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USE OF MODELING FOR THE PREVENTION OF SOLIDS FORMATION DURING CANYON PROCESSING OF LEGACY NUCLEAR MATERIALS AT THE SAVANNAH RIVER SITE

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ABSTRACT

The Savannah River Site (SRS) Environmental Management (EM) nuclear material stabilization program includes the dissolution and processing of legacy materials from various DOE sites. The SRS canyon facilities were designed to dissolve and process spent nuclear fuel and targets. As the processing of typical materials is completed, unusual and exotic nuclear materials are being targeted for stabilization. These unusual materials are often difficult to dissolve using historical flowsheet conditions and require more aggressive dissolver solutions. Solids must be prevented in the dissolver to avoid expensive delays associated with the build-up of insoluble material in downstream process equipment. Moreover, it is vital to prevent precipitation of all solids, especially plutonium-bearing solids, since their presence in dissolver solutions raises criticality safety issues.

To prevent precipitation of undesirable solids in aqueous process solutions, the accuracy of computer models to predict the formation of precipitate formation requires incorporation of plant specific fundamental data. These data are incorporated into a previously developed thermodynamic computer program that applies the Pitzer correlation to derive activity coefficient parameters. This improved predictive model will reduce unwanted precipitation in process solutions at DOE sites working with EM nuclear materials in aqueous solutions.

INTRODUCTION

Research and development focused on SRS canyon dissolver precipitation issues was important during the Sand, Slag, and Crucible (SS&C) campaign of 1997. During the flowsheet development for this campaign, high concentrations of potassium fluoride in the boric acid-nitric acid dissolver solution resulted in white solids. These solids were identified as potassium tetrafluoroborate (KBF_4), indicating a decrease in soluble boron, a neutron adsorbing poison that was required as a nuclear criticality control. The conditions that shift the equilibrium towards precipitation are qualitatively understood in terms of Le Chatelier's principle by considering the following equation:

$$K^+ (aq) + H_3BO_3 (aq) + 4\,F^- (aq) + 3\,H^+ (aq) = KBF_4 (s) + 3\,H_2O (l) \qquad \text{(Eq. 1)}$$

The Idaho National Engineering and Environmental Laboratory (INEEL) developed expertise in aqueous fluoride chemistry as a result of processing naval nuclear fuels at the Idaho Nuclear Technology and Engineering Center (INTEC, formerly the Idaho Chemical Processing Plant, ICPP). This process included nuclear material dissolution in hydrofluoric and nitric acids that incorporated boron as a soluble neutron poison for criticality control. This processing need required development of a thermodynamic speciation program for predicting multiple fluoride species equilibrium concentrations in representative plant solutions. As a result of the SS&C campaign issues, the INEEL model was used to predict nuclear material residue dissolution using calcium fluoride in the presence of boric acid and to predict the corrosion potential of the stainless steel dissolver vessel. However, the INEEL speciation program thermodynamic data are applicable at ionic strength conditions for the INEEL process solutions, i.e., do not have activity coefficient data. Therefore, application to SRS solutions with high ionic strength requires that the INEEL model be improved with specific chemical species information. Therefore, the INEEL speciation computer program is being updated with new basic chemical data in order to better predict and avoid the precipitation of undesirable solids in aqueous process solutions at SRS.

The objective of the project is to incorporate activity coefficients into the speciation program that has been developed to calculate individual component concentrations in acidic aqueous fluoride systems. The incorporation of relevant activity coefficients into the program will enable accurate predictions of solubilities of potentially precipitating species in plant solutions and provide the ability to calculate solution adjustments to assure stability. In order to do this, solubility and activity coefficient data must be fitted to a suitable activity coefficient model and its ion interaction parameters must be determined. Subsequently, the fitted model can be used to calculate the activity coefficients for process solution compositions. The computer program has potential applications at DOE sites working with EM materials in aqueous solutions.

MODELING TO ADDRESS PRECIPITATION IN THE CANYON DISSOLVER

In laboratory tests to support the Sand, Slag, and Crucible (SS&C) campaign and the Mark 42 Fuel Tube campaign, the presence of high concentration of fluoride ions in boric acid/nitric acid solutions led to the formation of a white solid (see Table 1). The white solids were collected from laboratory flowsheet simulations, and were identified as KBF_4.

Table 1. Identification of KBF_4 Precipitate in SRS Dissolver Simulation Tests.

Date	Test	$[HNO_3]_0$ (M)	$[F^-]_0^*$ (M)	$[B]_0^{**}$ (g/L)	Observation
Dec. 1997	SS&C - simulation	9.3	0.30	2.5	Unidentified white solid
May 1998	SS&C - simulation	1.0	0.23	1.7	White solid, KBF_4
Nov. 1998	SS&C – test 1	8.8	0.32	1.6	No solids
	SS&C – test 2	8.6	0.40	2.2	KBF_4 (s)
Feb. 1999	Mark 42 – simulation [Al] = 0.44 M	1.0	0.40	2.5	No solids
		1.0	0.50	2.5	KBF_4 (s), minor
		1.0	0.60	2.5	KBF_4 (s), more

*Added as KF. **Added as H_3BO_3

Without known KBF_4 activity coefficients at the conditions evaluated, the INEEL program under predicts the saturation of KBF_4, as shown in Table 2.

Table 2. Modeling Results for KBF_4 Experiments, 20°C

$[HNO_3]_0$	$[KF]_0$	$[B]_0$	$[Al]_0$	Mark-42: simulation	Using INEEL program, calculated:
M	M	(g/L)	(M)	Observation	
1.0	0.50	2.5	0.44	KBF_4 (s), few	$[BF_4^-]$ = 41.2% of saturation (i.e. no precipitation is predicted).
1.0	0.60	2.5	0.44	KBF_4 (s), some	Predicts saturated KBF_4. Calculated K_{SP}= 1.2724 x 10^{-3} [vs. literature: 1.27 x 10^{-3}] Precipitate composition: 1.9% of K^+ 7.6% of F (4.9% of F as KBF_4)

In recent years, the INEEL modeling capability has been expanded with the incorporation of complexation equilibrium calculations into a free energy minimization program with a database for over 15,000 compounds. To apply the model to new applications, the user incorporates data for the performance of phase equilibrium calculations. For incorporation of activity coefficients, the INEEL program will apply the Pitzer model,[1, 2] a widely used model for which parameters have been extensively tabulated for various salts and acids. For applications to multielectrolyte solutions, data from both single and binary salt solutions are required to obtain ion interaction parameters for all ions in solution. Figure 1 shows the prediction capability of Pitzer single-salt equation parameters for $NaNO_3$ activity coefficients.[3] The Pitzer equation is suitable to about 6 molal, but must be evaluated on a case-by case basis at higher ionic strengths.

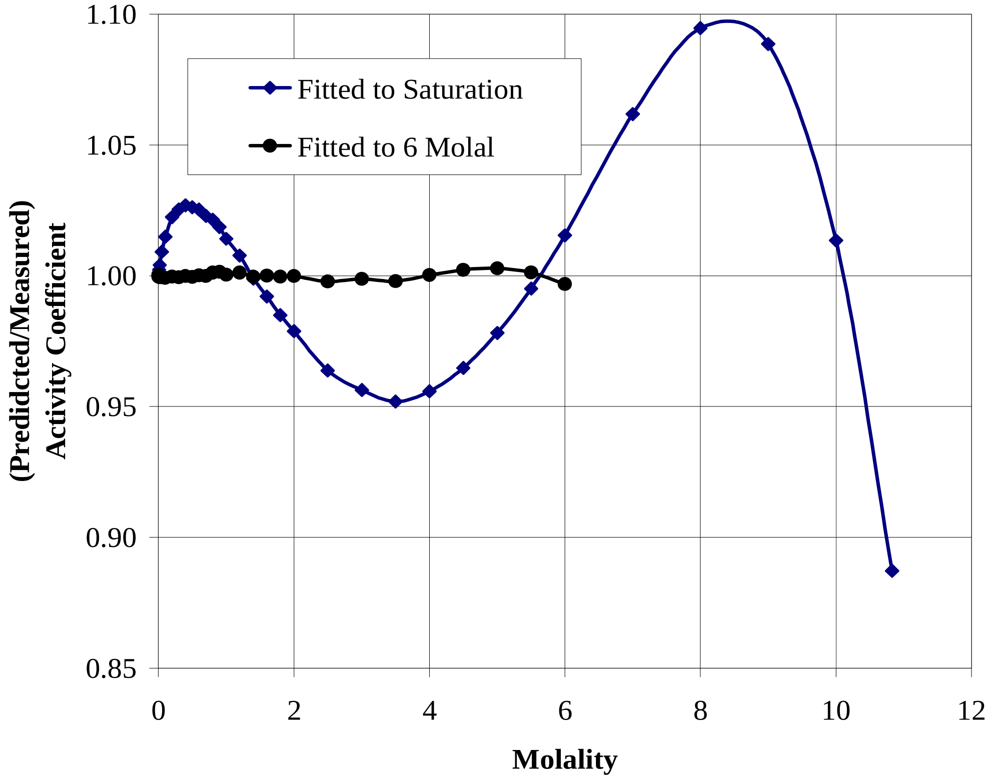


Fig. 1. Pitzer Coefficients for NaNO3 Single Salt Equation Fitted to Hamer & Wu Data.

The INEEL model incorporates multiple fluoride complexation constants and solubilities of fluoride species (e.g., aluminum fluoride and zirconium fluoride) that are involved in multiple complexation equilibria. This extensive database enables predictions of conditions (e.g., reagent concentrations and temperatures) that assure solution stability. The INEEL model will be applied to evaluate SRS dissolver solution compositions and predict equilibrium concentrations and the possible formation of undesirable solids. However, at ionic strengths pertinent to SRS plant solutions and specifically to the KBF_4 solubility product and activity coefficient determinations, the model needs improvement via incorporation of relevant salt solubilities and activity coefficients.

At SRS, the following interactions are important: KBF_4 – $NaNO_3$ (no common ion), KBF_4 – $NaBF_4$ (common anion), and KBF_4 – KNO_3 (common cation). Based on solubility measurements as functions of ionic strength of the interacting salt, binary and ternary KBF_4 activity coefficient parameters are being determined. These data enable solubility extrapolation to zero ionic strength and determination of Pitzer parameters.

Once the salt solubilities have been determined as a function of ionic strength, the activity coefficients are calculated as follows. For the general salt dissolution, Eq. (2), the molal concentration equilibrium constant (solubility product) and thermodynamic equilibrium constant are obtained by Eqs. (3) and (4).

$$A_xB_y = xA^{z+} + yB^{z-} \qquad \text{(Eq. 2)}$$

$$K_m = m_{A^{z+}}^{x} m_{B^{z-}}^{y} \qquad \text{(Eq. 3)}$$

$$K_{Th} = a_{A^{z+}}^{x} a_{B^{z-}}^{y} = K_m \gamma_{\pm}^{\nu} \qquad \text{(Eq. 4)}$$

Here, m is the molal concentration, a is the activity, $\gamma_\pm$ is the mean molal activity coefficient $[(\gamma_{A_{z+}}^{x}\gamma_{B_{z-}}^{y})^{1/\nu}]$, and ν is x + y. Let $K_{m,0}$ and γ_0 be the solubility product (molal) and the mean activity coefficient, respectively, of the salt in pure H_2O and K_m and $\gamma_\pm$ be the corresponding values in a solution with added electrolyte that increases the ionic strength, I [$I = ½(m_{A_{z+}} z_+^2 + m_{B_{z-}} z_-^2)$]. Then,

$$K_{Th} = K_{m,0}\,\gamma_0^{\nu} = K_m\,\gamma_\pm^{\nu} \qquad \text{(Eq. 5)}$$

so that $K_m\,\gamma_\pm^{\nu} = K_{m,0}\,\gamma_0^{\nu}$. Taking logarithms, we have

$$\log K_m = \log (K_{m,0}\,\gamma_0^{\nu}) - \log \gamma_\pm^{\nu} \qquad \text{(Eq. 6)}$$

Once $K_{m},_0\,\gamma_0^{\nu}$ is known, the activity coefficient at a given ionic strength can be calculated from the measured solubility product. To obtain $K_{m,0}\,\gamma_0^{\nu}$, log K_m is plotted against $I^{1/2}$. The plot is extrapolated to $I^{1/2} = 0$. The intercept gives $K_{m},_0\,\gamma_0^{\nu}$ at zero ionic strength, where $\gamma_0 = 1$. Then, from the measured solubility product at each ionic strength, Eq. (6) is solved for $\gamma_\pm$.

$$\gamma_\pm = \left(\frac{K_{m,0}\gamma_0^{\nu}}{K_m} \right)^{1/\nu} \qquad \text{(Eq. 7)}$$

The form of the suggested extrapolation equation arises from the limiting Debye-Hückel law, which predicts a linear relation between log $\gamma_{\pm}$ and $I^{1/2}$ at very low ionic strengths. An alternative, perhaps, better extrapolation plot[4] uses an extended Debye-Hückel equation developed by Davies[5] that translates to

$$\log K_m - \frac{A_\gamma \Delta z^2 I^{1/2}}{1+I^{1/2}} = \log K_{m,0} + bI \qquad \text{(Eq. 8)}$$

where A_γ, the Debye-Hückel limiting slope, is 0.511 at 25°C and Δz^2 is $\Sigma(z_{products})^2 - (z_{reactants})^2$. The left hand side of Eq. (8) is plotted against I and linearly extrapolated to zero I, yielding log $K_{m,0}$ at the intercept. Phillips has applied the linear function extrapolation to data up to 3 molal ionic strength.[4] Once $K_{m,0}$ has been determined from the lower ionic strength data, activity coefficients from all data, including at higher ionic strengths, are evaluated from Eq. (7).

A commercial free energy minimization program, HSC Chemistry® for Windows,[6] provides the capability of inputting enthalpy of formation, entropy, and heat capacity terms for individual species. Simple activity coefficient expressions or the values can also be inputted. In the case of experimental solubility constants, thermodynamic data are expressed for the reaction; individual species values are not provided. The INEEL model possesses general equations and methodology to convert equilibrium constants into a consistent set of thermodynamic parameters for use in the HSC database and program. Based on the experimental solubility data, the activity coefficients are obtained from the INEEL model. The plant solution stability is evaluated with the application of the HSC program. Solution compositions can be varied to determine the concentration limit at which precipitation will begin.

DETERMINATION OF BINARY AND TERNARY ACTIVITY COEFFICIENTS

Various well-established thermodynamic methods are known for determining the activity coefficients of electrolyte solutions.[7] These methods include vapor pressure, freezing point depression, boiling point elevation, osmotic pressure, solubility, and electromotive force measurements. Activity coefficients of KBF_4 as a function of ionic strength will be determined by simple solubility measurements at various ionic strengths. Specifically, the determination of KBF_4 binary and ternary activity coefficient parameters is based on KBF_4 solubility measurements as a function of the ionic strength of an adjuster salt ($NaNO_3$, $NaBF_4$, and KNO_3). The fluoroborate ion (BF_4^-) hydrolyzes slightly to yield H_3BO_3 and HF. Therefore, chemical additions (small amounts of HF and H_3BO_3 at levels that will not contribute to ion interactions) were made to the test solutions, preventing hydrolysis of BF_4^- that would otherwise occur to about 3.7%.[8] These data, along with literature values of Pitzer parameters for interactions of Na^+- NO_3^-, K^+- NO_3^-, Na^+- BF_4^-, and K^+-Na^+ enable evaluation of all pertinent two-salt interaction parameters yielding KBF_4 activity coefficients as a function of ionic strength. The KBF_4 solution was analyzed for B and K concentration by inductively couple plasma-atomic emission spectroscopy (ICP-AES).

RESULTS

KBF_4 Solubility Product and Activity Coefficients

Solubility products and activity coefficients obtained as discussed above are summarized in Figures 2 and 3. An important observation is that increasing the ionic strength increases the solubility of KBF_4 substantially, which means that plant solutions will be able to tolerate higher concentrations of boron than would be estimated in the absence of activity coefficients.

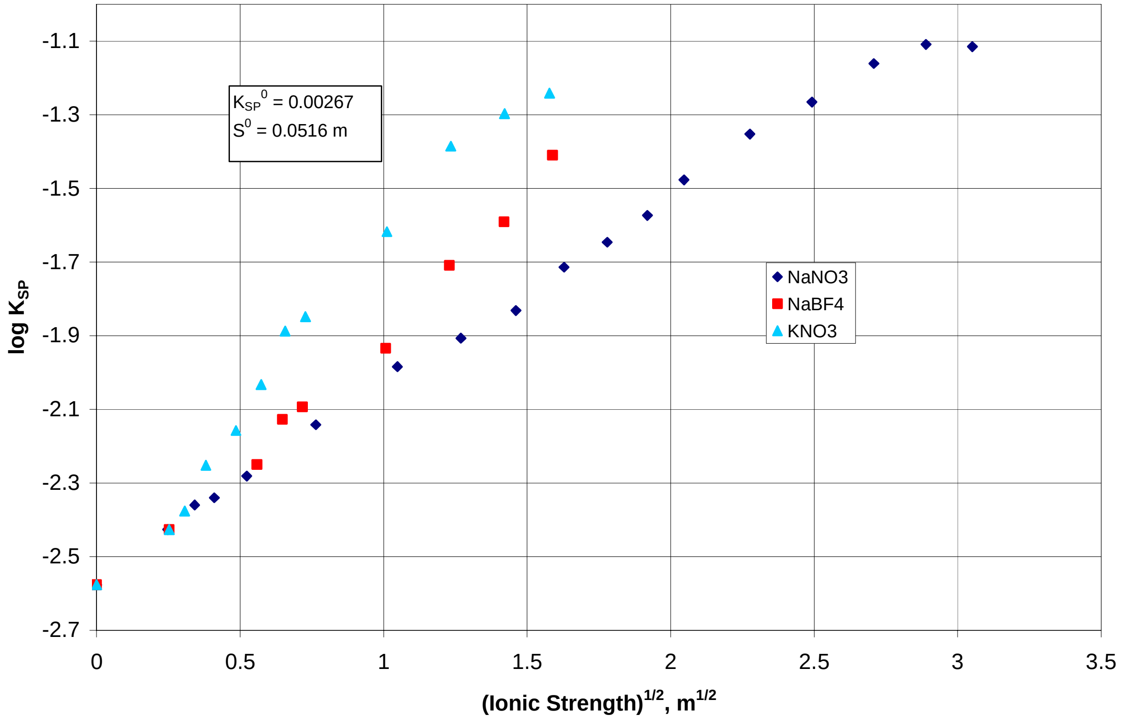
In order to obtain the Pitzer parameters in the multielectrolyte systems, the procedure developed by Pitzer and Kim[9] was followed. They developed a graphical procedure derived from empirical correlations for evaluation of the ternary system ion interaction parameters θ_{ij} and Ψ_{ijk}

$$\Delta \ln \gamma_{MX}\left(\frac{\nu}{2\nu_M m_N}\right) = \theta_{MN} + \frac{1}{2}\left(m_X + m_M \left|\frac{z_M}{z_X}\right|\right)\Psi_{MNX} \qquad \text{(Eq. 9)}$$

Here, m_n is the molality of the cation of the ionic strength adjuster salt. The term $\Delta \ln \gamma_{MX}$ is the difference between the experimental value of $\ln \gamma_{MX}$ with the appropriate single-salt parameters values for the pure single-electrolyte terms, by with $\theta_{MN} = \Psi_{MNX} = 0$ in the multielectrolyte activity coefficient equation. Pitzer used plotted the left-hand side of equation (9) against the coefficient of Ψ on the right-hand side to obtain a linear plot with intercept θ and slope Ψ. This simple approach avoids the need to solve the non-linear activity coefficient equations using multiple regression.

When we applied this approach to our data, which was obtained down to small concentrations of the ionic strength adjuster salt (m_N in equation (8)), a non-linear plot resulted because of the term in parentheses on the left-hand side approached infinity as m_N approached zero. This is evident in Figure 4 as an example. This problem was first identified by Khoo[10] and subsequently by Kim and Frederick.[11] Consequently, we will need to fit the data using multiple regression. The Number Cruncher Statistical Package (NCSS),[12] which was used by Kim and Frederick, has been ordered for that purpose. As a result, the fitting will be completed when that is available in order obtain the ion interaction parameters, after which a journal article will be prepared of the final results.

Figure 2. Solubility Product of KBF_4 in Ionic Strength Adjuster Salts, 25°C
Addition of Salts Increases Solubility



$K_{SP}{}^0$ = 0.00267
S^0 = 0.0516 m

Figure 3. Activity Coefficient of KBF_4 in Ionic Strength Adjuster Salts, 25°C

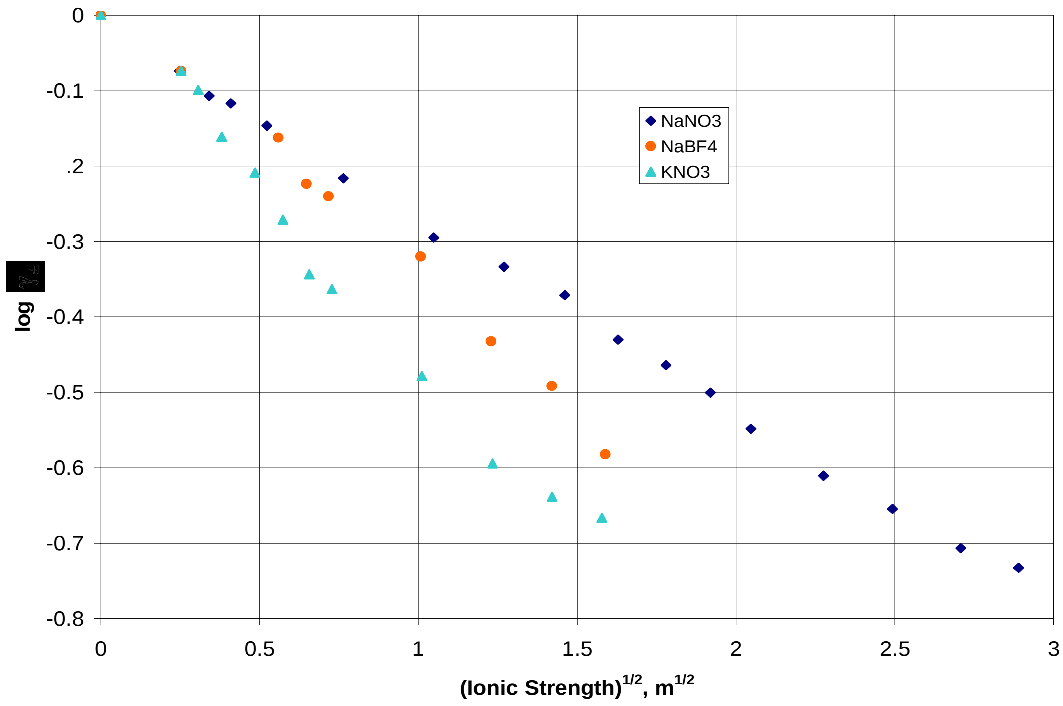
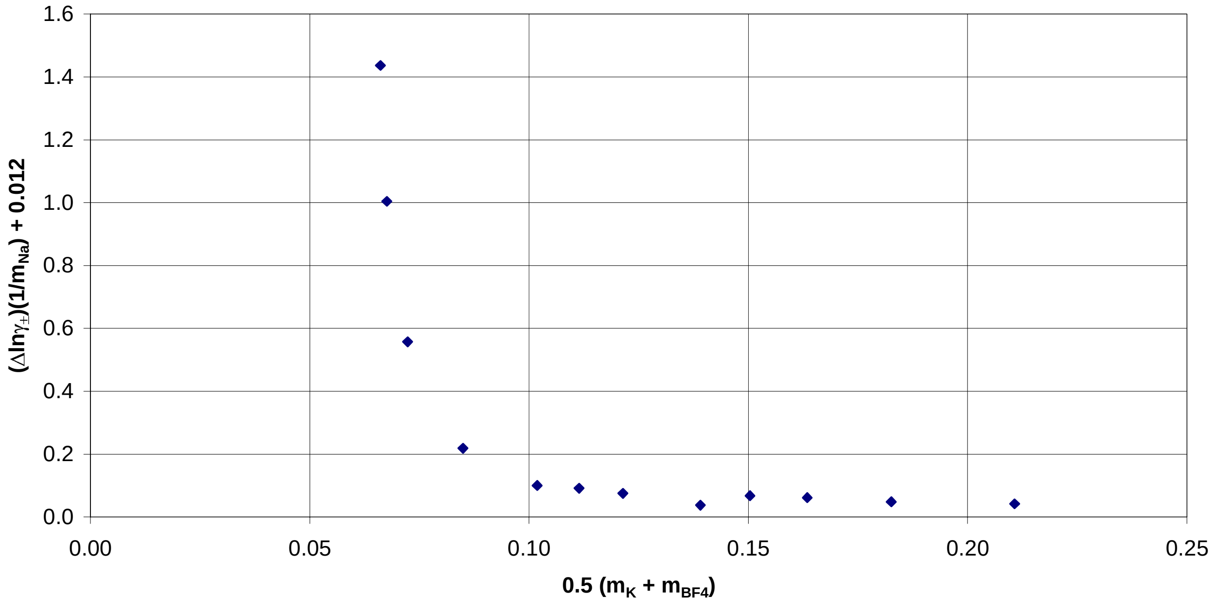


Figure 4. $(1/m_{Na})\Delta(\ln\gamma_{\pm}\ KBF_4)+0.012$ vs $(1/2)(m_K + m_{BF4})$

$NaNO_3$ System. Equil m_{BF4-} (= m_{BF4}+ m_X)

Slope = $\Psi_{K\text{-}Na\text{-}BF4}$ with intercept set = 0

Literature $\Theta_{K\text{-}Na}$ = -0.012



Demonstration of Computer Model to Predict the Precipitation of Solid Salts in the Dissolver

The INEEL fluoride speciation program was adapted to the species composition of the SRS plant dissolver solution. In laboratory tests to support the Sand, Slag, and Crucible campaign and the Mark 42 Fuel Tube campaign, the presence of high concentration of fluoride ions in boric acid/nitric acid solutions led to the formation of a white solid (see Table 3). The white solids were collected from these flow sheet simulations and were identified as potassium tetrafluoroborate (KBF_4).

Table 3. KBF_4 Saturation Experiments in SRS Plant Solutions

Date	**Test**	**[HNO3]$_0$ (M)**	**[F-]$_0$ (M)**	**[B]$_0$ (g/L)**	**Observation**
Dec-97	SS&C–sim.	9.3	0.30	2.5	Unidentified White solid
May-98	SS&C-sim. (gelatin strike)	1.0	0.23	1.7	White solid, KBF_4 (s)
Nov-98	SS&C-test 1	8.8	0.32	1.6	No solids
	SS&C-test 2	8.6	0.40	2.2	KBF_4 (s)
Feb-99	Mark 42 –sim [Al] = 0.44 M				
	Test Case **36**	1.0	0.40	2.5	No solids
	Test Case **37**	1.0	0.50	2.5	KBF_4 (s), few
	Test Case **38**	1.0	0.60	2.5	KBF_4 (s), some

The conditions that shift the equilibria towards precipitation are qualitatively understood in terms of Le Chatelier's principle by considering the following equations:

$$H_3BO_3\ (aq) + 3\ H^+(aq) + 4\ F^-\ (aq) = BF_4^-\ (aq) + 3H_2O$$
$$K+(aq) + BF_4^-\ (aq) = KBF_4(s)$$
$$K^+\ (aq) + H_3BO_3\ (aq) + 4\ F^-\ (aq) + 3\ H^+\ (aq) = KBF_4\ (s) + 3\ H_2O$$

Test Case 37 is just at saturation and Case 38 is over-saturated. These cases were modeled with the INEEL speciation program with the results in Table 4.

Table 4I. Modeling Results for KBF_4 Experiments, 20°C

Test Case	[HNO$_3$]$_0$ M	[KF]$_0$ M	[B]$_0$ g/L	[Al]$_0$ M	Mark-42-sim Observation	Using INEEL program, Calculated:
37	1.0	0.50	2.5	0.44	KBF_4 (s), few	[BF_4^-] = 41.2% of saturation (i.e. no precipitation is predicted).
38	1.0	0.60	2.5	0.44	KBF_4 (s), some	Predicts saturated KBF_4. Precipitate composition: 1.9% of K^+ 7.6% of F (4.9% of F as KBF_4)

The model properly predicts precipitation of KBF_4 at 0.60 M fluoride but slightly overpredicts solution stability at 0.50 M fluoride. This may be due to a complex interaction of activity coefficients of the ions in solution and the effect of HNO_3 on activity of HF. To complete the model development, it will be necessary to determine the activity coefficients of HF in HNO_3 and apply them in combination with calculated activity coefficients for the ionic species in solution that can be done following completion of the regression fitting of the Pitzer ion interaction parameters. As it stands, the model can predict the KF concentration stability limit to within about 12%. This is based on the 41% of saturation predicted at 0.50 M KF and correct prediction at 0.60 M KF [(1-0.41)*(0.60-0.50)/0.50]. This precision is sufficient for plant process control with safety factors.

SUMMARY

With the objective of preventing precipitation of undesirable solids during aggressive SRS dissolution processes of EM materials, the INEEL computer program is being updated with new basic chemical data resulting in a better ability to predict and avoid solids production in aqueous process solutions at SRS. The basic chemical data includes solubility, activity coefficients, and solubility products of potassium tetrafluoroborate (KBF_4) at ionic strengths expected in process solutions. This program will calculate the equilibrium position for a given starting dissolver solution composition and the solution stability is determined. Solution compositions can be varied to determine the concentration limit at which precipitation will begin in a dissolver solution.

This effort to develop a predictive model of the stability of aqueous solutions of nuclear materials will enable the avoidance of concentrations that may cause salts to precipitate. Therefore, for the processing of off-normal material, the risk of producing unwanted solids that require processing to stop will be reduced. Processing delays result in higher operating costs. In addition, the improved model may reduce the workscope for future flowsheet development by identifying the concentration of dissolver solutions that avoid the precipitation of salts. As an immediate impact, the improved INEEL model should reduce costs for the processing of difficult-to-dissolve residues from the Rocky Flats Environmental Technology Site by shortening the time it takes to determine dissolving solutions. As a long term impact, this model should improve schedules to dissolve other off-normal nuclear materials and process aqueous solutions that are stored throughout the DOE complex.

References:

1. K. S. Pitzer, J. Phys. Chem., **77**, 268 (1973).
2. K. S. Pitzer, "Ion Interaction Approach: Theory and Data Correlation," Chapter 3 in Activity Coefficients in Electrolyte Solutions, 2nd Edition, K. S. Pitzer, editor, CRC Press, Boca Raton, 1991.
3. W. J. Hamer and Y. Wu, "Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25°C," J. Phys. Chem. Ref. Data, Vol. 1, No. 4, 1047-1099 (1972).
4. S. L. Phillips, F. V. Hale, L. F. Silvester, and M. D. Siegel, Thermodynamic Tables for Nuclear Waste Isolation, Report NUREG/CR-4864/LBL-22860/SAND87-0323, Vol 1 (June 1988).
5. C. W. Davies, Ion Association (Butterworths, Washington, DC, 1962).
6. A. Roine, Outokumpo HSC Chemistry® for Windows, Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database, Version 4.0, Outokumpo Research Oy Information Service, P O Box 60, FIN-28101 Pori, Finland; available from ESM Software, Hamilton, Ohio.
7. C.F. Prutton and A.H. Maron, Fundamentals of Physical Chemistry (The MacMillan Company, 5th Edition, New York, 1957), 510.

8. R. F. Platford, “Osmotic and activity coefficients of simple borates in aqueous solution at 25°”, Canadian Journal of Chemistry, **47**, 2271-2273 (1969).

9. K. S. Pitzer and J. J. Kim, “Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mexed Electrolytes,” J. Amer. Chem. Soc., 96, 5701-5707 (1974).

10. H. H. Khoo, “Activity Coefficients in Mixed-electrolyte Solutions,” J. Chem. Soc., Faraday Trans. 1, 82, 1-12 (1986).

11. H-T. Kim and W. J. Frederick, Jr. “Evaluation of Pitzer Ion Interaction Parameters of Aqueous Mixed Electrolyte Solutions at 25 ° C. 2. Ternary Mixing Parameters,” J. Chem. Eng. Data, 33, 278-283 (1988).

12. Number Cruncher Statistical Systems, Kaysville, UT.

13. G. R. Choppin and P. J. Unrein, “Thermodynamic Study of Actinide Fluoride Complexation, in Transuranium Elements, W. Muller and R. Lindner (eds.), North Holland, Amsterdam (1976), p, 97.

14. G. R. Choppin, Radiochim. Acta, **32**, 43 (1983).

15. G. R. Choppin and L. F. Rao, “Complexation of Pentavalent and Hexavalent Actinides by Fluoride,” Radiochim. Acta, **37**, 143-146 (1984).

16. V. M. Vdovenko, L. N. Lazarev, and E. V. Shirvinskii, “Study of the Thermodynamic Characteristics of the System HF – HNO_3 – H_2O. I. Measurement of the Vapor Pressure of the Components of the Systems HF – H_2O and HF – HNO_3 – H_2O,” Soviet Radiochemistry, Vol. 7, No. 1, 45-47 (1965).

17. V. M. Vdovenko, L. N. Lazarev, E. V. Shirbinskii, and Yu. V. Gurikov, “Study of the Thermodynamic Characteristics of the System HF – HNO_3 – H_2O. II. Calculation of the Activity of Components of the System HF – HNO_3 – H_2O,” Soviet Radiochemistry, Vol. 7 No. 2, 154-160 (1965).

18. K. R. Brenneman and R. J. Donohoe, “Monitoring Hydrofluoric Acid Activity by Vapor-Phase Infrared Spectroscopy,” Appl. Spectroscopy, Vol. 48, No. 7, 808-812 (1994).