USE OF MODELING FOR 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 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 I). The white solids were collected from laboratory flowsheet simulations, and were identified as KBF_4.

Table I. 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 II.

Table II. 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	$\left[BF_4^-\right]$ = 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) widely used 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.

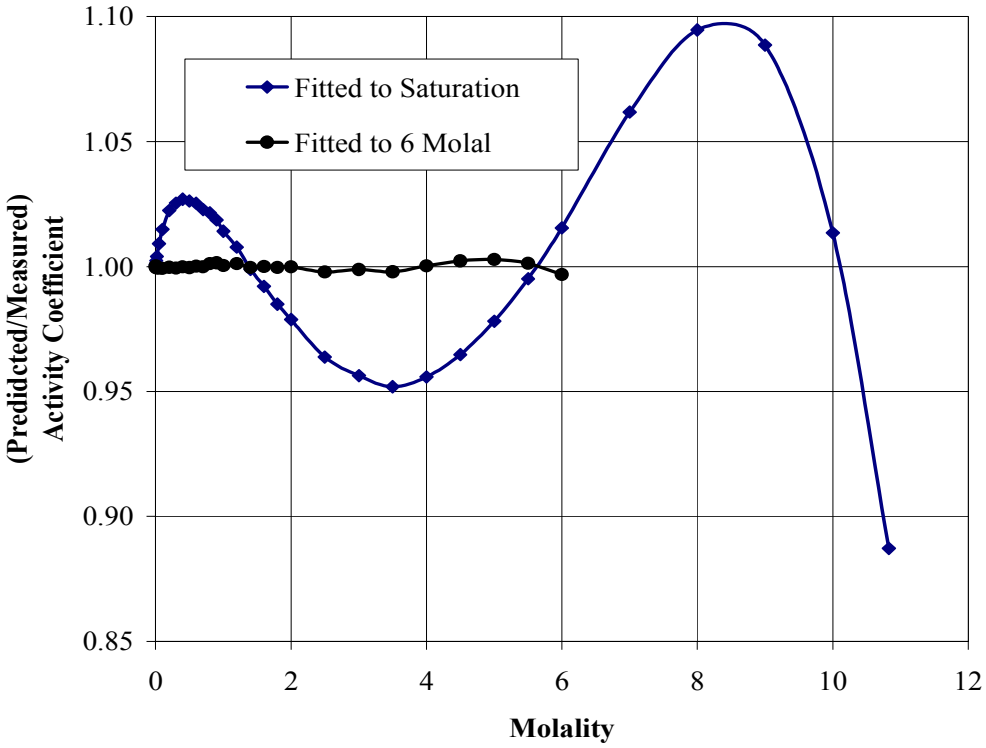

Fig. 1. Pitzer Coefficients for $NaNO_3$ Single Salt Equation Fitted to Hamer & Wu Data.

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).

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

$$K_m = m^x_{A^{z+}} m^y_{B^{z-}} \qquad \text{(Eq. 3)}$$

$$K_{Th} = a^x_{A^{z+}} a^y_{B^{z-}} = K_m \gamma^\nu_\pm \qquad \text{(Eq. 4)}$$

Here, m is the molal concentration, a is the activity, $\gamma_\pm$ is the mean molal activity coefficient $[(\gamma^x_{A_{z+}} \gamma^y_{B_{z-}})^{1/\nu}]$, 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 [$I = \frac{1}{2}(m_{A_{z+}} z_+^2 + m_{B_{z-}} z_-^2)$]. 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 $\sum(z_{products})^2 - \sum (z_{reactants})^2$. 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 are being 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). The KBF_4 solution was analyzed for B and K concentration by inductively couple plasma-atomic emission spectroscopy (ICP–AES). 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.

Preliminary data of the solubility of KBF_4 in $NaNO_3$, $NaBF_4$, and KNO_3 solutions are graphed as the Davies function in Figures 2, 3, and 4. More complete data are being obtained in the lower ionic strength regions to enable a more accurate extrapolation to zero ionic strength. Also, data in $NaNO_3$ are being obtained up to 9 molal ionic strength. The suppression of solubility due to the common ion effect in $NaBF_4$ and KNO_3 limit the collection of data in those solutions to about 2.5 molal.

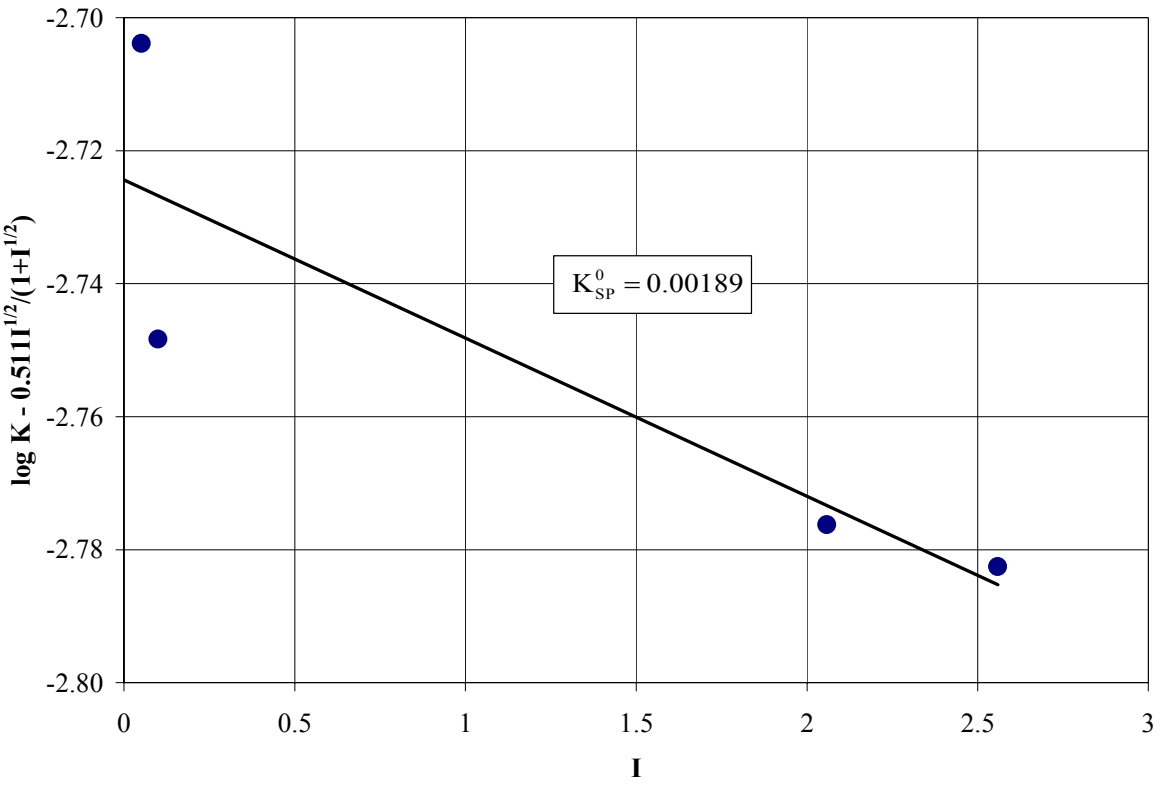

Fig. 2. KBF_4 Solubility Product as Function of Ionic Strength in $NaNO_3$, molal.

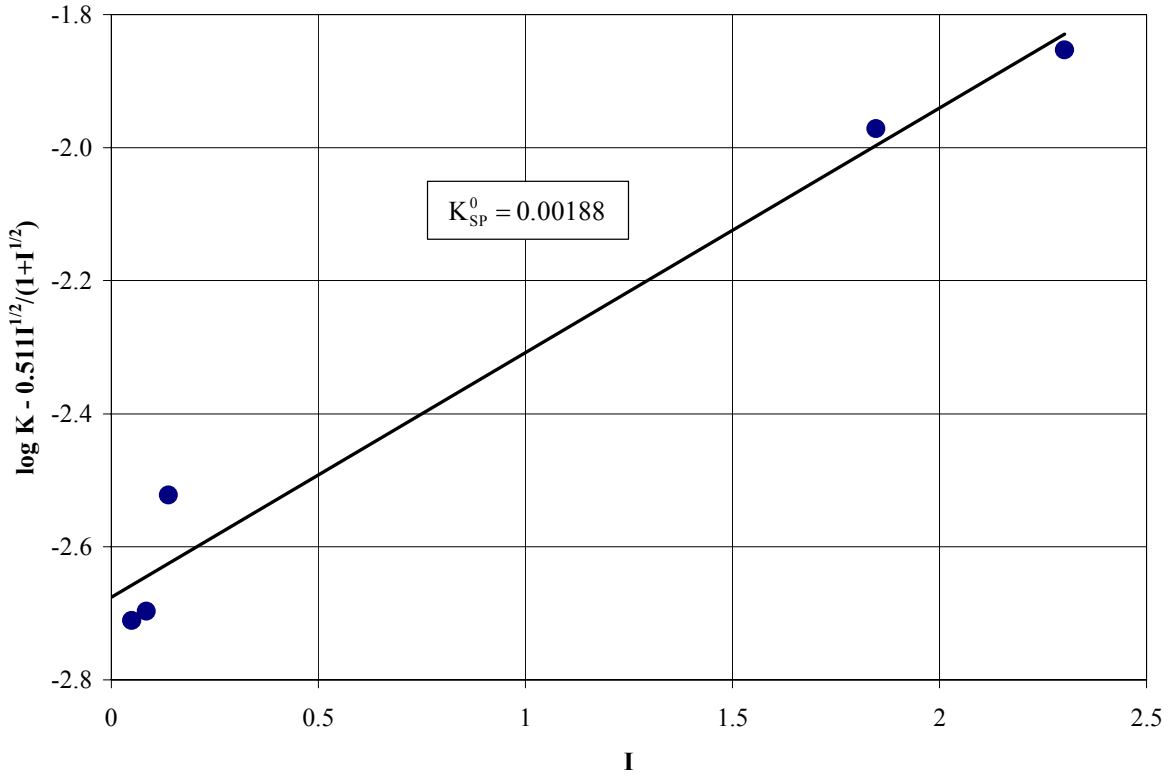

Fig. 3. KBF_4 Solubility Product as Function of Ionic Strength in $NaBF_4$, molal.

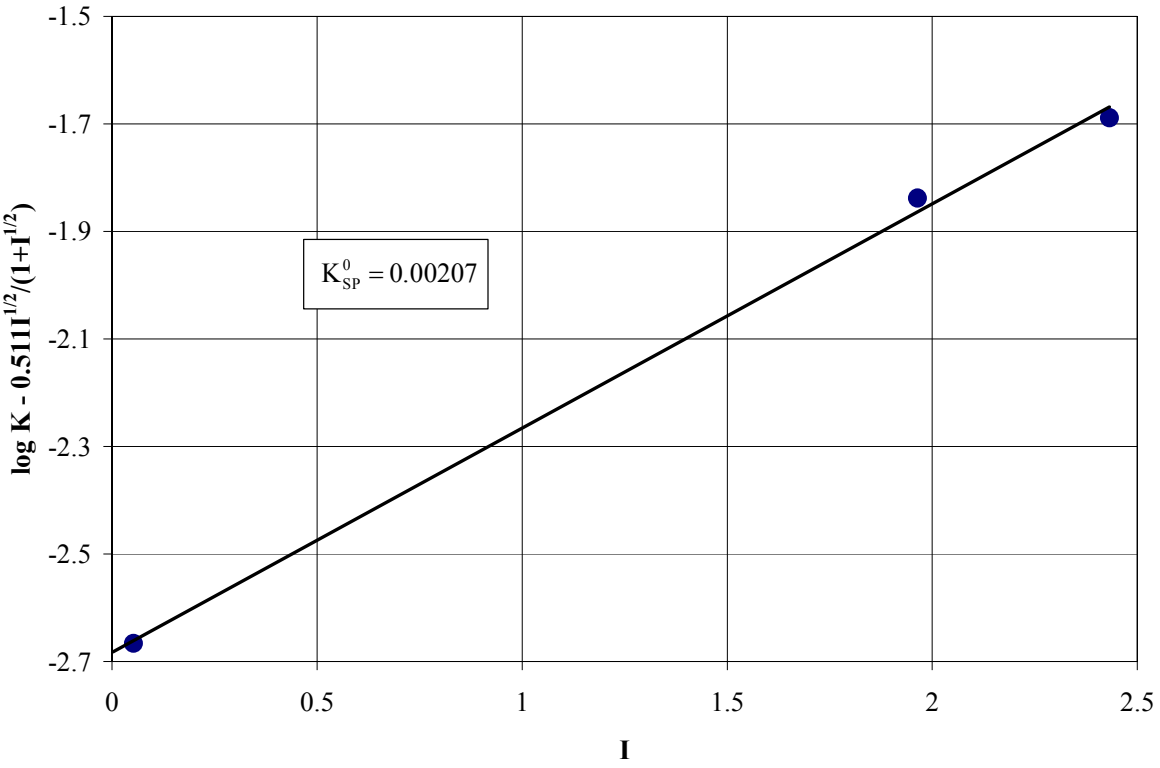

Fig. 4. KBF_4 Solubility Product as Function of Ionic Strength in KNO_3, molal.

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.

FUTURE WORK

Future efforts shall continue to address the INEEL speciation model with the incorporation of experimentally determined mercury fluoride (HgF_2) and plutonium fluoride (PuF_4) solubilities. The solubility and activity coefficients of PuF_4 will be determined by measuring the solubility of ThF_4 as a function of ionic strength, and correcting the determined complexation constants and activity coefficients to PuF_4 using the Born equation (9,10,11). Other specific solids of interest for future work include calcium fluoride, boric acid, aluminum nitrate, and plutonium salts.

In addition, hydrofluoric acid (HF) is an important species in modeling complexation equilibria and solubilities of fluoride salts in process solutions. In the current INEEL speciation program model, its activity coefficient is assumed to be unity. This has been adequate for INEEL process solutions in which the free HF and HNO_3 concentrations have been less than 0.1 and 1.8 molar, respectively. However, at the higher concentrations of HF and HNO_3 that occur in SRS process solutions, the activity coefficient of HF increases dramatically (12,13,14). Accordingly, the activity coefficients of HF as a function of ionic strength and HNO_3 concentration will be determined by measuring the partial pressure of HF above a solution by infrared spectroscopy or by an alternative transpiration technique. These new data will be incorporated into the predictive model as subsequent improvements.

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