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subject: Thermodynamic Data for phase 5 $(Mg_3Cl(OH)_5 \cdot 4H_2O)$ Determined from Solubility Experiments

The objective of this memorandum is to document the thermodynamic data for phase 5 $(Mg_3Cl(OH)_5 \cdot 4H_2O)$ determined from solubility experiments in the direction of undersaturation at SNL Carlsbad Facility. This memo supports the 2008 Milestone Report of MgO.

1 INTRODUCTION

Phase 5 is an important constituent in Sorel cements. It is also observed in experiments with GWB by using the Premier MgO supplied by the previous vendor (Xiong and Lord, 2008) (*magnesium chloride hydroxide hydrate* instead of phase 5 was used in Xiong and Lord (2008), although both of them refer to the same chemical species) (Figure 1), and in experiments with GWB and 1.0 M $MgCl_2$ + 3.6M NaCl solution by using Martin Marietta MgO supplied by the current vendor (Figure 2), conducted at SNL Carlsbad Facility. Therefore, this phase would be expected to be important to the near-field geochemical conditions when the engineered barrier MgO interacts with Mg-Cl-dominated brines. However, this phase is not in the current thermodynamic database, and reliable thermodynamic data for this phase is not available. Accordingly, SNL Carlsbad Facility has determined its thermodynamic properties. This memo reports its thermodynamic data determined from the solubility experiments from undersaturation.

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## 2 SOLUBILITY CONSTANT OF PHASE 5

In our solubility experiments, about 1 grams of the solubility controlling material—phase 5 were weighed out and placed into 150 mL plastic bottles. Then, 100 mL of supporting solutions were added into those bottles. After that the lids of the bottles were sealed with parafilm. The supporting solutions are a series of $MgCl_2$ + NaCl mixtures (Table 1). Phase 5 was synthesized with ACS reagent grade MgO and $MgCl_2 \cdot 6H_2O$, and it was recorded on Page 83 of WIPP-MM MgO-7. In the synthesis process, $MgCl_2$ solutions were first prepared with $MgCl_2 \cdot 6H_2O$ by dissolution with deionized water (resistance $\geq$ 18.0 MΩ). Then, MgO was reacted with $MgCl_2$ solutions at room temperature.

The dissolution reaction of phase 5 can be expressed as,

$$Mg_3Cl(OH)_5 \cdot 4H_2O + 5H^+ = 3Mg^{2+} + 9H_2O(l) + Cl^- \tag{1}$$
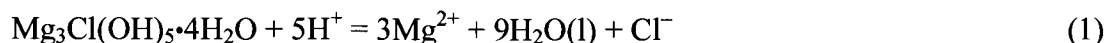
According to Reaction (1), the equilibrium quotient (log Q) for phase 5 can be computed from the molal concentrations of H^+, Mg^{2+}, and Cl^-. In the computation, the concentration of H^+ is calculated from the measured pH readings (pH_{ob}) with regard to the following equation,

$$pcH = pH_{ob} + A \tag{2}$$

In this report, the correction factors, A, are determined for a series of $MgCl_2$ + NaCl mixtures (Table 1) in a series of Gran titrations, which are recorded in the scientific notebook WIPP-MGO-CBD-26. Based on a multiple linear regression, A is fitted into an equation as a function of molalities of $MgCl_2$ and NaCl, and it will be of general use in the future experimental work:

$$A = -0.37647 + 0.66209 \times m_{MgCl_2} + 0.22791 \times m_{NaCl} \tag{3}$$

In Eq. (2), pcH is on molarity scale. In order that equilibrium quotients and equilibrium constants may be calculated on molality scale, pcH is converted to pmH on molality scale based on the measured densities of $MgCl_2$ + NaCl solutions (Table 2), which are recorded in the scientific notebook WIPP-MGO-CBD-27. The conversion factors are listed in Table 3. According these conversion factors, the correction factors for hydrogen ion concentrations on molal scale are also presented in Table 1.

Therefore, based on measured molal concentrations of H^+, Mg^{2+}, and Cl^-, the equilibrium quotients can be computed. The computed equilibrium quotients are listed in Table 4. Based on the specific interaction model (SIT), they are extrapolated to infinite dilution according to the following equation,

$$\log K_s^o = \log Q - 8D + 3\varepsilon(Mg^{2+}, Cl^-) I_m + \varepsilon(Na^+, Cl^-) I_m - 5\varepsilon(H^+, Cl^-) I_m + 9 \log a_{H_2O} \tag{4}$$

Where I_m is ionic strength on molal scale, $\varepsilon(Mg^{2+}, Cl^-)$, $\varepsilon(Na^+, Cl^-)$ and $\varepsilon(H^+, Cl^-)$ are SIT interaction coefficients at 25 °C, which are from Xiong (2006), and D is the Debye-Hückel term, which is given by:

$$D = \frac{A_\gamma \sqrt{I_m}}{1 + \rho \sqrt{I_m}} \qquad (5)$$

In which A_γ (0.509) is Debye-Hückel slope for activity coefficient at 25 °C from Helgeson and Kirkham (1974); ρ the minimum distance of approach between ions, which is taken as 1.5 (Ciavatta, 1980). The activities of water (a_{H_2O}) for $MgCl_2$ + $NaCl$ solutions are calculated by using the FMT code for the mixtures listed in Table 1. The activities of water are tabulated in Table 5.

　　　The solubility constants at infinite dilution for Phase 5 determined at this time are significantly different from the values of Mazuranic et al. (1982), which ranges from 39.41 to 39.48. This difference may be caused by the pH determination in their study. Mazuranic et al. (1982) mentioned that the precise determination of pH in their experiments was problematic. As the hydrogen concentrations are accurately determined, and the extrapolation to infinite dilution based on the reliable extrapolation method, in this study, we are confident that our values are more reliable.

3 DISCUSSIONS AND STANDARD THERMODYNAMIC PROPERTIES OF PHASE 5

　　　Based on the solubility constant of phase 5 determined in this study, and the solubility constant of phase 3 ($Mg_2Cl(OH)_3 \cdot 4H_2O$) in the EQ3/6 database, which is labeled as oxychloride-Mg in EQ3/6 database, the stability fields of phase 5 and phase 3 in the space of pH-log $a_{Mg^{2+}}$ are constructed as shown in Figure 3. Figure 3 suggests that phase 5 is stable under the conditions of higher activities of Mg^{2+} and lower activities of H^+. Phase 5 is also favored under higher activities of water. The experimental results with GWB and simplified GWB are overwhelmingly in the stability field of phase 5 (Figure 3).

　　　In Figure 4, the solubilities of phase 3 and phase 5 in the Mg-Cl binary system are displayed. The composition for the invariant point of phase 3 and phase 5 is m_{Mg} = 1.70 and pmH = 8.93. In the Mg-Cl binary system, the pmH buffered by phase 3 ranges from 9.10 to 8.70 in the range of $m_{Mg^{+2}}$ from 1 to 4. In contrast, the pmH buffered by phase 5 in the same range of $m_{Mg^{+2}}$ is from 9.03 to 8.83.

　　　In Figure 5, the solubilities of phase 3 and phase 5 in the Na-Mg-Cl ternary system typical of GWB are shown. In comparison with the solubilities in the Mg-Cl binary system, the stability fields of phase 3 and phase 5 are switched in terms of pmH in lower $m_{Mg^{+2}}$ range in the Na-Mg-Cl ternary system. For instance, at 1 m of Mg^{+2}, phase 3 is stable at higher pmH in the Mg-Cl binary system (Figure 4), whereas phase 5 is stable at higher pmH in the Na-Mg-Cl ternary system (Figure 5).

　　　In Figure 5, the experimental data from the simplified GWB are also plotted. It seems that those experimental data are close to the solubilities of phase 5, but far away from those of phase 3, in terms of pmH, implying that the formation of phase 5 is favored. Consequently, the formation of phase 3 is possible in simplified GWB is possible only after the conversion of phase 5 to phase 3 when pmH in the system is substantially decreased to those of phase 3.

　　　In Figure 6, the solubilities of brucite, phase 3 and Phase 5 in the Na-Mg-Cl ternary system typical of ERDA-6 are shown. Figure 6 shows that brucite is the stable phase in the high pmH and low $m_{Mg^{+2}}$ region. The conversion of brucite to either phase 5 or phase 3 requires the decrease in pmH and

the increase in $m_{Mg^{+2}}$. Some experimental data involving ERDA-6 are plotted into Figure 6. It seems that the solutions are still in the stability fields of brucite because of their nature in high pmH and lower $m_{Mg^{+2}}$.

The standard entropy of phase 5 is estimated in this study. The estimation follows the principle of Xiong (2007) which states that entropies of ternary or higher compounds can be estimated by stoichiometric summation of entropies of constituent binary compounds. The standard entropy of phase 5 is estimated according to the following equation:

$$S^o_{phase\ 5} = 2S^o_{Mg(OH)_2} + S^o_{MgOHCl} + 4S^o_{H_2O,\ structural} \tag{6}$$

The standard entropies of $Mg(OH)_2$ and MgOHCl are from the NBS table (Wagman et al., 1982) (Table 6). The entropy of the structural water in magnesium chloride compounds is calculated from the entropy of anhydrous magnesium chloride with corresponding entropies of hydrous magnesium chloride solids:

$$S^o_{MgCl_2 \cdot nH_2O(cr)} = S^o_{MgCl_2(cr)} + nS^o_{H_2O,\ structural} \tag{7}$$

Rearranging Eq. (7), we have,

$$nS^o_{H_2O,\ structural} = S^o_{MgCl_2 \cdot nH_2O(cr)} - S^o_{MgCl_2(cr)} \tag{8}$$

According to Eq. (8), a series of entropies of the structural water in magnesium chloride solids are calculated based on the entropies of magnesium chloride compounds listed in Table 6. The grand average entropy of structural water in magnesium chloride crystalline phases is calculated to be 46±3 (2σ) J mol^{-1} K^{-1}. Based on Eq. (6), the standard entropy of phase 5 is estimated as 394 J mol^{-1} K^{-1} (Table 7) according to the above principle. Other thermodynamic properties are also listed in Table 7.

The coefficients for the heat capacity equation of phase 5 in the following form are also estimated by using the estimation method of Mostafa et al. (1996) (Table 8),

$$C_p = a + bT + c/T^2 + dT^2 \tag{9}$$

Based on this heat capacity equation, the heat capacity of phase 5 at 25 °C is calculated as 374 J mol^{-1} K^{-1} (Table 7).

As our solubility experiments were conducted at 21 °C (294.15 K), equilibrium data are extrapolated to standard temperature, 298.15 K, by employing the following equation for temperature variations of Gibbs free energy, assuming constant heat capacity over this temperature range,

$$\Delta G^o_T = \Delta G^o_{298.15} - (T - 298.15)\Delta S^o_{298.15} + \int_{298.15}^{T} \Delta C^o_p dT - T \int_{298.15}^{T} \Delta C^o_p d\ln T \tag{10}$$

In the extrapolation, entropies of H_2O (l), Cl$^-$ and Mg^{2+} are from Wagman et al. (1982), and entropy of phase 5 is from this study. Heat capacities of H_2O (l) and Cl$^-$ are from Wagman et al. (1982), and those of Mg^{2+} and phase 5 are from Desnoyers et al. (1976) and this study, respectively. The equilibrium constant at 25 °C is 43.21±0.33 (2σ). This value is in agreement with a value of 43.37 within the quoted

uncertainty, when an independent extrapolation method, one-term isocoulombic approach using water a model substance, is applied. The one-term isocoulombic approach has been used before (e.g., Xiong, 2007, and references therein).

4 SUMMARY

The solubility constants for phase 5 from undersaturation experiments at SNL seem to be more reliable in comparison with the literature values owing to more precise determination of hydrogen concentrations in a wide range of brines.

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Table 1 Correction factors for hydrogen ion concentrations on both molar and molal scales for $MgCl_2$ + NaCl mixtures determined in this study

Brines	Correction Factor, A_M *	Correction Factor, A_m **
0.5 m $MgCl_2$ + 5.0 m NaCl (labeled as $MgCl_2$-A)	1.083	1.035
0.8 m $MgCl_2$ + 3.5 m NaCl (labeled as $MgCl_2$-B)	0.921	0.883
1.25 m $MgCl_2$ + 3.0 m NaCl (labeled as $MgCl_2$-C)	1.067	1.030
1.5 m $MgCl_2$ + 2.0 m NaCl (labeled as $MgCl_2$-D)	0.996	0.963
1.75 m $MgCl_2$ + 1.5 m NaCl (labeled as $MgCl_2$-E)	1.077	1.045
2.0 m $MgCl_2$ + 0.5 m NaCl (labeled as $MgCl_2$-F)	0.982	0.955

* Correction factor for hydrogen ion concentrations on molar scale originally determined by Gran titration

** Correction factor for hydrogen ion concentrations on molal scale based on the conversion factors from molarity to molality (see Table 3)

Table 2 Measured densities of $MgCl_2$ + NaCl mixtures

Brines	Density, g/mL
0.5 m $MgCl_2$ + 5.0 m NaCl (labeled as $MgCl_2$-A)	1.2007
0.8 m $MgCl_2$ + 3.5 m NaCl (labeled as $MgCl_2$-B)	1.1728
1.25 m $MgCl_2$ + 3.0 m NaCl (labeled as $MgCl_2$-C)	1.1890
1.5 m $MgCl_2$ + 2.0 m NaCl (labeled as $MgCl_2$-D)	1.1670
1.75 m $MgCl_2$ + 1.5 m NaCl (labeled as $MgCl_2$-E)	1.1654
2.0 m $MgCl_2$ + 0.5 m NaCl (labeled as $MgCl_2$-F)	1.1458

Table 3. Hydrogen concentration conversion factors from molarity scale to molality scale for $MgCl_2$ + NaCl mixtures based on the measured densities

Brines	Conversion Factor
0.5 m $MgCl_2$ + 5.0 m NaCl (labeled as $MgCl_2$-A)	1.1159
0.8 m $MgCl_2$ + 3.5 m NaCl (labeled as $MgCl_2$-B)	1.0920
1.25 m $MgCl_2$ + 3.0 m NaCl (labeled as $MgCl_2$-C)	1.0886
1.5 m $MgCl_2$ + 2.0 m NaCl (labeled as $MgCl_2$-D)	1.0794
1.75 m $MgCl_2$ + 1.5 m NaCl (labeled as $MgCl_2$-E)	1.0763
2.0 m $MgCl_2$ + 0.5 m NaCl (labeled as $MgCl_2$-F)	1.0644

Table 4.   Experimental results from undersaturation experiments, and solubility constants for Phase 5 at 21 °C.

Experimental Run #	Sample #	pH_{ob}	pmH	m_{Mg}^A, ±2σ	m_{Cl}^B	log Q, ±2σ	log K, ±2σ
P5-MgCl$_2$-A-1	1	8.46	9.50	0.472±0.000	4.790	47.18±0.00	44.06±0.00
P5-MgCl$_2$-A-2	1	8.44	9.48	0.477±0.004	4.853	47.10±0.01	43.98±0.01
P5-MgCl$_2$-B-1	1	8.44	9.32	0.724±0.004	4.245	46.82±0.01	43.93±0.01
P5-MgCl$_2$-B-2	1	8.42	9.30	0.723±0.002	4.228	46.72±0.00	43.83±0.00
P5-MgCl$_2$-C-1	1	8.13	9.16	1.201±0.011	4.718	46.71±0.01	43.69±0.01
P5-MgCl$_2$-C-2	1	8.13	9.16	1.214±0.000	4.573	46.71±0.00	43.69±0.00
P5-MgCl$_2$-D-1	1	8.14	9.10	1.467±0.007	4.429	46.66±0.01	43.76±0.01
P5-MgCl$_2$-D-2	1	8.10	9.06	1.477±0.020	4.309	46.46±0.02	43.56±0.02
P5-MgCl$_2$-E-1	1	8.04	9.09	1.716±0.021	4.430	46.78±0.02	43.86±0.02
P5-MgCl$_2$-E-2	1	8.05	9.10	1.728±0.000	4.344	46.83±0.00	43.91±0.00
P5-MgCl$_2$-F-1	1	8.05	9.00	1.994±0.020	4.084	46.53±0.01	43.75±0.01
P5-MgCl$_2$-F-2	1	8.03	8.98	2.000±0.042	4.092	46.44±0.03	43.65±0.03
P5-MgCl$_2$-A-1	2	8.48	9.52	0.491±0.004	4.569	47.31±0.01	44.19±0.01
P5-MgCl$_2$-A-2	2	8.49	9.53	0.485±0.005	4.537	47.34±0.01	44.22±0.01
P5-MgCl$_2$-B-1	2	8.48	9.36	0.756±0.005	3.905	47.04±0.01	44.15±0.01
P5-MgCl$_2$-B-2	2	8.47	9.35	0.735±0.006	4.865	47.05±0.01	44.16±0.01
P5-MgCl$_2$-C-1	2	8.19	9.22	1.256±0.017	4.519	47.05±0.02	44.03±0.02
P5-MgCl$_2$-C-2	2	8.19	9.22	1.232±0.018	4.476	47.02±0.02	44.00±0.02
P5-MgCl$_2$-D-1	2	8.17	9.13	1.555±0.027	4.129	46.86±0.02	43.96±0.02
P5-MgCl$_2$-D-2	2	8.17	9.13	1.514±0.032	4.158	46.82±0.03	43.92±0.03
P5-MgCl$_2$-E-1	2	8.08	9.13	1.762±0.027	4.194	46.99±0.02	44.07±0.02
P5-MgCl$_2$-E-2	2	8.08	9.13	1.755±0.055	4.238	46.99±0.04	44.07±0.04
P5-MgCl$_2$-F-1	2	8.11	9.06	1.998±0.026	4.065	46.84±0.02	44.05±0.02
P5-MgCl$_2$-F-2	2	8.09	9.04	1.970±0.035	3.784	46.69±0.02	43.90±0.02
Average						46.92±0.47	43.98±0.35

[A] Determined with ICP-AES.
[B] Determined with IC.

Table 5. Activity of water for MgCl$_2$+NaCl brines calculated from FMT*

Brines	Activity of water
0.5 m MgCl$_2$ + 5.0 m NaCl (labeled as MgCl$_2$-A)	0.75481
0.8 m MgCl$_2$ + 3.5 m NaCl (labeled as MgCl$_2$-B)	0.79700
1.25 m MgCl$_2$ + 3.0 m NaCl (labeled as MgCl$_2$-C)	0.77289
1.5 m MgCl$_2$ + 2.0 m NaCl (labeled as MgCl$_2$-D)	0.79683
1.75 m MgCl$_2$ + 1.5 m NaCl (labeled as MgCl$_2$-E)	0.79481
2.0 m MgCl$_2$ + 0.5 m NaCl (labeled as MgCl$_2$-F)	0.82035

* The corresponding FMT calculations are listed in Appendix A.

Table 6. Standard entropies employed for estimation of standard entropy of phase 5

Species	$S^o_{298.15}$, J mol^{-1} K^{-1}	Source
Mg(OH)$_2$ (cr)	63.18	Wagman et al. (1982)
MgOHCl (cr)	83.7	Wagman et al. (1982)
MgCl$_2$ (cr)	89.62	Wagman et al. (1982)
MgCl$_2$·H$_2$O (cr)	137.2	Wagman et al. (1982)
MgCl$_2$·2H$_2$O (cr)	179.9	Wagman et al. (1982)
MgCl$_2$·4H$_2$O (cr)	264.0	Wagman et al. (1982)
MgCl$_2$·6H$_2$O (cr)	366.1	Wagman et al. (1982)
H$_2$O (structural)	46±3 (2σ)	This study,

Table 7. Standard thermodynamic properties of phase 5 at 25 °C and 1 bar

Properties	Value (±2σ)	Reference
log K for Reaction 1	43.21±0.33	This study (measured)
$\Delta_f G^o$	−3384±2 kJ mol^{-1}	This study (derived)
$\Delta_f H^o$	−3896±6 kJ mol^{-1}	This study (derived)
S^o	394±20[A] J mol^{-1} K^{-1}	This study (estimated)[B]
C_p	372±19[A] J mol^{-1} K^{-1}	This study (estimated)[C]

[A] 5% uncertainty assigned
[B] Estimated based on the estimation principle of Xiong (2007)
[C] Estimated based on the method of Mostafa et al. (1996)

Table 8. Coefficients for the heat capacity equation of phase 5 estimated in this study

a	$b \times 10^{-3}$	$c \times 10^6$	$d \times 10^{-6}$
276.943	428.487	−1.733	−146.957

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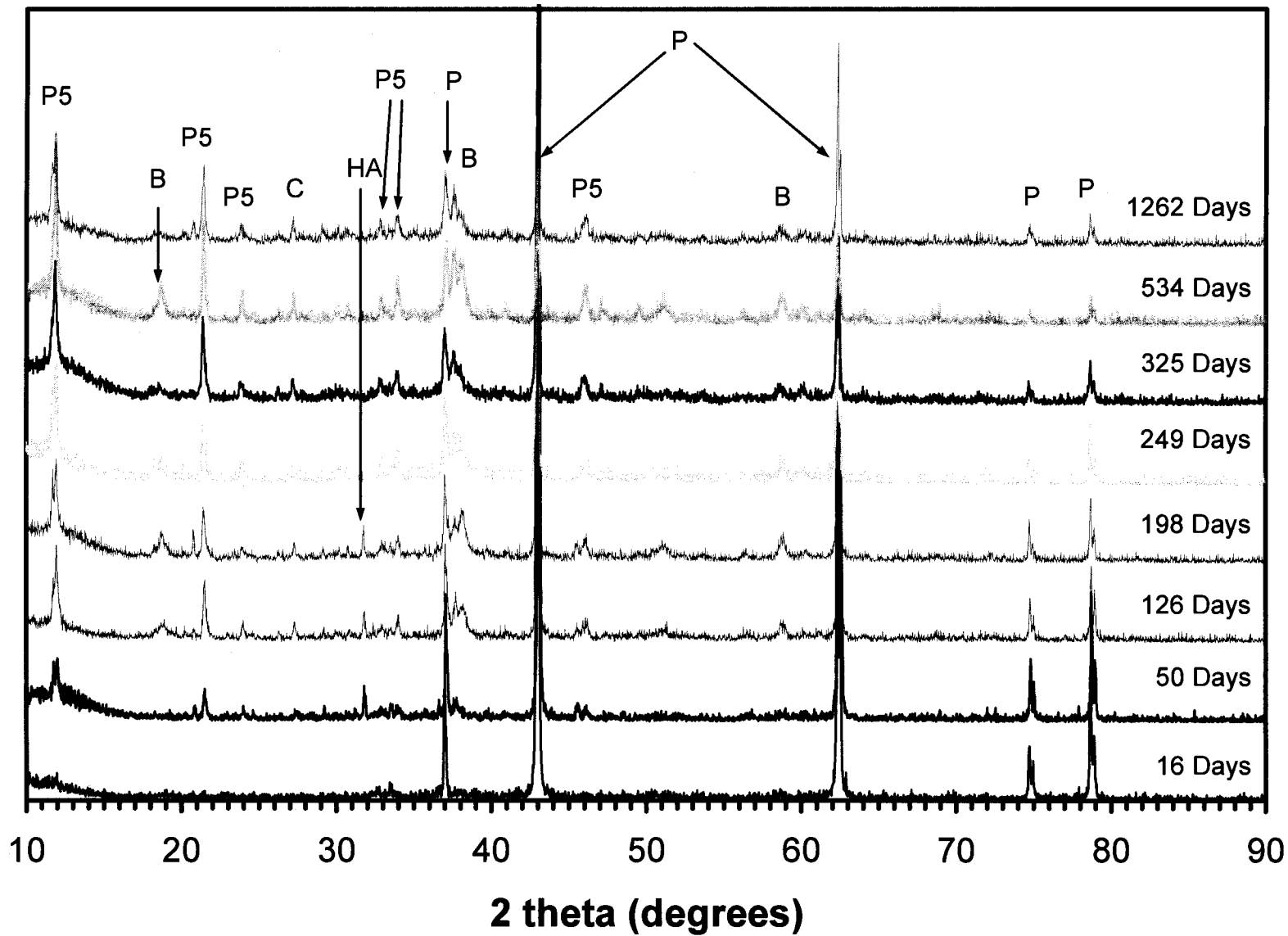
Figure 1. XRD patterns of experiments with Premier MgO in GWB at room temperature and atmospheric CO_2 partial pressure.
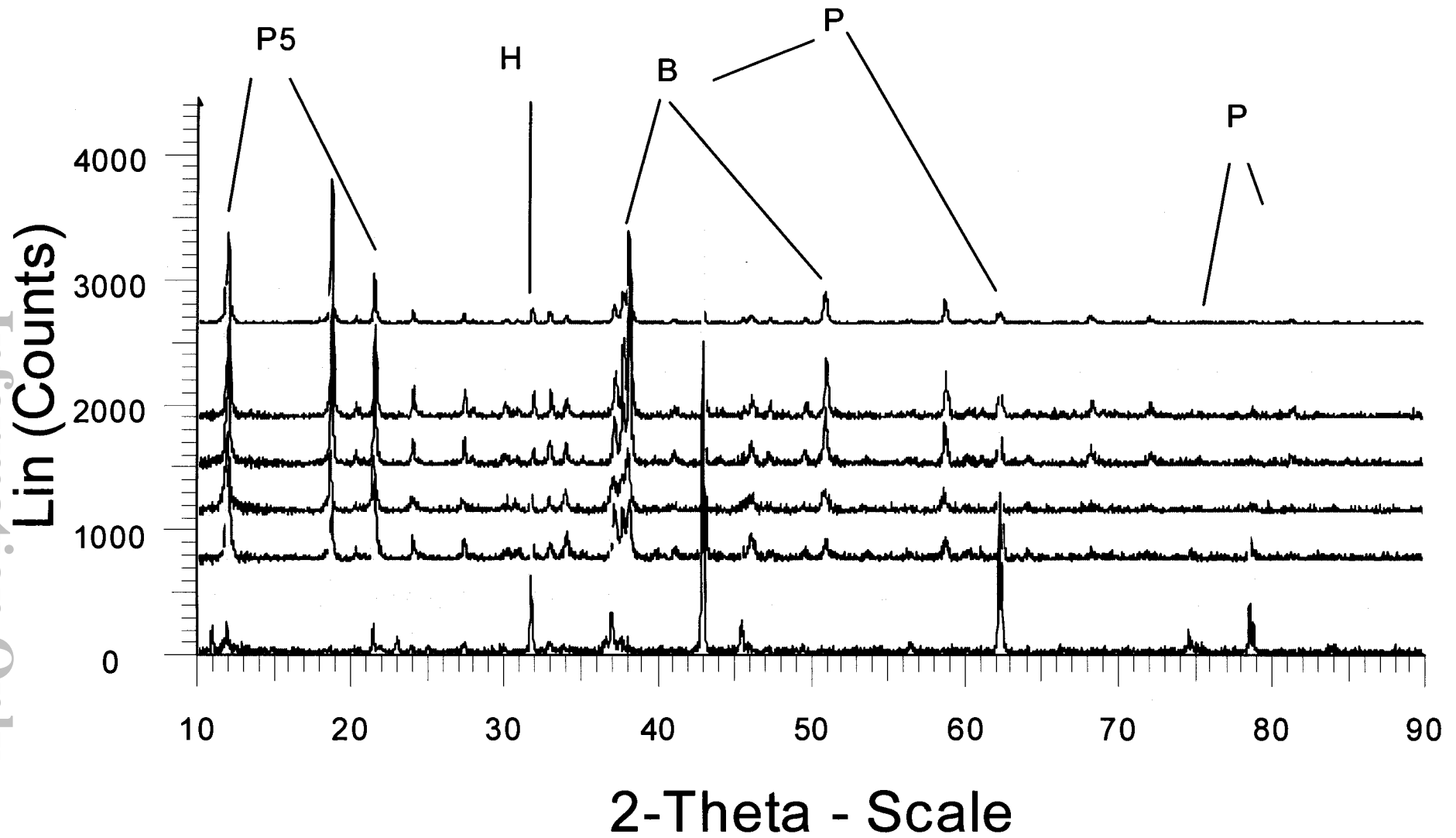
Figure 2. XRD patterns of experiments with Martin Marietta MgO in simplified GWB at room temperature and atmospheric CO_2 partial pressure.

WIPP:1.4.2.2:SFT:QA-L:519559
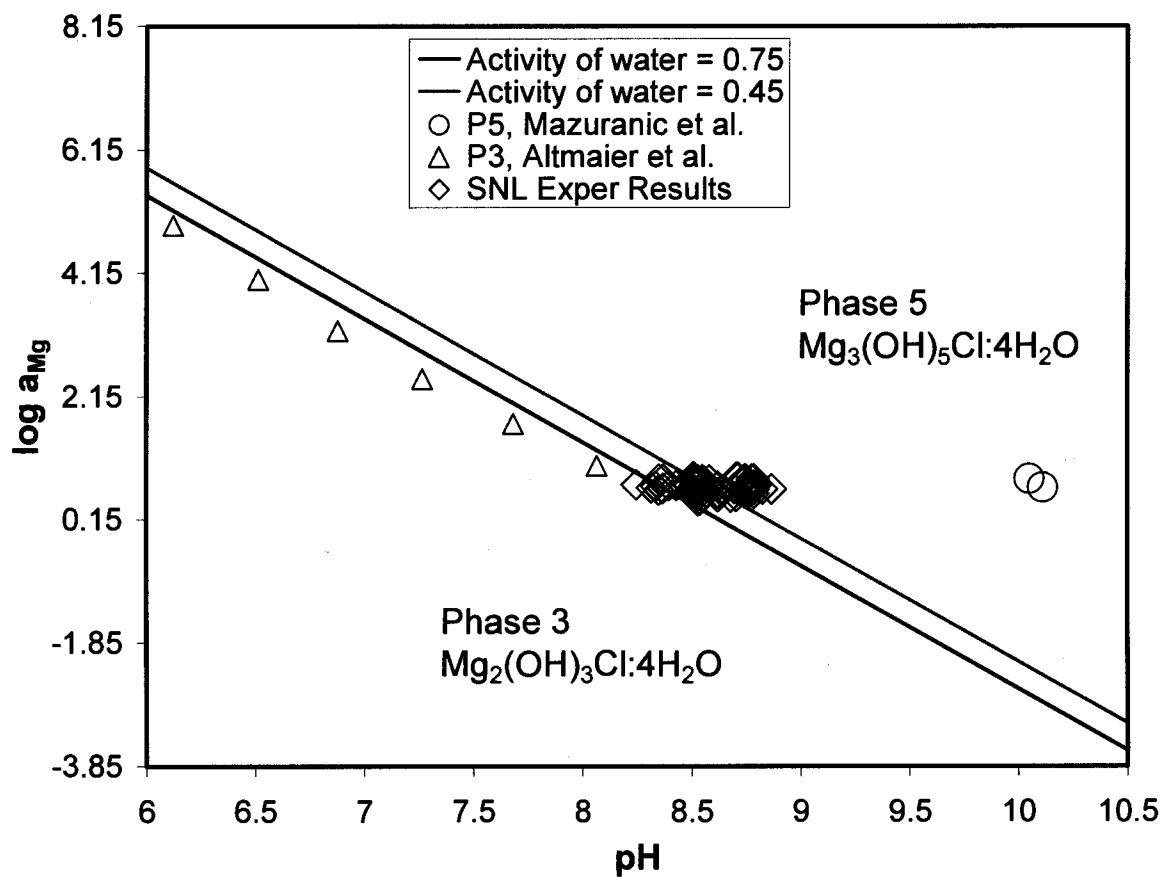
Figure 3. Activity diagram showing the stability fields of phase 3 and phase 5. Phase 3 data are from Altmaier et al. (2003), and phase 5 data from Mazuranic et al. (1982).
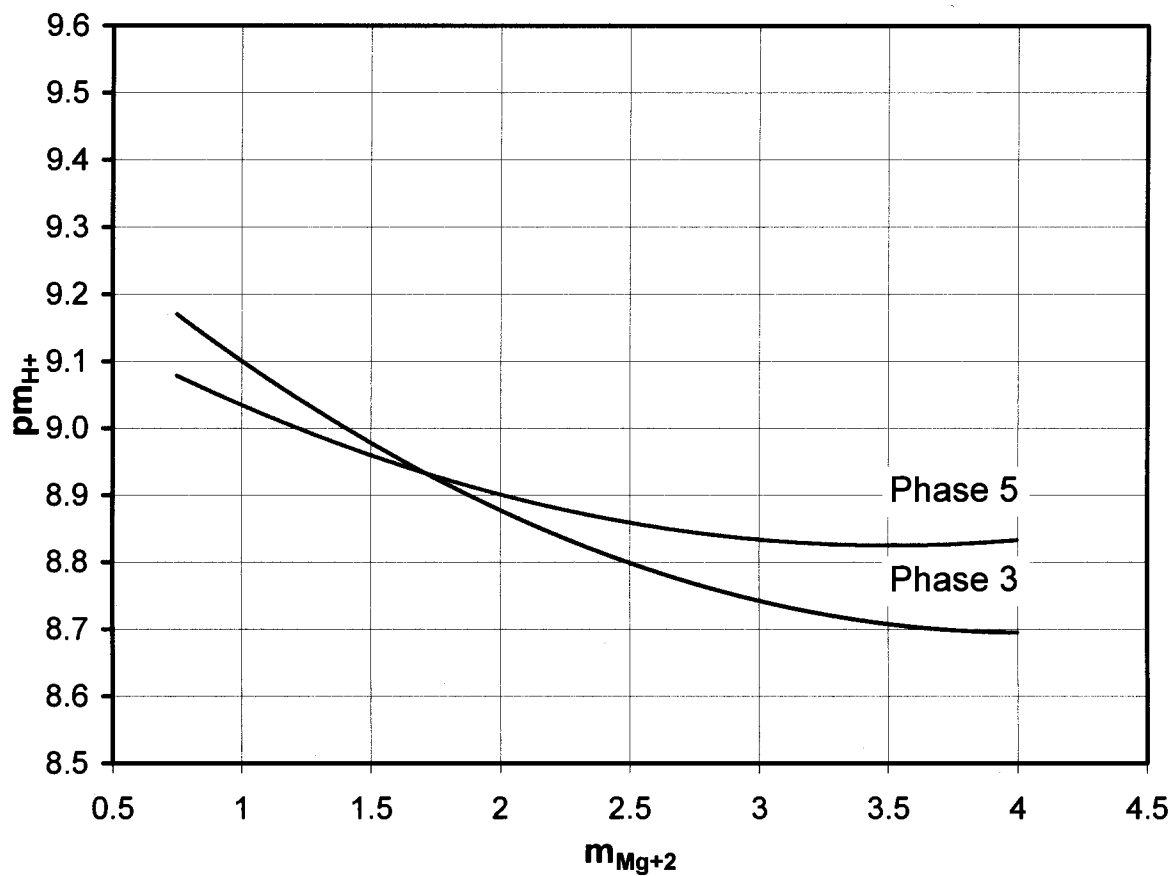
Figure 4. Solubilities of Phase 3 and Phase 5 in the Mg-Cl system.
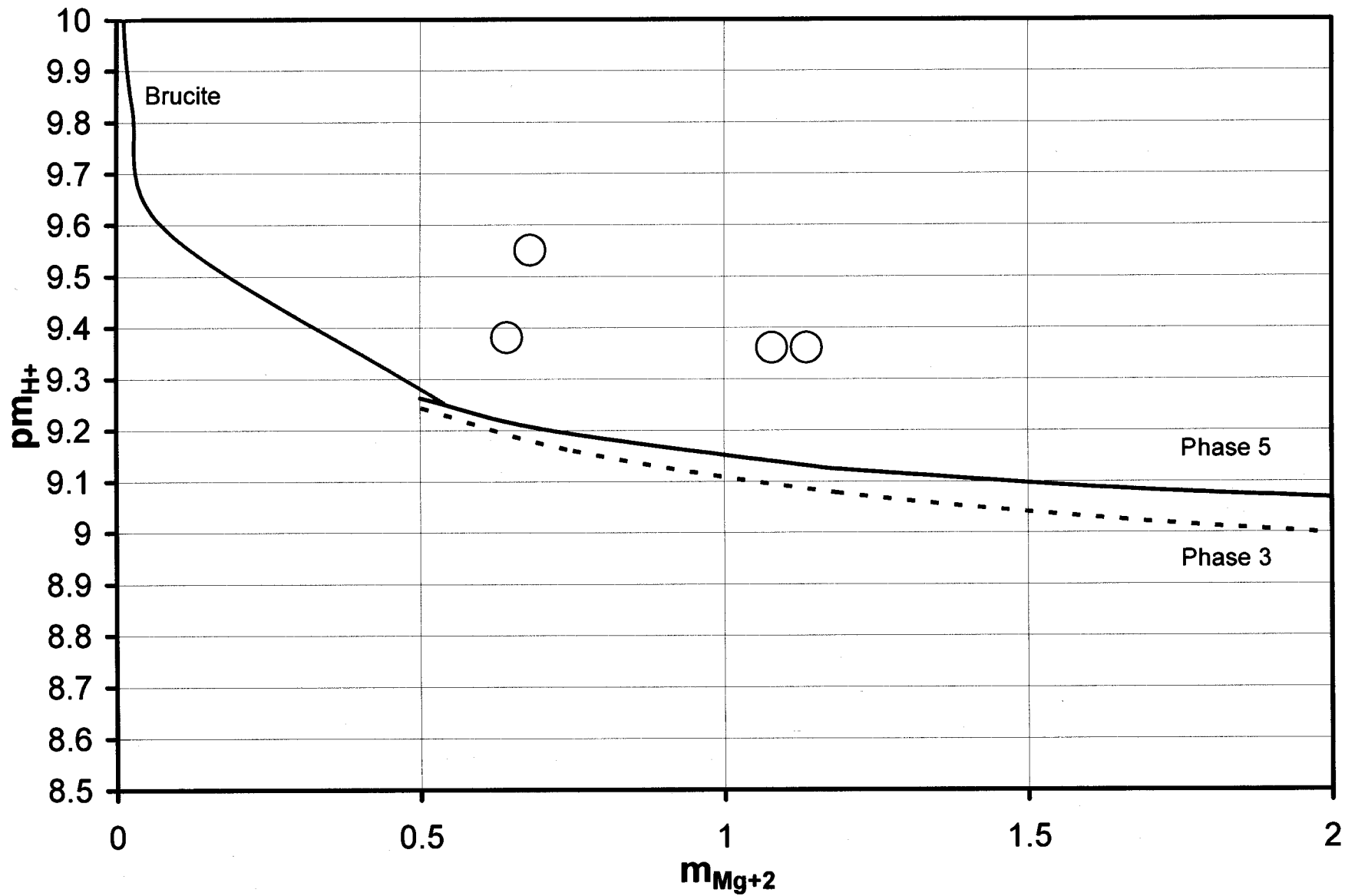
Figure 5. Solibilities of Phase 3 and Phase 5 in the Na-Mg-Cl system typical of GWB composition. Circles are experimental data in simplified GWB.
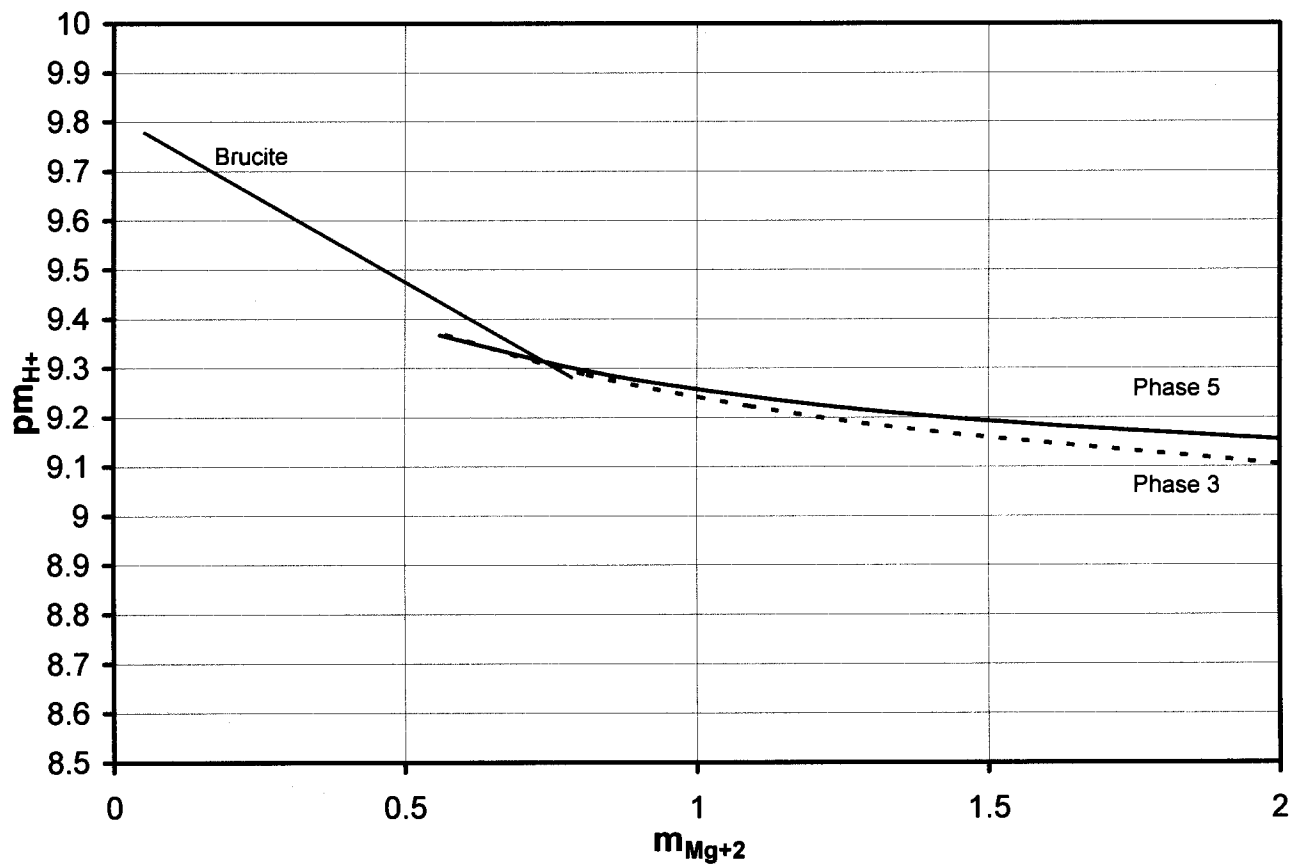
Figure 6. Solibilities of brucite, Phase 3 and Phase 5 in the Na-Mg-Cl system typical of ERDA-6 composition.

Appendix A. File names of FMT calculations

All FMT calculations are archived in the FMT library LIBACIDDIS_FMT

FMT_P5_MgCl2_001: Calculation of activity of water for the brine $MgCl_2$-A.

FMT_P5_MgCl2_002: Calculation of activity of water for the brine $MgCl_2$-B.

FMT_P5_MgCl2_003: Calculation of activity of water for the brine $MgCl_2$-C.

FMT_P5_MgCl2_004: Calculation of activity of water for the brine $MgCl_2$-D.

FMT_P5_MgCl2_005: Calculation of activity of water for the brine $MgCl_2$-E.

FMT_P5_MgCl2_006: Calculation of activity of water for the brine $MgCl_2$-F.

XIONG, 2009   May 6, 2009 Yongliang Xiong

MEMO: Thermodynamic Data for phase 5
($Mg_3Cl(OH)_5 \cdot 4H_2O$) Determined from Solubility Experiments.

Calculation of Heat Capacity equation of
phase 5   (Table 6)

Formula of phase 5:

$$Mg_3Cl(OH)_5 \cdot 4H_2O$$

According to Mostafa et al. (1996):

Group	Δa	Δb	Δc	Δd
Mg^{2+}	14.639	-0.637	-0.074	-0.609
Cl^-	26.609	10.376	-0.251	0.657
OH^-	28.917	30.730	-0.628	3.257
H_2O	15.458	66.593	0.470	-40.518

Therefore, for the heat capacity equation of
phase 5. in the form,

$$C_p = a + bT + c/T^2 + dT^2$$

$a = 3 \times 14.639 + 26.609 + 5 \times 28.917 + 4 \times 15.458$
$\quad = 276.943$

$b = 3 \times (-0.637) + 10.376 + 5 \times 30.730 + 4 \times 66.593$
$\quad = 428.487$

$c = 3 \times (-0.074) + (-0.251) + 5 \times (-0.628) + 4 \times 0.470$
$\quad = -1.733$

$d = 3 \times (-0.609) + 0.657 + 5 \times (3.257) + 4 \times (-40.518)$
$\quad = -146.957$

Computation of Conversion Factors (Table 3A)

The conversion factor will be the same for all species in a certain brine. Therefore, the following calculations are on Mg

(1) Brine MgCl₂ – A

The general equation for conversion of molality (m) to molarity (M) is expressed as:

$$M_i = \frac{1000 \, \rho \, m_i}{1000 + \sum_i^2 m_i E_i}$$

where M_i is the concentration of ith species on molarity scale; m_i the concentration of ith species on molality scale; ρ density of solution; E_i molecular weight of ith species.

In MgCl₂ – A brine,

$\rho = 1.2007$ ~~mg~~ g/mL

$m_{Mg} = 0.5$ $E_{Mg} = 24.305$

$m_{Na} = 5.0$ $E_{Na} = 22.98977$

$m_{Cl} = 6.0$ $E_{Cl} = 35.453$

$M_{Mg} = (1000 \times 1.2007 \times 0.5) / [1000 + 0.5 \times 24.305$

$5.0 \times 22.98977 + 6.0 \times 35.453]$

$= 600.35 / 1339.81935$

$= 4.4808 \times 10^{-1}$

Therefore, the conversion factor from molarity to molality should be

$$M_{Mg} / M_{Mg} = 0.5 / 0.44808$$
$$= 1.1159$$

(2) Brine $MgCl_2 - B$

$$M_{Mg} = 0.8$$
$$m_{Na} = 3.5$$
$$m_{Cl} = 2 \times 0.8 + 3.5 = 5.1$$

$$M_{Mg} = \frac{1000 \times 1.1728 \times 0.8}{1000 + 0.8 \times 24.305 + 3.5 \times 22.98977 + 5.1 \times 35.453}$$

$$= 938.24 / 1280.71895$$
$$= 7.3259 \times 10^{-1}$$

$$M_{Mg} / M_{Mg} = 0.8 / 0.73259 = 1.0920$$

(3) Brine $MgCl_2 - C$

$$M_{Mg} = 1.25$$
$$m_{Na} = 3.0$$
$$m_{Cl} = 1.25 \times 2 + 3 = 5.5$$

$$M_{Mg} = \frac{1000 \times 1.1890 \times 1.25}{1000 + 1.25 \times 24.305 + 3 \times 22.98977 + 5.5 \times 35.453}$$

$$= 1486.25 / 1294.34206$$
$$= 1.1483$$

$$m_{Mg}/M_{Mg} = 1.25/1.1483 = 1.0886$$

(4) Brine $MgCl_2 - D$

$\qquad m_{Mg} = 1.5$

$\qquad m_{Na} = 2.0$

$\qquad m_{Cl} = 1.5 \times 2 + 2 = 5.0$

$$M_{Mg} = \frac{1000 \times 1.1670 \times 1.5}{1000 + 1.5 \times 24.305 + 2 \times 22.98977 + 5.0 \times 35.453}$$

$$= 1750.50 / 1259.70204$$

$$= 1.3896$$

$$m_{Mg}/M_{Mg} = 1.5/1.3896 = 1.0794$$

(5) Brine $MgCl_2 - E$

$\qquad m_{Mg} = 1.75$

$\qquad m_{Na} = 1.5$

$\qquad m_{Cl} = 1.75 \times 2 + 1.5 = 5.0$

$$M_{Mg} = \frac{1000 \times 1.1654 \times 1.75}{1000 + 1.75 \times 24.305 + 1.5 \times 22.98977 + 5.0 \times 35.453}$$

$$= 2039.45 / 1254.283405$$

$$= 1.6260$$

$$m_{Mg}/M_{Mg} = 1.75/1.6260 = 1.0763$$

(6) Brine $MgCl_2 - F$

$$m_{Mg} = 2.0$$

$$m_{Na} = 0.5$$

$$m_{Cl} = 2.0 \times 2 + 0.5 = 4.5$$

$$M_{Mg} = \frac{1000 \times 1.1458 \times 2.0}{1000 + 2.0 \times 24.305 + 0.5 \times 22.98977 + 4.5 \times 35.453}$$

$$= 2291.60 / 1219.643385$$

$$= 1.87891$$

$$m_{Mg} / M_{Mg} = 2.0 / 1.87891 = 1.0644$$

According to $\log k = 43.21$,

$\Delta_r G$ is computed by using the following equation,

$$\log k = - \frac{\Delta_r G}{\ln 10 \, RT}$$

$$R = 8.314, \quad T = 298.15 \, K$$
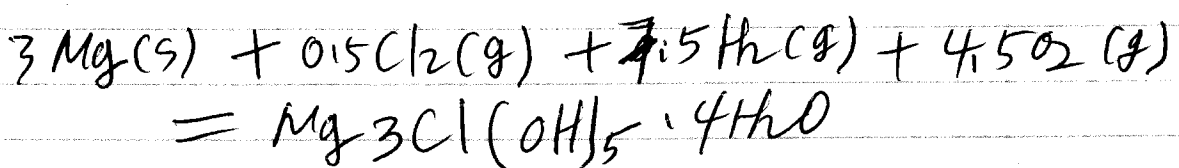
$$\Delta_r G = -246.629 \; KJ \, mol^{-1}$$

$$\Delta_f G_{phase\,5} = 3 \times \Delta_f G_{Mg^{2+}} + \Delta_f G_{Cl^-} + 9\Delta_f G_{H_2O}$$
$$- 5\Delta_f G_{H^+} - \Delta_r G$$

$$= 3 \times (-454.8) + (-131.228) + 9 \times (-237.18) - 5 \times 0$$
$$+ 246.629$$

$$= -3383.6 \approx -3384 \; KJ \, mol^{-1}$$

$$S^\circ_{phases} = 2 S^\circ_{Mg(OH)_2} + S^\circ_{MgOHCl} + 4 S^\circ_{H_2O, struct}$$

$$= 2 \times 63.18 + 83.7 + 4 \times 46$$
$$= 394 \; J \, mol^{-1} \, K^{-1}$$

For the reaction,

$$3\,Mg(s) + 0.5\,Cl_2(g) + 7.5\,H_2(g) + 4.5\,O_2(g)$$
$$= Mg_3Cl(OH)_5 \cdot 4H_2O$$

$$\Delta_r S = S^\circ_{phase\,5} - 3S^\circ_{Mg} - 0.5\,S^\circ_{Cl_2(g)} - 7.5\,S^\circ_{H_2(g)} - 4.5\,S^\circ_{O_2(g)}$$

$$= 394 - 3 \times (32.67) - 0.5 \times 223.066$$
$$- 7.5 \times 130.680 - 4.5 \times 205.152$$

$$= -1718.827$$

$$\Delta_r G = \Delta_f G\,_{phase\,5}$$

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$$\Delta_r H = \Delta_f H = \Delta_f G\,_{phase\,5} + T\Delta_r S$$

$$= -3384 + 298.15 \times (-1718.827)$$
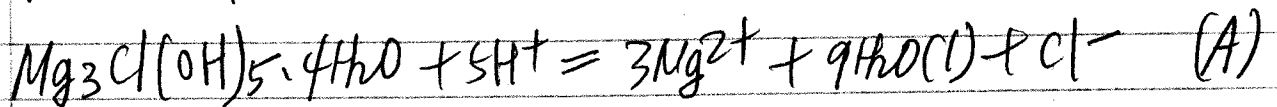$$\times 0.001$$

$$= -3896 \; KJ \; mol^{-1}$$

phase 5 MEMO

Explanation for one-term isocoulombic
method

For solubility reaction,

$$Mg_3Cl(OH)_5 \cdot 4H_2O + 5H^+ = 3Mg^{2+} + 9H_2O(l) + Cl^- \quad (A)$$

Usig H_2O as a model substance,

$$H_2O(l) = H^+ + OH^- \quad (B)$$
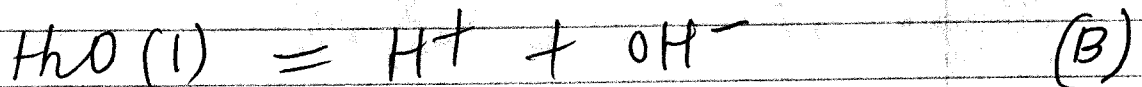
Combination of Reactions (A) and (B) leads to
the following isocoulombic reaction,

$$Mg_3Cl(OH)_5 \cdot 4H_2O + 6H^+ + OH^- = 3Mg^{2+} + 10H_2O(l) + Cl^- \quad (C)$$
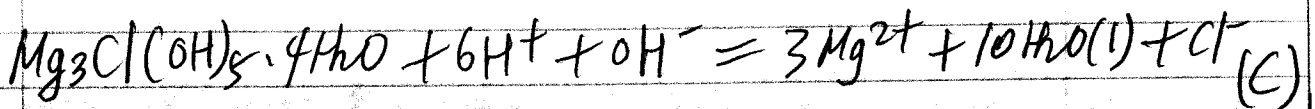
As $\log k$ for Reaction (A) is 43.98 at
21°C, and $\log k$ for Reaction (B) is
−14.1640 (based EQ3/6 database) at 21°C,

$\log k$ for Reaction (C) should be:

$$43.98 - (-14.1640) = 58.1440$$

$\Delta_r G$ for Reaction (C) should be:

$$\log k = - \frac{\Delta_r G}{\ln 10 \, RT} \quad (at \ 294.15)$$

$$\Delta_r G = -58.1440 \times \ln 10 \times 8.314 \times (294.15)$$

$$= -327.412 \ KJ \ mol^{-1}$$

Explanation for one-term isocoulombic method

According to one-term isocoulombic approach,

$$\Delta_r G_{298.15} = \Delta_r G_T = -RT \ln K_T$$

therefore, $\Delta_r G_{298.15} = \Delta_r G_{294.15} = -327.412$
$$KJ \, mol^{-1}$$

$\log K$ for Reaction (C) at $25°C$ should be

$$\log K_{298.15} = -\frac{(-327.412 \times 1000)}{\ln 10 \times 8.314 \times 298.15}$$

$$= 57.3634$$

As $\log K_{298.15}$ for Reaction (B) is -13.9951,

$\log K_{298.15}$ for Reaction (A) should be

$$57.3634 + (-13.9951) = 43.37$$