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# Solid-liquid equilibria of Sorel phases and Mg(OH)<sub>2</sub> in the system Na-Mg-Cl-OH-H<sub>2</sub>O. Part I: experimental determination of OH<sup>-</sup> and H<sup>+</sup> equilibrium concentrations and solubility constants at 25°C, 40°C, and 60°C

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Sorel phases are the binder phases of the magnesia building material (Sorel cement/concrete) and of special concern for the construction of long-term stable geotechnical barriers in repositories for radioactive waste in rock salt, as potentially occurring brines are expected to contain MgCl<sub>2</sub>. Sorel phases, in addition to Mg(OH)<sub>2</sub>, are equally important as pH buffers to minimize solubility and potential mobilization of radionuclides in brine systems. In order to obtain a detailed database of the relevant solid-liquid equilibria and the related pH<sub>m</sub> values of the equilibrium solutions, extensive experimental investigations were carried out. Solid phase formation was studied by suspending MgO and Mg(OH)<sub>2</sub> in NaCl saturated MgCl<sub>2</sub>-solutions at 25°C. Mg(OH)<sub>2</sub> and the 3-1-8 Sorel phase were identified as the stable solid phases, while the 5-1-8 Sorel phase is metastable. Equilibration at 40°C did not lead to any solid phase changes. Both OH<sup>-</sup> and H<sup>+</sup> equilibrium concentrations were analyzed as a function of MgCl<sub>2</sub> concentration at 25°C and 40°C. In addition to our already published solid-liquid equilibria for the ternary system Mg-Cl-OH-H<sub>2</sub>O (25°C–120°C), the equilibrium H<sup>+</sup> concentrations (pH<sub>m</sub>) determined at 25°C, 40°C and 60°C are now reported. Analyzing these data together with known ion-interaction Pitzer coefficients, the solubility constants for Mg(OH)<sub>2</sub> and the 3-1-8 phase at these three temperatures, for the metastable 5-1-8 phase at 25°C and for the 2-1-4 phase at 60°C have been consistently calculated.

## KEYWORDS

solubility equilibrium, system Na-Mg-Cl-OH-H<sub>2</sub>O, system Mg-Cl-OH-H<sub>2</sub>O, magnesium oxychloride, Sorel phases, Mg(OH)<sub>2</sub>, solubility constant

## 1 Introduction

Sorel phases are of particular importance for the construction of geotechnical barriers (plugs and sealing systems) in the host rock salt and the establishment of a favorable geochemical environment (i.e., by buffering of  $\text{pH}_m$  and limiting carbonate concentrations) to minimize radionuclide transport processes via potential aqueous solutions.

Sorel phases [named after Stanislas Sorel, who was the first to describe the formation of a hardening material by the reaction of caustic magnesium oxide with magnesium chloride solution (Sorel & Dumas, 1867)] are the binder phases of the magnesia building material (Sorel cement or concrete) with the general composition  $x\text{Mg}(\text{OH})_2 \cdot y\text{MgCl}_2 \cdot z\text{H}_2\text{O}$  ( $x$ - $y$ - $z$  phases). It has been empirically known for more than 100 years that Sorel cement does not corrode in salt (Unknown author, 1902). However, within the safety assessment of a repository, the long-term stability of the geotechnical barrier must be proven. This can be evidenced by analyzing the existing solubility equilibria between Sorel phases and salt solutions of the host rock. Depending on the ratio of  $\text{MgO}$  and the  $\text{MgCl}_2$  solution (and their concentration) in the building material formulation and the developing setting temperature, the 3-1-8, 5-1-8 and/or also 9-1-4 phase may be present when the setting reaction is complete. However, sufficient solubility equilibrium data of Sorel phases in  $\text{NaCl}$ -saturated solutions are not yet available in the literature.

In addition to the binder phase function, both Sorel phases and  $\text{Mg}(\text{OH})_2$  can act as pH buffers of salt solutions (Bodine, 1976) as is realized in the Waste Isolation Pilot Plant (WIPP) in New Mexico with  $\text{MgO}$  as additive of backfill materials (Monastra & Grandstaff, 1999). In case of a brine access a weakly alkaline milieu is generated, providing favorable geochemical conditions for radionuclide retention. Therefore, in addition to the usual data describing solubility equilibria [ $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$  solution concentrations in the presence of  $\text{Mg}(\text{OH})_2$  and Sorel phases], the  $\text{H}^+$  concentrations are of particular interest.

In recent decades, the Sorel phases occurring in the basic ternary system  $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$  - the 3-1-8, 5-1-8, 9-1-4, 2-1-4, 2-1-2, and 3-1-

0 phases - have been extensively characterized (de Wolff & Walter-Lévy, 1949; Bianco, 1951; Walter-Lévy & Bianco, 1951; de Wolff & Walter-Lévy, 1953; de Wolff & Kortlandt, 1954; Cole & Demediuk, 1955; Demediuk et al., 1955; Bianco, 1958; Sugimoto et al., 2007; Dinnebier et al., 2010; Dinnebier et al., 2012; Bette et al., 2015). Solubility data are available in terms of  $\text{OH}^-$  or  $\text{H}^+$  concentrations in  $\text{MgCl}_2$ -containing solutions (ternary system  $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$ ) or in  $\text{NaCl}$ - $\text{MgCl}_2$ -containing mixed solutions (system  $\text{Na}$ - $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$ ). For a conversion between concentration of free  $\text{OH}^-$  and  $\text{H}^+$  the ionic product of water,  $K_w^0$  (Eq. 1), must be known for  $\text{MgCl}_2$  and  $\text{NaCl}$ - $\text{MgCl}_2$  solutions at concentrations of interest.

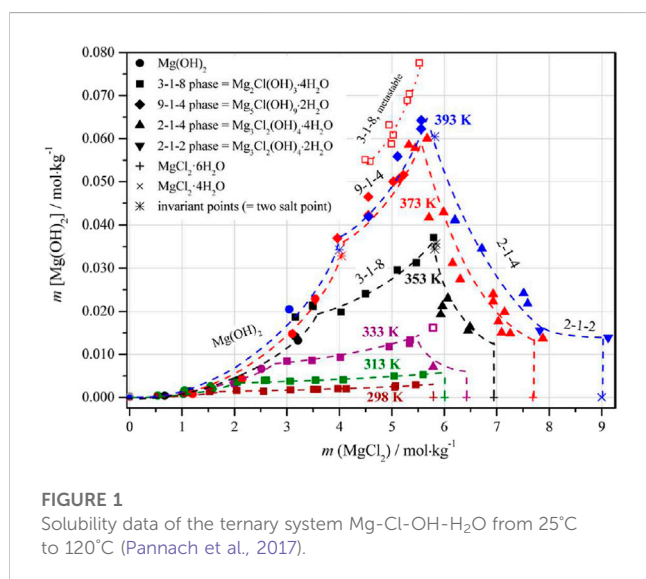
$$K_w^0 = \frac{[H^+] \cdot [OH^-] \cdot \gamma_{\pm}^2}{a_w} = \frac{K_w \cdot \gamma_{\pm}^2}{a_w} \quad (1)$$

In addition to the free  $\text{OH}^-$ , which is related to  $\text{H}^+$  via the  $K_w$ , in basic systems other hydroxide solution species [e.g.,  $\text{MgOH}^+$  (Palmer & Wesolowski, 1997)] exist, which yield together with the free  $\text{OH}^-$  the total  $\text{OH}^-$  concentration.

A comprehensive data set is available for the ternary system  $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$  from 25°C to 120°C by specifying the  $\text{OH}^-$  solution concentrations (Pannach et al., 2017), including the evaluation of earlier data (20°C: D'Ans & Katz, 1941, 25°C; Robinson & Waggaman, 1909, 50°C; Nakayama, 1960, 100°C; Nakayama, 1959, 120°C; Dinnebier et al., 2010). Accordingly, in addition to  $\text{Mg}(\text{OH})_2$ , the four basic magnesium chloride hydrates (Sorel phases) 3-1-8, 9-1-4, 2-1-4, and 2-1-2 occur as thermodynamically stable solid phases depending on temperature and solution concentration (Figure 1). The 3-1-8 phase exists between 25°C and 80°C and was found to be metastable at 100°C. The 9-1-4, 2-1-4, and 2-1-2 phases occur at the higher temperatures or higher  $\text{MgCl}_2$  concentrations. In general, the hydroxide solution concentration in the system increases with temperature. For the 5-1-8 phase, only a temporary occurrence was observed during the solubility studies. It is therefore a metastable phase of the system (Feitknecht, 1926; Feitknecht & Held, 1944; Bianco, 1951; Cole & Demediuk, 1955; Newman, 1955; Bianco, 1958; Pannach et al., 2017).

For the  $\text{NaCl}$ -containing system  $\text{Na}$ - $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$ , a data set exists only for 20°C at not specified  $\text{NaCl}$  solution concentrations (D'Ans et al., 1955). Analogous to the ternary system, the stable solids are  $\text{Mg}(\text{OH})_2$  in solutions with low  $\text{MgCl}_2$  concentrations, and the 3-1-8 phase at higher  $\text{MgCl}_2$  concentrations. The invariant point  $\text{Mg}(\text{OH})_2(\text{s}) + 3-1-8$  phase was given by D'Ans et al., 1955 with 0.555  $\text{MgCl}_2$  molal and 0.53  $\text{Mg}(\text{OH})_2$  mmolal. Metastable data points for  $\text{Mg}(\text{OH})_2$  are also given. A comparison of these 20°C data from D'Ans et al., 1955 with those of the ternary system  $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$  at 25°C from Pannach et al. (2017) in Figure 2 shows that in the presence of  $\text{NaCl}$  the stability range of the 3-1-8 phase extends towards lower  $\text{MgCl}_2$  concentrations.

Molal  $\text{H}^+$  concentrations ( $\text{pH}_m$ ) were determined in the ternary system at 22°C ± 2°C by Altmaier et al. (2003) in the presence of  $\text{Mg}(\text{OH})_2$  and the 3-1-8 phase; in the quaternary system  $\text{Na}$ - $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$  for  $\text{Mg}(\text{OH})_2$  in solutions with very low  $\text{NaCl}$  concentration by Altmaier et al. (2003); Xiong (2008) and in almost  $\text{NaCl}$ -saturated solutions for the 5-1-8 phase (Xiong et al., 2010). Comparison of these data in Figure 3 shows that the  $\text{pH}_m$  in the presence of  $\text{Mg}(\text{OH})_2$  decreases more with increasing  $\text{MgCl}_2$  concentration (from about 10.7 to 8.9) than in the region of the 3-1-8 phase (from about 8.9 to 8.7) as shown in the comprehensive data set for the ternary system  $\text{Mg}$ - $\text{Cl}$ - $\text{OH}$ - $\text{H}_2\text{O}$ . In agreement with the "OH<sup>-</sup> based data set" (Figures 1, 2), the invariant point of  $\text{Mg}(\text{OH})_2$  and the 3-1-8 phase is inferred to exist



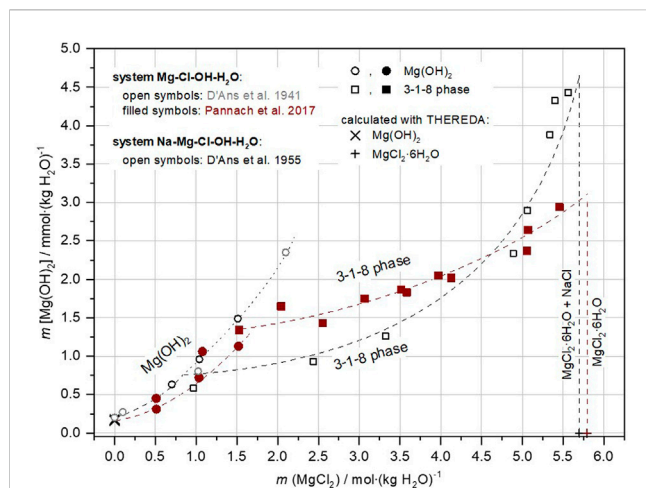


FIGURE 2

Comparison of solubility data in the quaternary system Na-Mg-Cl-OH-H<sub>2</sub>O at 20°C (D'Ans et al., 1955) and the ternary system Mg-Cl-OH-H<sub>2</sub>O at 25°C (Pannach et al., 2017).

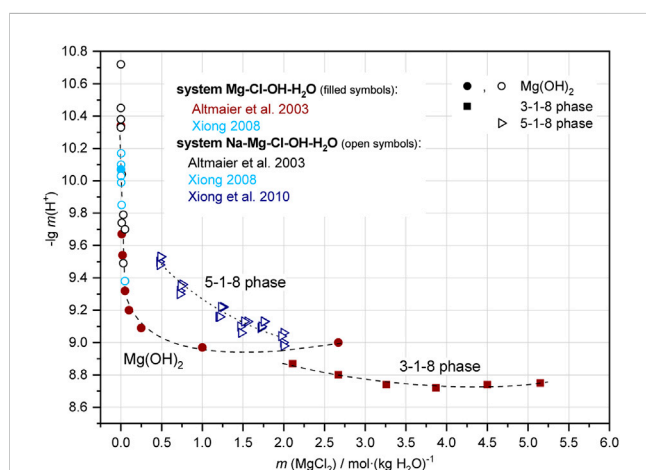


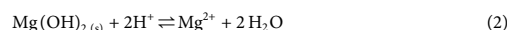
FIGURE 3

Molal H<sup>+</sup> concentrations (as  $-\lg m(\text{H}^+) = \text{pH}_m$ ) of the ternary Mg-Cl-OH-H<sub>2</sub>O and the quaternary Na-Mg-Cl-OH-H<sub>2</sub>O system at 25°C from literature. In the solutions containing very low MgCl<sub>2</sub> of Altmaier et al. (2003), the NaCl concentrations vary from 0.01 to 5.0 molal. In the measurements of Xiong et al., 2010, an approximated saturation concentration of NaCl was adjusted.

between 1.5 and 2.0 MgCl<sub>2</sub> molal in the ternary system. In the presence of NaCl there are no data for > 0.1 MgCl<sub>2</sub> molal for neither Mg(OH)<sub>2</sub> nor the 3-1-8 phase available. The pH<sub>m</sub> values determined by Xiong et al. (2010) in the presence of the 5-1-8 phase in the MgCl<sub>2</sub> concentration range from 0.5 to 2.0 molal in nearly NaCl-saturated solutions roughly compare to the trend of the 3-1-8 phase for the ternary system, but are shifted to a higher basicity.

With the determination of the H<sup>+</sup> molalities, solubility constants were calculated by Altmaier and Xiong using an activity coefficient model for 25 °C corresponding to the reactions (2), (3) and (4) (see also chapter 3.3):

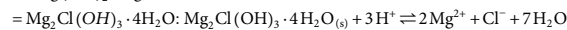
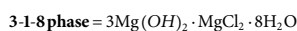
Mg(OH)<sub>2</sub>:



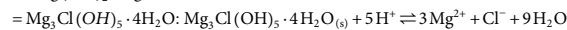
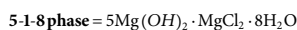
$$\lg K_{S,25^\circ\text{C},\text{Mg}(\text{OH})_2} = 17.16 \pm 0.1 \text{ from Mg-Cl-OH-H}_2\text{O system Altmaier et al. (2003)}$$

$$= 17.01 \pm 0.1 \text{ from Na-Mg-Cl-OH-H}_2\text{O system Altmaier et al. (2003)}$$

$$= 17.05 \pm 0.2 \text{ from Na-Mg-Cl-OH-H}_2\text{O system Xiong (2008)}$$



$$\lg K_{S,25^\circ\text{C},3\text{-1-8}} = 26.15 \pm 0.16 \text{ from Mg-Cl-OH-H}_2\text{O system Altmaier et al. (2003)}$$



$$\lg K_{S,25^\circ\text{C},5\text{-1-8}} = 43.21 \pm 0.33 \text{ from Na-Mg-Cl-OH-H}_2\text{O system Xiong et al. (2010)}$$

The solubility constant determined for Mg(OH)<sub>2</sub> in both the Mg-Cl-OH-H<sub>2</sub>O and Na-Mg-Cl-OH-H<sub>2</sub>O system agree very well within the given error limits.

In this work, the studies on the solubility equilibria of the Sorel phases and Mg(OH)<sub>2</sub> (brucite as mineral) were extended with the determination of the OH<sup>-</sup> and H<sup>+</sup> solution concentrations in the system Na-Mg-Cl-OH-H<sub>2</sub>O (NaCl-saturated) at 25°C and 40°C. In addition to the already known H<sup>+</sup> equilibrium concentrations in the ternary system Mg-Cl-OH-H<sub>2</sub>O at 25°C, measurements at 40°C and 60°C beside 25°C were presented together with the calculation of solubility constants for Mg(OH)<sub>2</sub> and the Sorel phases at 25°C, 40°C, and 60°C.

Part II of the paper present the geochemical model developing on the basis of the experimental data.

## 2 Materials and methods

### 2.1 Starting materials

MgCl<sub>2</sub>·6H<sub>2</sub>O, CAS No. 7791-18-6, (Fluka, purity > 99%, and Merck, ACS reagent, > 99%), Mg(OH)<sub>2</sub>, CAS No. 1309-42-8 (BioUltra, > 99%, from Fluka and M725 from Magnesia, 99%), MgO, CAS No. 1309-48-4 (M2923 from Magnesia, > 97%) and NaCl, CAS No. 7647-14-5 (from Merck, ACS reagent, ≥ 99.0%) were used for the investigations. The phase purity of all substances was checked by X-ray powder diffraction.

The magnesium chloride solutions were prepared by appropriate weighing of deionized water (CO<sub>2</sub>-free by boiling or flowing through with argon for 1 h) and MgCl<sub>2</sub>·6H<sub>2</sub>O. A suspension of NaCl ensured saturation in the respective MgCl<sub>2</sub> solutions.

All solution concentrations are given in molal (molality *m*) with the unit mol·(kg H<sub>2</sub>O)<sup>-1</sup> or mmolal = mmol·(kg H<sub>2</sub>O)<sup>-1</sup>.

### 2.2 Preparation of the solid-liquid mixtures for equilibrations in the quaternary system Na-Mg-Cl-OH-H<sub>2</sub>O (NaCl-saturated) at 25°C and 40°C

For the preparation of the mixtures of solutions with solids in the quaternary system Na-Mg-Cl-OH-H<sub>2</sub>O at 25°C (sample Series 1 of TUBAF, Table 1), 1 g MgO was weighed into 250 mL PP wide-neck bottles with 200 g NaCl-saturated, *n* molal in MgCl<sub>2</sub> each. The suspensions were annealed at 25°C ± 1°C and regularly shaken by hand every 1–3 days over a period of about 1 year.

Another sample series (sample Series 2 of KIT-INE, Table 3) was prepared by weighing 300 mg of Mg(OH)<sub>2</sub> (Fluka, BioUltra) into approximately 200 mL (240–270 g solution) of NaCl-saturated n molal MgCl<sub>2</sub> solutions. The suspensions were stored in sealed vessels at 24°C ± 2°C in a glove box under argon atmosphere and also shaken regularly by hand. Over a period of 6 years, the development of the H<sup>+</sup> solution concentrations were followed with a glass electrode (see chapter 2.4) and finally the solid phase was determined by X-ray.

The solids obtained after 1 year in sample series 1 [these were Mg(OH)<sub>2</sub> and the 3-1-8 phase] were filtered off and re-suspended in new solutions of 200 g NaCl-saturated n molal MgCl<sub>2</sub> solutions (partly in double approach) in 250 mL PP wide-neck bottles and equilibrated at 25°C for 131–144 days (sample Series 3a of TUBAF) and at 40°C for 32–84 days (sample Series 3b of TUBAF), see Table 4. In the case of the 40°C samples, the 2-1-4 Sorel phase (obtained in our previous studies on the ternary system Mg-Cl-OH-H<sub>2</sub>O (Pannach et al., 2017)) was also added. The temperature of the suspensions was controlled at 25°C ± 0.2°C and at 40°C ± 0.2°C in a water bath with continuous stirring using a Teflon magnetic stirrer. Subsequently, the solution and solid phases were separated using a micro glass fibre filter (Munktell, grade MGF = 0.7 μm).

### 2.3 Solid-liquid mixtures in the ternary system Mg-Cl-OH-H<sub>2</sub>O at 25°C, 40°C, and 60°C

In Pannach et al. (2017) we published our results on the determination of solubility equilibria in the ternary system Mg-Cl-OH-H<sub>2</sub>O at 25°C–120°C. In addition to the reported OH<sup>-</sup> solubility concentrations as a function of MgCl<sub>2</sub> concentration, we also finally measured the H<sup>+</sup> concentrations in the equilibrated suspensions at 25, 40°C and 60°C. These results are presented here as sample Series 4 (a-c) of TUBAF. The weights of the initial solution and solid components are given in Table 5 together with the equilibrium data. All suspensions were tempered in sealed 250 mL wide-necked PP bottles in water baths (25°C ± 0.2°C and 40°C ± 0.2°C, thermostat type EB, Julabo Labortechnik GmbH or 60°C ± 0.2°C shaking water bath, company GFL, model 1,083) and shaken regularly by hand (25°C, 40°C) or automatically (60°C). Further experimental details can be found in Pannach et al. (2017).

### 2.4 Analytics

**Solutions:** The Mg<sup>2+</sup> concentration was analyzed by complexometric titration in NH<sub>3</sub>/NH<sub>4</sub>Cl buffered solutions (pH 9–10) with Erio T as indicator and 0.05 M Na-EDTA solution (Biedermann & Schwarzenbach, 1948) (relative analytical error ± 0.3%). The Cl<sup>-</sup> concentration was determined according to the method of Mohr (Schulze & Simon, 2009) in a Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> buffered solution (pH 8–9) with K<sub>2</sub>CrO<sub>4</sub> as indicator and 0.1 M AgNO<sub>3</sub> solution (relative analytical error ± 0.2%). The total OH<sup>-</sup> concentrations were determined volumetrically by acid-base back titration (0.01 M HCl and 0.01 M NaOH solution) with potentiometric endpoint determination and a pH glass electrode (combination electrode, type ROSS, Thermo-

Orion 8103BN, filling solution 3 M KCl). Reported results are the mean of double or triple titrations, where for each the sample solution of 10–20 g was directly weighed (relative analytical error ± 0.3%). The analyzed OH<sup>-</sup> concentrations are given as Mg(OH)<sub>2</sub> concentrations in the following figures and tables. The Na<sup>+</sup> concentration was determined with the flame photometer (type BWB-XP, BWB-XP Technologies) and from sample No. 26 (Table 3, sample series 3) by ion chromatography due to equipment failure of the flame photometer.

The H<sup>+</sup> concentrations were determined potentiometrically according to the method of Altmaier et al. (2003) using glass electrodes calibrated to *m* (H<sup>+</sup>) at 25°C, 40°C and 60°C. At 25°C the potential measurements were carried out with a ROSS type pH glass electrode, Thermo-Orion 8103BN (combination electrode, filling solution 3 M KCl) - same for sample Series 2 (KIT-INE laboratory) and 3a and 4a (TUBAF laboratory). For the measurements at 40°C and 60°C (TUBAF sample Series 3b and 4b, 4c), a combination electrode with a temperature sensor of the type SenTix82 (company WTW, filling solution 3 M KCl solution) was used. Both pH electrodes were calibrated against standard pH buffer solutions (pH = 4–10, Riedel de Haën, Fisher Brand and Merck) at the corresponding temperatures. The pH value is defined in dilute aqueous solutions of ionic strength *I* < 0.1 molal by the activity of the H<sup>+</sup> concentration. Measurements in aqueous solutions of higher ionic strength give to an operative pH value (pH<sub>exp</sub>), from which the H<sup>+</sup> solution concentration is calculated using an empirical correction factor *A<sub>m</sub>* (Altmaier et al., 2003):

$$-\lg m(\text{H}^+) = \text{pH}_m = \text{pH}_{\text{exp}} + A_m \quad (5)$$

The correction factor *A<sub>m</sub>* depends on the solution composition, absolute concentration and temperature. This empirical relationship between *A* and a n molal salt solution of *I* > 0.1 molal is described by the following quadratic equations (in molal concentration units *m<sub>i</sub>*):

$$A_i = B_0 + B_1 \cdot \sum_i m_i + B_2 \cdot \left(\sum_i m_i\right)^2$$

Na-Mg-Cl-OH-H<sub>2</sub>O system:

25°C (for sample Series 2 and 3a with NaCl and MgCl<sub>2</sub> calibration solutions):

$$A_{\text{NaCl/MgCl}_2} = A_{\text{NaCl}} + A_{\text{MgCl}_2} \quad (6)$$

$$\text{with } A_{\text{NaCl}} = -0.0988 + 0.1715 \cdot m_{\text{NaCl}} + 0.0013 \cdot (m_{\text{NaCl}})^2$$

$$A_{\text{MgCl}_2} = -0.0887 + 0.2275 \cdot m_{\text{MgCl}_2} + 0.0043 \cdot (m_{\text{MgCl}_2})^2$$

40°C (for sample Series 3b with NaCl/MgCl<sub>2</sub> mixing solutions):

$$A_{\text{NaCl/MgCl}_2} = 0.04853 + 0.13377 \cdot m_{\text{NaCl/MgCl}_2} + 0.00188 \cdot (m_{\text{NaCl/MgCl}_2})^2 \quad (7)$$

Mg-Cl-OH-H<sub>2</sub>O system (for sample Series 4):

25°C (for Series 4a):

$$A_{\text{MgCl}_2} = -0.0887 + 0.2275 \cdot m_{\text{MgCl}_2} + 0.0043 \cdot (m_{\text{MgCl}_2})^2 \quad (8)$$

40°C (for Series 4b):

$$A_{\text{MgCl}_2} = -0.0968 + 0.4474 \cdot m_{\text{MgCl}_2} + 0.0141 \cdot (m_{\text{MgCl}_2})^2 \quad (9)$$

60°C (for Series 4c):

$$A_{\text{MgCl}_2} = -0.1926 + 0.4025 \cdot m_{\text{MgCl}_2} + 0.0126 \cdot (m_{\text{MgCl}_2})^2 \quad (10)$$

Using the correction factor  $A_m$  and the measured  $\text{pH}_{\text{exp}}$  values, the molal  $\text{H}^+$  concentrations of the solutions were determined with an accuracy of  $\pm 0.05$  pH units.

**Solids:** The solid phases (after filtration from the solution washed with cold ( $T < 5^\circ\text{C}$ ) deionized water and subsequently with cold ( $T < 5^\circ\text{C}$ ) ethanol to remove adhering wash water; finally dried at room temperature in an exsiccator) were identified by X-ray powder diffraction (Bruker D8 Discover with linear detector Vantec-1 at TUBAF or Bruker AXS D8 Advance at KIT-INE; each with Cu-K $\alpha$  radiation). The samples were prepared as flat plates after grinding.

SEM images (exemplarily from the appropriately washed solids) were taken by TUBAF on gold-coated samples using a TESCAN Vega 5130 SB scanning electron microscope with a cathode voltage of 20 kV.

## 3 Results and discussions

### 3.1 Solid phase development in the quaternary system Na-Mg-Cl-OH-H<sub>2</sub>O at 25°C

The development of the solid phase composition in the system Na-Mg-Cl-OH-H<sub>2</sub>O was followed at 25°C in NaCl saturated  $n$  molal  $\text{MgCl}_2$  solutions by suspending caustic MgO (sample Series 1 of TUBAF) as well as  $\text{Mg}(\text{OH})_2$  (sample Series 2 of KIT-INE) with  $\leq 1$  g solid in 200 g solution.

MgO suspension in dilute  $\text{MgCl}_2$  solutions (0.2 molal) resulted in the formation of  $\text{Mg}(\text{OH})_2(\text{s})$  beside the present NaCl.  $\text{Mg}(\text{OH})_2(\text{s})$  was also formed in 0.5  $m_{\text{MgCl}_2}$  solution. Finally, after 349 days, a mixture of  $\text{Mg}(\text{OH})_2(\text{s})$  and 3-1-8 phase was detected. The  $\text{MgCl}_2$  concentration was slightly increased to 0.56 molal (Table 1). In a 1.0  $m_{\text{MgCl}_2}$  solution,  $\text{Mg}(\text{OH})_2(\text{s})$  was also identified within the first weeks and transformed into the 3-1-8 phase over months (see powder diffractograms taken within 1 year

in Figure 4A). The SEM image (Figure 4C) shows the typical long needles of the 3-1-8 phase, between which particles of  $\text{Mg}(\text{OH})_2(\text{s})$  are still visible in the “212-day sample” (Figure 4B).

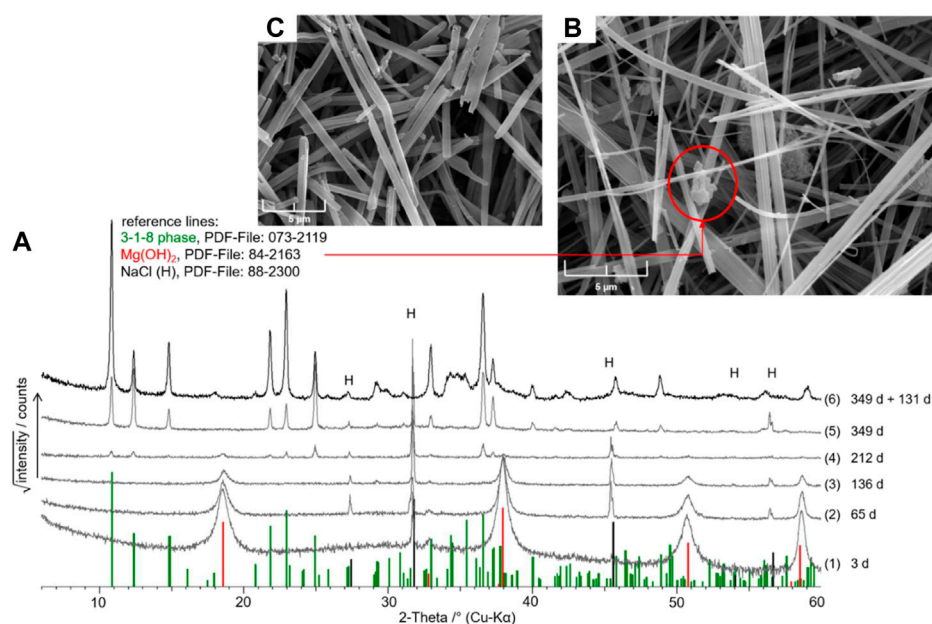
In 2 or 3  $m_{\text{MgCl}_2}$  solutions, the formation of the 5-1-8 phase in addition to  $\text{Mg}(\text{OH})_2$  and/or the 3-1-8 phase was observed within the first few days (Figure 5). After a few weeks, only the 3-1-8 phase was present in addition to NaCl(s). In the concentrated  $\text{MgCl}_2$  solutions (4 and 5.5  $m_{\text{MgCl}_2}$ , NaCl-saturated), the 3-1-8 phase could be identified as a solid phase after 3 days already. This time-dependent change of the solid phase composition in the differently concentrated  $\text{MgCl}_2$  solutions (NaCl-saturated) at  $25^\circ\text{C} \pm 1^\circ\text{C}$  is schematically summarized in Figure 6. All values of the initial solid-solution samples as well as the analyzed solution are given in Table 1.

In the case of the  $\text{Mg}(\text{OH})_2(\text{s})$  suspension (sample Series 2), the development of the  $\text{pH}_m$  was monitored over an even longer period of 2,394 days (6.5 years) (Figure 7). At the beginning of the measurements, three samples (the 0.5, 2.0 and 4.0  $m_{\text{MgCl}_2}$  suspensions, all NaCl-saturated) were selected, from which a few milligrams of solid phase were taken after 16 days to determine their composition. At this time, only the 3-1-8 phase was identified in the 4.0  $m_{\text{MgCl}_2}$  solution, whereas a mixture of  $\text{Mg}(\text{OH})_2(\text{s})$  and 3-1-8 phase was found in the 2.0  $m_{\text{MgCl}_2}$  solution. In this solution, the  $\text{Mg}(\text{OH})_2(\text{s})$  continued to transform into the 3-1-8 phase with time, as shown in the final diffractograms recorded after 2,394 days (6.5 years) in Figure 8. Only in the 0.5  $m_{\text{MgCl}_2}$  solution  $\text{Mg}(\text{OH})_2$  could be detected as the remaining solid.

The measured  $\text{pH}_m$  show values (of the otherwise weakly acidic NaCl- $\text{MgCl}_2$  solutions) that are buffered in the weakly basic range within the first 400 days. After a maximum value is reached, a decrease to a constant value is observed, indicating that the equilibrium state has been established. The difference between the intermediate maximum value and the equilibrium value was up to 0.2  $\text{pH}_m$  units in the solutions with lower  $\text{MgCl}_2$  concentrations, in the more concentrated  $\text{MgCl}_2$  solutions (3, 4  $m_{\text{MgCl}_2}$ ) it was significantly smaller. Within the analytical error of  $\pm 0.05$   $\text{pH}_m$  units, it can be assumed that equilibrium was reached in all suspensions after approximately 500 days. In general,

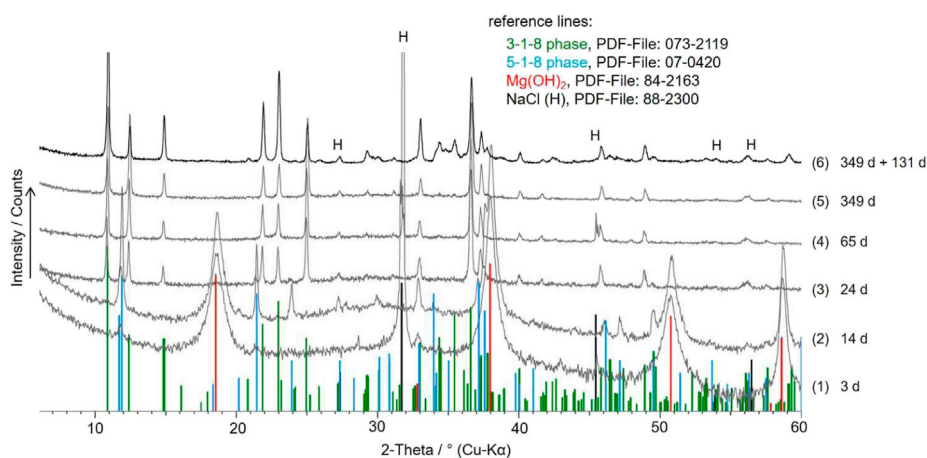
TABLE 1 Set of samples used in Series 1. Sample compositions and analytical results after 349 days of equilibration at 25°C.

No.	initial solid—liquid system				solid—liquid system			
	solid phases		MgCl <sub>2</sub> solution		MgCl <sub>2</sub>	NaCl	Mg(OH) <sub>2</sub>	solid + NaCl <sub>(s)</sub>
	MgO	NaCl	[g]	[molal]				
	[g]		[g]	[molal]	[molal]	[mmolal]		
1	1.0007	70.73	199.99	0.2	0.20	5.57	0.34	Mg(OH) <sub>2</sub>
2	1.0004	60.60	200.00	0.5	0.56	4.86	0.78	Mg(OH) <sub>2</sub> + 3-1-8
3	1.0013	47.17	200.00	1.0	1.00	4.19	1.71	3-1-8
4	1.0026	29.57	200.01	2.0	1.97	2.35	2.22	3-1-8
5	1.0006	15.51	200.01	3.0	3.01	0.98	2.88	3-1-8
6	1.0005	8.55	200.01	4.0	3.94	0.29	3.21	3-1-8
7	1.0051	4.05	199.99	5.5	5.51	0.04	3.89	3-1-8



**FIGURE 4**

(A) X-ray powder diffractograms of the solids obtained after different times of MgO suspension in NaCl-saturated  $1.0 m_{\text{MgCl}_2}$  solution (diff. No. 1–5); diff. No. 6: solid after re-suspension of the “349-day solid” (diff. No. 5) in new NaCl-saturated  $1.0 m_{\text{MgCl}_2}$  solution and further 131 days of suspension (= sample No. 18 of Series 3, Table 4); (B) SEM images of the solid after 212 days (diff. No. 4) and (C) after 349 days (diff. No. 5).



**FIGURE 5**

X-ray powder diffractograms of the solids obtained after different times of MgO suspension in NaCl-saturated  $2.0 m_{\text{MgCl}_2}$  solution (diff. No. 1–5); diff. No. 6: solid after re-suspension of the “349-day solid” (diff. No. 5) in new NaCl-saturated  $2.0 m_{\text{MgCl}_2}$  solution and further 131 days of suspension (= sample No. 20 of Series 3, Table 4).

higher  $\text{pH}_m$  values can be observed in solutions of lower  $\text{MgCl}_2$  concentration (Figure 7). All analytical results obtained at the end of the measurements, after 2,394 days, are shown in Table 3 together with the initial data of this sample Series 2.

The results of the sample Series 1 and 2 show unanimously that, starting from MgO or  $\text{Mg}(\text{OH})_2(\text{s})$  in  $\text{MgCl}_2$  solutions of medium concentration ( $0.5 < m_{\text{MgCl}_2} < 4$ ), the approach to equilibrium needs longer periods of time (months—about 1 year), but is relatively quickly (hours - days) in  $4 m_{\text{MgCl}_2}$ , where the equilibrium phase is 3-1-8 phase. Up to  $0.5 m_{\text{MgCl}_2}$ ,  $\text{Mg}(\text{OH})_2(\text{s})$  is identified as the stable

solid phase. In the case of sample Series 1, the intermediate occurrence of the 5-1-8 phase was also observed.

### 3.2 Solid-liquid equilibria

#### 3.2.1 Na-Mg-Cl-OH- $\text{H}_2\text{O}$ system: $\text{OH}^-$ and $\text{H}^+$ equilibrium concentrations at $25^\circ\text{C}$ and $40^\circ\text{C}$

The stable solids,  $\text{Mg}(\text{OH})_2(\text{s})$  and 3-1-8 phase, as well as their mixture (all being obtained from sample Series 1, where respective

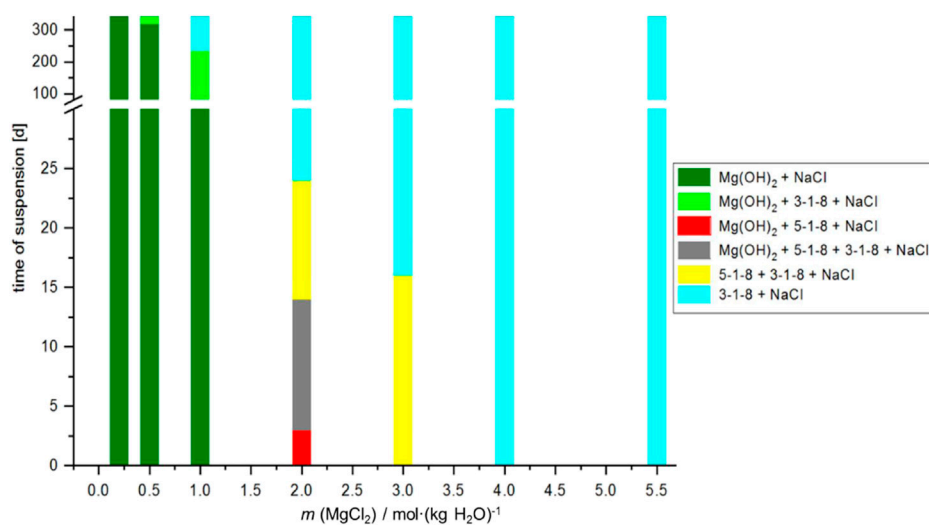


FIGURE 6

Time-dependent solid phase formation at 25°C starting from MgO suspension in the NaCl-saturated MgCl<sub>2</sub> solutions (sample Series 1, Table 1). The solution concentrations subsequently analyzed are shown in Figure 9 (blue symbols).

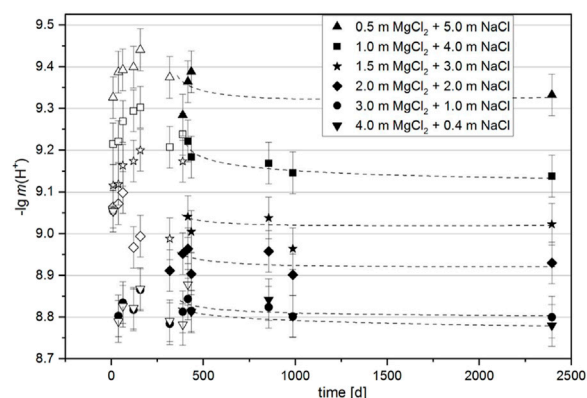


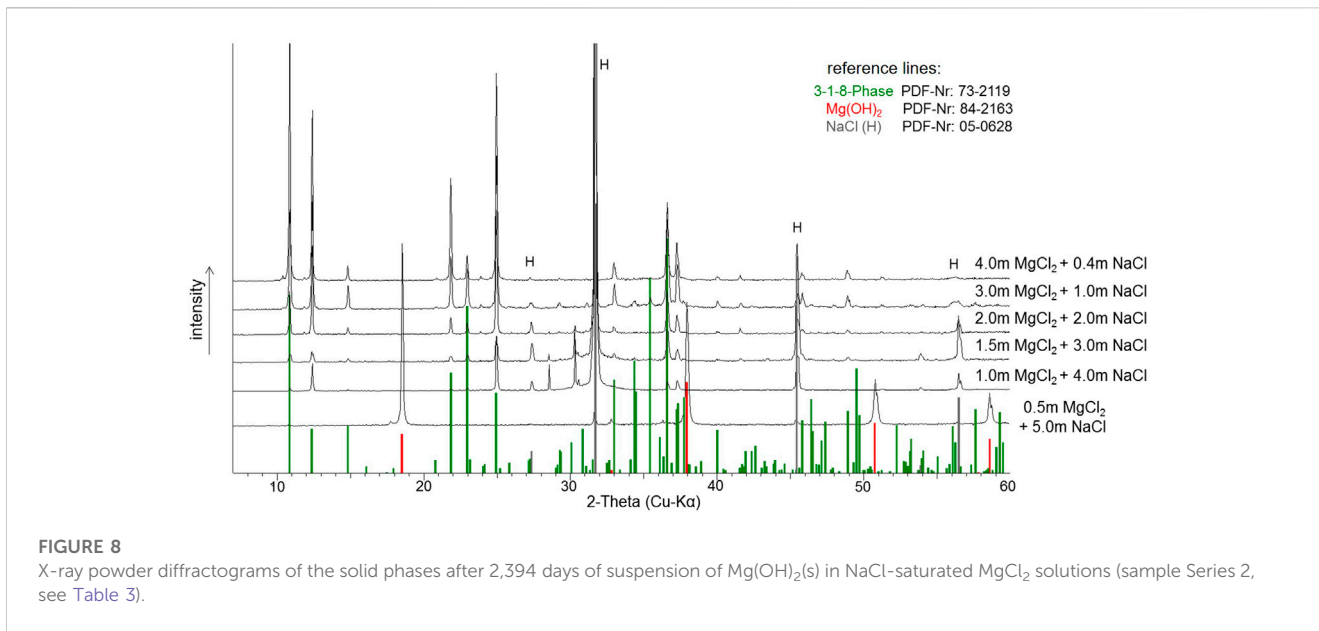
FIGURE 7

Time-dependent development of  $\text{pH}_m$  in samples with initial  $\text{Mg}(\text{OH})_2(\text{s})$  suspended in NaCl-saturated  $\text{MgCl}_2$  solutions (sample Series 2). Filled symbols indicate measured values with deviations from each other smaller than the analytical error of  $\text{pH}_m = \pm 0.05$  (the beginning of gradually stabilizing values).

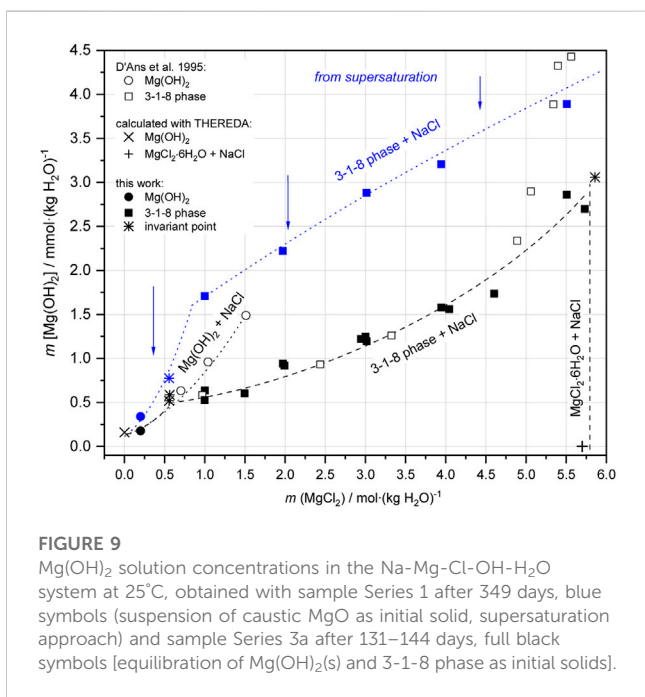
solids were filtered off), were again suspended as a new sample Series 3a in corresponding NaCl-MgCl<sub>2</sub> solutions at 25°C and analyzed after 131–140 days. No further changes in the composition of the solid phases were observed. The analyzed OH<sup>-</sup> solution concentrations (for Series 1 in Table 1 and Series 3 in Table 4) are shown in Figure 9 as a function of MgCl<sub>2</sub> concentration. The comparison in Figure 9 shows that the OH<sup>-</sup> solution concentrations of sample Series 1 are significantly higher than those of sample Series 3, despite their long-term suspension of almost 1 year (349 days). We have already observed such a behavior (remaining in the OH<sup>-</sup> supersaturated region) in our investigations on the solid-solution equilibria in the ternary system Mg-Cl-OH-H<sub>2</sub>O at 25°C (not at higher temperatures), using caustic MgO as the initial phase

(Pannach et al., 2017). The causes seem to be structural defects (stacking faults in the H<sub>2</sub>O-Mg-OH polyhedral layer sequences) and amorphous fractions, especially of the 3-1-8 phase, which arise during its formation from highly OH<sup>-</sup> supersaturated solutions. These stacking fault (domains) cause a higher inner energy of the 3-1-8 lattice and are the reason for the slightly higher solubility. On contact or suspension in appropriate OH<sup>-</sup> free solution, they dissolve with recrystallisation (defect-free) until equilibrium is reached at low OH<sup>-</sup> solution concentrations according to sample Series 3. Still further, i.e., multiple recrystallisation tests did not lead to any further lowering of the OH<sup>-</sup> solution concentration. Therefore, in the following, only the OH<sup>-</sup> concentrations determined by means of sample Series 3 will be considered as equilibrium concentrations. They agree well with those of D'Ans et al., 1955 at unknown NaCl concentration (open black squares in Figure 9 (cf; Figure 2) up to  $\leq 5 m_{\text{MgCl}_2}$ . A clear deviation to higher values can be seen in 5.0–5.5  $m_{\text{MgCl}_2}$  solution, suggesting still supersaturated states. The reported invariant point between  $\text{Mg}(\text{OH})_2(\text{s})$  and 3-1-8 phase at a MgCl<sub>2</sub> concentration of 0.555 molal and 0.53 Mg(OH)<sub>2</sub> mmolal agrees very well with our values of 0.56 MgCl<sub>2</sub> molal and  $0.55 \pm 0.03$  Mg(OH)<sub>2</sub> mmolal. Furthermore, D'Ans et al., 1955 still give metastable data points for Mg(OH)<sub>2</sub>(s) at higher MgCl<sub>2</sub> concentrations (open circles in Figure 9).

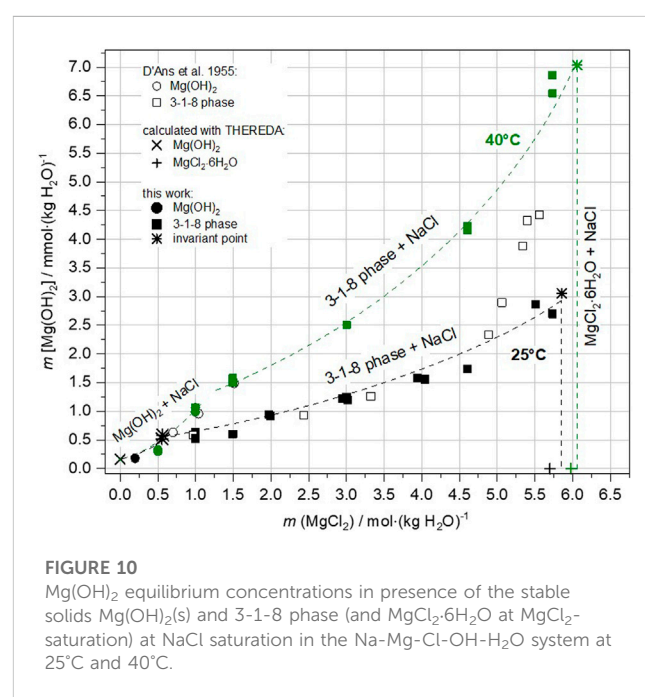
In addition to the samples equilibrated at 25°C, Mg(OH)<sub>2</sub>(s) and the 3-1-8 phase as well as the 2-1-4 phase were also suspended at 40°C in corresponding NaCl-saturated MgCl<sub>2</sub> solutions for 32–84 days (sample Series 3b). Again, only Mg(OH)<sub>2</sub>(s) and the 3-1-8 phase remained as the stable solids at this temperature, the 2-1-4 phase converted either into Mg(OH)<sub>2</sub>(s) or the 3-1-8 phase as shown in Table 4. Compared to the 25°C data, higher OH<sup>-</sup> concentrations are analyzed at 40°C with a consistent trend towards increasing OH<sup>-</sup> concentrations with increasing  $m_{\text{MgCl}_2}$ . The highest values are reached at MgCl<sub>2</sub> saturation. At 40°C its value is twice the one at 25°C. The invariant point between Mg(OH)<sub>2</sub>(s) and 3-1-8 phase



**FIGURE 8**  
X-ray powder diffractograms of the solid phases after 2,394 days of suspension of Mg(OH)<sub>2</sub>(s) in NaCl-saturated MgCl<sub>2</sub> solutions (sample Series 2, see Table 3).



**FIGURE 9**  
Mg(OH)<sub>2</sub> solution concentrations in the Na-Mg-Cl-OH-H<sub>2</sub>O system at 25°C, obtained with sample Series 1 after 349 days, blue symbols (suspension of caustic MgO as initial solid, supersaturation approach) and sample Series 3a after 131–144 days, full black symbols [equilibration of Mg(OH)<sub>2</sub>(s) and 3-1-8 phase as initial solids].



**FIGURE 10**  
Mg(OH)<sub>2</sub> equilibrium concentrations in presence of the stable solids Mg(OH)<sub>2</sub>(s) and 3-1-8 phase (and MgCl<sub>2</sub>·6H<sub>2</sub>O at MgCl<sub>2</sub>-saturation) at NaCl saturation in the Na-Mg-Cl-OH-H<sub>2</sub>O system at 25°C and 40°C.

(+NaCl) has shifted from 0.56  $m_{\text{MgCl}_2}$  at 25°C to about 1.1–1.3  $m_{\text{MgCl}_2}$  at 40°C in the NaCl-saturated solutions (Figure 10). The corresponding OH<sup>-</sup> concentration has approximately tripled from about 0.0005 m Mg(OH)<sub>2</sub> to 0.0013–0.0015 m.

The pH<sub>m</sub> analyzed in sample Series 2 at 25°C and sample Series 3a and 3b at 25°C and 40°C respectively (Tables 3, 4) are presented in Figure 11. The 25°C values of Series 2 form a common isotherm with those determined for Series 3a. Obviously, equilibrium with respect to H<sup>+</sup> solution concentrations had been reached with both sample series in the different laboratories. As no OH<sup>-</sup> concentrations were analyzed for sample Series 2 (KIT-INE), it is not possible to say whether equilibrium has also been reached for the OH<sup>-</sup> solution

concentration in these suspensions over the long monitoring period of 6.5 years in comparison with sample Series 3a.

The pH<sub>m</sub> measured at 25°C are highest (H<sup>+</sup> concentrations lowest) in the solutions with lowest MgCl<sub>2</sub> concentrations in equilibrium with Mg(OH)<sub>2</sub>(s) (pH<sub>m</sub> = 9.57 in 0.2  $m_{\text{MgCl}_2}$  NaCl saturated solution, see all values in Tables 3, 4). In MgCl<sub>2</sub>-free NaCl-saturated solution, pH<sub>m</sub> still increases to 10.72, as shown by the data point from Altmaier et al. (2003) in Figure 11. At the invariant point of Mg(OH)<sub>2</sub>(s) + 3-1-8-phase + NaCl in 0.56  $m_{\text{MgCl}_2}$  solution, the pH<sub>m</sub> was determined to be 9.32. As the MgCl<sub>2</sub> concentration increases, the pH<sub>m</sub> in the presence of 3-1-8 phase + NaCl(s) decreases only gradually over the wide concentration range to pH<sub>m</sub> = 8.7 in 5.5  $m_{\text{MgCl}_2}$  solution. Compared



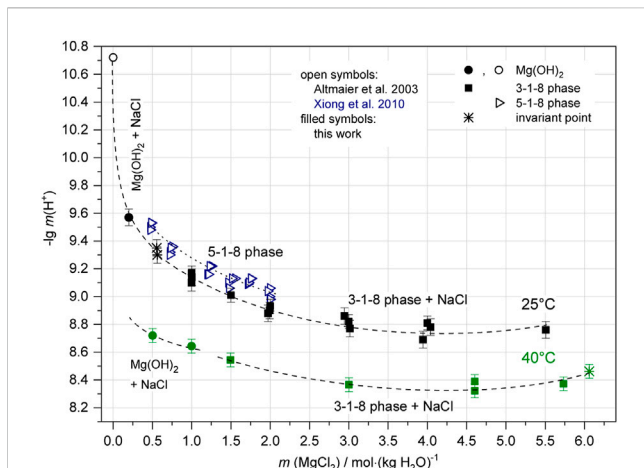


FIGURE 11

$pH_m$  in the system Na-Mg-Cl-OH-H<sub>2</sub>O at NaCl saturation and 25°C (filled black symbols: sample Series 2 and sample Series 3a) in comparison with literature values (open circle: Altmaier et al., 2003, blue; Xiong et al., 2010, cf; Figure 3) and 40°C (green symbols: sample Series 3b).

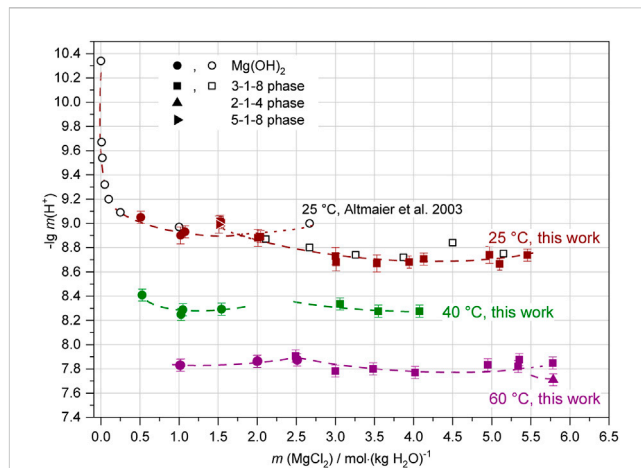


FIGURE 13

$pH_m$  in the Mg-Cl-OH-H<sub>2</sub>O system at 25°C (after 1,172 or 1,417 days of equilibration), 40°C (after 1,885–2,148 days) and 60°C (after 1,081–1,830 days) in comparison with the literature (open black symbols: Altmaier et al., 2003).

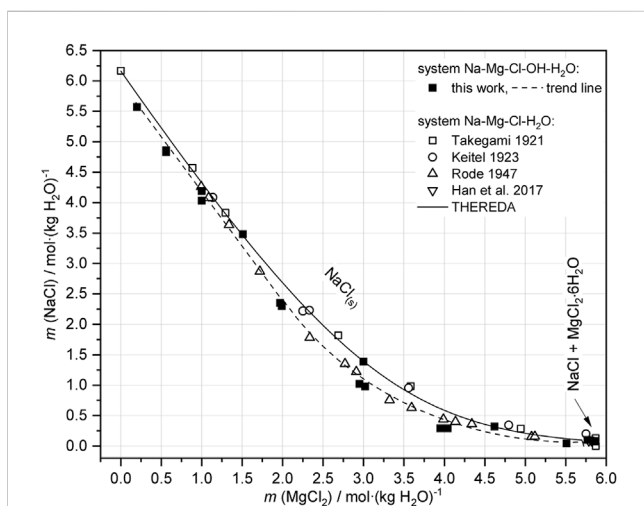


FIGURE 12

Analyzed NaCl saturation concentrations in the system Na-Mg-Cl-OH-H<sub>2</sub>O in presence of Mg(OH)<sub>2</sub>(s) resp. 3-1-8 phase (see Table 4, Series 3a) in compare to the OH<sup>-</sup> free, ternary Na-Mg-Cl-H<sub>2</sub>O system (literature data) at 25°C (Takegami, 1921, Keitel, 1923, Rode, 1947, Han et al., 2017).

to the 25°C data of Xiong et al. (2010) for the 5-1-8 phase in the investigated range of  $0.5 \geq m_{MgCl_2} \geq 2$  (NaCl saturated), the  $pH_m$  are at higher values compared to both Mg(OH)<sub>2</sub>(s) and the 3-1-8 phase. This indicates a metastable occurrence of the 5-1-8 phase, which is consistent with our observations of solid phase formation in the system (see Section 3.1), showing the intermediate occurrence of the 5-1-8 phase.

The data curve shown in Figure 11 for the samples at 40°C runs nearly parallel to the respective curve for 25°C, shifted to lower  $pH_m$  by about 0.6 units in the presence of Mg(OH)<sub>2</sub>(s) and about 0.4 units in the presence of the 3-1-8 phase (see also Table 4). With Mg(OH)<sub>2</sub>(s) as solid phase in 0.5 and 1  $m_{MgCl_2}$  solution, the  $pH_m$  was measured as 8.72 and 8.64 respectively. In the presence of the 3-1-8 phase, the values again

decrease only slightly with increasing  $m_{MgCl_2}$ . Between  $4 < m_{MgCl_2} < 5$  a flat minimum occurs at  $pH_m \sim 8.3$ . At the invariant point of 3-1-8 phase + MgCl<sub>2</sub>·6H<sub>2</sub>O(s) + NaCl(s) the  $pH_m$  is 8.4–8.5.

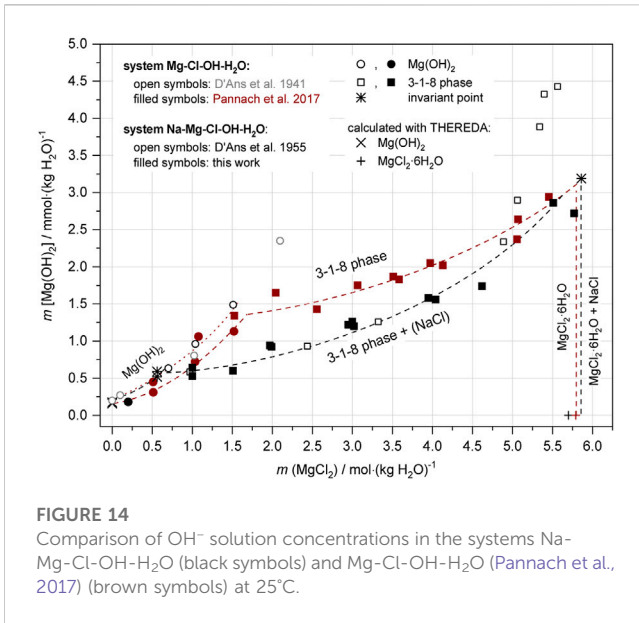
Beside the analyzed OH<sup>-</sup> and H<sup>+</sup> solution concentration, also the NaCl concentrations of saturation determined in sample Series 3a are plotted for 25°C in Figure 12. As the data show, at least approximate NaCl saturation is approached with the initial compositions of sample Series 2 (Table 3) after equilibration in the Na-Mg-Cl-OH-H<sub>2</sub>O system. Compared to the OH<sup>-</sup> free, ternary Na-Mg-Cl-H<sub>2</sub>O system, the adjustment of the very low OH<sup>-</sup> saturation concentration causes within the scatter of the experimental data only a very slight decrease of the NaCl saturation concentration in the Na-Mg-Cl-OH-H<sub>2</sub>O system.

### 3.2.2 Mg-Cl-OH-H<sub>2</sub>O system: H<sup>+</sup> equilibrium concentrations at 25°C, 40°C and 60°C

In the study on the solubility equilibria in the ternary system Mg-Cl-OH-H<sub>2</sub>O from 25°C to 120°C (Pannach et al., 2017), the  $pH_m$  in the samples equilibrated at 25°C, 40°C and 60°C were measured but not yet published. The results are given now in Table 4 (as sample Series 4a, b and c) together with all initial components. Figure 13 shows the  $pH_m$  as a function of MgCl<sub>2</sub> concentration for all three temperatures. The values for 40°C and 60°C are shifted to lower  $pH_m$  by about 0.6–0.4 units. The intersection of the branches for Mg(OH)<sub>2</sub>(s) and 3-1-8 phase data indicate the invariant points, which shift from 1.7–1.8  $m_{MgCl_2}$  at 25°C to about 2 at 40°C and 2.5 at 60°C (as already observed by Pannach et al. (2017) on the basis of the “OH<sup>-</sup> isotherms”). At 60°C a further Sorel phase, the 2-1-4 phase, increases relative to the 3-1-8 phase near the MgCl<sub>2</sub> saturation. Thus, we could measure also a  $pH_m$  value in presence of this phase in 5.8  $m_{MgCl_2}$  solution.

### 3.2.3 Comparison of NaCl-free and NaCl saturated system at 25°C

Comparing the two systems at 25°C shows that the stability field of the 3-1-8 phase in NaCl-saturated solutions expands towards lower MgCl<sub>2</sub> concentrations, as can be seen by the shift of the invariant point with Mg(OH)<sub>2</sub>(s) from  $m_{MgCl_2}$  of 1.7–1.8 in NaCl-free to 0.56 in NaCl-saturated solution (Figures 14, 15).



**FIGURE 14**  
Comparison of OH<sup>-</sup> solution concentrations in the systems Na-Mg-Cl-OH-H<sub>2</sub>O (black symbols) and Mg-Cl-OH-H<sub>2</sub>O (Pannach et al., 2017) (brown symbols) at 25°C.

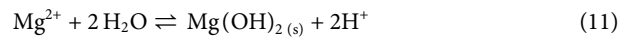
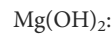
The OH<sup>-</sup> concentrations and thus the solubility of the 3-1-8 phase are lower in NaCl-saturated than in NaCl-free solutions. However, the OH<sup>-</sup> concentrations approach each other when reaching saturation concentration of MgCl<sub>2</sub> (Figure 14).

With the invariant point at 0.56 *m*<sub>MgCl<sub>2</sub></sub>, a MgO-based concrete geotechnical barrier consisting of 3-1-8 binder phase (besides inert aggregates) will be in equilibrium with NaCl-saturated solutions as soon as concentrations of MgCl<sub>2</sub> as low as 0.56 *m*<sub>MgCl<sub>2</sub></sub> are present. For solutions not saturated with NaCl higher concentrations are needed to ensure stability of the binder phase against the solution. In NaCl-free solutions a minimum of 1.7–1.8 *m*<sub>MgCl<sub>2</sub></sub> is required.

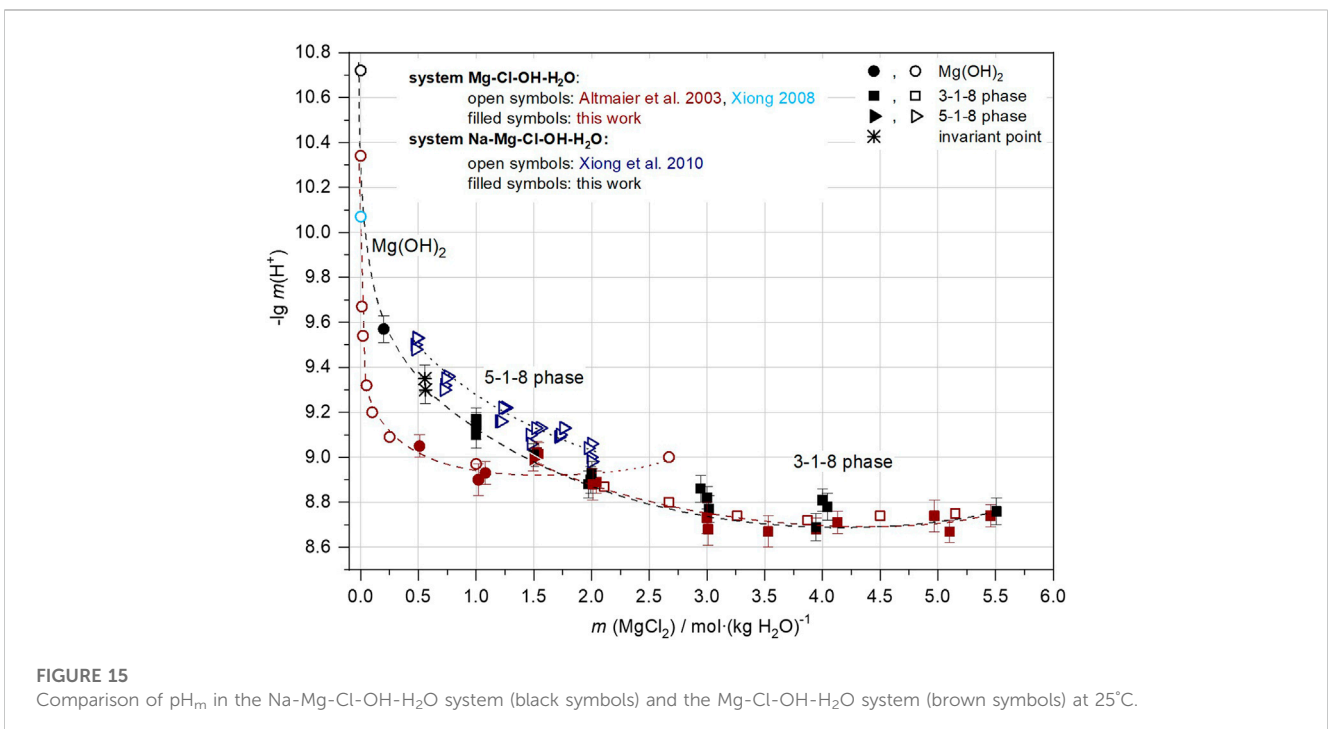
As can be seen in Figure 15, Mg(OH)<sub>2</sub>(s) buffers a pH<sub>m</sub> range from 9.3 to 9.6 in NaCl-saturated solutions, and if they are free of MgCl<sub>2</sub> up to 10.7. From 0.56 *m*<sub>MgCl<sub>2</sub></sub>, a pH<sub>m</sub> of about 9.3 is established by the 3-1-8 phase, decreasing to pH<sub>m</sub> = 8.7 with further increase in MgCl<sub>2</sub> concentration. This pH<sub>m</sub> range also is found in NaCl-free solutions in the presence of the 3-1-8 phase. An analogous situation would be found when comparing the 40°C data of both systems, however, shifted by 0.6–0.4 units to lower pH<sub>m</sub> values.

### 3.3 Solubility constants for Mg(OH)<sub>2</sub>(s) and the Sorel phases 3-1-8, 2-1-4 and 5-1-8 at 25°C, 40°C und 60°C

The solubility constants, lg *K*<sub>S</sub>, for Mg(OH)<sub>2</sub>(s) and the Sorel phases 3-1-8 and 2-1-4 were calculated from the molal equilibrium H<sup>+</sup> concentrations in the NaCl-saturated MgCl<sub>2</sub> solutions at 25°C and 40°C (Tables 3, 4) and in the MgCl<sub>2</sub> solutions free of NaCl at 25°C, 40°C and 60°C (Table 5) according to Eqs 11–18. The calculation of lg *K*<sub>S</sub> was also possible for the metastable 5-1-8 phase by measuring the H<sup>+</sup> concentration during its intermediate appearance in a 25°C suspension (sample No. 46 in Table 5). The activity coefficients γ<sub>1</sub> of Mg<sup>2+</sup>, H<sup>+</sup> und Cl<sup>-</sup> and the water activity *a*<sub>W</sub> were calculated using the Pitzer data set of THEREDA for the hexary system of oceanic salts including acids and bases [THEREDA, Voigt (2020)].



$$\lg K_{S, \text{Mg(OH)}_2}^{\circ} = \lg \left( \frac{m_{\text{H}^+}^2}{m_{\text{Mg}^{2+}}} \cdot \frac{\gamma_{\text{H}^+}}{\gamma_{\text{Mg}^{2+}}} \cdot \frac{1}{a_{\text{W}}^2} \right) \tag{12}$$



**FIGURE 15**  
Comparison of pH<sub>m</sub> in the Na-Mg-Cl-OH-H<sub>2</sub>O system (black symbols) and the Mg-Cl-OH-H<sub>2</sub>O system (brown symbols) at 25°C.

**TABLE 2 Solubility constants (lg  $K_S$ ) for Mg(OH)<sub>2</sub>(s), and the Sorel phases 3-1-8, 5-1-8 und 2-1-4 in compare to available data from literature.**

Solid	T [°C]	System Mg-Cl-OH-H <sub>2</sub> O		System Na-Mg-Cl-OH-H <sub>2</sub> O		Overall mean value, lg $K_S$
		lg $K_S \pm \sigma$	Reference	lg $K_S \pm \sigma$	Reference	
Mg(OH) <sub>2</sub>	25	-17.16 ± 0.10	Altmaier et al. (2003)	-17.05 ± 0.20	Xiong (2008)	-17.1 ± 0.2
		-17.16 ± 0.08	this work	-17.01 ± 0.10	Altmaier et al. (2003)	
	40	-15.86 ± 0.09	this work	-16.00 ± 0.06	this work	-15.9 ± 0.1
	60	-14.92 ± 0.02	this work	-	-	
3-1-8 phase	25	-26.15 ± 0.16	Altmaier et al. (2003)	-26.16 ± 0.13	this work	-26.1 ± 0.2
		-26.10 ± 0.13	this work	-	-	
	40	-24.72 ± 0.04	this work	-24.88 ± 0.16	this work	-24.8 ± 0.2
	60	-23.04 ± 0.11	this work	-	-	
5-1-8 phase	25	-43.39 ± 0.25*	this work	-43.21 ± 0.33	Xiong et al. (2010)	-43.3 ± 0.3
2-1-4 phase	60	-32.95 ± 0.20*	this work	-	-	

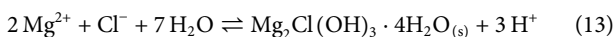
\*as only one sample was available, the deviation was calculated from the H<sup>+</sup> concentration determination uncertainty of ± 0.05 pH units.

**TABLE 3 Initial components and sample composition for sample Series 2 (KIT-INE). Solution composition after equilibration (6.5 years) and calculated solubility constants for the stable solids Mg(OH)<sub>2</sub> and 3-1-8 phase in the Na-Mg-Cl-OH-H<sub>2</sub>O (NaCl-saturated) system at 25°C.**

No.	Initial solid-liquid system				Equilibrated solid-liquid system				
	Solid Mg(OH) <sub>2</sub>	NaCl-saturated MgCl <sub>2</sub> solution			MgCl <sub>2</sub>	NaCl	-lg $m$ (H <sup>+</sup> )	Solid + NaCl <sub>(s)</sub>	-lg $K_S$
		MgCl <sub>2</sub> ·6H <sub>2</sub> O	NaCl	H <sub>2</sub> O					
	[g]				[molal] <sup>a</sup>				
8	0.3	20.330	58.440	189.191	0.50	5.00	9.34	Mg(OH) <sub>2</sub>	17.14
9	0.3	40.660	46.752	178.382	1.00	4.00	9.17	3-1-8	26.19
10	0.3	60.990	35.064	167.573	1.50	3.00	9.01	3-1-8	26.11
11	0.3	81.320	23.376	156.764	2.00	2.00	8.93	3-1-8	26.16
12	0.3	121.980	11.688	135.147	3.00	1.00	8.82	3-1-8	26.18
13	0.3	162.640	4.675	113.529	4.00	0.40	8.81	3-1-8	26.40

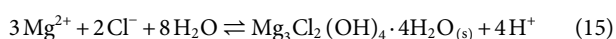
<sup>a</sup>Calculated from initial solution compounds (not analyzed).

3-1-8 phase:



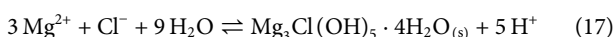
$$\lg K_{S,3-1-8}^\circ = \lg \left( \frac{m_{\text{H}^+}^3}{m_{\text{Mg}^{2+}}^2 \cdot m_{\text{Cl}^-}} \cdot \frac{\gamma_{\text{H}^+}^3}{\gamma_{\text{Mg}^{2+}}^2 \cdot \gamma_{\text{Cl}^-}} \cdot \frac{1}{a_W^7} \right) \quad (14)$$

2-1-4 phase:



$$\lg K_{S,2-1-4}^\circ = \lg \left( \frac{m_{\text{H}^+}^4}{m_{\text{Mg}^{2+}}^3 \cdot m_{\text{Cl}^-}^2} \cdot \frac{\gamma_{\text{H}^+}^4}{\gamma_{\text{Mg}^{2+}}^3 \cdot \gamma_{\text{Cl}^-}^2} \cdot \frac{1}{a_W^8} \right) \quad (16)$$

5-1-8 phase:



$$\lg K_{S,5-1-8}^\circ = \lg \left( \frac{m_{\text{H}^+}^5}{m_{\text{Mg}^{2+}}^3 \cdot m_{\text{Cl}^-}} \cdot \frac{\gamma_{\text{H}^+}^5}{\gamma_{\text{Mg}^{2+}}^3 \cdot \gamma_{\text{Cl}^-}} \cdot \frac{1}{a_W^9} \right) \quad (18)$$

All calculated lg  $K_S$  values are given as mean values in Table 2 for each system and temperature (single values in Tables 3–5) compared with literature data where available. For Mg(OH)<sub>2</sub>(s) a mean value at 25°C of lg  $K_S = -17.17 \pm 0.03$  is obtained for NaCl-saturated solutions (Tables 3, 4) and lg  $K_S = -17.16 \pm 0.08$  for NaCl-free solutions (Table 5). The values are in a very good agreement with those of Altmaier et al. (2003) and Xiong (2008) within the given error range as can be seen in Table 2. There are some more studies on solubility constants for Mg(OH)<sub>2</sub>(s) discussed and evaluated by Altmaier et al. (2003), which agree within an overall mean value of lg  $K_{S,\text{Mg}(\text{OH})_2,25^\circ\text{C}} = -17.1 \pm 0.2$ . For 40°C we determined lg  $K_{S,\text{Mg}(\text{OH})_2,40^\circ\text{C}} = -15.9 \pm 0.2$  from the two mean values, lg  $K_S = -16.00 \pm 0.06$  from NaCl-saturated solutions (Table 4) and lg  $K_S = -15.86 \pm 0.09$  from the NaCl-free solutions (Table 5). At 60°C a value of lg  $K_{S,\text{Mg}(\text{OH})_2,60^\circ\text{C}} = -14.92 \pm 0.02$  was calculated from the NaCl-free MgCl<sub>2</sub> solutions (Table 5).

For the 3-1-8 phase the obtained value of lg  $K_{S,3-1-8,25^\circ\text{C}} = -26.10 \pm 0.13$  agrees very well with Altmaier et al. (2003) (-26.15 ± 0.16) from

**TABLE 4** Initial components and sample composition for sample Series 3 (TUBAF). Analyzed solution composition after equilibration at 25°C (131–144 days), at 40°C (32–84 days) and calculated solubility constants for the stable solids Mg(OH)<sub>2</sub> and 3-1-8 phase in the Na-Mg-Cl-OH-H<sub>2</sub>O (NaCl-saturated) system.

No.	Initial solid-liquid system					Equilibrated solid-liquid system					
	Solids		MgCl <sub>2</sub> solution		MgCl <sub>2</sub>	NaCl	Mg(OH) <sub>2</sub>	-lg <i>m</i> (H <sup>+</sup> )	Solid + NaCl <sub>(s)</sub>	-lg <i>K</i> <sub>S</sub>	
	[g]	NaCl	[g]	[mmolal]	[mmolal]		[mmolal]				
<b>T = 25°C (sample Series 3a)</b>											
14	Mg(OH) <sub>2</sub>	<2	70.07	199.99	0.2	0.20	5.57	0.18	9.57	Mg(OH) <sub>2</sub>	17.20
15	Mg(OH) <sub>2</sub> + 3-1-8	<2	60.20	200.00	0.5	0.56	4.86	0.59	9.30	Mg(OH) <sub>2</sub>	
16	Mg(OH) <sub>2</sub> + 3-1-8	<2	60.21	200.01	0.5	0.56	4.83	0.52	9.35	Mg(OH) <sub>2</sub> + 3-1-8	
17	Mg(OH) <sub>2</sub> + 3-1-8	<2	47.15	201.02	1.0	1.00	4.03	0.53	9.10	3-1-8	25.98
18	3-1-8	<2	47.15	200.01	1.0	1.00	4.19	0.64	9.14	3-1-8	26.08
19	3-1-8	<2	29.59	199.98	2.0	1.97	2.35	0.94	8.88	3-1-8	25.99
20	3-1-8	<2	29.56	200.03	2.0	1.99	2.30	0.92	8.90	3-1-8	26.04
21	3-1-8	<2	15.58	200.01	3.0	2.95	1.02	1.22	8.86	3-1-8	26.33
22	3-1-8	<2	15.56	200.05	3.0	3.02	0.98	1.20	8.77	3-1-8	26.07
23	3-1-8	<2	8.95	200.01	4.0	3.95	0.29	1.58	8.69	3-1-8	26.06
24	3-1-8	<2	8.58	200.99	4.0	4.04	0.29	1.56	8.78	3-1-8	26.32
25	3-1-8	<2	4.05	200.01	5.5	5.51	0.04	2.86	8.76	3-1-8	26.32
26	3-1-8	2.0	0.96	98.67	1.5	1.51	3.48	0.60	n. d.	3-1-8	
27	3-1-8	2.0	0.99	100.04	3.0	3.00	1.39	1.26	n. d.	3-1-8	
28	3-1-8	2.0	1.05	99.95	4.5	4.62	0.32	1.74	n. d.	3-1-8	
29	3-1-8	2.1	0.98	101.77	5.75	5.77	0.10	2.72	n. d.	3-1-8	
30	3-1-8 + MgCl <sub>2</sub> ·6H <sub>2</sub> O	2.0	1.00	95.31	5.9	5.86	0.08	3.19	n. d.	3-1-8 + MgCl <sub>2</sub> ·6H <sub>2</sub> O	
<b>T = 40°C (sample Series 3b)</b>											
31	Mg(OH) <sub>2</sub>	2.0	0.98	100.70	0.5	0.50	4.98	0.29	n. d.	Mg(OH) <sub>2</sub>	
32	2-1-4	3.0	1.00	100.68	0.5	0.50	4.98	0.33	8.72	Mg(OH) <sub>2</sub>	15.93
33	Mg(OH) <sub>2</sub>	2.0	1.00	99.78	1.0	1.0	4.04	0.99	n. d.	Mg(OH) <sub>2</sub>	
34	2-1-4	2.0	1.01	101.17	1.0	1.0	4.04	1.06	8.64	Mg(OH) <sub>2</sub>	16.06
35	3-1-8	2.0	1.02	100.98	1.5	1.49	3.25	1.50	n. d.	3-1-8	
36	2-1-4	3.0	1.00	100.70	1.5	1.49	3.25	1.58	8.54	3-1-8	24.65
37	2-1-4	3.0	1.02	99.81	3.0	3.00	1.22	2.50	8.37	3-1-8	24.75
38	3-1-8	3.0	1.01	100.03	4.5	4.60	0.30	4.23	8.32	3-1-8	24.89
39	2-1-4	3.1	1.01	100.30	4.5	4.60	0.30	4.16	8.39	3-1-8	25.09
40	3-1-8	3.0	1.01	99.45	5.75	5.73	0.03	6.86	n. d.	3-1-8	
41	2-1-4	3.1	0.99	100.16	5.75	5.73	0.03	6.54	8.37	3-1-8	25.02
42	3-1-8 + MgCl <sub>2</sub> ·6H <sub>2</sub> O	2.1	1.01	98.36	6.06	6.01	0.10	7.04	8.46	3-1-8 + MgCl <sub>2</sub> ·6H <sub>2</sub> O	

n. d.: not determined.

**TABLE 5** Initial components and sample composition for sample Series 4 (TUBAF). Analyzed solution composition after equilibration at 25°C (3 years), at 40°C (3 years) and 60°C (205–318 days) in the system Mg-Cl-OH-H<sub>2</sub>O. Calculated solubility constants for the stable solids Mg(OH)<sub>2</sub>, 3-1-8 and 2-1-4 phase and the metastable 5-1-8 phase.

No.	Initial solid-liquid system				Equilibrated solid-liquid system				
	Solid	MgCl <sub>2</sub> solution			MgCl <sub>2</sub>	Mg(OH) <sub>2</sub>	-lg <i>m</i> (H <sup>+</sup> )	Solid	-lg <i>K</i> <sub>s</sub>
	[g]	[g]	[molal]	[molal]	[mmolal]				
<i>T</i> = 25°C (sample Series 4a)									
43	(MgO	1.0013) <sup>a</sup>	199.99	0.5	0.51	0.45	9.05	Mg(OH) <sub>2</sub>	17.27
44	(MgO	1.0019) <sup>a</sup>	200.00	1.0	1.02	n. d.	8.90	Mg(OH) <sub>2</sub>	17.08
45	(MgO	1.0000) <sup>a</sup>	200.00	1.0	1.08	1.06	8.93	Mg(OH) <sub>2</sub>	17.14
46	(MgO	1.0313) <sup>a</sup>	201.42	1.5	1.51	2.84	8.99	5-1-8 <sup>b</sup>	43.39
47	(MgO	1.0015) <sup>a</sup>	200.01	1.5	1.54	2.31	9.01	3-1-8 <sup>b</sup>	26.19
48	(MgO	0.0948) <sup>a</sup>	200.01	2.0	2.01	n. d.	8.88	3-1-8	26.06
49	(MgO	1.0003) <sup>a</sup>	200.00	3.0	3.00	n. d.	8.73	3-1-8	25.99
50	(MgO	0.0949) <sup>a</sup>	200.03	3.0	3.01	n. d.	8.68	3-1-8	25.84
51	(MgO	1.0087) <sup>a</sup>	200.97	3.5	3.53	n. d.	8.67	3-1-8	25.94
52	(MgO	0.9293) <sup>a</sup>	185.81	4.0	3.95	2.74	8.68	3-1-8	26.04
53	(MgO	0.0947) <sup>a</sup>	200.02	5.0	4.97	n. d.	8.74	3-1-8	26.29
54	(MgO	1.0011) <sup>a</sup>	200.00	5.0	5.10	3.41	8.67	3-1-8	26.08
55	3-1-8	0.1018	157.25	1.5	1.53	1.34	9.02	3-1-8	26.21
56	3-1-8	0.1010	150.00	2.0	2.04	1.65	8.89	3-1-8	26.11
57	3-1-8	0.1080	149.99	4.0	4.13	2.02	8.71	3-1-8	26.15
58	3-1-8	0.1104	150.09	5.5	5.46	2.94	8.74	3-1-8	26.27
<i>T</i> = 40°C (sample Series 4b)									
59	(MgO	1.0011) <sup>a</sup>	200.00	0.5	0.53	1.25	8.41	Mg(OH) <sub>2</sub>	15.99
60	(MgO	1.0009) <sup>a</sup>	200.00	1.0	1.05	1.63	8.28	Mg(OH) <sub>2</sub>	15.83
61	(MgO	1.0035) <sup>a</sup>	200.00	1.0	1.03	0.83	8.24	Mg(OH) <sub>2</sub>	15.75
62	(MgO	1.0003) <sup>a</sup>	200.00	1.5	1.55	2.58	8.29	Mg(OH) <sub>2</sub>	15.86
63	3-1-8	0.1514	150.01	3.0	3.06	3.76	8.34	3-1-8	24.74
64	3-1-8	0.1513	150.01	3.5	3.55	3.99	8.28	3-1-8	24.67
65	3-1-8	0.1546	150.00	4.0	4.08	4.10	8.28	3-1-8	24.75
<i>T</i> = 60°C (sample Series 4c)									
66	(MgO	0.9999) <sup>a</sup>	199.99	1.0	1.01	1.26	7.83	Mg(OH) <sub>2</sub>	14.90
67	(MgO	1.0004) <sup>a</sup>	200.37	2.5	2.49	8.57	7.87	3-1-8 <sup>b</sup>	23.00
68	(MgO	1.0006) <sup>a</sup>	200.01	5.5	5.34	12.53	7.82	3-1-8	23.06
69	Mg(OH) <sub>2</sub>	0.1004	199.95	1.0	1.02	0.96	7.83	Mg(OH) <sub>2</sub>	14.90
70	Mg(OH) <sub>2</sub>	0.1110	200.06	2.0	1.99	3.39	7.86	Mg(OH) <sub>2</sub>	14.94
71	3-1-8	0.2307	200.01	2.0	2.00	3.11	7.86	Mg(OH) <sub>2</sub>	14.95
72	3-1-8	0.2551	200.02	2.5	2.51	6.63	7.87	Mg(OH) <sub>2</sub>	14.93
73	3-1-8	0.2679	200.01	3.0	2.99	8.41	7.78	3-1-8	22.86

(Continued on following page)

**TABLE 5 (Continued) Initial components and sample composition for sample Series 4 (TUBAF). Analyzed solution composition after equilibration at 25°C (3 years), at 40°C (3 years) and 60°C (205–318 days) in the system Mg-Cl-OH-H<sub>2</sub>O. Calculated solubility constants for the stable solids Mg(OH)<sub>2</sub>, 3-1-8 and 2-1-4 phase and the metastable 5-1-8 phase.**

No.	Initial solid-liquid system				Equilibrated solid-liquid system				
	Solid	MgCl <sub>2</sub> solution			MgCl <sub>2</sub>	Mg(OH) <sub>2</sub>	-lg <i>m</i> (H <sup>+</sup> )	Solid	-lg <i>K<sub>s</sub></i>
	[g]	[g]	[molal]	[molal]	[mmolal]				
<i>T</i> = 60°C (sample Series 4c)									
74	3-1-8	0.2893	200.00	3.5	3.48	8.59	7.80	3-1-8	22.99
75	3-1-8	0.2730	200.02	4.0	4.02	9.29	7.77	3-1-8	22.95
76	3-1-8	0.3378	200.02	5.0	4.95	11.77	7.83	3-1-8	23.13
77	3-1-8	0.1984	200.00	5.5	5.35	13.36	7.88	3-1-8	23.24
78	3-1-8	0.6237	200.04	6.0	5.78	16.24	7.85	3-1-8 <sup>b</sup>	23.10
79	2-1-4	0.4122	200.07	6.3	5.79	7.13	7.71	2-1-4	32.95

No's in italics: already listed in Pannach et al. (2017). All other No's are additional equilibrated samples.

<sup>a</sup>clear OH<sup>-</sup>-supersaturated MgCl<sub>2</sub>-solution after filtration of the remaining MgO [see exp. part in Pannach et al. (2017)].

<sup>b</sup>metastable.

n. d. not determined.

measurements in MgCl<sub>2</sub> solutions at 25°C. Our measurements in NaCl-saturated MgCl<sub>2</sub> solutions (Tables 3, 4) yield a consistent value of lg *K<sub>s,3-1-8,25°C</sub>* = -26.16 ± 0.13. At 40°C, equally consistent values with lg *K<sub>s,3-1-8,40°C</sub>* = -24.88 ± 0.16 and -24.72 ± 0.04 were calculated from the NaCl-saturated (Table 4) and NaCl-free solutions (Table 5). From the measurements at 60°C in MgCl<sub>2</sub> solutions a lg *K<sub>s,3-1-8,60°C</sub>* = -23.04 ± 0.11 results accordingly. For the 2-1-4 phase occurring at and above 60°C in concentrated MgCl<sub>2</sub> solution, the solubility constant could only be determined from one sample (in 5.79 molal MgCl<sub>2</sub>-solution, Table 5) with lg *K<sub>s,2-1-4,60°C</sub>* = -32.95 ± 0.2.

## 4 Conclusion

Sorel phases are binder phases of the magnesia building material (Sorel cement/concrete) highly suitable for construction of geotechnical barriers in rock salt formations. Compared with classical concrete, materials based on Sorel phases possess the principal property of being stable against saline MgCl<sub>2</sub> containing solutions. This specific feature represents a crucial prerequisite for the construction of geotechnical barriers in repositories for radioactive waste in rock salt, as potentially occurring brines are expected to contain MgCl<sub>2</sub>. In addition, to minimize solubility and possible mobilization of actinides in brines systems, the pH should preferably be buffered in the weakly alkaline range. Detailed understanding of relevant solid-liquid equilibria and related pH<sub>m</sub> data for the equilibrium solutions provide the scientific basis and information in the context of safety analysis.

In this work, the solid-liquid equilibria of the Sorel phases and Mg(OH)<sub>2</sub>(s) in the system Na-Mg-Cl-OH-H<sub>2</sub>O at saturation of NaCl were determined at 25°C and 40°C. Starting from the suspension of MgO (sample Series 1, ss 1) and Mg(OH)<sub>2</sub>(s) (sample Series 2, ss 2), the solid phase formation was followed at

25°C over a period of one (ss 1) and 6 years, respectively, including the determination of H<sup>+</sup> solution concentrations, pH<sub>m</sub>, (ss 2) as a function of MgCl<sub>2</sub> molality.

Mg(OH)<sub>2</sub>(s) and the 3-1-8 phase were identified as the stable solids in the system. Following their further equilibration at 25°C and 40°C (ss 3), the equilibrium OH<sup>-</sup> and H<sup>+</sup> concentrations (pH<sub>m</sub>) were determined. Mg(OH)<sub>2</sub>(s) is the stable phase in the presence of NaCl-saturated solutions with low MgCl<sub>2</sub> content (up to about 0.56 *m*<sub>MgCl<sub>2</sub></sub>) and the 3-1-8 phase in the more concentrated MgCl<sub>2</sub> solutions at 25°C. At 40°C, the invariant point shifts to 1–1.5 *m*<sub>MgCl<sub>2</sub></sub>. The 5-1-8 Sorel phase was found to occur only intermediately during the study period of ss1 and is therefore only a metastable phase in the solid-solution system.

In addition to the already published solid-liquid equilibria for the ternary system Mg-Cl-OH-H<sub>2</sub>O (25°C–120°C) in Pannach et al. (2017), the pH<sub>m</sub> determined at 25°C, 40°C and 60°C are reported here. Using these and with known ion-interaction Pitzer coefficients, the solubility constants for Mg(OH)<sub>2</sub>(s) and the 3-1-8 phase could be calculated for 25°C, 40°C and 60°C. From the measurements in the ternary system it was also possible to calculate the solubility constant for the metastable 5-1-8 phase at 25°C and for the 2-1-4 phase at 60°C, which was found only at higher temperature in the ternary system at high MgCl<sub>2</sub> concentrations.

On the basis of the solid-liquid equilibria determined in this work, it is now possible to predict the long-term stability of magnesia building material in contact with solutions in a saline environment on a significantly improved scientific level and with high robustness. The pH<sub>m</sub> values developing in equilibrium with the respective Sorel phases or Mg(OH)<sub>2</sub>(s) are identified as a function of the solution composition for the system Na-Mg-Cl-OH-H<sub>2</sub>O at NaCl saturation.

The data also allow an extension of the Pitzer dataset in THEREDA to calculate the solubility equilibria of Sorel phases

and  $\text{Mg}(\text{OH})_2(\text{s})$  in complex salt solutions of the hexary system of oceanic salts, which is presented in Part II of this work.

## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

## Author contributions

DF: initiator of the investigation, head of the research area, data evaluation and writer of the paper. MP: experimenter, analysis and data evaluation, preparation of figures and tables. IP: experimenter, analysis. VM: experimenter and data evaluation. MA: experimenter, analysis, data evaluation, and co-writer of the paper. WV: initiator of some measurements, advisor, and co-writer of the paper.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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