgO , leading to lower effective Mg/PO_4 ratios at early times. The XRD data in Figure 8C confirm the predominance of K-struvite and the presence of cattite at high water to solid ratio. $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was not observed after long reaction times at w/s 5 or 10, but traces were present after 60 days.

In MKP cements with much higher nominal Mg/PO_4 ratios, the same trends have been observed as in our simplified suspensions. A low water to solid ratio leads to higher potassium, magnesium and phosphate concentrations and promotes the formation of K-struvite in MKP cements (Lahalle et al., 2018; Xu et al., 2018a; Xu et al., 2019).

Figure 8: A) Aqueous concentrations as a function of the water/solid ratio at $\text{Mg}/\text{PO}_4 = 1$ in solutions at 20°C: solid lines: calculated concentrations; dotted and dashed lines: variation of solubility products by ± 0.2 log units; symbols: measured values; full symbols: Samples 1_57, 1_10 and 1_5 after 480 or 750 days; empty symbols: Samples 1_57, 1_10 and 1_5 after 60 or 75 days. The formation of bobierrite has been suppressed in the calculations as its formation at 20°C was kinetically hindered. B) Calculated amount of solid phases; the shadowed areas indicate the composition of the samples shown. C) XRD of samples 1_57 (750 days), 1_10 (480 days) and 1_5 (480 days). C: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$; S: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

4.4 Effect of reaction temperature

Also the temperature affects the stable hydrates as illustrated below for K-struvite re-dissolved in water and for samples with Mg/PO_4 ratio of 0.5 and 1.

The dissolution of K-struvite in water and equilibration at 20, 40 and 80°C resulted in the formation of both cattite and K-struvite at 20°C, of K-struvite and $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at 40°C and of bobierrite at 80°C as summarised in Table 3 and Figure 9C. For a sample which contained initially cattite only, similar observations could be made; cattite remained stable at 20°C, bobierrite was formed instead at 40°C, while at 80°C MO_4 precipitated (Table 3). Thus in both cases it was observed that cattite destabilises at above 20°C in agreement with the calculated relative stability in Figure 5C. As the solubilities of bobierrite and MO_4 are very similar between 40 and 80°C (Figure 5B and C), both of the solids seem to nucleate at 40°C, without any clear preference. K-struvite is destabilised at higher temperature; less K-struvite is observed at 40°C than at 20°C, and none at 80°C (Figure 9C, Table 3). At 40°C the formation of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ is observed, indicated by an additional reflection at $12.5^\circ 2\theta$ CoK α and a broadening and increased intensity of the reflections at 22.4° and $25.0^\circ 2\theta$ CoK α (Figure 9C).

Thermodynamic modelling using the data selected in this paper reproduces the trends in aqueous concentrations and solid phases well as shown in Figure 9A and B. Modelling, however, predicts the destabilisation of K-struvite at slightly lower temperatures (at $25 \pm 15^\circ\text{C}$) than observed in the experiments as well as the formation of MO_4 or bobbierite at below 40°C.

Figure 9: A) Aqueous concentrations as a function of temperature for K-struvite dissolved in water at 20, 40 and 80°C and equilibrated for 30 days: solid lines: calculated concentrations; dotted and dashed lines: variation of solubility products by ± 0.2 log units; empty symbols: measured values. The formation of bobierrite has been suppressed in the calculations as its formation at 20°C was kinetically hindered. B) Calculated amount of solid phases; the shadowed areas indicate the temperature of the samples shown. C) XRD of after 30 days of reaction. B: $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; C: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$; S: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$; 1: $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$; *: unidentified phase (UP1).

For samples with $\text{Mg}/\text{PO}_4 = 1$ (sample 1_57) similar observations were made (Figure 10C): at 5°C and 20°C catiite and K-struvite dominated the solid phases. At early ages (30 or 60 days) in addition some $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ was present (Table 3), which was destabilised after 1 and 2 years. At 50°C, again catiite is destabilised while some K-struvite, $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ and MO4 are observed, at 80°C MO4 was identified as summarised in Table 3 and Figure 10C. In addition, at 50 and 80°C also unidentified phase(s) with main reflections at 9.8° and 11.0° 2θ $\text{CoK}\alpha$ (d-values = $10.4\text{\AA}$ and $9.4\text{\AA}$) was observed, which could not be assigned to any known structure. Mass balance calculations indicated for this unidentified phase an approximate total composition of $\text{K}_{0.0.3}\text{Mg}_{1.5.2}\text{PO}_4 \cdot 4\text{-}5\text{H}_2\text{O}$.

The destabilisation of K-struvite and catiite at higher temperature led to an increase of the phosphate concentrations, magnesium concentrations decreased with temperature, while potassium concentration did not vary significantly between 50°C (where K-struvite is present) and 80°C where no K-struvite was observed (Figure 10A, Table 3). Both at 50 and 80°C the measured K-concentrations are with 59 to 79 mM significantly lower than the maximum K-concentrations of 179 mM, indicating the presence of a potassium-containing solid (possible some $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$) also at 80°C. In fact, the broadening and increased intensity of the reflections at 22.4° and 25.0° 2θ $\text{CoK}\alpha$ points towards the presence of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at 50°C

Thermodynamic modelling reproduces the trends observed experimentally: catiite and K-struvite were calculated to be present at 5 and 20°C, formation of MO4 at slightly above 20°C and destabilisation of K-struvite to $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at around 25°C as shown in Figure 10B. The formation of the unidentified magnesium phosphate phase could not be reproduced due to the lack of compositional and thermodynamic data.

Figure 10: A) Aqueous concentrations as a function of temperature at $\text{Mg}/\text{PO}_4 = 1$ (sample 1_57) at 5, 20, 50 and 80°C: solid lines: calculated concentrations; dotted and dashed lines: variation of solubility products by ± 0.2 log units; symbols: measured values; full symbols: after 360 d (5, 50°C) and 750 days (20°C); empty symbols: after 30 d (5, 50, 80°C) or 60 days (20°C). The formation of bobierite has been suppressed in the calculations as its formation at 20°C was kinetically hindered. B) Calculated amount of solid phases; the shadowed areas indicate the composition of the samples shown. C) XRD of sample 1_57 after 30 (80°C), 360 (5, 50°C) and 750 days (20°C). C: $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$; S: $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$; 1: $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$; 4: $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; 15: $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$; *: unidentified phase(s) (UP1).

Thermodynamic modelling indicates that the destabilisation of cattite to MO4 or bobbierite occurs at slightly above 20°C and of K-struvite to $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at around 25°C both at high and low water to solid ratio. The calculated destabilisation of K-struvite at higher temperatures agrees with experimental data in a hydrated MKP cements where the dehydration of K-struvite at higher temperature either to $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ (Gao et al., 2016) or to a X-ray amorphous solid was reported (Gardner et al., 2015b). The formation of $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ instead of K-struvite results in a lower volume of the hydrates, which is consistent with the observed decrease in compressive and flexural strength observed at higher temperature (Gao et al., 2016; Gardner et al., 2015b).

5 Conclusions

The paper summarises a thermodynamic database built for magnesium potassium phosphate hydrates based on experimentally determined solubilities of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite), $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ (phosphorösslerite), $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite), $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (bobierrite), and $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ (cattiite). Phosphorösslerite is formed as an intermediate phase only and destabilises to newberyite with time. $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ (cattiite) are stable at 20°C and below, while higher temperatures lead to the stabilisation of $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and bobierrite. The precipitation of bobierrite was found to be kinetically hindered at room temperature and in the absence of calcium or potassium. In addition in some sample, the formation of an unidentified, poorly crystalline solid was observed.

Application of thermodynamic modelling to magnesium potassium phosphates and comparison with the experimental results illustrated the effect of several factors on the hydrates observed in the MKP systems

- pH plays a major role in the stabilisation of different solids: at low pH values ($\text{pH} < 7$) only newberyite is expected, at intermediate pH values $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, while at $\text{pH} > 8$ and high K concentrations, K-struvite becomes stable. This sequence also corresponds to the sequence of phases formed during the reaction of magnesium potassium phosphate cements, during the hydration of such cements a distinct pH increase occurs.
- An increase of the Mg/PO_4 has a comparable effect on the hydrates and the composition of the solution; pH increases, Mg and phosphate concentrations decrease and K-struvite instead of newberyite is formed.
- The same sequence from low to high Mg/PO_4 , from low to high pH and from newberyite to K-struvite is also observed during the hydration of MKP cements. The dissolution of KH_2PO_4 in MKP cements occurs very fast, while the reaction of MgO is slower and occurs only partially, such that an hydrating MKP cement has initially a very low Mg/PO_4 , which increases with

time. This slow reaction of MgO leads initially to the formation of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, which react to K-struvite only with time.

- A decrease of the water to solid ratio increases potassium, magnesium and phosphate concentrations, which stabilises K-struvite and destabilises cattite. In MKP cements with much higher nominal Mg/PO₄ ratios, the same trends have been observed. A low water to solid ratio leads to higher potassium, magnesium and phosphate concentrations and promotes the formation of K-struvite.
- An increase in temperature leads to a destabilisation of cattite to MO₄ or bobbierite occurs at slightly above 20°C and to a dehydration of K-struvite to $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ at above 25°C.

The database for (potassium) magnesium phosphate hydrates derived in this paper can reliably calculate the type, composition, amount and volume of hydrates formed as a function of initial composition and temperature. The database, compiled in the Table S.1 (Supplementary Material) and in Table 5, includes carefully selected thermodynamic data based on a critical review of the available literature data supplemented with new experimental data. The magnesium phosphate database is fully compatible with the GEMS version of the PSI/Nagra 12/07 TDB (Thoenen et al., 2014; Thoenen and Kulik, 2003) and Cemdata18 database (Lothenbach et al., 2019) developed for Portland cements and blended cements. This database for magnesium potassium phosphate cements is freely downloadable at <http://www.empa.ch/cemdata> in formats supporting the computer programs GEM-Selektor (Kulik et al., 2013; Wagner et al., 2012).

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