Development of a Thermodynamic Model for the
Hanford Tank Waste Operations Simulator – 12193

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ABSTRACT

The Hanford Tank Waste Operations Simulator (HTWOS) is the current tool used by the Hanford Tank Operations Contractor for system planning and assessment of different operational strategies. Activities such as waste retrievals in the Hanford tank farms and washing and leaching of waste in the Waste Treatment and Immobilization Plant (WTP) are currently modeled in HTWOS. To predict phase compositions during these activities, HTWOS currently uses simple wash and leach factors that were developed many years ago. To improve these predictions, a rigorous thermodynamic framework has been developed based on the multi-component Pitzer ion interaction model for use with several important chemical species in Hanford tank waste. These chemical species are those with the greatest impact on high-level waste glass production in the WTP and whose solubility depends on the processing conditions. Starting with Pitzer parameter coefficients and species chemical potential coefficients collated from open literature sources, reconciliation with published experimental data led to a self-consistent set of coefficients known as the HTWOS Pitzer database. Using Gibbs energy minimization with the Pitzer ion interaction equations in Microsoft Excel,[1] a number of successful predictions were made for the solubility of simple mixtures of the chosen species. Currently, this thermodynamic framework is being programmed into HTWOS as the mechanism for determining the solid-liquid phase distributions for the chosen species, replacing their simple wash and leach factors.

INTRODUCTION

There are currently 212 million liters of radioactive and chemically hazardous waste stored in 177 underground tanks at the Department of Energy's (DOE) Hanford Site. The mission of the DOE River Protection Project (RPP) is to protect the Columbia River by eliminating the risk to the environment posed by this tank waste. The Hanford Waste Treatment and Immobilization Plant (WTP), currently being constructed, will immobilize the waste by vitrification in glass to allow safe long-term storage of the waste. Hanford tank waste is complex in that it contains many chemical and radionuclide species and distinctly separate phases, including a supernatant (liquid) phase, a sludge solid phase, and a salt-cake solid phase. An accurate prediction of the solid-liquid phase distribution of the Hanford tank waste during retrieval and subsequent processing is vital for planning for and successful future operation of the WTP.

To prepare for effective and efficient retrieval and treatment of the tank waste and to assess different operational strategies, Washington River Protection Solutions (WRPS) has developed an integrated, dynamic process model of the Hanford tank farms and the WTP known as the Hanford Tank Waste Operations Simulator (HTWOS) [1]. Currently, HTWOS calculates phase speciation using prescribed simple wash and leach factors during retrieval operations in the tank farms and for washing and leaching operations in the WTP. To improve these speciation calculations, constituents currently tracked in HTWOS have been divided into categories based on their relative solubility and impact to the mission [2]. Constituents of intermediate solubility and high impact include sodium salts of aluminate, carbonate, oxalate, fluoride, phosphate, and

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[1] Excel is a registered trademark of the Microsoft Corporation, Redmond, Washington.

sulfate ions. An internally self-consistent thermodynamic model has been developed to predict phase speciation for these constituents. This model will replace the use of the simple wash and leach factors for these species in HTWOS.

The thermodynamic model chosen for this application is the Pitzer ion interaction model for multi-component electrolytes [3]. This model is widely accepted in the scientific community, underpinning many software programs, and a version of it has been used in limited individual calculations to predict Hanford waste speciation in the past [4]. The Pitzer model calculates ion activity coefficients and water activity for a given mixture composition and temperature based on a set of empirically derived parameters (known as binary parameters and mixing parameters) for each solute. Binary and mixing parameters of the solutes chosen for this application were collected from open literature sources. Pitzer's equations defined by this database were used in combination with a Gibbs free energy minimization technique to predict speciation in many simple binary and tertiary systems. The resulting predictions are compared to experimentally derived solubility data, also obtained from open literature sources, to test the self-consistency of the database of parameters and to test the ability of the integrated model to predict simple system compositions.

Work is underway to install the Pitzer ion interaction model in HTWOS as the mechanism for determining the solid-liquid phase distributions of select waste constituents during tank retrievals and subsequent washing and leaching of the waste. This HTWOS model change is expected to elicit shifts in mission criteria (e.g., mission end date and quantity of high-level waste glass produced) as predicted by HTWOS. These improvements to the speciation calculations in HTWOS, however, will establish a better planning basis and eventually facilitate more effective and efficient operations.

METHOD

The solutes of interest for the HTWOS thermodynamic model are sodium aluminate (NaAl[OH]$_4$), sodium carbonate (Na$_2$CO$_3$), sodium oxalate (Na$_2$C$_2$O$_4$), sodium fluoride (NaF), trisodium phosphate (Na$_3$PO$_4$), and sodium sulfate (Na$_2$SO$_4$) [2]. With ionic strength being a key variable in the Pitzer model, additional solutes are included as they dominate the liquid phase in Hanford tank waste. These additional ionic strength contributing species are sodium nitrate (NaNO$_3$), sodium nitrite (NaNO$_2$), and sodium hydroxide (NaOH). The compounds chosen to represent the solid species in Hanford tank waste are listed in Table I. The original list of solids in [2] had to be expanded during development of the model to ensure correct prediction of solubility over the entire temperature range considered.

Table I. Solids Included in the HTWOS Thermodynamic Model

Solid Compounds Included in the Pitzer Ion Interaction Model in HTWOS		
Al(OH)$_3$	Na$_2$HPO$_4$·7H$_2$O	Na$_3$PO$_4$·6H$_2$O
Na$_2$C$_2$O$_4$	Na$_2$HPO$_4$·12H$_2$O	Na$_3$PO$_4$·8H$_2$O
NaCl[a]	Na$_2$SO$_4$	Na$_7$F(PO$_4$)$_2$·19H$_2$O
Na$_2$CO$_3$·10H$_2$O	Na$_2$SO$_4$·10H$_2$O	NaF
Na$_2$CO$_3$·7H$_2$O	Na$_3$FSO$_4$	NaHCO$_3$
Na$_2$CO$_3$·H$_2$O	Na$_3$SO$_4$NO$_3$·H$_2$O	NaNO$_2$
Na$_2$HPO$_4$·2H$_2$O	Na$_3$PO$_4$·0.25NaOH·12H$_2$O	NaNO$_3$

 [a] NaCl was required to model the experimental solubility data for gibbsite [5].

To predict phase speciation at equilibrium accurately, information on the solubility of the solid species is required. This information includes activity coefficients, solubility constants and water activity (for hydrated solids), and their temperature and pressure dependence. The most efficient way of solving an equilibrium speciation problem is to use a Gibbs free energy minimization technique [6]. To use this technique, the Gibbs free energies of all of the chosen solutes and solids must be known.

It is very important that any set of Pitzer parameters, used for calculating activity coefficients and water activity, is consistent with the Gibbs free energies of all of the species involved, otherwise predictions of phase speciation will not be accurate. An initial set of Pitzer parameters and Gibbs free energies was collated from open literature sources [7, 8, 9,10]. A Microsoft Excel workbook was developed to test the Pitzer model for consistency of the initial set of parameters and to reconcile them with solubility data into a self-consistent database, referred to as the HTWOS Pitzer database.

Multi-Component Pitzer Ion Interaction Model

To calculate activity coefficients of the species and water activity, required to predict phase speciation, the multi-component Pitzer ion interaction model was used. The model is based on an expression for the Gibbs free energy of the solution, which is a combination of the Debye-Hückel theory for long-range ionic interactions with a second and third order virial coefficient expansion to account for short-range interactions [3]. Pitzer's original model has been extended by several researchers to include the effects of neutral molecular species [4, 11]. With appropriate differentiation of his expression, the activity coefficient is given for cation M, by:

$$\ln \quad = \quad (\ ) + \quad (2 \quad + \quad) + \quad \quad + \quad 2\Phi \quad +$$

$$+ \quad \quad \quad + 2$$

$$+ \quad \quad \quad \text{(Eq. 1)}$$

for anion X, by:

$$\ln \quad = \quad (\ ) + \quad (2 \quad + \quad) + | \ | \quad \quad + \quad 2\Phi \quad +$$

$$+ \quad \quad ,\quad ,\ + 2 \quad + \quad \quad \text{(Eq. 2)}$$

and for neutral species N, by:

$$\ln \quad = 2 \quad \quad + \quad \quad \text{(Eq. 3)}$$

The osmotic coefficient is given by:

$$-1 = \frac{2}{\Sigma} - \frac{/}{1+\sqrt{}}$$

$$+ \qquad + \quad + \qquad \Phi \quad +$$

$$+ \qquad \Phi \quad + \qquad + \qquad +$$

$$+ \qquad + \frac{1}{2} \qquad + \qquad \qquad \text{(Eq. 4)}$$

where y_i is the activity coefficient of ion i,   is the osmotic coefficient,   is a subscript extending over all anions,   extends over all cations, and   extends over all neutral solute molecules. The summations denoted by $c<c'$, $a<a'$ or $n<n'$ mean that only unique pairs are considered,   is the magnitude of charge on ion i, and m_c, m_a, m_n are molality of cation, anion, and neutral species, respectively. The term F is given by:

$$= - \qquad \frac{\sqrt{}}{1+\sqrt{}} + \frac{2}{}\ln\left(1+\sqrt{}\right) + \qquad \qquad - + \qquad \qquad \frac{\Phi}{}$$

$$+ \qquad \qquad \frac{\Phi}{} \qquad \qquad \text{(Eq. 5)}$$

where   is the Debye-Hückel osmotic constant, with a value of 0.3915 $kg^{1/2}\ mol^{-1/2}$ at 25°C and 1 bar. The remaining terms in Equations 1 to 5 are defined as:

$$= \quad + \quad — = \quad {}^{()} + {}^{()} \quad \sqrt{} + {}^{()} \quad \sqrt{} \qquad \text{(Eq. 6)}$$

$$= 2|\quad|^{/} \qquad \text{(Eq. 7)}$$

$$= {}^{()} + {}^{()} \quad \sqrt{} + {}^{()} \quad \sqrt{} \qquad \text{(Eq. 8)}$$

$$(\ ) = 2\frac{(1-(1+\ )\quad)}{} \qquad \text{(Eq. 9)}$$

$$— = \frac{{}^{()}h \quad \sqrt{}}{} + \frac{{}^{()}h \quad \sqrt{}}{} \qquad \text{(Eq. 10)}$$

$$h(\ ) = {}'(\ )\frac{}{2} = -\frac{2\left(1-\left(1+\quad+—\right)\right)}{} \qquad \text{(Eq. 11)}$$

$$\Phi = \Phi + \frac{\Phi}{} \qquad \text{(Eq. 12)}$$

$$\Phi \quad = \quad + \quad (\ ) \tag{Eq. 13}$$

$$\frac{\Phi}{\quad} = \quad (\ ) \tag{Eq. 14}$$

$$= \frac{1}{2} \tag{Eq. 15}$$

$$= \quad |\ | \tag{Eq. 16}$$

The exponential coefficient $= 2.0$ kg$^{1/2}$ mol$^{-1/2}$, except for 2-2 electrolytes, where $= 1.4$ kg$^{1/2}$ mol$^{-1/2}$ is used in combination with $= 12$ kg$^{1/2}$ mol$^{-1/2}$. For electrolytes other than 2-2, the term $(\ ) \quad \surd \quad$ is not used. The value of b is fixed at 1.2 for all electrolytes.

Higher Order Unsymmetrical Mixing Parameters

To account for long-range electrical forces between ions of the same charge but different magnitudes, the unsymmetrical mixing parameters $(\ )$ and $(\ )$, appearing in Equations 13 and 14, are needed. These terms are dependent on the charges of the ions , , the total ionic strength, I, and on the dielectric constant and density of the solvent. They are evaluated from the following equations [12]:

$$(\ ) = \quad \frac{}{4} \quad -\frac{1}{2} (\ ) -\frac{1}{2} \tag{Eq. 17}$$

$$'(\ ) = -\frac{(\ )}{8} + \quad \quad ' \quad -\frac{1}{2} \quad '(\ ) -\frac{1}{2} \quad ' \tag{Eq. 18}$$

where

$$= 6 \quad \surd \tag{Eq. 19}$$

$$(\ ) = \frac{1}{} \quad 1+ \quad +\frac{1}{2} \quad - \tag{Eq. 20}$$

$$= - \ - \tag{Eq. 21}$$

Pitzer [12] describes a method to evaluate both J(x) and J'(x) using Chebyshev polynomial approximations.

Solute Parameters Required by the Pitzer Model

For a single solute, the parameters required by Equations 1 to 16 are the binary coefficients, $(\ )$, $(\ )$, $(\ )$, and , sometimes called Pitzer parameters, which can be temperature and pressure dependent, but are independent of ionic strength. For a mixture of solutes, the

additional parameters,   ,   ,   ,   ,   ,   ,   , and   , are required, which have to be determined experimentally and can be temperature and pressure dependent.

The temperature dependency of the solute parameters was fit to Equation 22 [7, 8, 9, 10]:

$$ (\ ) = \ + \ (\ - \ ) + \ \frac{1}{\ } - \frac{1}{\ } + \ \ln \frac{\ }{\ } + \ (\ - \ ) \qquad \text{(Eq. 22)} $$

where P(T) is one of the binary coefficients, a mixing parameter, or a reduced chemical potential (dimensionless form of the Gibbs free energy, $\mu°/RT$). T_r is the reference temperature of 298.15 K, and A to E are constants that define the temperature dependence of the parameter. The pressure dependency was not required, as the temperature range chosen was from 0 to 100°C only.

Evaluation of the Hanford Tank Waste Operations Simulator Thermodynamic Model Parameters

To evaluate the initial set of Pitzer parameters, predictions of the osmotic coefficient for single solutes at a number of different temperatures, via Equation 4, were compared to published experimental values. If necessary, the binary coefficients were adjusted (the constants in Equation 22) to better fit the experimental values. During this analysis, an additional two neutral species, $NaNO_2(aq)$ and $NaNO_3(aq)$, were included in order for the model to accurately predict the experimental data.

Next, the chemical potentials of the solids were tested for consistency with the final Pitzer parameters by comparing the model's prediction of solute concentration at saturation as a function of temperature with experimental solubility data from the literature [13]. If necessary, the chemical potential coefficients of the solids were adjusted to match the experimental data. When experimental osmotic coefficients were not available in the literature for a particular solute, the Pitzer coefficients and experimental solubility data had to be reconciled simultaneously.

Once the Pitzer parameters and specie chemical potentials were optimized, the model's prediction of the solubility for mixtures of solutes was tested. The purpose of this exercise was twofold: first to reconcile the chemical potential coefficients of the double salts (e.g., $Na_3SO_4NO_3 \cdot H_2O$, $Na_7F[PO_4]_2 \cdot 19H_2O$, and Na_3FSO_4), and second, to evaluate any required mixing parameters   ,   ,   ,   ,   ,   ,   , and   .

RESULTS

Evaluation of Single Solutes

As an example of the evaluation of single solutes, the osmotic coefficients for the $NaNO_3$-H_2O system between 0 and 100°C and up to saturation molality were obtained from open literature sources. The data types ranged from vapor pressure measurement to isopiestic molality to freezing point depression, as well as solubility measurements. Each dataset was converted to an osmotic coefficient and compared to model predictions (Equation 4) from the initial set of Pitzer coefficients and then, if necessary, from a final reconciled set. The results of these analyses using the initial parameters and final reconciled set are shown in Figure 1 and Figure 2 at 0 and 100°C, respectively.
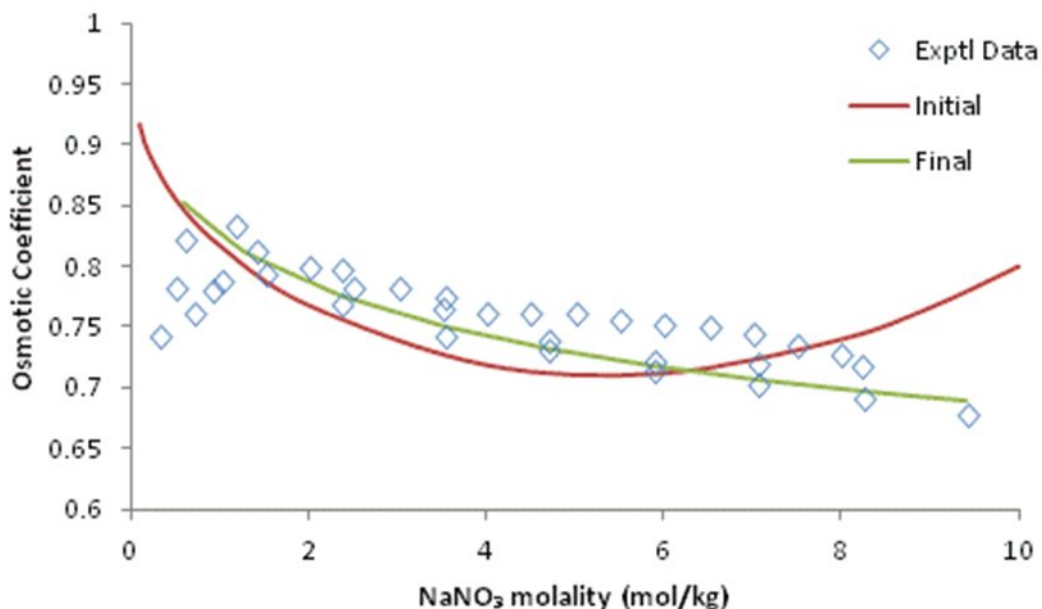
Fig.1. Experimental NaNO$_3$ osmotic coefficient at 0°C
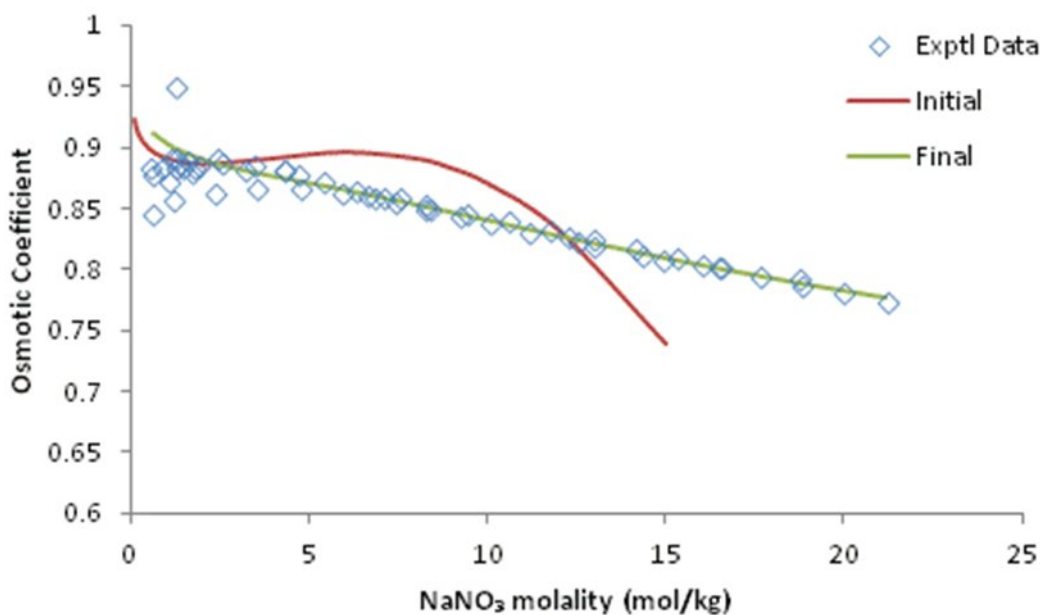compared to the initial and final model predictions

Fig. 2. Experimental NaNO$_3$ osmotic coefficient at 100°C
compared to the initial and final model predictions

During reconciliation of the Pitzer coefficients, it became necessary to include the neutral NaNO$_3$(aq) molecule to better fit the experimental osmotic coefficient, especially at the higher temperatures, as Felmy and co-workers found [4]. In addition, this required evaluating the coefficients for the reduced chemical potentials of the neutral molecule.

Evaluation of Solute Mixtures

Table II lists the solute mixtures that were analyzed during the development of the HTWOS Pitzer database and the temperature range of the experimental data over which a particular system was evaluated. The experimental data was collected from many open literature sources, with the majority taken from Seidell [13].

Table II. List of Solute Mixtures Analyzed and Applicable Range of Temperature

Chemical System	Temperature Range (°C)	Chemical System	Temperature Range (°C)	Chemical System	Temperature Range (°C)
Na-OH-NO$_3$-H$_2$O	0 – 100	Na-NO$_2$-NO$_3$-H$_2$O	0 – 103	Na-CO$_3$-SO$_4$-H$_2$O	15 – 25
Na-OH-NO$_2$-H$_2$O	20 – 25	Na-NO$_2$-CO$_3$-H$_2$O	20 – 25	Na-CO$_3$-PO$_4$-H$_2$O	25
Na-OH-F-H$_2$O	0 – 94	Na-NO$_2$-SO$_4$-H$_2$O	0 – 50	Na-F-SO$_4$-H$_2$O	0 – 80
Na-OH-Cl-H$_2$O	0 – 90	Na-NO$_3$-F-H$_2$O	25 – 50	Na-F-PO$_4$-H$_2$O	25 – 50
Na-OH-CO$_3$-H$_2$O	0 – 100	Na-NO$_3$-CO$_3$-H$_2$O	25	Na-Al-OH-H$_2$O	6 – 80
Na-OH-SO$_4$-H$_2$O	0 – 100	Na-NO$_3$-C$_2$O$_4$-H$_2$O	20 – 75		
Na-OH-C$_2$O$_4$-H$_2$O	0 – 50	Na-NO$_3$-SO$_4$-H$_2$O	0 – 100		

Examples of the significance of Hanford tank waste chemistry are illustrated by the last two systems in Table II. For the Na-F-PO$_4$-H$_2$O system, predictions of the solubility isotherms were compared against experimental data extracted from OLI Systems mixed solvent electrolyte data set validations [14]. Figure 3 shows the model prediction and experimental data at 25°C. The model predicted that three solids would precipitate. At extremely low concentrations of fluoride, the solid predicted was trisodium phosphate, but quickly changed to the double salt, which in turn reduced the phosphate concentration in solution. Upon further additions of fluoride, the double salt remained the only solid predicted until, at around 0.9 molal, solid sodium fluoride was predicted to form. Similar plots were obtained at 35 and 50°C, but are not shown.
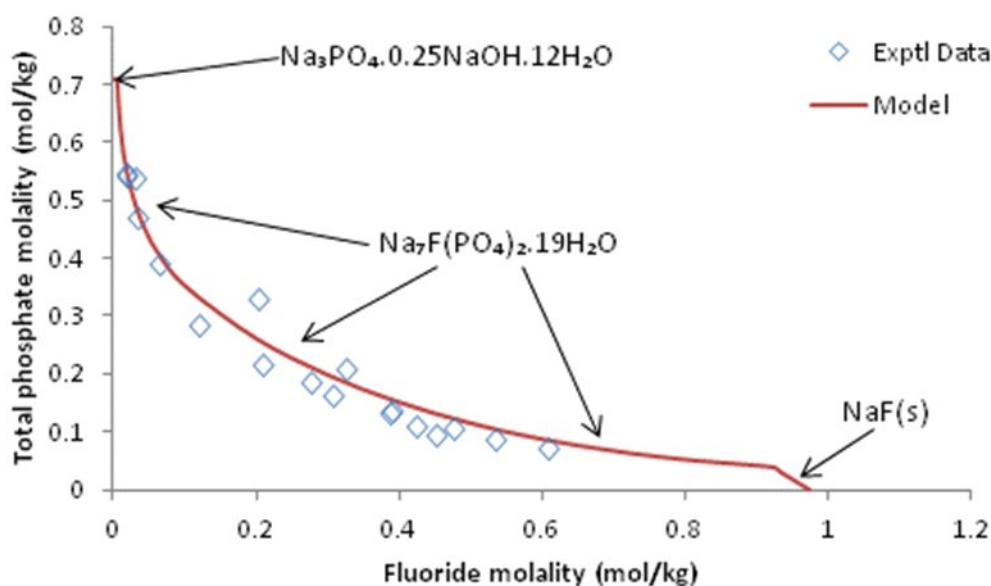

Fig. 3. Prediction of the solubility of Na$_3$PO$_4$ in NaF solutions at 25°C

Aluminum chemistry is also of significance for Hanford tank wastes, as the majority of tanks contain gibbsite, boehmite, or both, as the dominant aluminum-containing solid. Accurate prediction of phase equilibrium in the Na-Al-OH-H_2O system can help to estimate the amount of sodium hydroxide that would be required to leach the gibbsite from the solid phase during processing of waste through WTP. Such a prediction of the amount of aluminum in solution for a given concentration of hydroxide is shown in Figure 4 at temperatures of 40, 70, and 100°C, where it is compared to the experimental data of Russell [15].
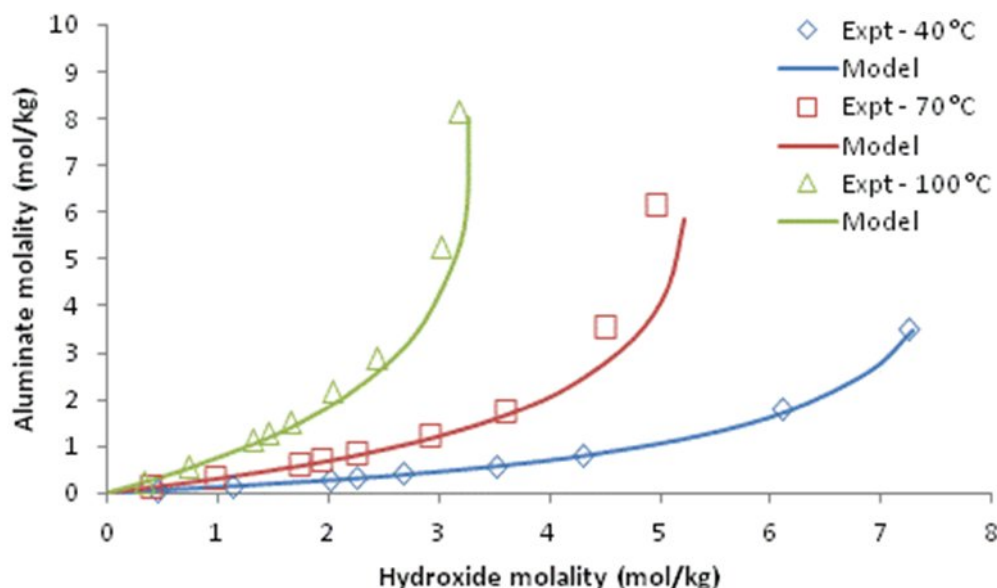

Fig. 4. Prediction of the solubility of gibbsite in NaOH solutions at 40, 70, and 100°C

CONCLUSIONS

Starting from a variety of open literature sources, a collection of Pitzer parameters and species chemical potentials, as functions of temperature, was tested for consistency and accuracy by comparison with available experimental thermodynamic data (e.g., osmotic coefficients and solubility). Reconciliation of the initial set of parameter coefficients with the experimental data led to the development of the self-consistent set known as the HTWOS Pitzer database. Using Microsoft Excel to formulate the Gibbs energy minimization method and the multi-component Pitzer ion interaction equations, several predictions of the solubility of solute mixtures at various temperatures were made using the HTWOS Pitzer database coefficients. Examples of these predictions are shown in Figure 3 and Figure 4. A listing of the entire HTWOS Pitzer database can be found in RPP-RPT-50703 [16].

Currently, work is underway to install the Pitzer ion interaction model in HTWOS as the mechanism for determining the solid-liquid phase distributions of select waste constituents during tank retrievals and subsequent washing and leaching of the waste. Validation of the Pitzer ion interaction model in HTWOS will be performed with analytical laboratory data of actual tank waste. This change in HTWOS is expected to elicit shifts in mission criteria, such as mission end date and quantity of high-level waste glass produced by WTP, as predicted by HTWOS. These improvements to the speciation calculations in HTWOS, however, will establish a better planning basis and facilitate more effective and efficient future operations of the WTP.

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