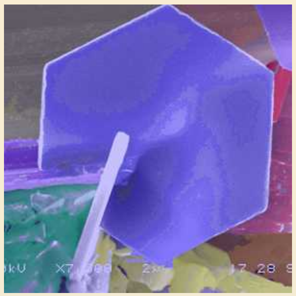
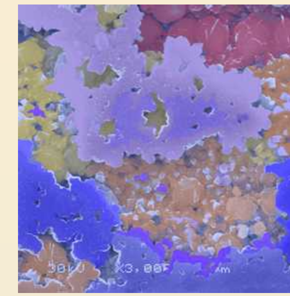
SAND2013-2885P

Exceptional service in the national interest

Sandia National Laboratories







Speciation and Solubility of Aluminum in High Ionic Strength Solutions at Elevated Temperatures to 250 ^{o}C

Yongliang Xiong, Ph.D.

Repository Performance Department, 6212

This research is funded by the Salt Research and Development (Salt R&D) programs administered by the Office of Nuclear Energy (NE) of the U.S Department of Energy.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Outline of Presentation

- Introduction
  - Importance of Studying Aqueous Chemistry/Geochemistry of Aluminum at Elevated Temperatures
  - Speciation of Aluminum at 25°C and 150°C
  - The Pitzer Activity Coefficient Model
- Objectives of This Work
- Results
  - log K
  - Binary Interaction Parameters for Na^{+}—$Al(OH)_4^{-}$
- Model Verification/Validation
- Summary

INTRODUCTION: Aluminum

- Aluminum is the third most abundant element in the earth's crust, forming numerous minerals.
- Borosilicate glasses in which aluminum is a major component, are strong candidate waste forms for immobilization of high level nuclear waste (HLW).
- Sodalite, $Na_8(Al_6Si_6O_{24})(OH, Cl, I)_2$, is a candidate waste form for electrorefinery contaminated salt wastes and radioactive iodine waste.
- Hanford and Savannah River Tank wastes have significant inventories of aluminum and silica.
- Solutions associated with geological repositories such as those in salt formations and deep boreholes are of high ionic strengths.

INTRODUCTION: Aluminum Speciation at 25°C

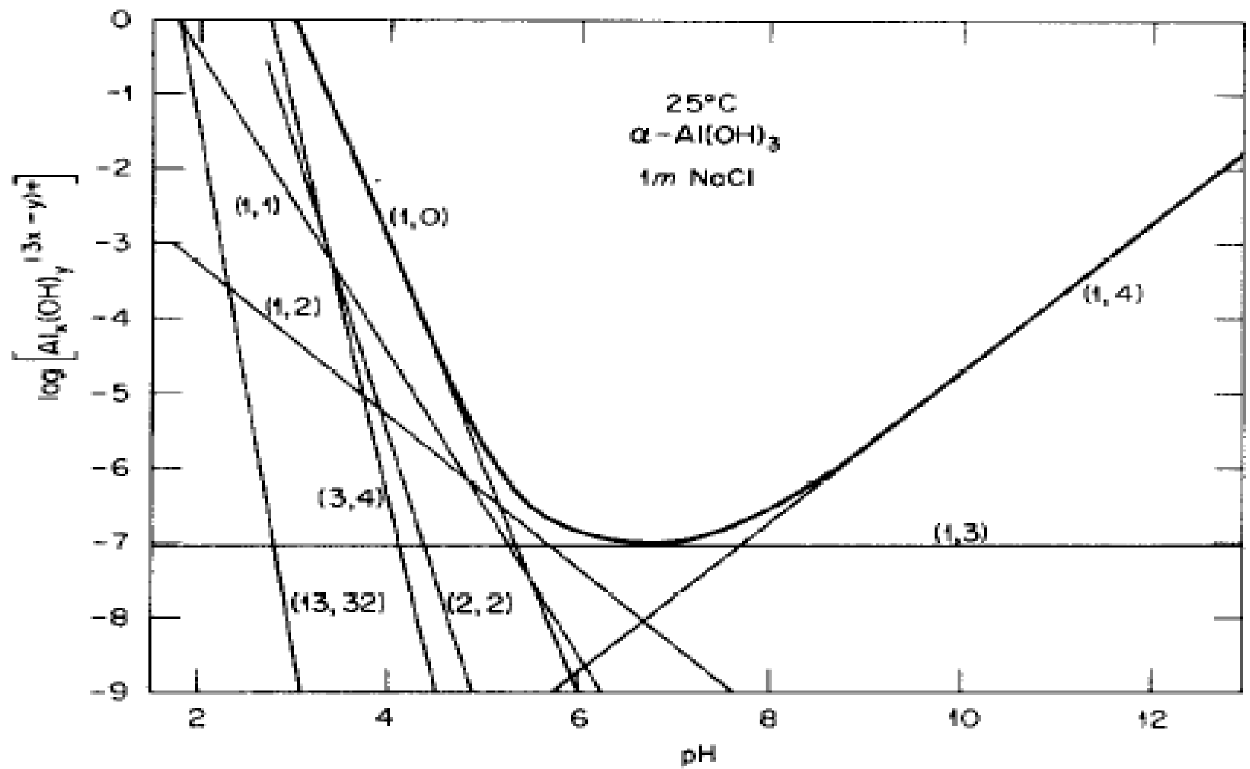
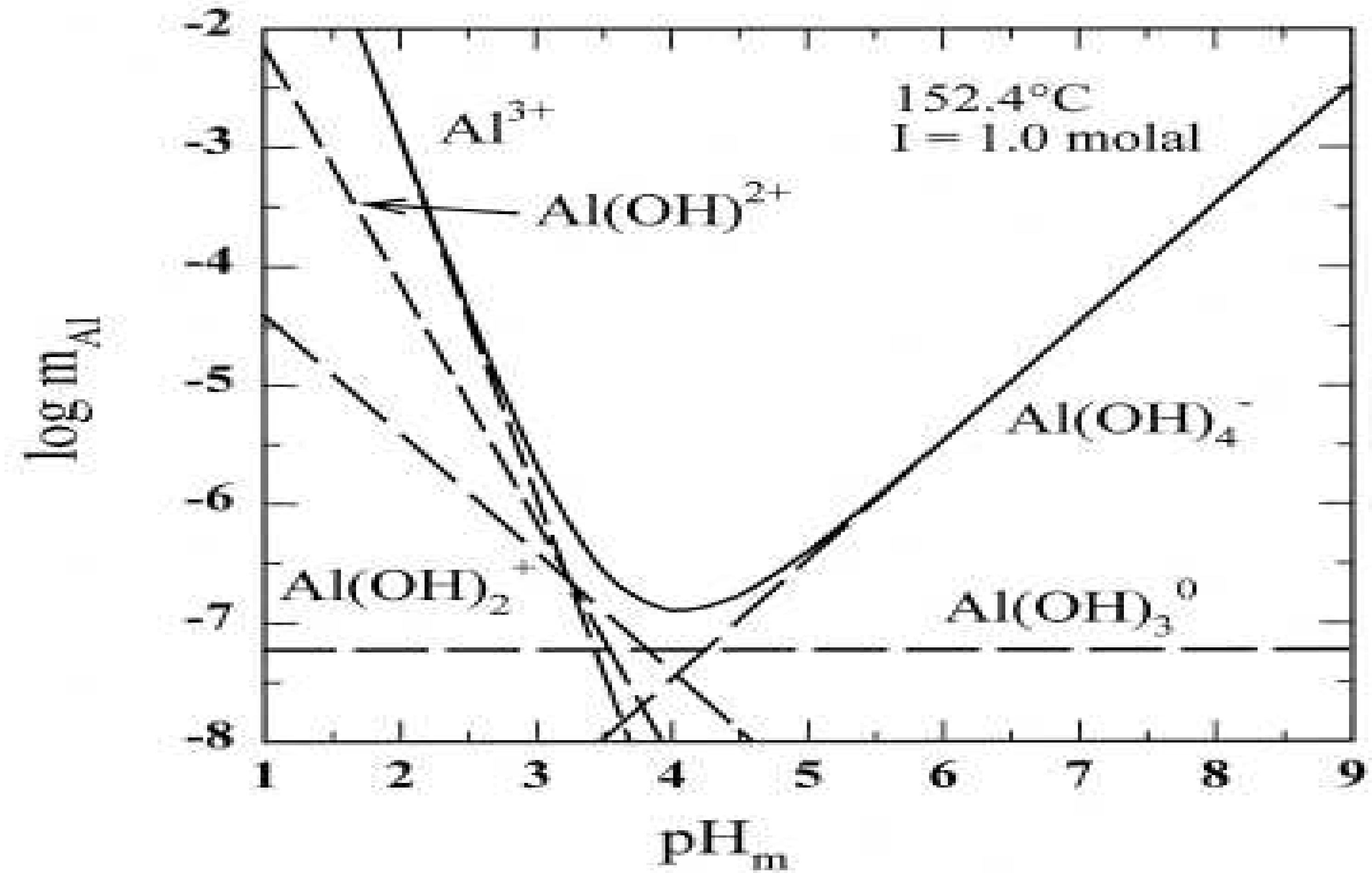


FIG. 1. Molal concentrations of aluminum hydroxyl species in equilibrium with α-$Al(OH)_3$ (gibbsite) in 1 molal NaCl solution at 25°C and 1 bar. The straight lines represent the concentrations of individual species (x, y), indicating the stoichiometries of species of the type $Al_x(OH)_y^{3x-y}$. The heavy curve is the total concentration of all aqueous aluminum species in equilibrium with gibbsite at these conditions. This figure is taken from HITCH et al. (1980).

INTRODUCTION: Aluminum Speciation at 150°C

From Palmer et al. (2001)



INTRODUCTION: Activity Coefficient Models—low to moderate ionic strength

- Davies Equation:

$$\log\gamma_i = -A_\gamma z_i^2 \left(\frac{\sqrt{\mathrm{I}_m}}{1+\sqrt{I_m}} + 0.3 I_m\right)$$

- Extended Debye-Hückel (or WATEQ Debye-Hückel) Equation:

$$\log\gamma_i = -A_\gamma z_i^2 \times \frac{\sqrt{\mathrm{I}_m}}{1+B_{DH} a_i^0 \sqrt{I_m}} - b_i I_m$$

- B dot Equation:

$$\log\gamma_i = -A_\gamma z_i^2 \times \frac{\sqrt{\mathrm{I}_m}}{1+B_{DH} a_i^0 \sqrt{I_m}} + \dot{B}\, I_m$$

INTRODUCTION: Activity Coefficient Model—up to ~3.5 m

- Brønsted-Guggenheim-Scatchard Specific Ion Interaction Theory (SIT) Model

$$\log \gamma_i = -A_\gamma z_i^2 \times \frac{\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \sum_k \varepsilon(i,k) m_k$$

INTRODUCTION: Activity Coefficient Model—to high ionic strength, up to saturation of most salts

- Pitzer Model, using mean activity coefficient for NaCl as an example:

$$\ln\gamma_{\pm} = -A_{\phi}\left[\frac{\sqrt{I_m}}{1+1.2\sqrt{I_m}} + \frac{2}{1.2}\ln(1+1.2\sqrt{I_m})\right] + m\left\{2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 \times I_m}\left[1-(1+\alpha\sqrt{I_m} - \frac{\alpha^2 I_m}{2})e^{-\alpha\sqrt{I_m}}\right]\right\} + \frac{3m^2}{2}C^{\phi}$$

Pitzer Model for Na^{+}—$Al(OH)_4^{-}$ interaction

- Wesolowski (1992) recommended two sets of Pitzer parameters for Na^{+}—$Al(OH)_4^{-}$ interaction.

- One set at 25°C was calculated based on the equations of Pitzer and Mayorga (1973).
  - This set of Pitzer parameters was successfully adopted in the Al-Si high ionic strength model to 100°C to model solubilities of zeolite A (Xiong, 2013), assuming they are constant over 25°C-100°C.
- The other set at 0°C-100°C was calculated based on the equations of Simonson et al. (1989).
  - This set was used by Königsberger et al. (2006).

Objectives of This Work

- The need to obtain Pitzer parameters for Na^+—$Al(OH)_4^-$ interaction to higher temperatures:
  - The peak temperatures in the near field for geological repositories for HLW/used nuclear fuel in salt formations are up to 200°C or slightly higher.
  - The peak temperatures in the near field for deep boreholes for HLW/used nuclear fuel are expected to be higher than 200°C.
- The first objective of this work is to evaluate Pitzer binary interaction parameters for Na^+—$Al(OH)_4^-$ as a function of temperature to 250°C.
- The second objective is to evaluate the temperature dependence of the psi parameters, $\Psi_{Na\text{-}Al(OH)4\text{-}OH}$.

Experimental Data Used for Evaluation

- Equilibrium quotients for the following reaction in NaCl solutions up to 5.0 m from Palmer et al. (2001) are used for evaluation of binary parameters for Na^+—$Al(OH)_4^-$ up to 250°C:

$$AlOOH(cr) + 2H_2O = Al(OH)_4^- + H^+$$

$$Q_{s4} = [Al(OH)_4^-][H^+]$$

- Boehmite (AlOOH(cr)) solubility data in NaOH solutions to 170°C from Russell et al. (1955) are used for evaluation of $\Psi_{Na\text{-}Al(OH)4\text{-}OH}$.

Auxiliary Data

- Binary interaction parameters for H^+—Cl^- valid to 375°C from Holmes et al. (1987)
- Binary interaction parameters for Na^+—Cl^- valid to 300°C from Pitzer et al. (1984)
- Binary interaction parameters for Na^+—OH^- valid to 350°C from Pabalan and Pitzer (1987)
- Modeling platform: EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011) with data0.ypf (Wolery, and Jarek. 2003)

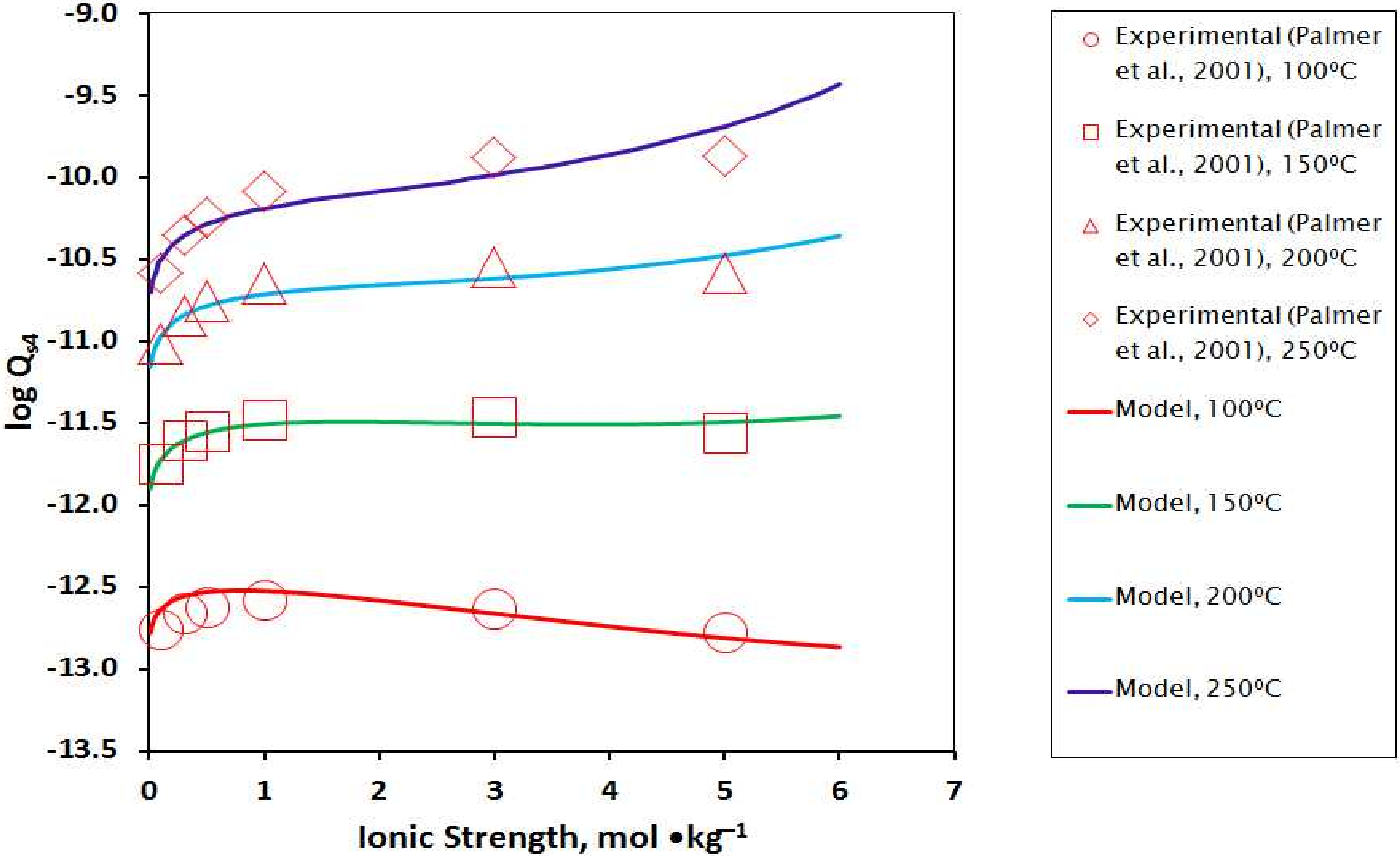
Modeling Results

- log K_{s4}
  - T = 100°C, log K_{s4} = -12.89
  - T = 150°C, log K_{s4} = -12.03
  - T = 200°C, log K_{s4} = -11.34
  - T = 250°C, log K_{s4} = -10.98
- Pitzer Parameters for Na^+—$Al(OH)_4^-$
  - $\beta^{(0)}$ = 0.051 from Wesolowski (1992), constant
  - T = 100°C, $\beta^{(1)}$ = 0.330, C^{ϕ} = -0.00550
  - T = 150°C, $\beta^{(1)}$ = 0.376, C^{ϕ} = -0.00834
  - T = 200°C, $\beta^{(1)}$ = -0.223, C^{ϕ} = 0.00745
  - T = 250°C, $\beta^{(1)}$ = -0.720, C^{ϕ} = 0.00673

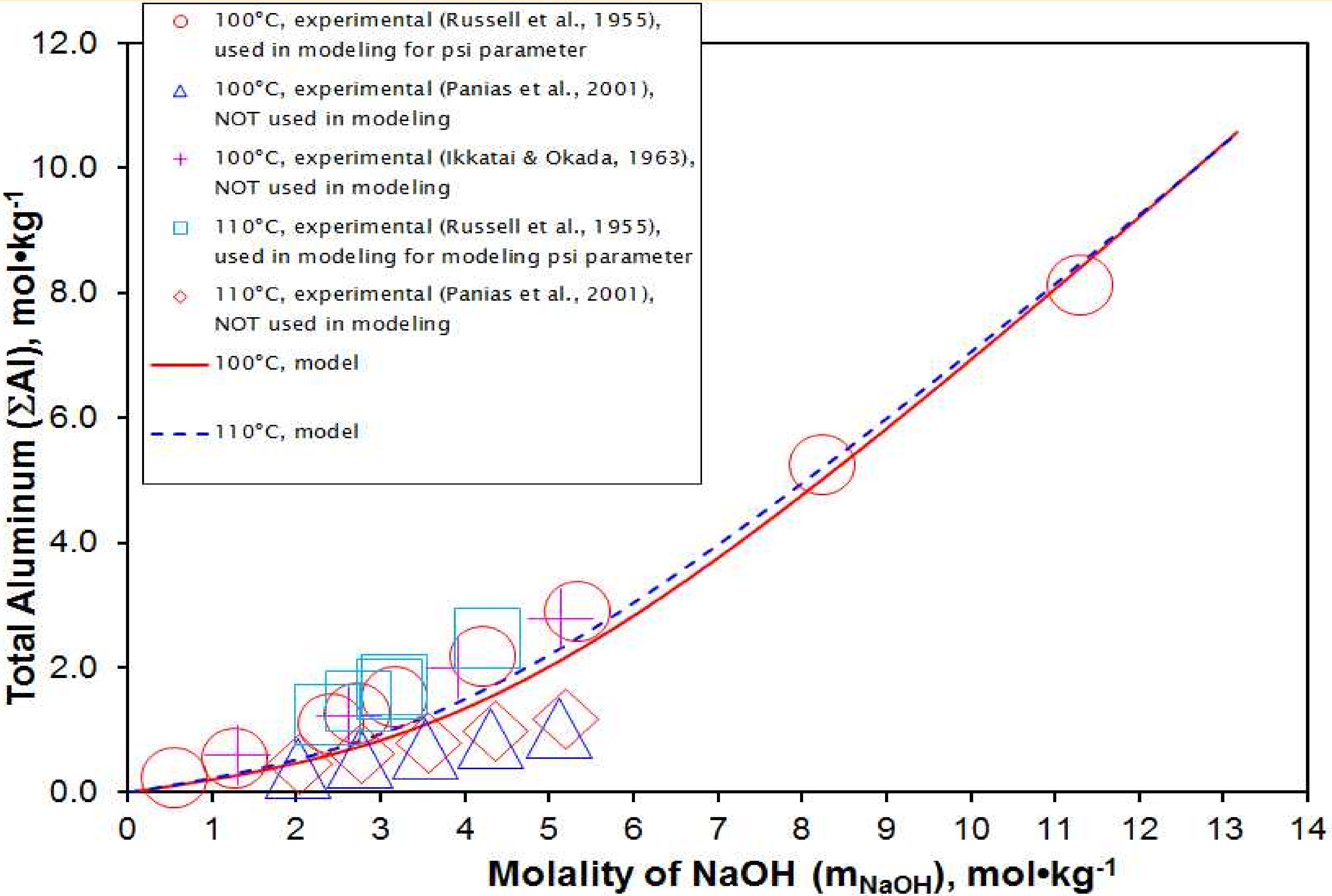
Modeling Results

- Pitzer Parameters for OH^-—$Al(OH)_4^-$
  - θ = 0.014 from Wesolowski (1992), constant
- Pitzer Parameters for Na^+—OH^-—$Al(OH)_4^-$
  - T = 100°C, Ψ = 0.129
  - T = 110°C, Ψ = 0.139
  - T = 120°C, Ψ = 0.135
  - T = 130°C, Ψ = 0.132
  - T = 140°C, Ψ = 0.128
  - T = 150°C, Ψ = 0.125
  - T = 160°C, Ψ = 0.122
  - T = 170°C, Ψ = 0.119

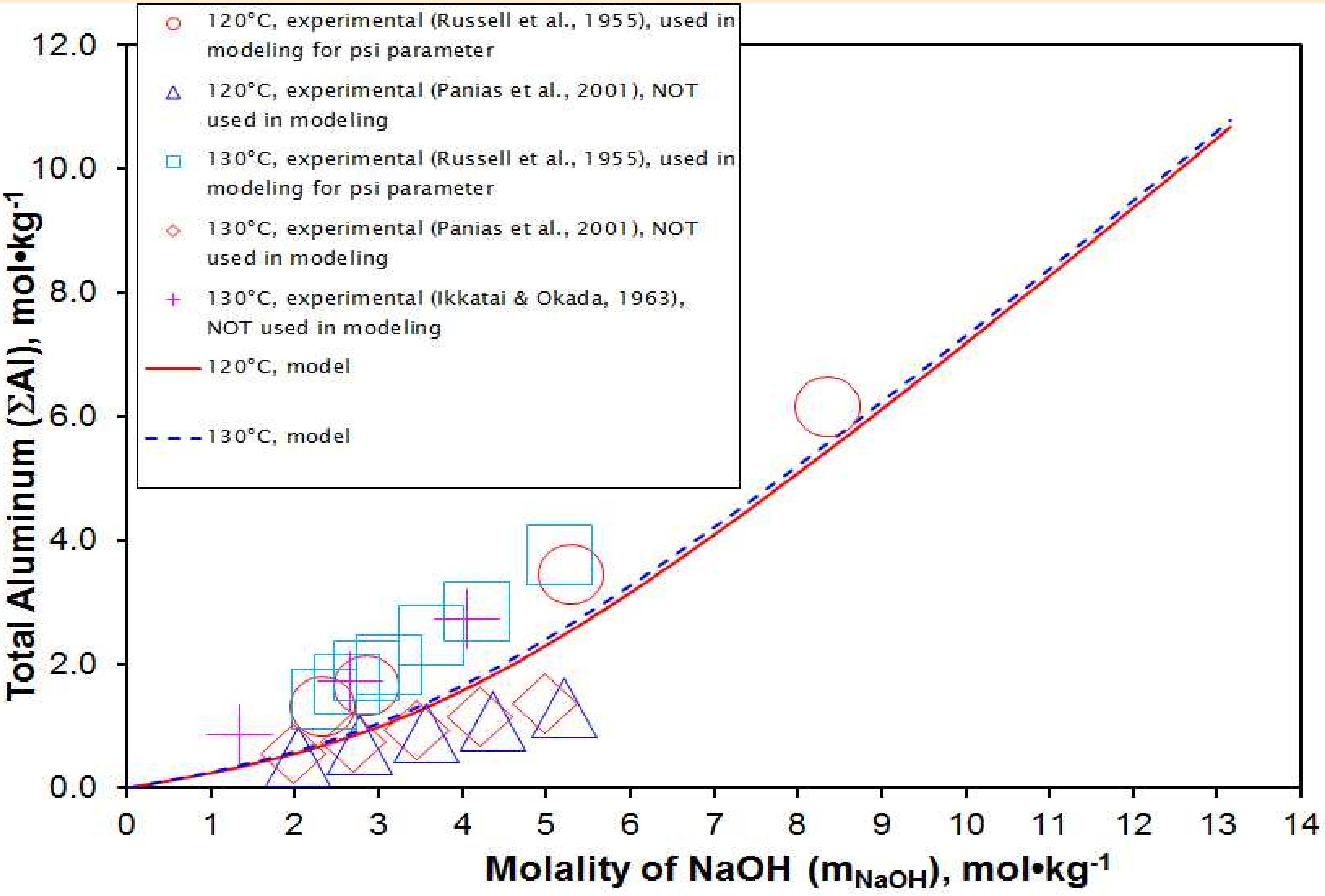
Model Verification



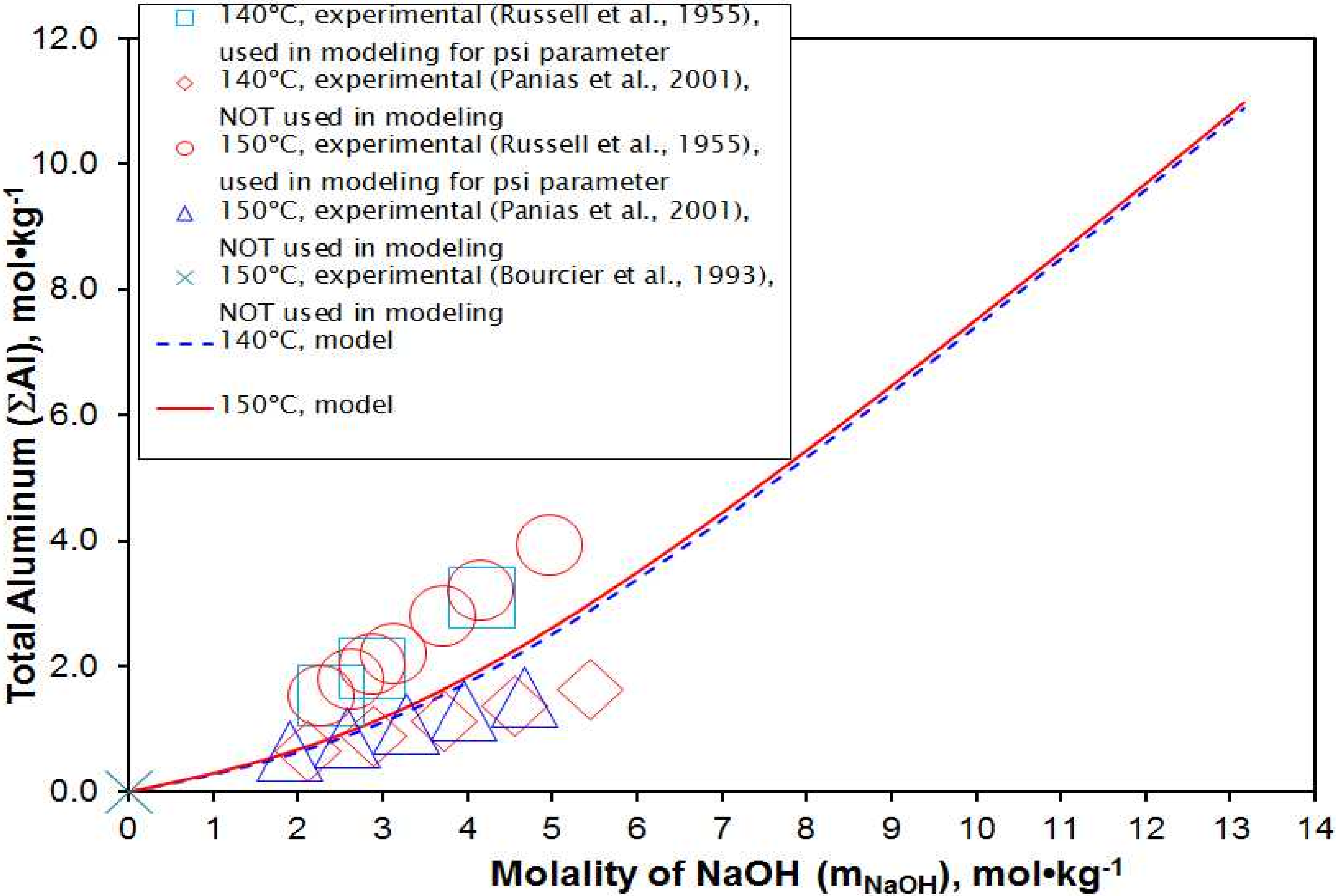
Model Verification/Validation



Model Verification/Validation



Model Verification/Validation



Summary

- In this study, a Pitzer model for the Na-Cl-OH-Al$(OH)_4$ system is tentatively established to 250^oC to ionic strength of 5.0 m, and to 170^oC to ionic strength of 13 m.

- Solubilities of boehmite in NaOH solutions predicted by the model are in good agreement with independent experimental data.

References

- Bourcier, W. L., Knauss, K. G., and Jackson, K. J., 1993. Aluminum hydrolysis to 250°C from boehmite solubility measurements. Geochim. Cosmochim. Acta 57**,** 747–762.
- Hitch, B. F., Mesmer, R. E., Baes, C. F., Jr., and Sweeton, F. H., 1980. The solubility of (α-$Al(OH)_3$,) in 1 molal NaCl as a function of pH and temperature. ***Oak Ridge National Laboratory Report ORNL-5623.***
- Holmes, H.F., Busey, J.M., Simonson, J.M., Mesmer, R.E., Archer, D.G., and Wood, R.H., 1987, The enthalpy of dilution of HCl(aq) to 648 K and 4p MPa. Thermodynamic properties. Journal of Chemical Thermodynamics, 19, 863-890.
- KÖnigsberger, E., May, P.M., and Helfter, G., 2006. Comprehensive model of synthetic Bayer liquors. Part 3. Sodium aluminate solutions and the solubility of gibbsite and boehmite. Monatishefte fur Chemie, 137, 1139–1149.
- Pabalan, R.T., and Pitzer, K.S., 1987. Thermodynamics of NaOH(aq) in hydrothermal solutions. Geochimica et Cosmochimica Acta, 51, 829-837.
- Palmer, D.A., Benezeth, P., Wesolowski, D.J., 2001. Aqueous high-temperature solubility studies. I. The solubility of boehmite as functions of ionic strength (to 5 molal, NaCl), temperature (100–290°C), and pH as determined by in situ measurements. Geochimica et Cosmochimica Acta, 65, 2081–2095.
- Panias, D., Asimidis, P., Paspaliaris, I., 2001. Solubility of boehmite in concentrated sodium hydroxide solutions: model development and assessment. Hydrometallurgy, 59, 15-29.

References

- Pitzer, K. S., and Mayorga, G., 1973. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. J. Phys. Chem. 77, 2300-2308.
- Pitzer, K. S., Peiper, J. C. and Busey, R. H., 1984. Thermodynamics properties of aqueous sodium chloride solutions. J. Phys. Chem Ref Data, 13, 1-102.
- Russell, A . S., Edward, SJ. D., and Taylor, C . S., 1955. Solubility and density of hydrated aluminas in NaOH solutions. J. Metals 7, 1123-l 128.
- Simonson, J. M., Mesmer, R. E., and Rogers P. S. Z., 1989. The enthalpy of dilution and apparent molar heat capacity of NaOH(aq) to 523 K and 40 MPa. J. Chem. Therm. 21,561-584.
- Wesolowski, D.J., 1992. Aluminum speciation and equilibrium in aqueous solution: I. The solubility of gibbsite in the system Na-K-Cl-OH-$Al(OH)_4$ from 0 ^{o}C to 100 ^{o}C. Geochimica et Cosmochimica Acta, 56, 1065–1091.
- Wolery, T.J., and R.L. Jarek. 2003. "Software User's Manual: EQ3/6, Version 8.0." Doc. No. 10813 UM-8.0-00. Albuquerque, NM: Sandia National Laboratories.
- Wolery, T.W., 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.

References

- 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.
- Xiong, Y.-L., 2013. A thermodynamic model for silica and aluminum in alkaline solutions with high ionic strength at elevated temperatures up to 100 °C: Applications to zeolites. American Mineralogist, 98, 141–153.