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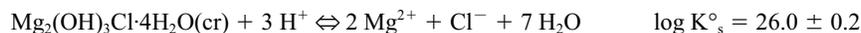
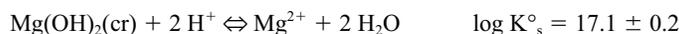
Solid-liquid equilibria of $\text{Mg}(\text{OH})_2(\text{cr})$ and $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ in the system $\text{Mg-Na-H-OH-Cl-H}_2\text{O}$ at 25°C

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Abstract—The solubility of crystalline $\text{Mg}(\text{OH})_2(\text{cr})$ was determined by measuring the equilibrium H^+ concentration in water, 0.01–2.7 m MgCl_2 , 0.1–5.6 m NaCl , and in mixtures of 0.5 and 5.0 m NaCl containing 0.01–0.05 m MgCl_2 . In MgCl_2 solutions above 2 molal, magnesium hydroxide converted into hydrated magnesium oxychloride. The solid-liquid equilibrium of $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ was studied in 2.1–5.2 m MgCl_2 . Using known ion interaction Pitzer coefficients for the system $\text{Mg-Na-H-OH-Cl-H}_2\text{O}$ (25°C), the following equilibrium constants at $I = 0$ are calculated:



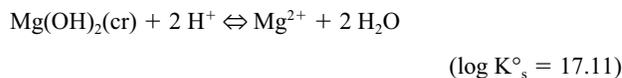
The experimental results are discussed with regard to discrepancies in frequently used databases and computer codes for geochemical modeling, such as EQ3/6, Geochemist's Workbench and CHES. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

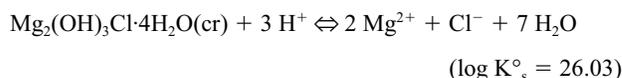
The solubility of brucite $\text{Mg}(\text{OH})_2(\text{cr})$ and magnesium oxychloride $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ is of particular interest with regard to natural aquifer systems containing predominantly magnesium or sodium chloride. In the context of nuclear waste disposal in underground salt mines, MgO has been proposed as additive to backfill materials in the Waste Isolation Pilot Plant (WIPP) in New Mexico (e.g., Monstra and Grandstaff, 1999; Krumhansl et al., 2000). For the Asse salt mine in Germany, the addition of brucite has been proposed recently by Schüssler et al. (2002). The capacity of brucite to buffer pH and to scavenge carbonate (due to the limited solubility of magnesium carbonates) is considered to minimize radionuclide, in particular actinide solubilities which are very sensitive to variation of pH and carbonate concentration. As the geochemical environment of a potential nuclear waste repository is severely affected by the addition of brucite, performance assessment calculations on the long-term safety require reliable and precise thermodynamic data. Geochemical modeling of highly saline systems relies on computer codes like EQ3/6 (Wolery, 1992) or Geochemist's Workbench (GWB) (Bethke, 2000) in combination with thermodynamic databases including standard state equilibrium constants and ion interaction coefficients to calculate the water activity and activity coefficients of aqueous species with the ion interaction model of Pitzer (1991) implied in these codes.

The standard states (index °) adopted for solids and solvent H_2O is one unit activity and that for aqueous species corresponds to unit activity of the species in a hypothetical one molal solution. If not otherwise stated, they refer to $T = 298.15$ K and $p = 1$ bar. A comprehensive data set for the system

$\text{Mg-Na-H-OH-Cl-H}_2\text{O}$ (25°C) was evaluated by Harvie et al., 1984 (Table 1). The standard Gibbs energies proposed in the HMW model and the corresponding solubility constants for the reactions:



and



were adopted in the databases “data0.hmw.V8.R6(1997)” of the EQ3/6 code and “thermo_hmw.dat” (release GWB 3.1.2, 2001) of the GWB code. The frequently used database “data0.pit.V8.R6(1997)” for the EQ3/6 code includes also the HMW set of ion interaction parameters but considerably changed values of $\log K_s^\circ(\text{Mg}(\text{OH})_2(\text{cr})) = 16.30$ and $\log K_s^\circ(\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}) = 25.83$. The latter $\log K_s^\circ$ values are also included in databases for systems of low or moderate salinity (in combination with extended Debye-Hückel formalisms for the calculation of activity coefficients), such as “data0.com.V8.R6” of the EQ3/6 code, “thermo_com.dat” of the GWB code and “chess.tdb” of the CHES code (Van der Lee, 1998).

The difference in the solubility constant of magnesium oxychloride (0.2 log-units) seems to be due to inconsistencies arising from the different $\Delta_f G^\circ$ values for $\text{H}_2\text{O}(\text{l})$, OH^- and particularly Mg^{2+} (cf. Table 1), because the only reference cited in the databases for the EQ3/6 code is that of Harvie et al. (1984). In this context it should be mentioned that (Harvie et al., 1984) pointed out that the experimental data available for $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ are inconsistent. The large discrepancy in the solubility constant of brucite (0.8 log-units) is mainly due

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Table 1. Molar standard Gibbs energies of formation and ion interaction Pitzer coefficients for the system Mg-Na-H-OH-Cl-H₂O at 25°C.

Ion interaction coefficients ^{a)} taken from Harvie et al. (1984)				
i	j	$\beta^{(0)}_{ij}(\text{kg mol}^{-1})$	$\beta^{(i)}_{ij}(\text{kg mol}^{-1})$	$C^{\phi}_{ij}(\text{kg}^2 \text{mol}^{-2})$
Na ⁺	Cl ⁻	0.0765	0.2664	0.00127
Mg ²⁺	Cl ⁻	0.35235	1.6815	0.00519
MgOH ⁺	Cl ⁻	-0.10	1.658	0
H ⁺	Cl ⁻	0.1775	0.2945	0.0008
Na ⁺	OH ⁻	0.0864	0.253	0.0044

i	j	k	$\theta_{ij}(\text{kg mol}^{-1})$	$\psi_{ijk}(\text{kg}^2 \text{mol}^{-2})$
Na ⁺	Mg ²⁺	Cl ⁻	0.07	-0.012
H ⁺	Na ⁺	Cl ⁻	0.036	-0.004
H ⁺	Mg ²⁺	Cl ⁻	0.10	-0.011
MgOH ⁺	Na ⁺	Cl ⁻	0	0
MgOH ⁺	Mg ²⁺	Cl ⁻	0	0.028
OH ⁻	Cl ⁻	Na ⁺	-0.050	-0.006

$\Delta_f G_m^\circ(\text{kJ mol}^{-1})$		
	Harvie et al. (1984) “data0.hmw”	SUPCRT 92 (Johnson et al., 1992) “data0.pit”, “data0.com”, “data0.sup”
H ⁺ (aq)	0	0
OH ⁻ (aq)	-157.25	-157.30
H ₂ O(l)	-237.14	-237.18
Cl ⁻ (aq)	-131.27	-131.29
Mg ²⁺ (aq)	-454.81	-453.98
MgOH ⁺ (aq)	-624.55	-623.90 ^{b)}
Mg(OH) ₂ (cr)	-831.44	-835.32 ^{c)}
Mg ₂ (OH) ₃ Cl·4H ₂ O(cr)	-2552.33	-2552.08

^{a)} As the ion product of water in Mg solutions is not known, the binary parameters for Mg-OH, $\psi_{\text{Mg-OH-Cl}}$ and $\psi_{\text{Mg-Na-OH}}$ cannot be determined. They are set equal to zero.

^{b)} Only included in “data0.sup” (neglected in “data0.pit” and “data0.com”).

^{c)} From Helgeson et al. (1978).

to the different values of $\Delta_f G_m^\circ(\text{Mg(OH)}_2(\text{cr})) = -831.44 \text{ kJ mol}^{-1}$ (Harvie et al., 1984) and $-835.32 \text{ kJ mol}^{-1}$ included in the other databases mentioned above. The latter value comes from the SUPCRT 92 algorithm (Johnson et al., 1992) including data from Helgeson et al. (1978). The discrepant values of $\log K_s^\circ(\text{Mg(OH)}_2(\text{cr}))$ included in databases relying on the HMW model and in other databases lead to significantly different equilibrium pH values in performance assessment calculations for the near field in a nuclear waste repository. Ultimately, this can cause pronounced errors in the predicted actinide solubilities, which considerably depend on pH (cf., Fanghänel and Neck, 2002). For these reasons we have re-investigated the solubility equilibria of brucite and magnesium oxychloride. In addition, the applicability of the HMW set of ion interaction Pitzer coefficients is tested for dilute to concentrated MgCl₂ and NaCl solutions.

2. EXPERIMENTAL

2.1. Chemicals

Crystalline Mg(OH)₂(cr) (purity = 99%) was purchased from Fluka, MgCl₂·6H₂O (p.a.) and NaCl (p.a.) from Merck. The crystallite diameter of the solid Mg(OH)₂(cr) was determined by scanning electron microscopy (SEM) to be in the range of 0.3–1.0 μm. The stoichiometric composition, i.e., the water content of the MgCl₂·6H₂O was confirmed by chloride analysis. The H⁺ and OH⁻ standard solutions used for the calibration of the pH electrodes were prepared with HCl titrisol (Merck) and carbonate-free NaOH solution (Baker). All solutions were

prepared with purified water from a Milli-Q-academic apparatus (Millipore). Before its use, CO₂ was removed by bubbling argon through the Milli-Q water.

2.2. Solubility Experiments

All samples were prepared and stored at $22 \pm 2^\circ\text{C}$ (constant room temperature) in an argon glove box. An amount of 0.3 g Mg(OH)₂(cr) was added to 200 mL solution. The H⁺ concentrations were measured in aliquots taken from the samples as a function of equilibration time ranging from a few days to 14 months. In a first set of experiments performed in Duran glass vials, the dissolution of glass (SiO₂(am) + (4-x) OH⁻ → H_xSiO₄^{(4-x)-} + (2-x) H₂O) caused a significant and continuous decrease in pH and no equilibrium state was reached up to 130 d. Therefore, all further experiments were performed in polyethylene vials. In solutions of low Mg concentrations ($m_{\text{MgCl}_2} = 0-0.05 \text{ mol kg}^{-1}$), the values of m_{Mg} were determined at the end of each experiment. The analytical uncertainty of the ICP-MS analysis (ELAN 6100, Perkin Elmer) is 5–10%. For this purpose aliquots of the samples were measured in duplicate, after ultracentrifugation for 60 min at 90000 rpm (relative centrifugal force $\sim 5 \cdot 10^5 \text{ g}$) and after 30 kD ultrafiltration (MicrosepTM, Filtron), to ensure that the measured Mg concentration does not include contributions from solid particles or colloids. The initial and final solids were investigated by X-ray powder diffraction with a Bruker D8 diffractometer equipped with a Si(Li) solid state detector.

2.3. pH Measurements

Combination pH electrodes (type ROSS, Orion), freshly calibrated against dilute standard pH buffers (pH 1–10, Merck), were used to determine the molal H⁺ concentration m_{H^+} . The pH value measured in

dilute test solutions, for which the individual ionic activity coefficient γ_{H^+} can be calculated with extended Debye-Hückel equations, is related to the H^+ activity a_{H^+} by

$$\text{pH} = -\log a_{\text{H}^+} = -\log m_{\text{H}^+} - \log \gamma_{\text{H}^+} \quad (1)$$

In salt solutions of ionic strength $I > 0.1 \text{ mol kg}^{-1}$, the measured pH value (pH_{exp}) is an operational apparent value (Felmy et al., 1991; Fanghänel et al., 1996), which is related to the molal H^+ concentration by

$$-\log m_{\text{H}^+} = \text{pH}_{\text{exp}} + A \quad (2)$$

with

$$A = \log \gamma_{\text{H}^+} + \Delta E_j (F/RT \ln 10) \quad (3)$$

where F , R , and T are the Faraday constant, gas constant, and temperature (in Kelvin), respectively. The parameter A includes the individual activity coefficient γ_{H^+} and a contribution ΔE_j from the variation of the liquid junction potential E_j when measuring dilute pH buffer solutions for calibration and saline test solutions. For a given pH electrode system, junction electrolyte, and temperature, A depends only on the composition and concentration of the test solution. It was determined as a function of the NaCl and MgCl_2 molality by measuring pH_{exp} in corresponding salt solutions containing known concentrations of 0.001–0.05 m HCl . The experimental values of A in NaCl and MgCl_2 solutions of $I > 0.1 \text{ mol kg}^{-1}$ can be expressed empirically by the following polynoms:

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

$$A_{\text{MgCl}_2} = -0.0887 + 0.4549 m_{\text{MgCl}_2} + 0.0172 (m_{\text{MgCl}_2})^2$$

In addition, $-\log m_{\text{H}^+}$ was determined by an independent second method proposed by Knauss et al. (1990), i.e., by measuring the activity of HCl (a_{HCl}) with a liquid junction free cell consisting of a H^+ sensitive glass electrode and a chloride sensitive electrode:

$$\log a_{\text{HCl}} = 1/2 (\log m_{\text{H}^+} + \log m_{\text{Cl}^-} + \log \gamma_{\text{H}^+} + \log \gamma_{\text{Cl}^-}) \quad (4)$$

This cell was calibrated against 0.001–0.1 m HCl solutions and 0.01 m NaOH solutions in 0.05–5.6 m NaCl . The H^+ molality of a test solution was then derived from measured $\log a_{\text{HCl}}$, given $\log m_{\text{Cl}^-}$ and $\log \gamma_{\text{HCl}} = 1/2 (\log \gamma_{\text{H}^+} + \log \gamma_{\text{Cl}^-})$ calculated with the Pitzer equations and the HMW set of ion interaction coefficients. It should be noted that a_{HCl} measurements in concentrated MgCl_2 solutions exceed the proposed application range of the chloride sensitive electrode (Orion). To avoid potential effects of corrosion, the electrode surface was polished after each measurement to ensure a reproducibility within $\pm 0.02 \log a_{\text{HCl}}$ units.

$\log a_{\text{HCl}}$ was measured at the end of each experiment and at different times in 0.5 and 5.6 m NaCl and in 0.25, 2.67 and 5.15 m MgCl_2 . H^+ concentrations measured by the two methods described above were generally consistent within $\pm 0.04 \log$ -units, with the exception of the values in concentrated MgCl_2 which showed a certain systematic deviation. The average deviation between the $-\log m_{\text{H}^+}$ values determined with ROSS electrodes and those calculated from a_{HCl} measurements was 0.01 ± 0.03 in 0.5 m NaCl , 0.00 ± 0.03 in 5.6 m NaCl , 0.02 ± 0.04 in 0.25 m MgCl_2 , 0.04 ± 0.03 in 2.67 m MgCl_2 , and 0.08 ± 0.04 in 5.15 m MgCl_2 .

3. RESULTS AND DISCUSSION

Figures 1 and 2 show typical results obtained in solubility experiments with $\text{Mg}(\text{OH})_2(\text{cr})$, i.e., the H^+ molality measured as a function of time. After a slight decrease of $-\log m_{\text{H}^+}$ within the first month, the constant values measured after 50 to 350 d indicate that equilibrium was achieved. The pH decrease observed at the higher MgCl_2 molalities of 2.67 and 5.15 mol kg^{-1} (cf. Fig. 3) is caused by the transformation of $\text{Mg}(\text{OH})_2(\text{cr})$ into magnesium oxychloride. The reproducible results obtained in two experiments (shown in Fig. 3) as filled

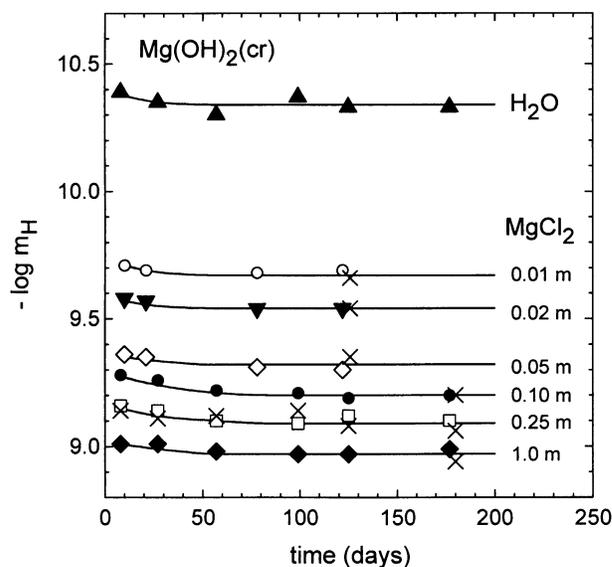


Fig. 1. Molal H^+ concentrations measured as a function of time after adding $\text{Mg}(\text{OH})_2(\text{cr})$ to pure water and 0.01–1.0 m MgCl_2 solutions. The values shown as crosses (\times) were derived from a_{HCl} measurements.

circles and open triangles) clearly indicate that in 2.67 m MgCl_2 solution, the initial magnesium hydroxide remained (meta)stable for some weeks and then slowly converted into oxychloride, whereas in 5.15 m MgCl_2 the solid transformation started from the beginning. The solid conversion was confirmed by X-ray diffraction (cf. Fig. 4). The initial $\text{Mg}(\text{OH})_2(\text{cr})$ used, which remains stable in water and NaCl and dilute MgCl_2

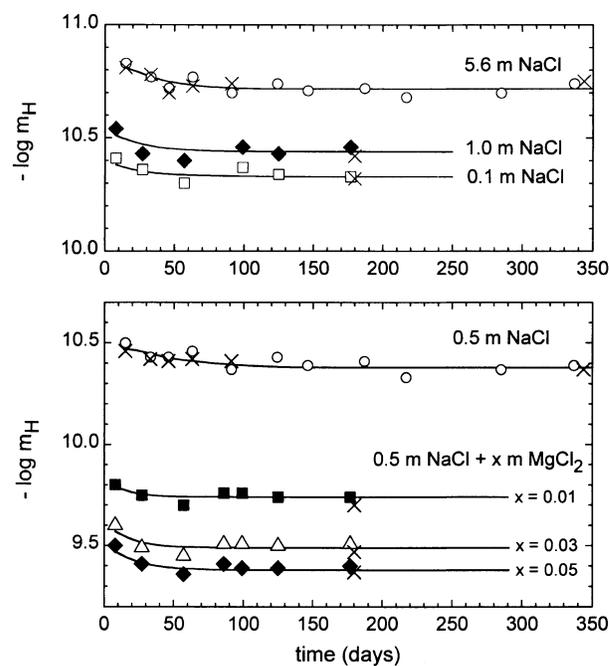


Fig. 2. Molal H^+ concentrations measured as a function of time during the solubility experiments with $\text{Mg}(\text{OH})_2(\text{cr})$ in NaCl solutions (\times from a_{HCl} measurements).

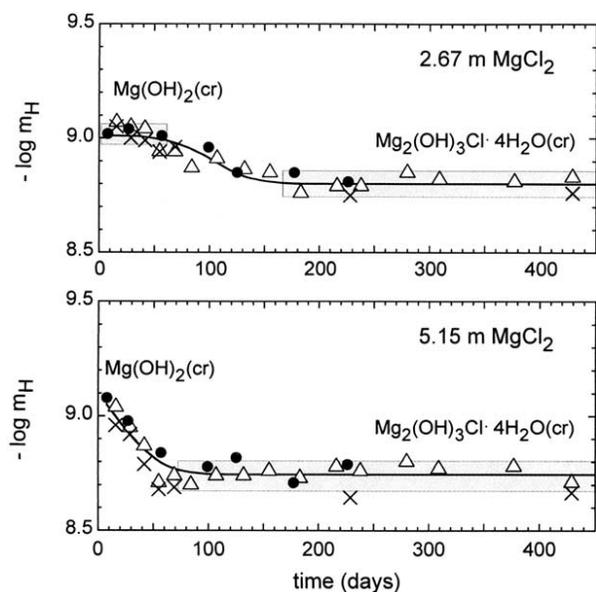


Fig. 3. Molal H^+ concentrations measured as a function of time during the solubility experiments in 2.67 and 5.15 m $MgCl_2$ solution. The filled circles and open triangles show the two runs of experiments (\times from a_{HCl} measurements).

solutions, shows the typical X-ray diffraction pattern of brucite as sharp peaks. These peaks are absent in the XRD patterns recorded from the solids in the final 2.67 and 5.15 m $MgCl_2$ solutions. These solids are identified as triclinic $Mg_2(OH)_3Cl \cdot 4H_2O(cr)$ according to the JCPDS files 36-0388 and 07-0412 (JCPDS, 2001). Moreover there are no indications of the presence of other magnesium oxychloride hydrate phases like $Mg_3(OH)_5Cl \cdot 4H_2O(cr)$. Scanning electron microscopy

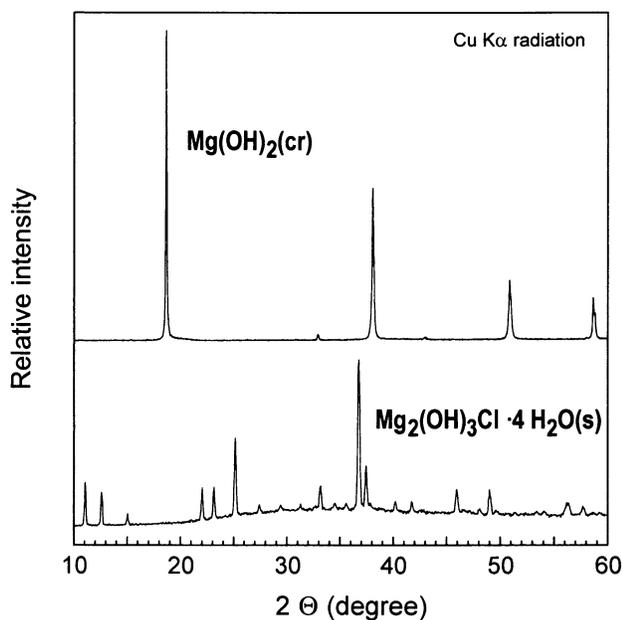


Fig. 4. X-ray diffraction patterns of the $Mg(OH)_2(cr)$ used and the magnesium oxychloride formed in 2.67 m $MgCl_2$.

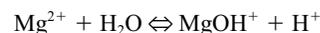
(SEM) coupled with energy-dispersive spectrometry (EDS) showed needle-like crystals with a length of 10–100 μm and confirmed the element ratio of $Mg:Cl:O = 2:1:7$.

3.1. Solubility Constant of $Mg(OH)_2(cr)$

The solubility constant of brucite is calculated from the equilibrium H^+ molalities in the various $MgCl_2$ - $NaCl$ - H_2O solutions (cf. Table 2) according to

$$\log K_s^\circ(Mg(OH)_2(cr)) = \log(m_{Mg^{2+}} \gamma_{Mg^{2+}}) - 2(\log(m_{H^+} \gamma_{H^+}) + 2 \log a_w) \quad (5)$$

The activity coefficients γ_{H^+} and $\gamma_{Mg^{2+}}$ and the water activity a_w are calculated with the Pitzer parameters of the HMW model. The formation of the magnesium hydroxide complex $MgOH^+$



with $\log K_1^\circ = -11.81$ (Harvie et al., 1984) or $\log K_1^\circ = -11.68 \pm 0.05$, as determined more recently by Palmer and Wesolowski (1997) from potentiometric experiments in 0.1–5 m $NaCl$, is calculated to be negligible in all $MgCl_2$ containing solutions ($-\log m_{H^+} \leq 10$). In 0–5.6 m $NaCl$ the complex $MgOH^+$ is also of minor importance. In equilibrium with $Mg(OH)_2(cr)$ it contributes less than 5% to the total Mg concentration. The $\log K_1^\circ$ value of the HMW model (also included in the EQ3/6 databases “data0.hmw” and “data0.sup” but neglected in “data0.pit” and “data0.com”) was taken from the study of McGee and Hostetler (1975). These authors also demonstrated that possible experimental errors would generally lead to an overestimation of $MgOH^+$, e.g., in the studies of Stock and Davies (1948) and Hostetler (1963) from which Baes and Mesmer (1976) selected $\log K_1^\circ = -11.44 \pm 0.1$. However, even this larger hydrolysis constant or the use of the most recent values determined by Palmer and Wesolowski (1997) would have no significant impact on the calculated solubility constants.

The total Mg concentrations determined by ICP-MS at the end of the experiments in water and 0.1–5.6 m $NaCl$ were significantly higher than $m_{OH^-}/2$ as expected from the dissolution reaction. As a large excess of Mg ($m_{Mg} \gg m_{OH^-}/2$) cannot be explained by the hydrolysis species $MgOH^+$, it must be due to trace impurities of soluble Mg salts in the chemicals used, i.e., in $Mg(OH)_2(cr)$ and $NaCl$ p.a. (reported Mg content: $< 0.001\%$). Using the experimentally determined Mg concentrations to calculate $\log K_s^\circ$ from the equilibrium H^+ molalities in these experiments, the solubility constants are reasonably consistent with those derived from the measurements in 0.01–2.67 m $MgCl_2$ and in 0.5 and 5.0 m $NaCl$ containing 0.01–0.05 m $MgCl_2$ (Table 2).

A small but noticeable difference is observed for the mean values ($\pm 2\sigma$, where σ is the standard deviation) from the experiments in 0–2.67 m $MgCl_2$ ($\log K_s^\circ = 17.16 \pm 0.10$) and from those in $NaCl$ -predominant solutions with $m_{Mg^{2+}} \ll m_{Na^+}$ ($\log K_s^\circ = 17.01 \pm 0.10$). In this context it should be noted that the $\log K_s^\circ$ values calculated by applying Eqn. 5 include an experimental uncertainty from the measured concentrations ($\log m_{Mg^{2+}} - 2 \log m_{H^+}$), which is below ± 0.1 , and also an uncertainty from the calculated trace activity coeffi-

Table 2. Solutions in equilibrium with Mg(OH)₂(cr) and evaluation of the solubility constant (all concentrations are in mol/kg H₂O)

input concentrations		measured equilibrium concentrations		
m _{MgCl₂}	m _{NaCl}	−log m _{H⁺}	log m _{Mg}	log K ^o _s ^{a)}
0	0	10.34	−3.55	17.10
0.01	0	9.67	−2.02	17.19
0.02	0	9.54	−1.73	17.17
0.05	0	9.32	−1.30 ^{b)}	17.10
0.10	0	9.20	−1.00 ^{b)}	17.10
0.25	0	9.09	−0.60 ^{b)}	17.17
1.00	0	8.97	0.00 ^{b)}	17.21
2.67	0	9.00	0.43 ^{b)}	17.22
mean value: 17.16 ± 0.10				
0	0.10	10.33	−3.38	17.04
0	0.50	10.38	−3.28	17.07
0	1.00	10.45	−3.30	17.08
0	5.61	10.72	−3.33	16.92
0.01	0.50	9.74	−1.99	17.08
0.03	0.50	9.49	−1.53	17.03
0.05	0.50	9.38	−1.31	17.02
0.01	5.00	10.04	−1.94	17.03
0.03	5.00	9.79	−1.50	16.96
0.05	5.00	9.70	−1.30	16.98
mean value: 17.01 ± 0.10				

^{a)} Calculated with the HMW model (including the complex MgOH⁺) from the equilibrium −log m_{H⁺} values and the total Mg concentration measured by ICP-MS.

^{b)} Not measured, m_{Mg} is taken from the initial solution composition.

cients of Mg²⁺ and H⁺. In particular for traces of Mg²⁺ in concentrated NaCl solutions, the values of $\gamma_{\text{Mg}^{2+}}$ may become somewhat inaccurate, because the ternary interaction parameters $\theta_{\text{Mg-Na}}$ and $\psi_{\text{Mg-Na-Cl}}$ are based on isopiestic data in MgCl₂-NaCl mixtures where Mg²⁺-Mg²⁺ interactions are not negligible (Pitzer, 1991). On the other hand, all experimental results are reasonably well described with the HMW set of ion interaction coefficients and an overall mean value of

$$\log K_s^o(\text{Mg(OH)}_2(\text{cr})) = 17.1 \pm 0.2$$

which agrees with numerous previous studies. The most extensive study of the brucite solubility at 25°C was made by Hostetler (1963). Using somewhat different experimental procedures, three sets of dissolution experiments in dilute solutions led to log K^o_s = 16.95 ± 0.16, 17.26 ± 0.10 and 16.84 ± 0.05 (2σ). The decrease of pH and log K^o_s observed in precipitation experiments was ascribed to the increase in particle size during the aging process. Hostetler (1963) also discussed the literature data at 18–25°C published before his study and the lowest value cited was log K^o_s = 16.70. The solubility constant of log K^o_s = 16.84 proposed by Hostetler (1963) was accepted in the reviews of Baes and Mesmer (1976) and Robie and Hemingway (1995). Harvie et al. (1984) selected log K^o_s = 17.11 from a later study of McGee and Hostetler (1973, 1977) who extended the solubility studies with Mg(OH)₂(cr) to the temperature range of 10–90°C. Liu and Nancollas (1973) determined a very similar value of log K^o_s = 17.14 ± 0.03 by conductometric methods in dissolution-precipitation experiments at 25°C. Brown et al. (1996) determined log K^o_s at 60–200°C from precipitation experiments in 0.1 and 1.0 m NaCl. Combining their data with those of McGee and Hostetler (1977)

they calculated log K^o_s = 17.13 at 25°C. For 22 ± 2°C, the temperature of the present study, the linear regression of Brown et al. (1996) yields a somewhat higher constant of log K^o_s = 17.32 ± 0.13. These experimental solubility constants are further corroborated by a value of log K^o_s(Mg(OH)₂(cr)) = 16.97 derived by Baes and Mesmer (1976) from thermochemical data given by (Pitzer and Brewer 1961). To our knowledge there is no experimental solubility study which would justify the selection of thermodynamic data corresponding to an equilibrium constant close to log K^o_s = 16.30 at 25°C as calculated from Δ_rG^o₂₉₈, Δ_rH^o₂₉₈ and S^o₂₉₈ selected for brucite in the review of Helgeson et al. (1978) and included in many databases. Helgeson et al. (1978) used high pressure/temperature data on the univariant equilibrium between Mg(OH)₂(cr) and MgO(cr) in combination with calorimetric data for MgO(cr) and auxiliary data for the standard molal volume, heat capacity coefficient and entropy for brucite. It will be shown below that the discrepant solubility constant is primarily due to the standard entropy of brucite (S^o₂₉₈ = 63.14 J K^{−1} mol^{−1}) adopted from Robie and Waldbaum (1968).

The standard enthalpy of reaction derived by Brown et al. (1996) from their own solubility data and those of McGee and Hostetler (1977), Δ_rH^o₂₉₈ = −112 kJ mol^{−1}, is in good agreement with Δ_rH^o₂₉₈ = −111.15 kJ mol^{−1} derived by Königsberger et al. (1999) from brucite solubilities in 3.5 and 3.0 m NaClO₄ at 25 and 50°C, respectively. It is also fairly consistent with Δ_rH^o₂₉₈ = −114.0 kJ mol^{−1} calculated from the data selected by Wagman et al. (1982) and Robie and Hemingway (1995). However, Königsberger et al. (1999) rely on an entropy value of S^o₂₉₈(Mg(OH)₂(cr)) = 63.2 J K^{−1} mol^{−1} adopted by Robie and Hemingway (1995) from the tables of Wagman et al. (1982), which finally leads to log K^o_s = 16.3.

None of the reviews cited above discuss this entropy value for brucite and the underlying original data. They all lead back to Robie and Waldbaum (1968) who cite an uncritical collection of entropy data (Kelley and King, 1961) which includes the value of S^o₂₉₈ = 15.09 ± 0.05 cal K^{−1} mol^{−1} calculated by Giauque and Archibald (1937) from experimental heat capacities of Mg(OH)₂ from 20 to 300 K. As calculated by Königsberger et al. (1999), the solubility studies of McGee and Hostetler (1977) and Brown et al. (1996), combined with CODATA values for Mg²⁺(aq) and H₂O(l) (Cox et al., 1989), lead to Δ_rH^o₂₉₈(Mg(OH)₂(cr)) = −926.7 kJ mol^{−1}, Δ_rG^o₂₉₈(Mg(OH)₂(cr)) = −831.9 kJ mol^{−1} and a considerably lower standard entropy of S^o₂₉₈(Mg(OH)₂(cr)) = 50.6 J K^{−1} mol^{−1}. Königsberger et al. (1999) assumed that the solids in the precipitation experiments of Brown et al. (1996) possibly refer to less crystalline small brucite particles with a higher Gibbs energy and solubility. This can be ruled out for the solid used in the present study, which gave a similar solubility constant corresponding to Δ_rG^o₂₉₈(Mg(OH)₂(cr)) = −832.1 kJ mol^{−1}. The crystallite diameter determined by SEM analysis was in the range of 0.3–1.0 μm and for Mg(OH)₂(cr) crystals of this size the Gibbs energy contribution from the surface energy is known to be negligible (Hostetler, 1963).

3.2. Solubility Constant of Mg₂(OH)₃Cl·4H₂O(cr)

Harvie et al. (1984) pointed out that the few and widely scattered experimental data available for Mg₂(OH)₃Cl·4H₂O(cr) do

Table 3. Solutions in equilibrium with $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ and evaluation of the solubility constant (all concentrations in mol/kg H_2O)

m_{MgCl_2}	$-\log m_{\text{H}^+}$	$\log K_s^{\circ \text{a}}$	$\log a_{\text{HCl}}$	$\log K_s^{\circ \text{b}}$
2.11	8.87	26.08 (25.96)	-3.83	25.94
2.67	8.80	26.10 (25.91)	-3.59	25.97
3.26	8.74	26.08 (25.78)	-3.33	25.88
3.87	8.72	26.14 (25.72)	-3.09	25.86
4.50	8.74	26.25 (25.66)	-2.87	25.94
5.15	8.75	26.25 (25.49)	-2.65	26.00
	mean value:	26.15 ± 0.16		25.93 ± 0.11

^a) Calculated from $-\log m_{\text{H}^+}$ measured with ROSS electrodes and activity coefficients based exclusively on the HMW model. The values in brackets are calculated with $\theta_{\text{Mg-H}} = 0.062$ and $\psi_{\text{Mg-H-Cl}} = 0.001$ from Roy et al. (1980).

^b) Calculated from the measured $\log a_{\text{HCl}}$ values.

not yield any definitive information. They selected a solubility constant assuming that the brucite-oxychloride invariant point is below 2 M MgCl_2 since Bodine (1976) observed solid phase conversion slightly above this concentration. In the present study, the solubility constant is determined directly from equilibrium data. The molal H^+ concentrations and HCl activities measured in MgCl_2 solutions equilibrated with $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ are summarized in Table 3. In addition to the measurements shown in Figure 3, the magnesium oxychloride formed in 2.5 M (2.67 m) and 4.5 M (5.15 m) MgCl_2 was used to determine further solubility data in 2.0 M (2.11 m), 3.0 M (3.26 m), 3.5 M (3.86 m), and 4.0 M (4.49 m) MgCl_2 . The solubility constant at $I = 0$ is given by

$$\log K_s^{\circ}(\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})) = 2 \log (m_{\text{Mg}^{2+}} \gamma_{\text{Mg}^{2+}}) + \log (m_{\text{Cl}^-} \gamma_{\text{Cl}^-}) - 3 \log (m_{\text{H}^+} \gamma_{\text{H}^+}) + 7 \log a_w \quad (6)$$

Using the $-\log m_{\text{H}^+}$ values measured with ROSS electrodes and applying the Pitzer parameters of the HMW model to calculate the activity coefficients and the water activity in Eqn. 6, the mean value of the solubility constant of $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$ is found

to be $\log K_s^{\circ} = 26.15 \pm 0.16$ (2σ uncertainty interval). However, the $\log K_s^{\circ}$ values calculated from the experimental data in 2.11–5.15 m MgCl_2 show a slight systematic increase (cf. Table 3). The corresponding deviation between the measured $-\log m_{\text{H}^+}$ equilibrium values and those predicted by the HMW model is illustrated in Figure 5. It may be due to a slight systematic error either in the experimental data or in the calculated activity coefficients of $\log \gamma_{\text{H}^+}$. Harvie et al. (1984) derived the mixing parameters $\theta_{\text{Mg-H}} = 0.1$ and $\psi_{\text{Mg-H-Cl}} = -0.011$ from emf data in HCl-MgCl_2 mixtures at $m_{\text{MgCl}_2} \leq 3 \text{ mol kg}^{-1}$ (Khoo et al., 1977), while Roy et al. (1980) performed similar emf measurements up to $m_{\text{MgCl}_2} = 5 \text{ mol kg}^{-1}$ and calculated $\theta_{\text{Mg-H}} = 0.062$ and $\psi_{\text{Mg-H-Cl}} = 0.001$ (based on the same binary parameters for HCl and MgCl_2). However, if the mixing parameters of Roy et al. (1980) are used, the $\log K_s^{\circ}$ values derived from $-\log m_{\text{H}^+}$ in 2.11–5.15 m MgCl_2 show a considerable systematic decrease (cf. Table 3, values in brackets). Therefore the solubility constant is also calculated from the $\log a_{\text{HCl}}$ values measured at the end of the experiments. The calculation of $\log K_s^{\circ}$ according to Eqn. 7, obtained by combining Eqn. 6 and 4, does not require the calculation of $\log \gamma_{\text{H}^+}$. It depends only on the well ascertained binary Pitzer parameters for MgCl_2 :

$$\log K_s^{\circ}(\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})) = 2 \log (m_{\text{Mg}^{2+}} \gamma_{\text{Mg}^{2+}}) + 4 \log (m_{\text{Cl}^-} \gamma_{\text{Cl}^-}) - 6 \log a_{\text{HCl}} + 7 \log a_w \quad (7)$$

The $\log K_s^{\circ}$ values derived from $\log a_{\text{HCl}}$ in 2.11–5.15 m MgCl_2 according to Eqn. 7 show no systematic variation (cf. Table 3) and yield a mean value of $\log K_s^{\circ} = 25.93 \pm 0.11$ (2σ). Since the a_{HCl} measurements in concentrated MgCl_2 solutions are related to certain problems mentioned in section 2, the $\log K_s^{\circ}$ values obtained with both approaches are taken into account and the best value is considered to be

$$\log K_s^{\circ}(\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})) = 26.0 \pm 0.2$$

Figure 5 shows the experimental and calculated H^+ molalities in MgCl_2 solutions saturated with $\text{Mg}(\text{OH})_2(\text{cr})$ and $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})$. The present experimental results predict the invariant point at $m_{\text{MgCl}_2} = 1.8 \pm 0.1 \text{ mol kg}^{-1}$ and $-\log m_{\text{H}^+} = 8.95 \pm 0.05$. They are well reproduced by the solid lines calculated with the HMW model (EQ3/6 database “data0.hmw”). For comparison, the dotted lines in Figure 5 are calculated with the EQ3/6 database “data0.pit.” The equilibrium constant $\log K_s^{\circ}(\text{Mg}(\text{OH})_2(\text{cr})) = 16.30$ included in this database leads to significant errors in the calculation of equilibrium pH values. Moreover, the magnesium concentration predicted at the magnesium hydroxide-oxychloride invariant point ($m_{\text{MgCl}_2} = 4.0 \text{ mol kg}^{-1}$) is more than twice of that observed in the present study.

4. CONCLUSIONS

The solubility constants determined in the present study for brucite, $\log K_s^{\circ}(\text{Mg}(\text{OH})_2(\text{cr})) = 17.1 \pm 0.2$, and magnesium oxychloride, $\log K_s^{\circ}(\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}(\text{cr})) = 26.0 \pm 0.2$, confirm the values of 17.11 and 26.03 at 25°C proposed by Harvie et al. (1984) and included in the databases “data0.hmw” of the EQ3/6 code and “thermo_hmw.dat” of the GWB code. The solid-liquid equilibria in dilute to concentrated solutions of the system $\text{Mg-Na-H-Cl-H}_2\text{O}$ (25°C) are consistently described

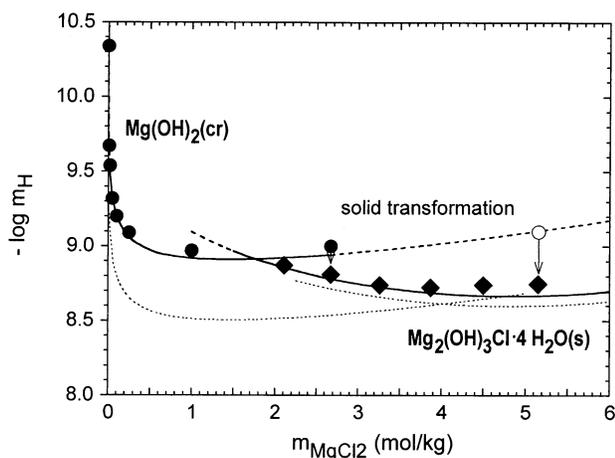


Fig. 5. Experimental and calculated equilibrium H^+ molalities in MgCl_2 solutions saturated with brucite or magnesium oxychloride. The solid lines are based on the HMW model (EQ3/6 database “data0.hmw”). The dotted lines are calculated for comparison using the EQ3/6 database “data0.pit.”

with the HMW set of ion interaction coefficients. The maximum deviation between experimental and calculated H^+ concentration is ≤ 0.08 log-units.

The equilibrium constant $\log K_s^\circ(\text{Mg}(\text{OH})_2(\text{cr})) = 16.3$ (25°C) included in various other thermodynamic databases of the EQ3/6, GWB and CHES codes is considerably too low. It arises from an erroneous standard entropy value for brucite used to calculate its standard Gibbs energy. Geochemical modeling based on these data leads to significant errors in the calculated pH value and in the magnesium concentration at the magnesium hydroxide-oxychloride invariant point. This has a considerable impact on the calculated mass balance, reaction progress and equilibrium state of magnesium salt-solution systems and hence on the predicted radionuclide solubilities in the performance assessment of a potential nuclear waste repository in underground salt mines.

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