

# A Pitzer Model for Hydrolysis of Lead to High Ionic Strength: Applications to Low Temperature Geochemical Processes

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# Outline of Presentation

- Introduction
- Objective of This Work
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- Experimental Results
- The Pitzer Model
- Summary

# INTRODUCTION

- An accurate understanding of solution chemistry/geochemistry of lead over a wide range of ionic strengths is important to many fields.
- In the field of mineral deposits,
  - Non-sulfide lead and zinc deposits: supergene alteration of various types of sulfidic lead and zinc deposits; solutions with multiple components including sulfate and chloride responsible for transport and deposition of lead and zinc
- In the field of nuclear waste management,
  - Significant inventories of lead in nuclear waste stream destined for disposal in geological repositories.
    - In the Waste Isolation Pilot Plant (WIPP), the lead inventory was estimated as 1,256,796 kg
  - Lead in geological repositories is likely to interact with brines that are part of the geological formations.
  - Cerussite ( $\text{PbCO}_3$ ) as a waste form for geological disposal of radioactive  $^{14}\text{C}$  generated in the heavy-water moderator systems of nuclear reactors
- In the field of environmental management,
  - Lead is present in soils and shooting ranges as a contaminant.
  - Lead is present in mine tailings as a contaminant.
  - Lead in acid mine drainages
- In the field of recycling lead
  - Lead acid batteries in concentrated solutions

# THE WASTE ISOLATION PILOT PLANT (WIPP)



# WIPP



TRI-6342-1076-1

# WIPP Brines

## Appendix B Concentration Scales in Molarity (Moles/L Solution) and Molality (Moles/kg H<sub>2</sub>O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines

Chemical Species	GWB	GWB	ERDA-6	ERDA-6
	Moles/L sol'n	Moles/kg H <sub>2</sub> O	Moles/L sol'n	Moles/kg H <sub>2</sub> O
Na <sup>+</sup>	3.53	3.98	4.85	5.44
K <sup>+</sup>	0.467	0.526	9.70×10 <sup>-2</sup>	0.109
Li <sup>+</sup>	4.48×10 <sup>-3</sup>	5.05×10 <sup>-3</sup>	None	None
Ca <sup>2+</sup>	1.38×10 <sup>-2</sup>	1.56×10 <sup>-2</sup>	1.20×10 <sup>-2</sup>	1.34×10 <sup>-2</sup>
Mg <sup>2+</sup>	1.02	1.15	1.90×10 <sup>-2</sup>	2.13×10 <sup>-2</sup>
Cl <sup>-</sup>	5.61	6.32	4.64	5.20
Br <sup>-</sup>	2.66×10 <sup>-2</sup>	3.00×10 <sup>-2</sup>	1.10×10 <sup>-2</sup>	1.23×10 <sup>-2</sup>
SO <sub>4</sub> <sup>2-</sup>	0.178	0.200	0.167	0.187
B <sub>4</sub> O <sub>7</sub> <sup>2-</sup>	3.95×10 <sup>-2</sup>	4.45×10 <sup>-2</sup>	1.57×10 <sup>-2</sup>	1.76×10 <sup>-2</sup>

From Xiong (2008)

Xiong (2008), Preparing synthetic brines for geochemical experiments, WIPP SP 20-4

# Objective of This Study

- To determine solubilities of PbO(cr), litharge, in a wide range of ionic strengths.
- Based on solubility data obtained, to develop a Pitzer model to describe accurately the  $\text{Na}^+ - \text{Pb}^{2+} - \text{Cl}^- - \text{ClO}_4^- - \text{SO}_4^{2-}$  system.
- Modeling platform: EQ3/6 Version 8.0a (Wolery, Xiong, Long, 2010; Xiong, 2011)

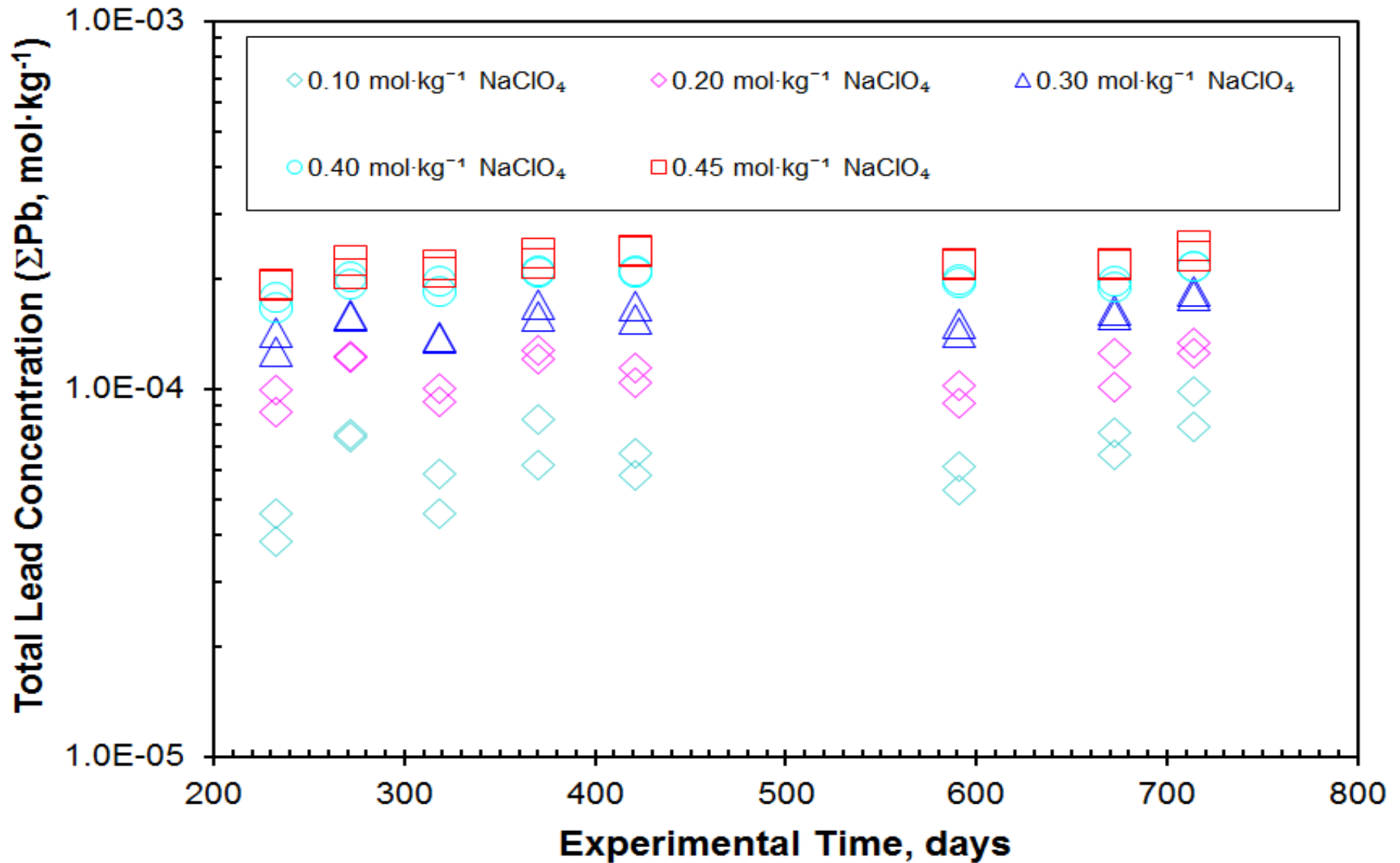
Wolery, T.J., Xiong, Y.-L., and Long, J., 2010. Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10. Carlsbad, NM: Sandia National laboratories. ERMS 550239.

Xiong, Y.-L., 2011. WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1, Document Version 8.20. Supersedes ERMS 550239. Carlsbad, NM. Sandia National Laboratories. ERMS 555358.

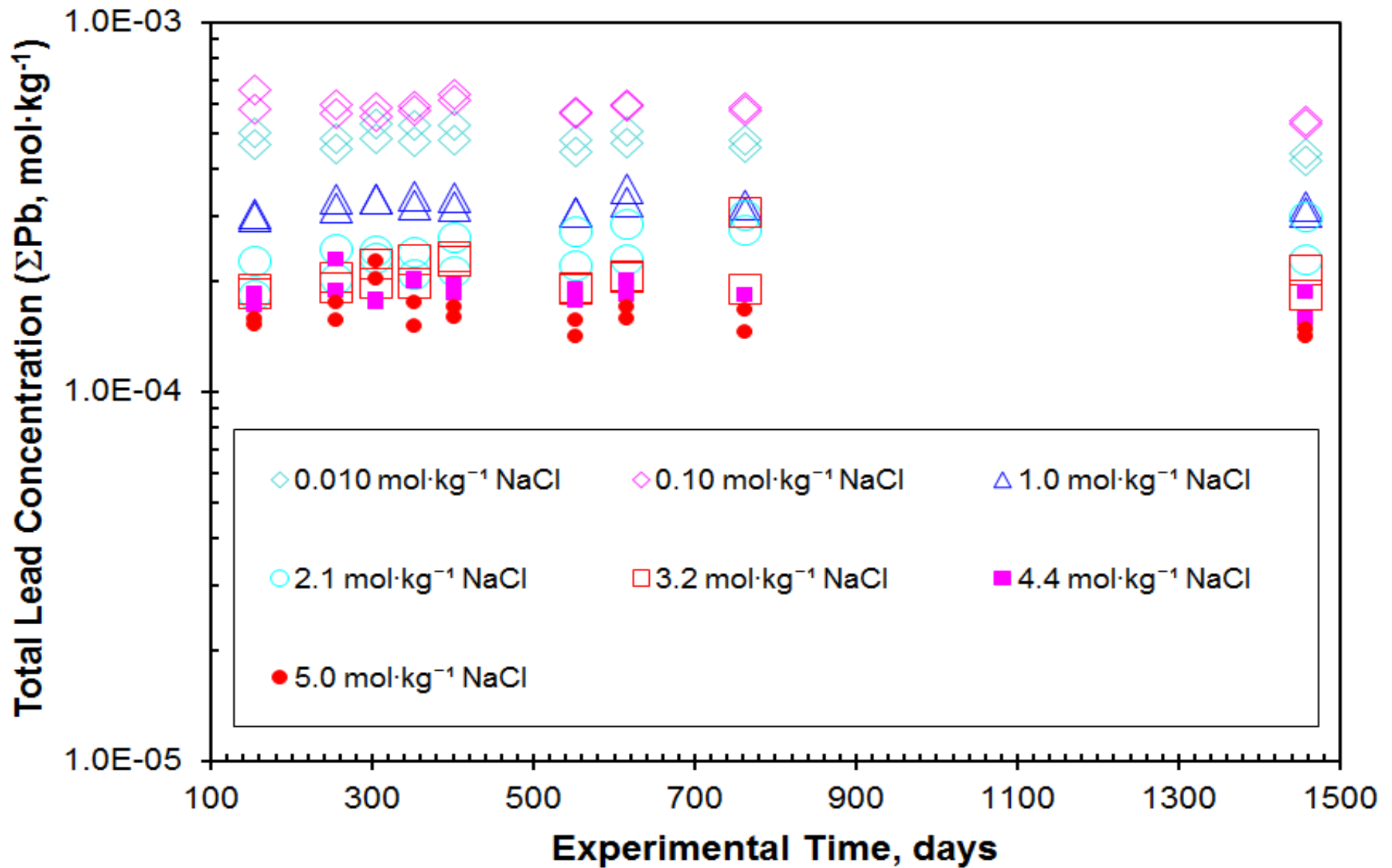
# Experimental Method

- Experimental conditions:  $T = 22.5 \pm 0.5 \text{ }^\circ\text{C}$
- Starting material: high purity  $\text{PbO}(\text{cr})$  from MP Biomedicals
- Long-term undersaturation experiments
- Supporting solutions:
  - $0.10\text{-}0.45 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$
  - $0.010\text{-}5.0 \text{ mol}\cdot\text{kg}^{-1} \text{ NaCl}$
  - $0.010\text{-}1.8 \text{ mol}\cdot\text{kg}^{-1} \text{ Na}_2\text{SO}_4$  with ionic strengths up to  $5.4 \text{ mol}\cdot\text{kg}^{-1}$
- Pb and Na concentrations determined by using inductively coupled plasma atomic emission spectrometer (ICP-AES). Anions by using ion chromatograph (IC)
- pCH measured using pH electrode with correction factors

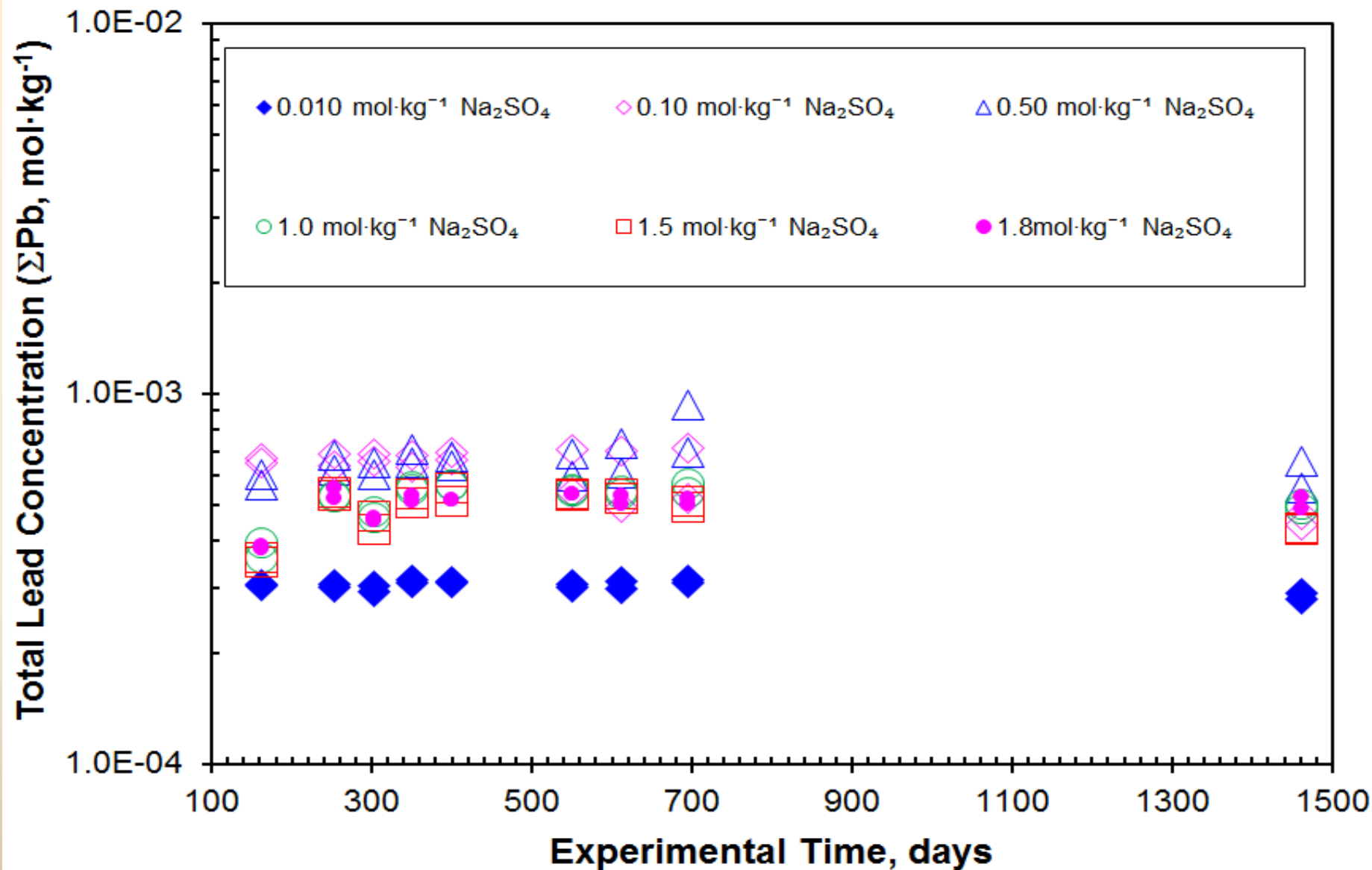
# Experimental Results



# Experimental Results



# Experimental Results



# Pitzer Model

Table 1. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the  $\text{Na}^+ - \text{Pb}^{2+} - \text{Cl}^- - \text{ClO}_4^- - \text{SO}_4^{2-}$  system

Pitzer Parameters					
Species, $i$	Species, $j$	$\beta^{(0)}$	$\beta^{(1), A}$	$C^\phi$	References
$\text{Na}^+$	$\text{Pb}(\text{OH})_3^-$	0.3354	0.29	0	This work
$\text{PbOH}^+$	$\text{ClO}_4^-$	0	0	0	This work
$\text{PbOH}^+$	$\text{Cl}^-$	0	0	0	This work
$\text{Na}^+$	$\text{PbCl}_3^-$	-0.0605	0	0.091	Xiong et al. (2013)
Pitzer Mixing Interaction Parameters and Interaction Parameters Involving Neutral Species					
Species $i$	Species $j$	Species $k$	$\theta_{ij}$	$\psi_{ijk}$	References
$\text{ClO}_4^-$	$\text{Pb}(\text{OH})_2(\text{aq})$		0		This work
$\text{Cl}^-$	$\text{Pb}(\text{OH})_2(\text{aq})$		-0.1721		This work
$\text{Na}^+$	$\text{Pb}(\text{OH})_2(\text{aq})$		0		This work
$\text{SO}_4^{2-}$	$\text{Pb}(\text{OH})_2(\text{aq})$		-0.5581		This work
$\text{SO}_4^{2-}$	$\text{Pb}(\text{OH})_3^-$		-0.4046		This work
$\text{Na}^+$	$\text{PbCl}_2(\text{aq})$		-0.11		Felmy et al. (2000)
$\text{Cl}^-$	$\text{PbCl}_3^-$		0		This work
$\text{Na}^+$	$\text{Pb}^{2+}$		0.10		Felmy et al. (2000)
$\text{Na}^+$	$\text{PbCl}_2(\text{aq})$	$\text{Cl}^-$		0	Xiong et al. (2013)

# Pitzer Model (Table 1 Continued)

Equilibrium Constants for Dissolution Reaction of Litharge and Formation Reactions for Lead Hydroxyl Species		
Reaction	$\log K_{sp}$ and $\log \beta_1$ , $\log \beta_2$ , $\log \beta_3$ at 25 °C	References
$\text{PbO}(\text{cr}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{O}(\text{l})$	12.59	Data0.ymp.R2 (Wolery & Jarek, 2003)*
$\text{Pb}^{2+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{PbOH}^+ + \text{H}^+$	-7.46	Powell et al. (2009)
$\text{Pb}^{2+} + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Pb}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-17.05	This work
$\text{Pb}^{2+} + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	-27.99	This work

<sup>A</sup> Values are set according to AP-154, Revision 2 (Xiong, 2013).

Felmy, A.R., Onishi, L.M., Foster, N.S., Rustad, J.R., Rai, D. and Mason, M.J., 2000. An aqueous thermodynamic model for the  $\text{Pb}^{2+}$ - $\text{Na}^+$ - $\text{K}^+$ - $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{H}^+$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$  system to high concentration: application to WIPP brines. *Geochimica et Cosmochimica Acta*, 64(21), pp.3615-3628.

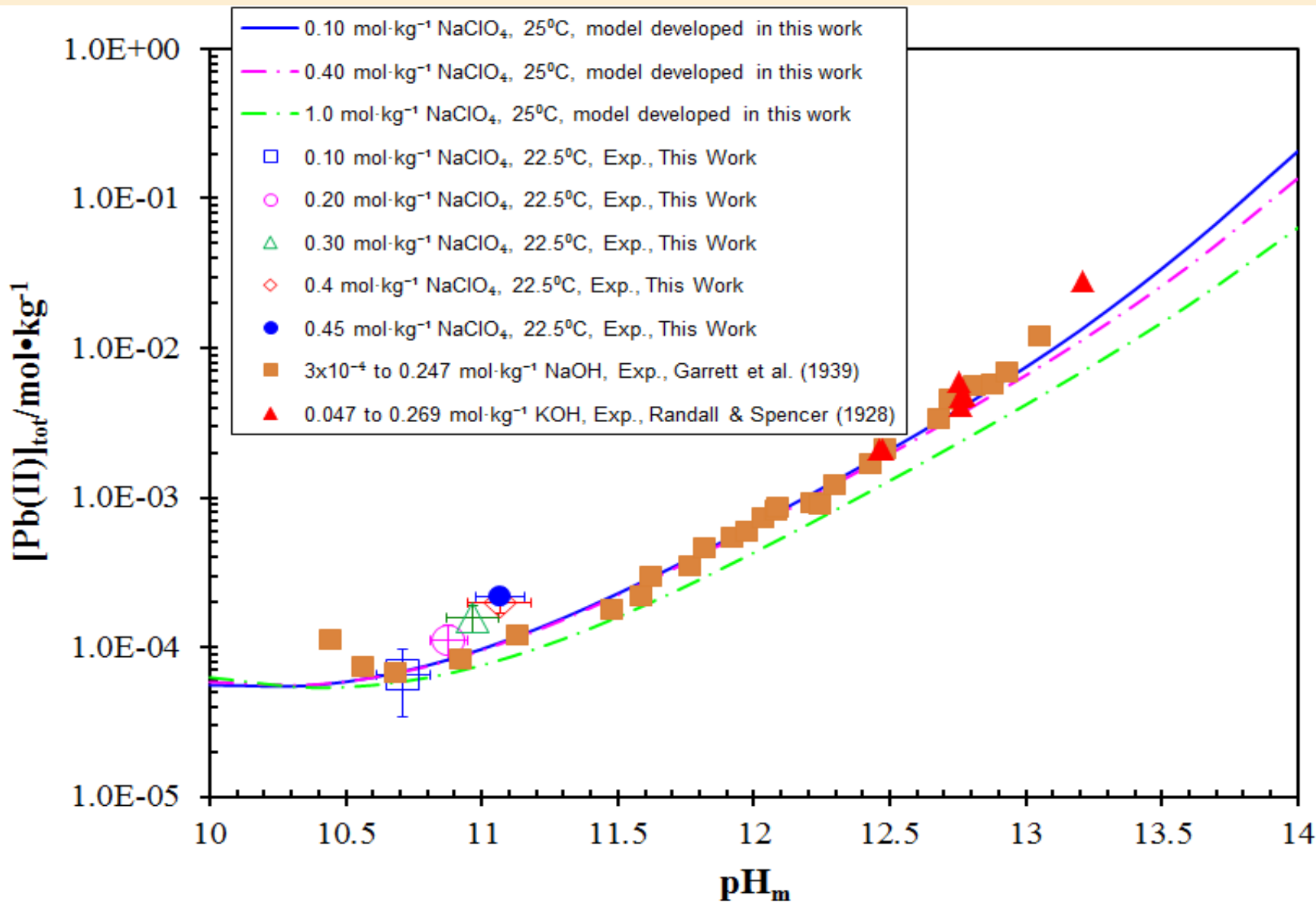
Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Luez, A.-K., Sjöberg, S., and Wanner, H., 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The  $\text{Pb}^{2+}$  +  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  systems (IUPAC Technical Report). *Pure and Applied Chemistry* 81 (12), 2425-2476.

Wolery, T.J., Jarek, R.L., 2003. Software user's manual EQ3/6 (version 8.0). Sandia National Laboratories, Albuquerque/New Mexico.

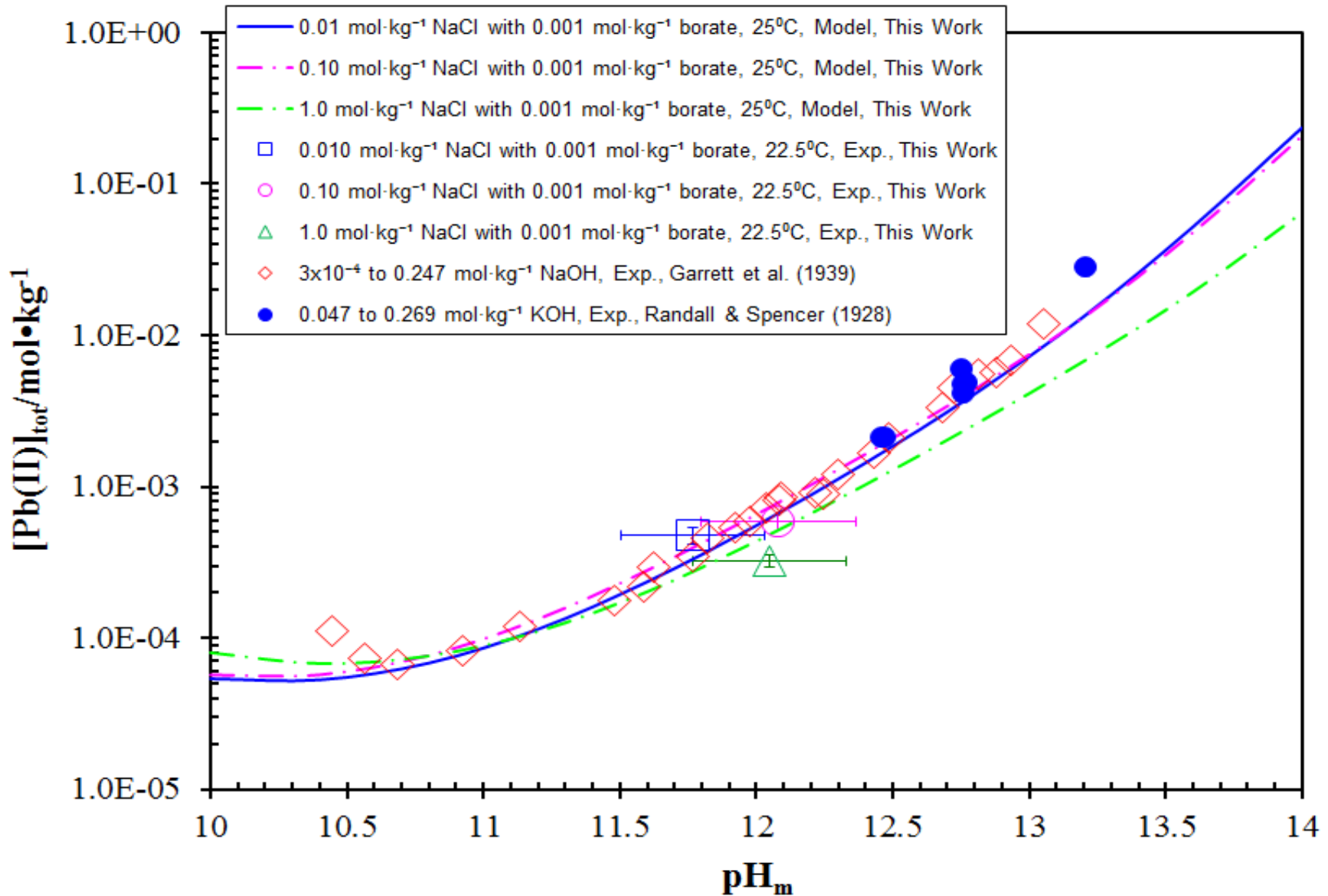
Xiong, Y.-L., 2013. Sandia National Laboratories Waste Isolation Pilot Plant (WIPP) Analysis AP-155, Revision 2, Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA. Carlsbad, NM: Sandia National Laboratories. ERMS 561114.

Xiong, Y., Kirkes, L., Westfall, T. and Roselle, R., 2013. Experimental determination of solubilities of lead oxalate ( $\text{PbC}_2\text{O}_4(\text{cr})$ ) in a NaCl medium to high ionic strengths, and the importance of lead oxalate in low temperature environments. *Chemical Geology*, 342, pp.128-137.

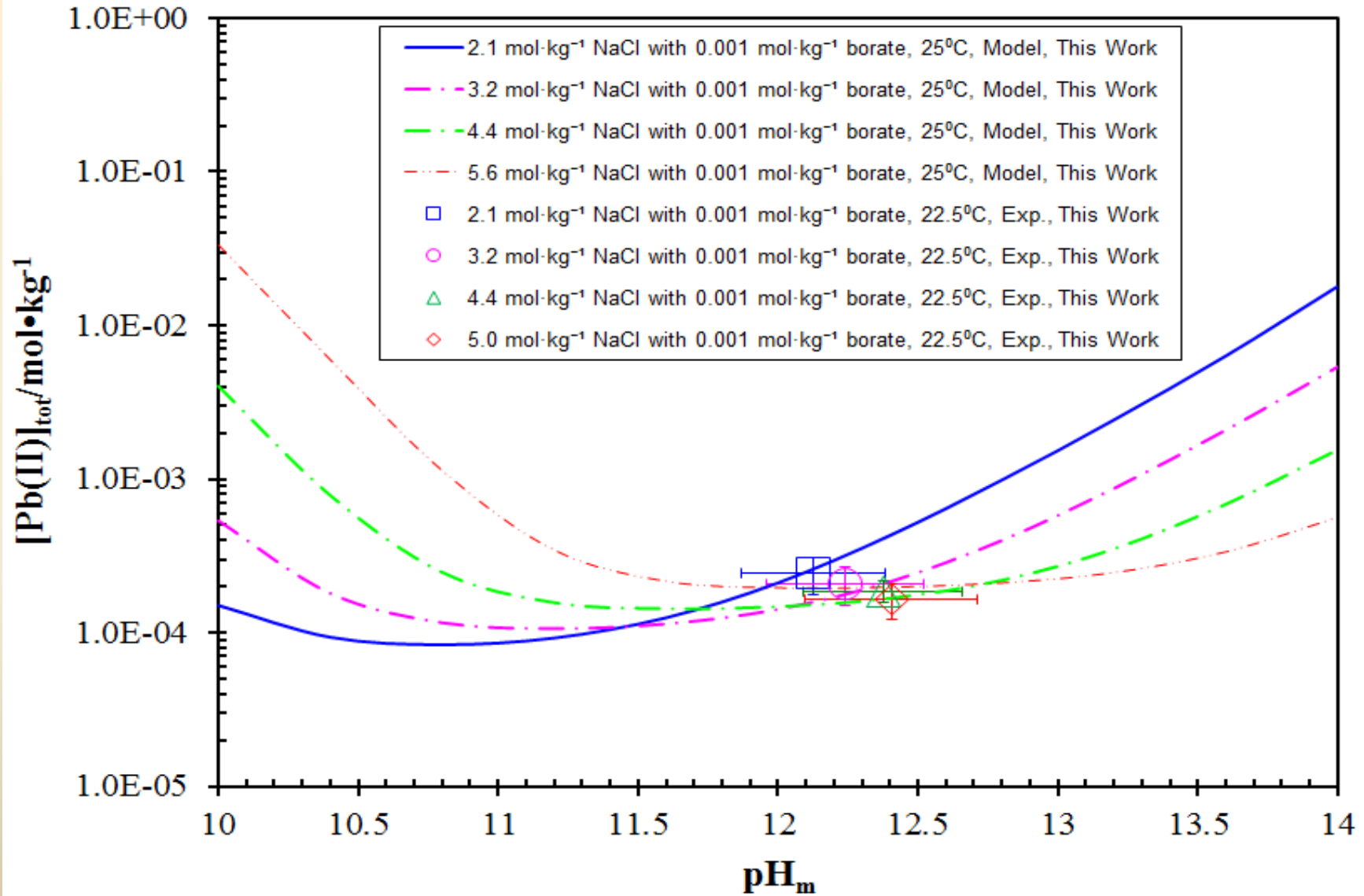
# Model Verification/Validation



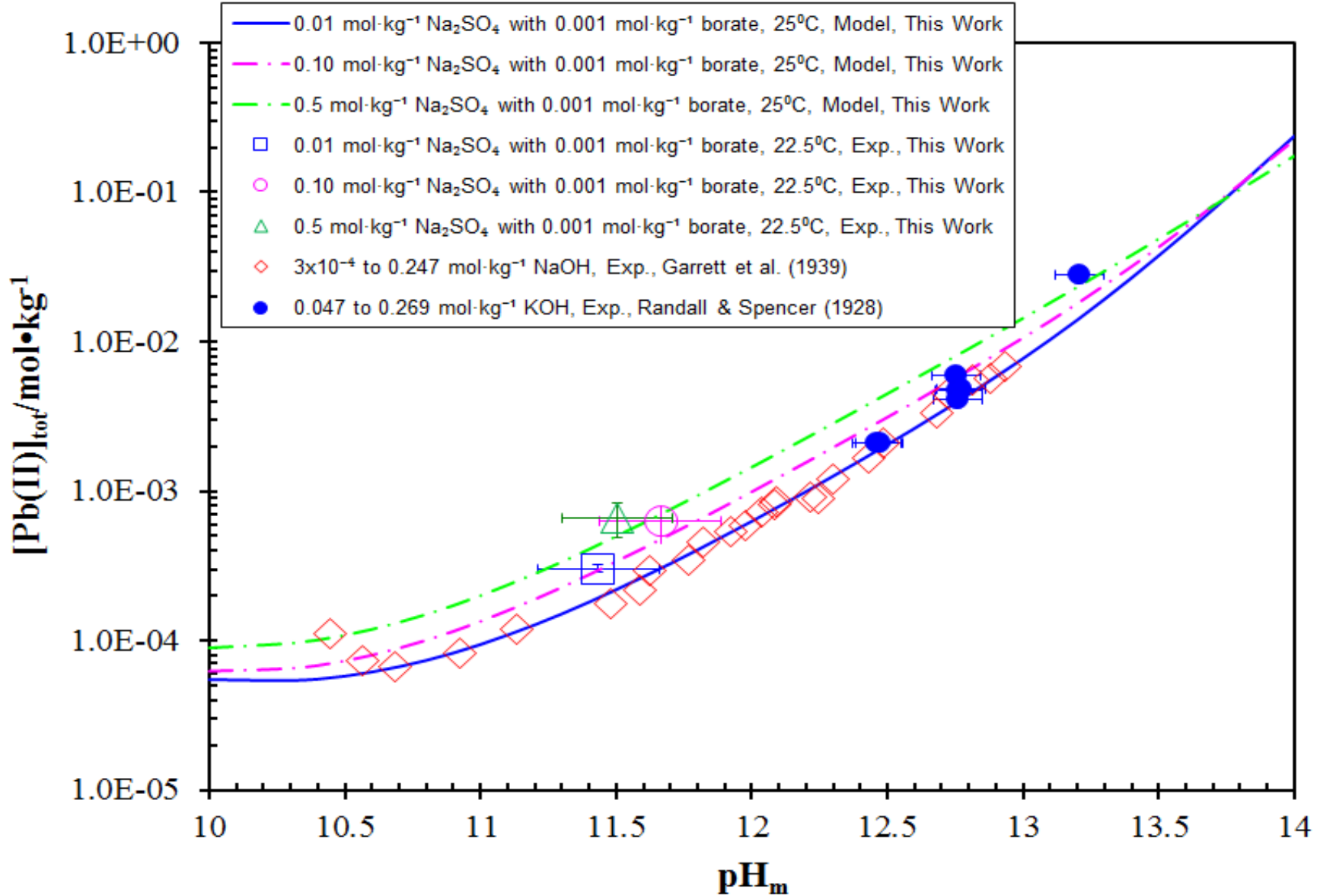
# Model Verification/Validation (Continued)



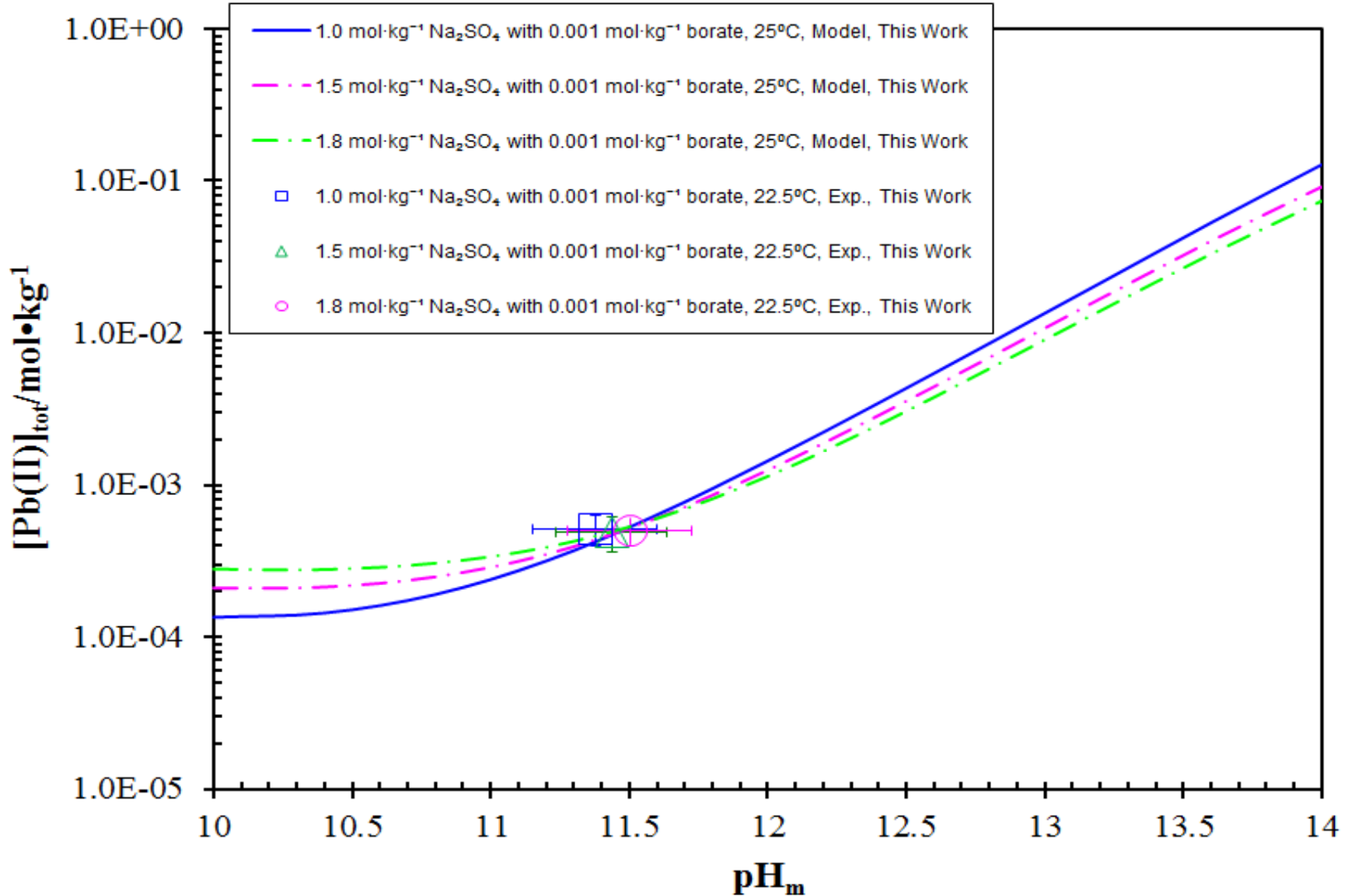
# Model Verification/Validation (Continued)



# Model Verification/Validation (Continued)



# Model Verification/Validation (Continued)



# Summary

- In this study,
  - We experimentally determined solubilities of PbO(cr) in NaClO<sub>4</sub>, NaCl, and Na<sub>2</sub>SO<sub>4</sub> solutions in a wide range of ionic strengths in our long-term experiments.
  - Based on our experimental data, we developed a Pitzer model that can accurately describe lead chemistry in Na<sup>+</sup>—Pb<sup>2+</sup>—Cl<sup>-</sup>—ClO<sub>4</sub><sup>-</sup>—SO<sub>4</sub><sup>2-</sup> system.
- In combination with our previous work on lead oxalate (Xiong et al., 2013) and lead carbonate (Xiong, 2015), lead in low temperature geochemical processes in a wide range ionic strengths can be modeled, including:
  - Geological repositories
  - Acid mine drainages
  - Non-sulfide Pb-Zn deposits
  - Recycling lead acid batteries in alkaline media

Xiong, Y., Kirkes, L., Westfall, T. and Roselle, R., 2013. Experimental determination of solubilities of lead oxalate (PbC<sub>2</sub>O<sub>4</sub>(cr)) in a NaCl medium to high ionic strengths, and the importance of lead oxalate in low temperature environments. *Chemical Geology*, 342, pp.128-137.

Xiong, Y.-L., 2015. Experimental determination of lead carbonate solubility at high ionic strengths: a Pitzer model description. *Monatshefte fuer Chemie/Chemical Monthly*, 146:1433-1443.