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Experimental Determination of Solubilities of Brucite [$Mg(OH)_2(cr)$] In Na_2SO_4 Solutions with Borate to High Ionic Strength: Formation Constant for $MgSO_4(aq)$ and Pitzer Interaction Parameters for $MgB(OH)_4^{+}$—SO_4^{2-}

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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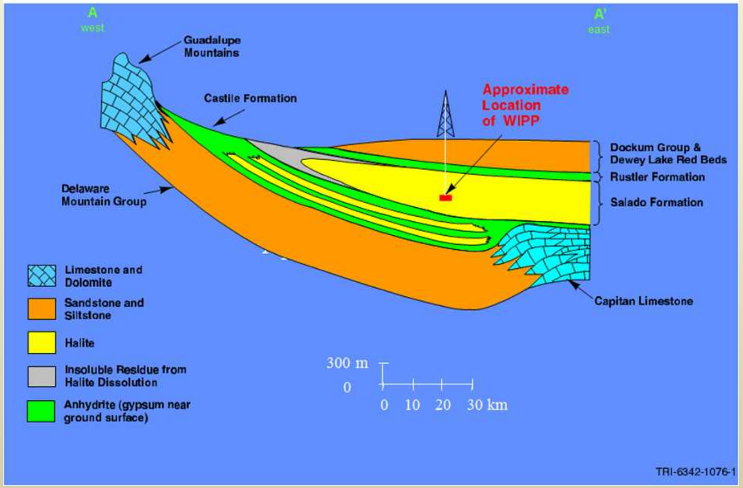
INTRODUCTION

- Industrial grade magnesium oxide (MgO) is the only engineered barrier certified by EPA for emplacement in the Waste Isolation Pilot Plant (WIPP). MgO hydrates as brucite [$Mg(OH)_2(cr)$] [1].
- $Mg(OH)_2$-based engineered barrier for the Asse repository, Germany [2].
- Sulfate is a major species in natural brines:
  - The sulfate concentrations in the WIPP brines
    - Generic Weep Brine (GWB): 0.203 mol•kg^{-1} and
    - U.S. Energy Research and Development Administration Well 6 (ERDA-6): 0.187 mol•kg^{-1} [1]
  - The sulfate concentrations in the Q-brine at the Asse: 0.2 mol•kg^{-1} [2]
  - In the low level and intermediate level radioactive sulfate liquid waste (LLW and ILW), they are very rich in SO_4^{2-} , up to 2.2 mol•kg^{-1} [3].



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[1] Y.-L. Xiong, A.C. Lord, Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with various ionic strengths, and their applications to nuclear waste isolation, Applied Geochemistry, Vol.23, p. 1634, 2008.

[2] Schuessler et al., 2002. Materials Research Society Meeting at Boston, MA

[3] A. Guerrero, S. Goni, M.-S. Hernandez, 2000. Thermodynamic solubility constant of $Ca(OH)_2$ in simulated radioactive sulfate liquid waste. Journal of American Ceramics Society, Vol. 83, p. 882, 2000.

INTRODUCTION (Continued)

- When magnesium alloys such as AZ91D and AZ30 are corroded in sulfate solutions, brucite forms [4-6].
  - Accurate knowledge of brucite solubility in sulfate solutions will provide a better understanding of corrosion behavior.
- Portland cement pastes are subject to $MgSO_4$ solution attack by formation of brucite [7].
  - Accurate knowledge of brucite solubility in sulfate solutions will provide a better understanding of sulfate attack to cement.
- Borate forms an aqueous complex with Mg^{2+}, $MgB(OH)_4^+$, which could increase solubility of brucite
- Solubilities of brucite in NaCl solutions have been well established, and they can serve as baseline solubilities.
- Accurate knowledge of brucite solubility in sulfate-bearing solutions will impact a wide range of fields.
- In this work, we investigate solubilities of brucite in Na_2SO_4 solutions in the presence of borate, with a wide range of ionic strengths up to 5.4 mol•kg^{-1} under well-constrained conditions.

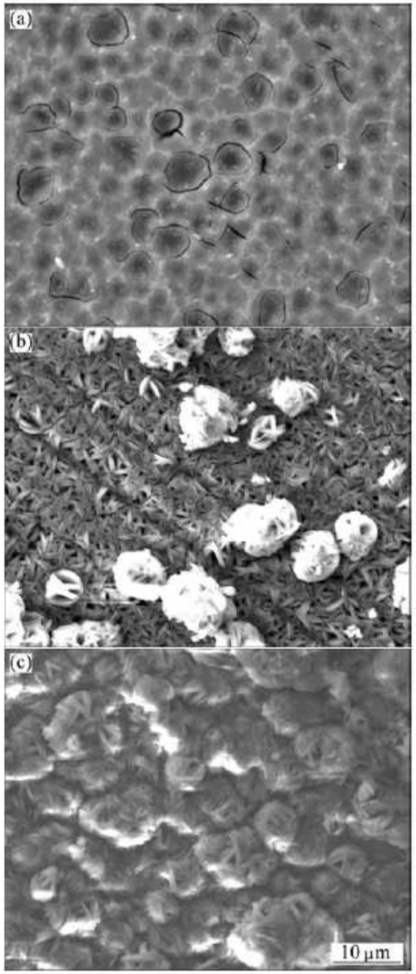

Fig.8 SEM images of specimens immersed in Na_2SO_4 solution with pH 9 for various time: (a) 96 h; (b) 330 h; (c) 480 h

Tian et al. (2011)

[4] Yang, L.J., Wei, Y.H., Hou, L.F. and Zhang, D., 2010. Corrosion behaviour of die-cast AZ91D magnesium alloy in aqueous sulphate solutions. *Corrosion Science*, *52*(2), pp.345-351.

[5] Zeng, R.C., Hu, Y., Guan, S.K., Cui, H.Z. and Han, E.H., 2014. Corrosion of magnesium alloy AZ31: The influence of bicarbonate, sulphate, hydrogen phosphate and dihydrogen phosphate ions in saline solution. *Corrosion Science*, *86*, pp.171-182.

[6] Tian, Y., Yang, L.J., Li, Y.F., Wei, Y.H., Hou, L.F., Li, Y.G. and Murakami, R.I., 2011. Corrosion behaviour of die-cast AZ91D magnesium alloys in sodium sulphate solutions with different pH values. *Transactions of Nonferrous Metals Society of China*, *21*(4), pp.912-920.

[7] Santhanam, M., Cohen, M.D. and Olek, J., 2001. Sulfate attack research—whither now?. *Cement and concrete research*, *31*(6), pp.845-851.

PURPOSE OF THIS STUDY

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- To measure solubility of $Mg(OH)_2$(cr) in Na_2SO_4 solutions with borate to high ionic strengths at 22.5^oC.
- To investigate the interactions of $MgB(OH)_4^+$ with sulfate, in addition to the interactions of magnesium with sulfate.
- To develop a Pitzer model to describe solubilities of brucite in Na_2SO_4 solutions in the presence of borate, with high ionic strengths
  - Fundamental understanding of brucite solubility behavior in Na_2SO_4 solutions

EXPERIMENTAL METHOD

- DI water for making supporting solutions: CO_2 are removed by following the procedure of Wood et al. [8].
- Experimental conditions: T = 22.5°C
- Starting material: Synthetic $Mg(OH)_2(cr)$ from Fisher Scientific
- pH_m are determined by applying correction factors to pH readings obtained using a pH meter.
  - $pH_m = pH_{ob} + A_m = pH_{ob} + A_M - \log \Theta$
- Mg(II) concentrations are analyzed using ICP-AES.
- Na concentrations are analyzed using ICP-AES.
- Sulfate concentrations are analyzed using IC.
- Approaching equilibrium from undersaturation.
- Supporting solutions: 0.01 to 1.8 $mol \bullet kg^{-1}$ Na_2SO_4 with 0.001 $mol \bullet kg^{-1}$ H_3BO_3

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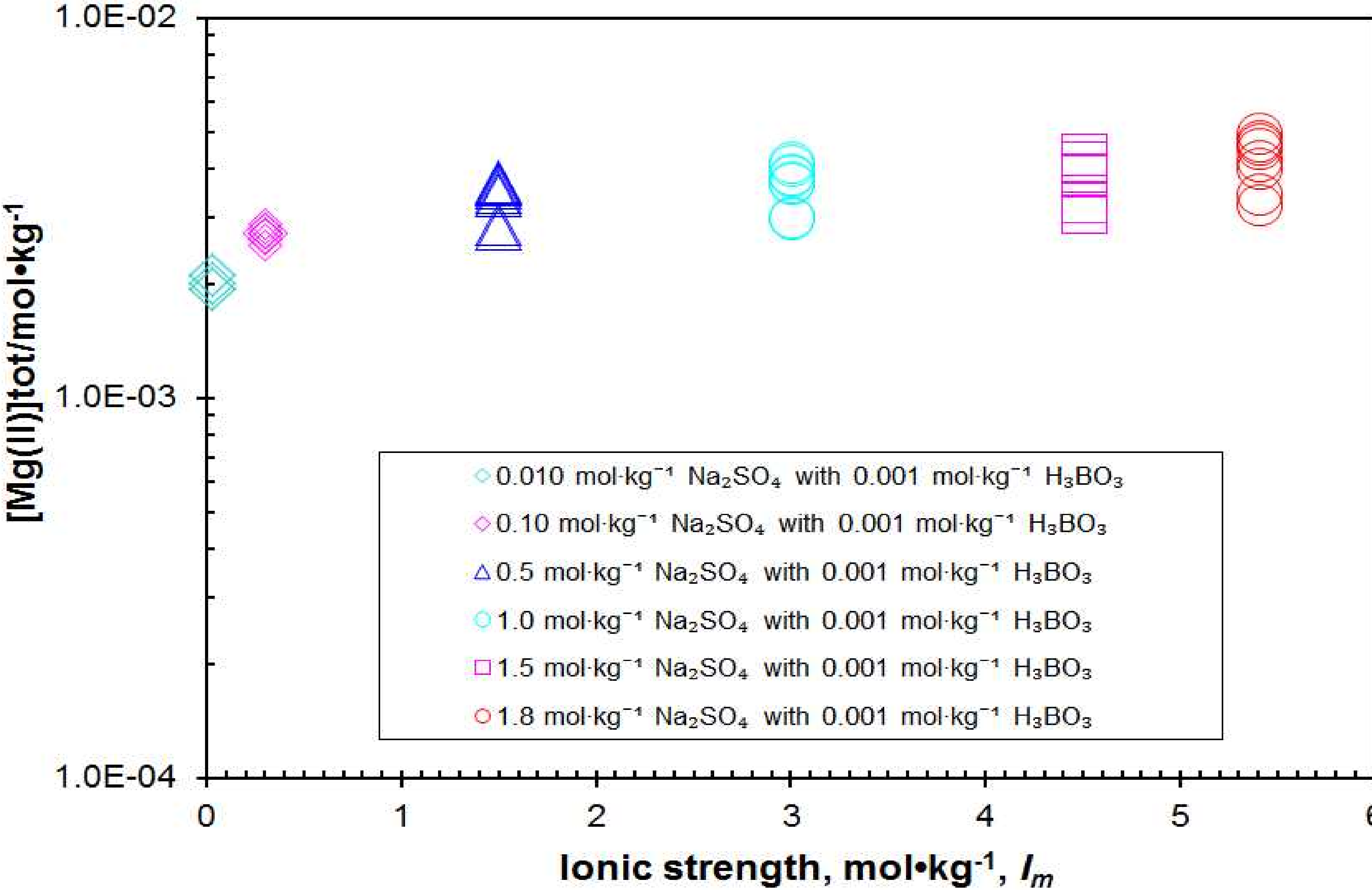
[8] S.A. Wood, D.A. Palmer, D.J. Wesolowski, and P. Bénézeth, In Hellmann, R. and Wood, S.A., ed., Special Publication 7, The Geochemical Society, pp. 229–256, 2002.

Experimental Results: As a function of I_m



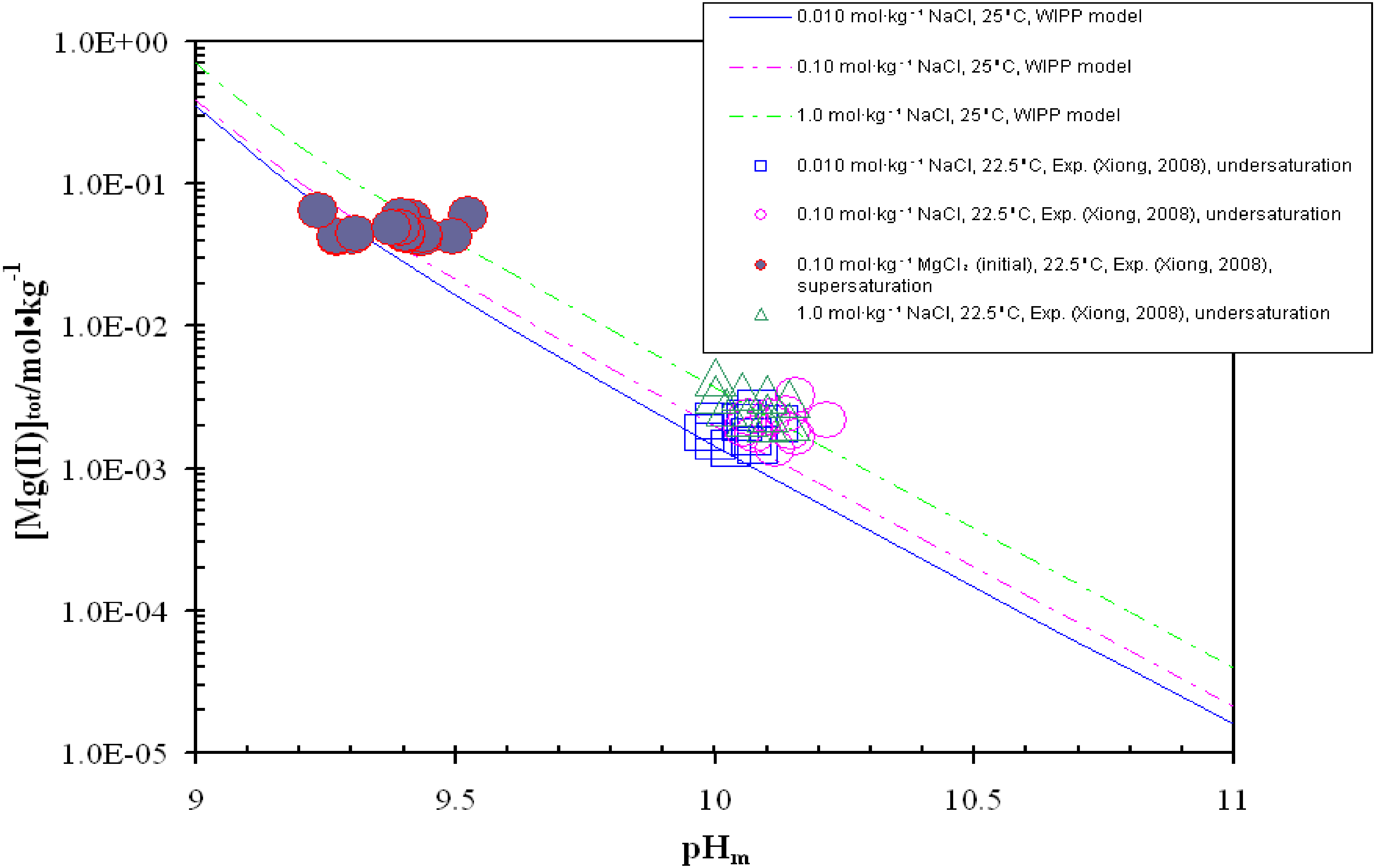
Baseline Solubility of Brucite in NaCl Solutions

Table 1. Key parameters describing solubility of brucite in NaCl solutions at 25°C (from the WIPP thermodynamic database, data0.fm1)

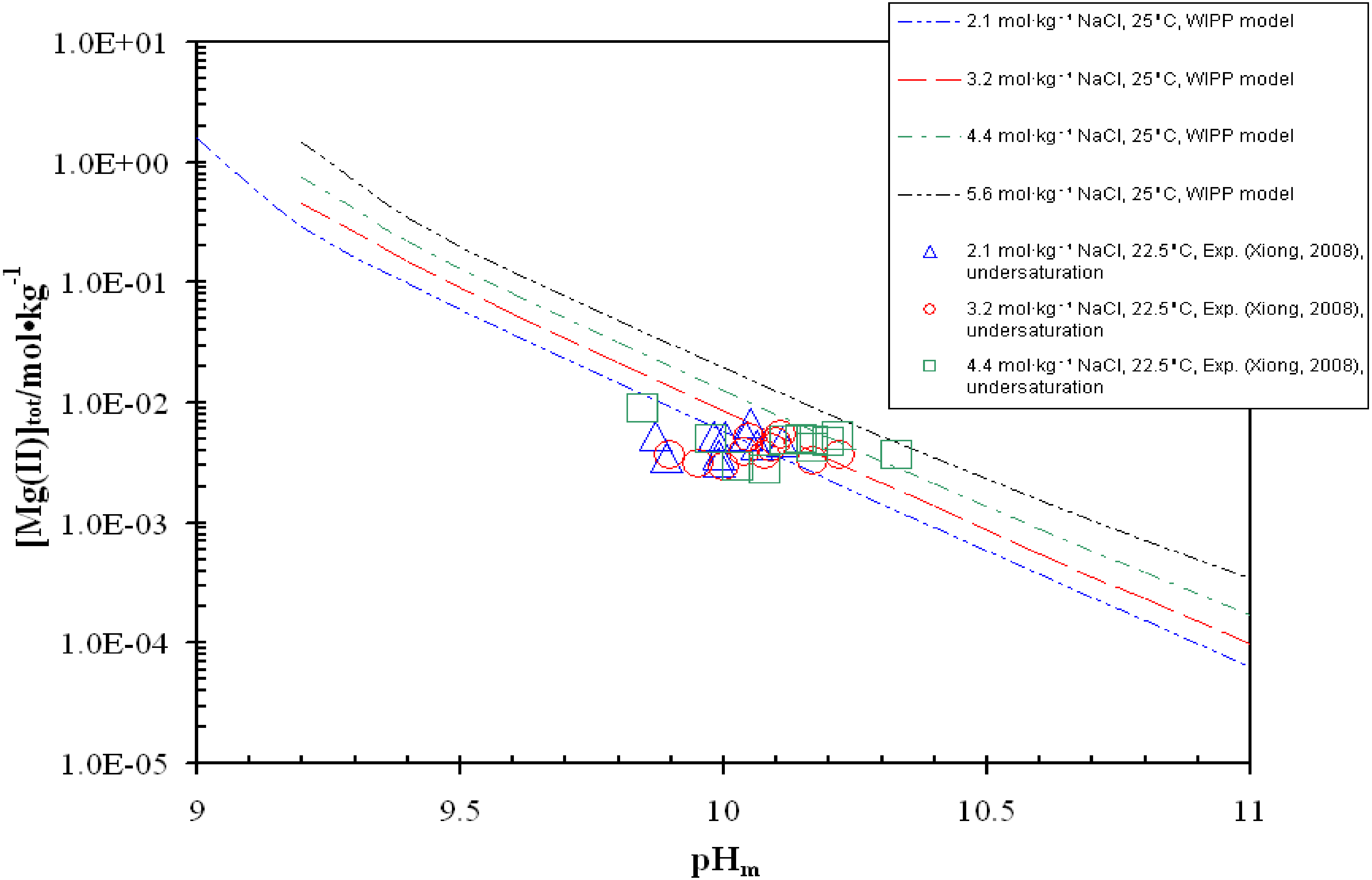
Pitzer Binary Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^+	Cl^-	0.0765	0.2664	0.00127
Mg^{2+}	Cl^-	0.35235	1.6815	0.00519
$MgOH^+$	Cl^-	–0.30	1.658	0
Na^+	OH^-	0.0864	0.253	0.0044
Pitzer Mixing Parameters				
Species, *i*	Species, *j*	Species, *k*	θ_{ij}	Ψ_{ijk}
Mg^{2+}	$MgOH^+$	Cl^-	0	0.028
Mg^{2+}	Na^+	Cl^-	0.07	–0.012
Equilibrium constants at infinite dilution for dissolution reaction of brucite and dissociation reaction of $MgOH^+$				
Reactions			$\log K^0$	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.1090	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.05 [A]	
$MgOH^+ + H^+ = Mg^{2+} + H_2O(l)$			11.8091	

[A] Xiong, Y.-L., 2008. Thermodynamic properties of brucite determined by solubility studies and their significance to nuclear waste isolation. ***Aquatic Geochemistry***, 14: 223–238.

Baseline Solubility of Brucite in NaCl Solutions (continued)



Baseline Solubility of Brucite in NaCl Solutions (continued)



Solubility of Brucite in Na_2SO_4 Solutions without $MgSO_4(aq)$

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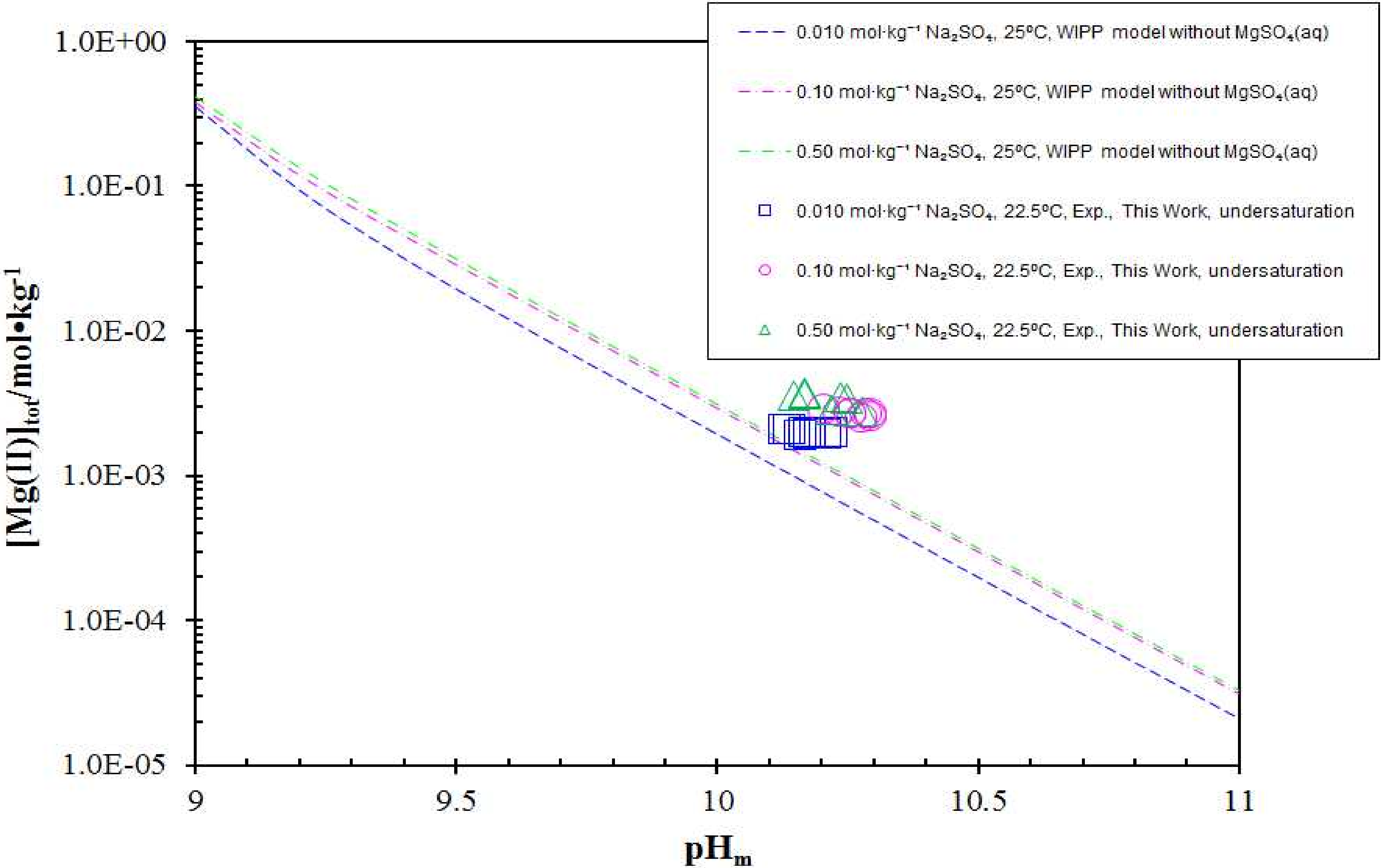
Table 2. Key parameters describing solubility of brucite in Na_2SO_4 solutions with borate at 25°C (from the WIPP thermodynamic database, data0.fm1)

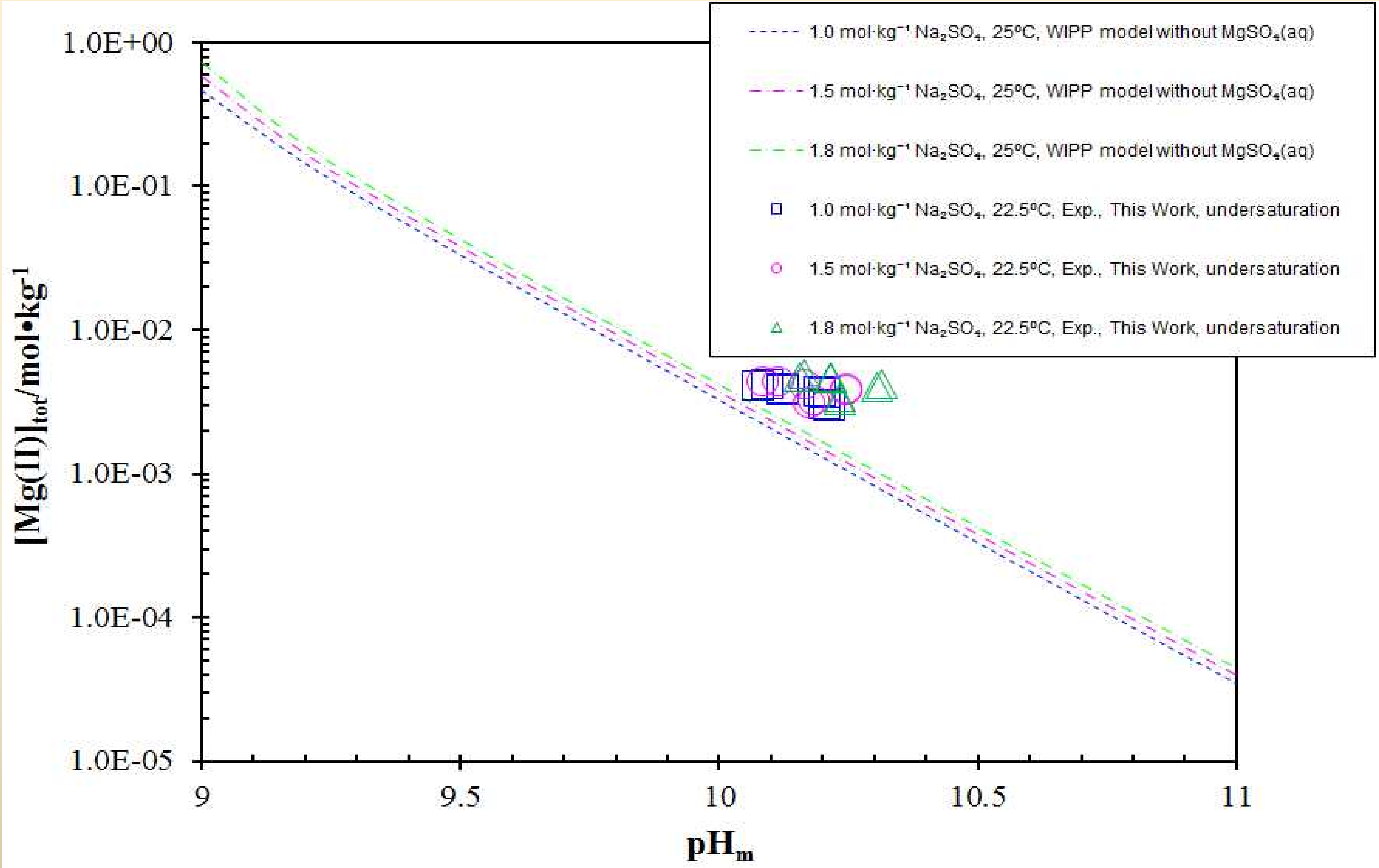
Pitzer Binary Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}/\beta^{(2)}$	C^{ϕ}
Mg^{2+}	SO_4^{2-}	0.221	3.343/-37.23	0.025
Na^{+}	SO_4^{2-}	0.01958	1.113	0.00497
Na^{+}	OH^{-}	0.0864	0.253	0.0044
Pitzer Mixing Parameters				
Species, *i*	Species, *j*	Species, *k*	θ_{ij}	Ψ_{ijk}
Mg^{2+}	Na^{+}	SO_4^{2-}	0.07	–0.015
Equilibrium constants at infinite dilution for dissolution reaction of brucite and dissociation reactions of $MgOH^{+}$ and $MgB(OH)_4^{+}$				
Reactions			$\log K^0$	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.1090	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.05 [A]	
$MgOH^+ + H^+ = Mg^{2+} + H_2O(l)$			11.8091	
$MgB(OH)_4^+ = Mg^{2+} + B(OH)_4^-$			-1.3993	

[A] Xiong, Y.-L., 2008. Thermodynamic properties of brucite determined by solubility studies and their significance to nuclear waste isolation. ***Aquatic Geochemistry***, 14: 223–238.

Solubility of Brucite in Na_2SO_4 Solutions without $MgSO_4(aq)$



Solubility of Brucite in Na_2SO_4 Solutions without $MgSO_4(aq)$



Solubility of Brucite in Na_2SO_4 Solutions with $MgSO_4(aq)$

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Table 3. Key parameters describing solubility of brucite in Na_2SO_4 solutions with borate and $MgSO_4(aq)$ at 25°C (from the updated WIPP thermodynamic database, data0.fm2)

Pitzer Binary Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}/\beta^{(2)}$	C^{ϕ}
Mg^{2+}	SO_4^{2-}	0.221	3.343/-37.23	0.025
Na^+	SO_4^{2-}	0.01958	1.113	0.00497
Na^+	OH^-	0.0864	0.253	0.0044
$MgB(OH)_4^+$	SO_4^{2-}	0.7806	1.74	0
Pitzer Mixing Parameters				
Species, *i*	Species, *j*	Species, *k*	θ_{ij}	Ψ_{ijk}
Mg^{2+}	Na^+	SO_4^{2-}	0.07	–0.015
Na^+	$MgB(OH)_4^+$		–0.2975	
Equilibrium constants at infinite dilution for dissolution reaction of brucite and dissociation reactions of $MgOH^+$, $MgB(OH)_4^+$ and $MgSO_4(aq)$				
Reactions			$\log K^0$	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.1090	
$Mg(OH)_2(cr) + 2H^+ = Mg^{2+} + 2H_2O(l)$			17.05 [A]	
$MgOH^+ + H^+ = Mg^{2+} + H_2O(l)$			11.8091	
$MgB(OH)_4^+ = Mg^{2+} + B(OH)_4^-$			–1.3993	
$MgSO_4(aq) = Mg^{2+} + SO_4^{2-}$			–2.38	

[A] Xiong, Y.-L., 2008. Thermodynamic properties of brucite determined by solubility studies and their significance to nuclear waste isolation. ***Aquatic Geochemistry***, 14: 223–238.

Solubility of Brucite in Na_2SO_4 Solutions with $MgSO_4$(aq)

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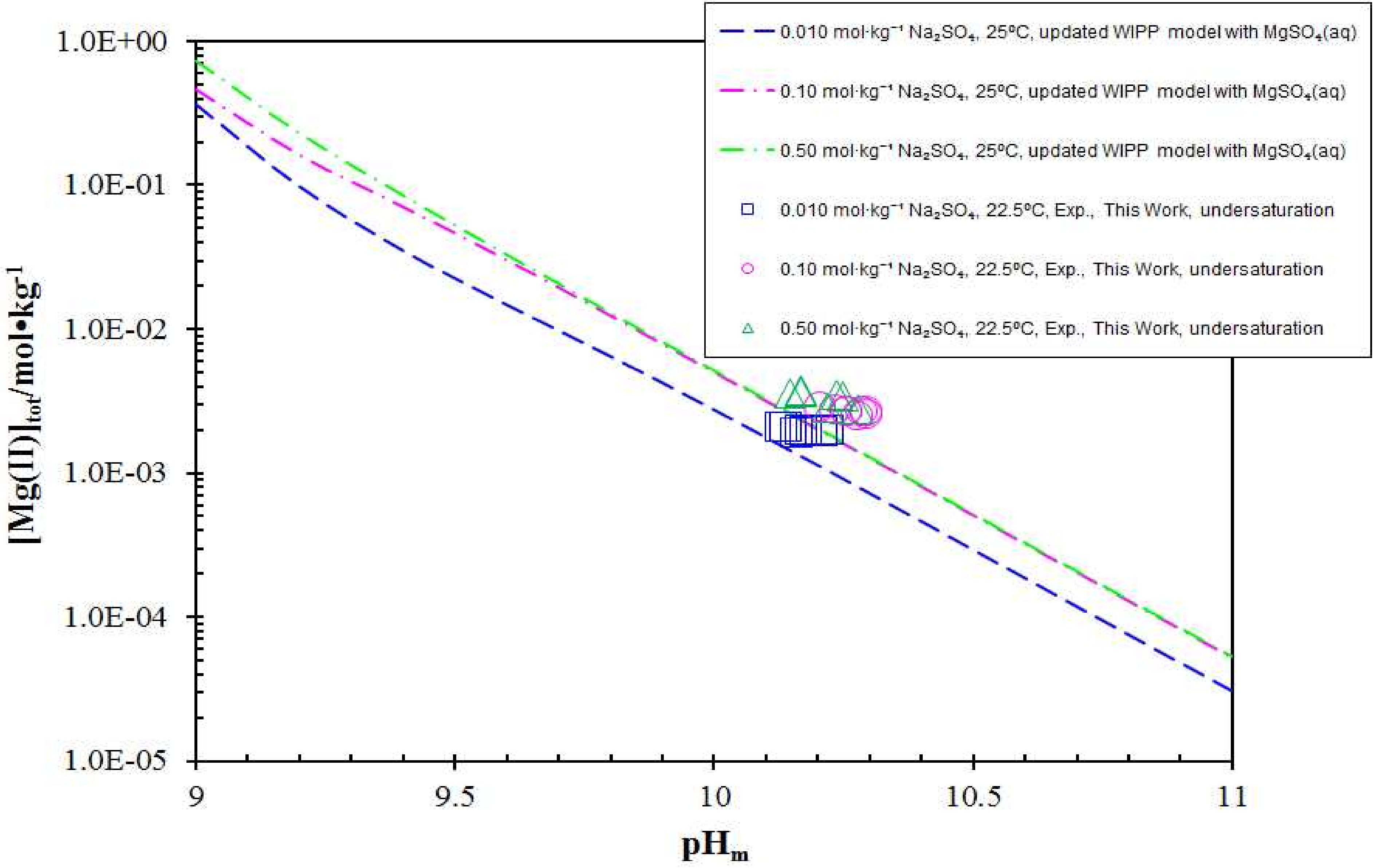

Solubility of Brucite in Na_2SO_4 Solutions with $MgSO_4(aq)$

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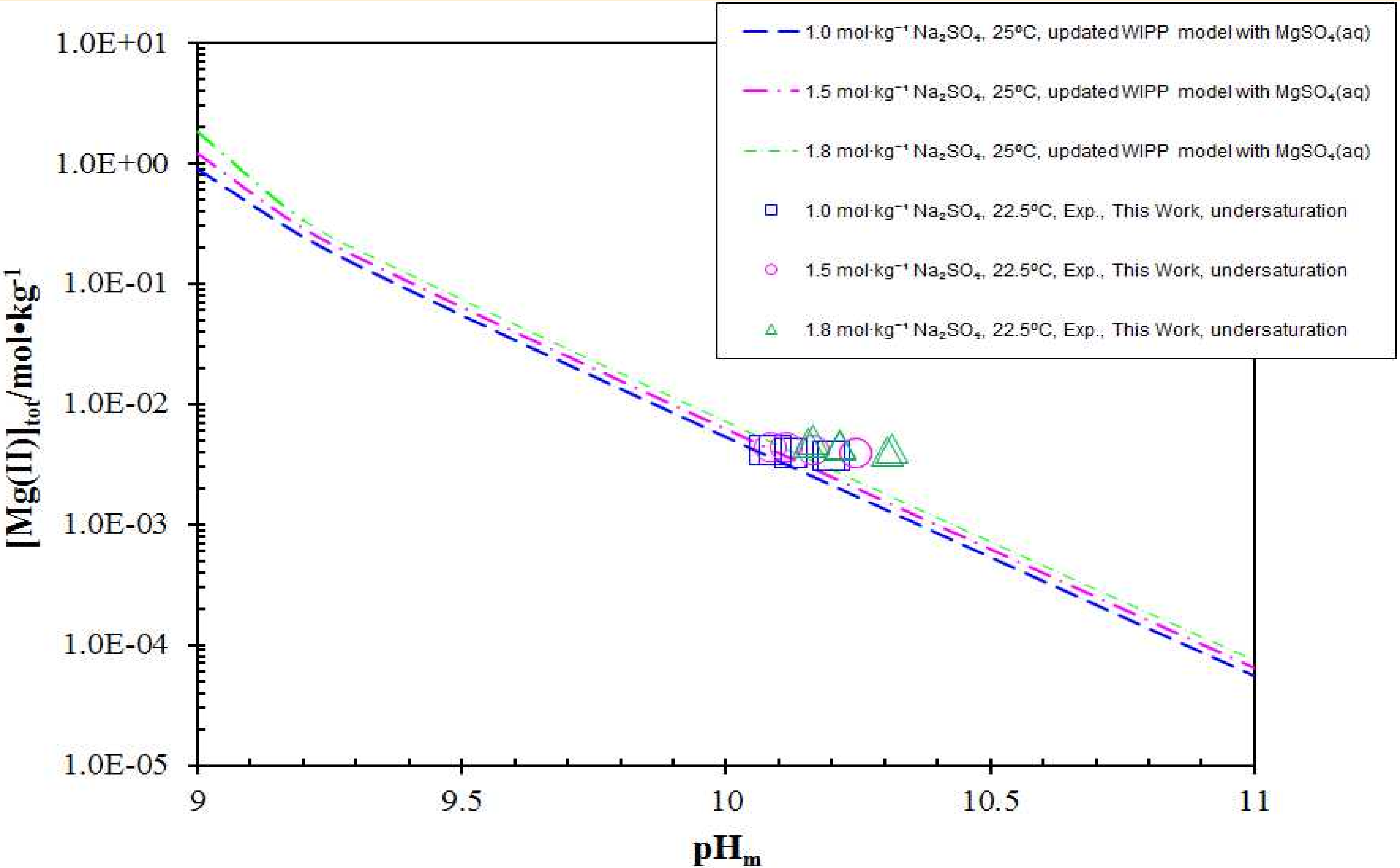

$MgSO_4$(aq): Comparison with the literature data

- Kratsis et al. (2001)
  - Potentiometric study of association constants for $MgSO_4$(aq)

    $Mg^{2+} + SO_4^{2-} = MgSO_4(aq)$
  - CsCl, up to 6.0 mol•dm^{-3}
  - Magnesium ion-selective electrode
  - Extended Debye-Hückel equation for extrapolation
  - $\log \beta^0 = 2.38 \pm 0.03$
- The $\log \beta^0$ obtained in this work via modeling solubility of brucite in Na_2SO_4 with borate
  - Excellent agreement with Kratsis et al. (2001)

Kratsis, S., Hefter, G., May, P., 2001. **Potentiometric Study of the Association of Magnesium and Sulfate Ions at 25°C in High Ionic Strength Media. Journal of Solution Chemistry, 30:19-29**

Summary

- Solubility experiments concerning brucite have been conducted at Sandia National Laboratories Carlsbad Facility
  - in 0.01 to 1.8 mol•kg^{-1} Na_2SO_4 with 0.001 mol•kg^{-1} borate (initially as H_3BO_3) at 22.5°C.
- The updated WIPP model developed based on our experimental data
  - can accurately predict solubility of brucite in sulfate solutions to high ionic strengths.
  - It would have a wide range of applications such as:
    - Nuclear waste management (e.g., WIPP, Asse)
    - Portlandite cement degradation by attack from $MgSO_4$ solutions
    - Corrosion of magnesium-based alloys in sulfate solutions