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Solubility of Np(V) in K-Cl-CO_3 and Na-K-Cl-CO_3 Solutions to High Concentrations: Measurements and Thermodynamic Model Predictions

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Summary

The solubility of Np(V) in K-Cl-CO_3 and Na-K-Cl-CO_3 solutions was measured to confirm a published thermodynamic model for Np(V) solubility and solubility-controlling solid phases. Undersaturation experiments starting with NpO_2OH(am), $KNpO_2CO_3$(s), or $Na_3NpO_2(CO_3)_2$(s) were conducted in KCl + K_2CO_3 and NaCl + KCl + Na_2CO_3 solutions to high electrolyte concentrations. Steady-state dissolved Np(V) concentrations were obtained within 180 days, at which time the final solid phases were characterized by X-ray diffraction techniques. The thermodynamic model and data base, based on the Pitzer ion interaction formalism for activity coefficients, has been parameterized in the NaCl, $NaClO_4$, NaCl-CO_2(g), $NaClO_4$-CO_2(g), Na_2CO_3, and K_2CO_3 systems but has not been parameterized using data from K-Cl-CO_3 and Na-K-Cl-CO_3 solutions. Predictions from the thermodynamic model match measured Np(V) solubilities in K-Cl-CO_3 solutions to within 0.3 log units, confirming recent parameter values. Np(V) solubilities in Na-K-Cl-CO_3 solutions agree within 0.5 log units when $KNpO_2CO_3$(s) was the equilibrium solid phase. A deviation of up to 0.8 log units resulted when $Na_3NpO_2(CO_3)_2$(s) was the equilibrium solid phase. Additionally, the data base provides satisfactory predictions of oversaturation solubility experiments in three complex synthetic brines. This work demonstrates that thermodynamic models can provide reliable predictions of Np(V) solubility in concentrated groundwaters such as may exist in the near- and far-field environments of nuclear waste repositories located in salt beds.

Introduction

A thermodynamic data base for describing the solubility of Np(V) in concentrated Na-K-Cl-CO_3 electrolytes has been proposed [1]. The data base is an extension of the Harvie *et al.* [2] and Felmy and Weare [3] thermodynamic data bases describing mineral solubilities in concentrated ground waters. Activity coefficients are calculated using the Pitzer activity coefficient formalism [4]. The Np(V) parameters were based on measurements in which the dominant anionic bulk electrolyte was either Cl^- or CO_3^{2-}, but not when both the chloride and carbonate ions were simultaneously present in large concentrations.

The chemical systems used to parameterize the model resulted in a redundancy between the parameter describing K^+-$NpO_2(CO_3)_3^{5-}$ interactions and the parameter describing CO_3^{2-}-$NpO_2(CO_3)_3^{5-}$ interactions. That is, a linear combination of the values was determined because the individual effects were not separable. To eliminate this redundancy, additional measurements of the solubility of $KNpO_2CO_3$(s) in K-Cl-CO_3 solutions over large concentration ranges were required. Also, further experimental support was needed for the observation that $KNpO_2CO_3$(s), not $NaNpO_2CO_3 \cdot 3.5\ H_2O$(s), controls solubility even in solutions with large sodium concentrations [5]. Such experiments would provide independent chemical data to verify the thermodynamic data base developed for the Np(V)-Na-K-Cl-CO_3 system.

Reliable predictions of data not used to generate model parameters are required to establish the predictive capabilities of the model and data base. This manuscript provides such comparisons for increasingly complex systems approaching those conditions that may occur in the near-field and far-field environments of a nuclear waste repository situated in salt media.

This work was performed in support of the Waste Isolation Pilot Plant (WIPP), a U.S. department of Energy facility for the disposal of transuranic nuclear waste, located in Southeastern New Mexico.

Experimental

All chemicals were A.R. grade, KOH from J. T. Baker and K_2CO_3 from Matheson, Coleman, and Bell. Filtration was performed with 4.1 nm Centricon filters from Amicon Corporation. X-ray capillaries were loaded into a Philips Debye-Scherrer 57.3 mm camera, type 52056-B, using Kodak DEF392 films and copper K_α radiation filtered through a nickel filter. The equilibration vessels were made from polyetheretherketone (from Cadillac Plastics). All experiments were conducted under argon atmosphere at slightly elevated room temperature, 22 ± 1 °C.

Aqueous Np concentrations were measured using the 29.4 keV gamma ray. We used a high purity germanium (HPGe) detector of Lawrence Berkeley National Laboratory design with a full width half-

Table 1. Solution compositions and measured Np(V) concentrations under steady-state conditions for the K-Cl-CO_3 series of experiments

KCl (mol kg^{-1})	K_2CO_3 (mol kg^{-1})	Np(V) total (mol dm^{-3})	Initial solid	Final solid
0.0034	0.0010	$(1.21 \pm 0.08) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.0032	0.0101	$(6.61 \pm 0.57) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.0323	0.0010	$(5.89 \pm 0.28) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.0320	0.0101	$(3.47 \pm 0.24) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.0321	0.100	$(2.50 \pm 0.32) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.320	0.0010	$(2.32 \pm 0.24) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.320	0.0101	$(3.92 \pm 0.38) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.320	0.100	$(3.71 \pm 0.25) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
3.20	0.0010	$(1.94 \pm 0.24) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
3.20	0.0101	$(2.24 \pm 0.32) \times 10^{-7}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
3.20	0.100	$(1.46 \pm 0.12) \times 10^{-5}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
1.00	0.996	$(1.68 \pm 0.10) \times 10^{-5}$	$KNpO_2CO_3(s)$	$K_3NpO_2(CO_3)_2(s)$
1.08	1.07	$(1.82 \pm 0.12) \times 10^{-5}$	$NpO_2OH(am)$	$K_3NpO_2(CO_3)_2(s)$

Table 2. Solution compositions and measured Np(V) concentrations under steady-state conditions for the Na-K-Cl-CO_3 series of experiments

Na_2CO_3[a] (mol kg^{-1})	Np(V) total (mol dm^{-3})	Initial solid	Final solid
0.00035	$(1.04 \pm 0.41) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.00100	$(1.15 \pm 0.42) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.00310	$(2.11 \pm 0.99) \times 10^{-6}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.00995	$(6.32 \pm 0.23) \times 10^{-5}$	$KNpO_2CO_3(s)$	$KNpO_2CO_3(s)$
0.00995	$(1.40 \pm 0.45) \times 10^{-5}$	$Na_3NpO_2(CO_3)_2(s)$	$Na_3NpO_2(CO_3)_2(s)$
0.0454	$(3.55 \pm 0.13) \times 10^{-4}$	$Na_3NpO_2(CO_3)_2(s)$	$Na_3NpO_2(CO_3)_2(s)$
0.215	$(4.09 \pm 0.13) \times 10^{-4}$	$Na_3NpO_2(CO_3)_2(s)$	$Na_3NpO_2(CO_3)_2(s)$
1.00	$(3.47 \pm 0.11) \times 10^{-4}$	$Na_3NpO_2(CO_3)_2(s)$	unidentified

[a] Added to (5.00 mol kg^{-1} NaCl + 0.100 mol kg^{-1} KCl).

maximum (FWHM) resolution of about 0.5 keV. The overlap from the ^{233}Pa gamma ray peak at 28.6 keV was removed by applying spectral deconvolution. The correction was only necessary in the samples at very low Np concentrations ($< 10^{-6}$ mol dm^{-3}).

Experiment preparation

Two series of experiments were conducted, one in K-Cl-CO_3 solutions and one in Na-K-Cl-CO_3 solutions. Thirteen reaction vessels were prepared for the K-Cl-CO_3 series with K_2CO_3 molalities ranging from 0.001 to 1.0 mol kg^{-1} and KCl concentrations ranging from 0.0032 to 3.2 mol kg^{-1}. The K-Cl-CO_3 solution compositions are reported in Table 1. Undersaturation experiments were started by adding freshly precipitated $KNpO_2CO_3(s)$ (or $NpO_2OH(am)$ in one reaction vessel) prepared as described previously [1]. Eight reaction vessels were prepared for the Na-K-Cl-CO_3 series with Na_2CO_3 concentrations ranging from 0.00032 to 1 mol kg^{-1} in solutions of (5.0 mol kg^{-1} NaCl + 0.10 mol kg^{-1} KCl). The Na-K-Cl-CO_3 solution compositions are reported in Table 2. Undersaturation experiments were started with $KNpO_2CO_3(s)$ for carbonate concentrations less than or equal to 0.01 mol kg^{-1} and with $Na_3NpO_2(CO_3)_2(s)$ for carbonate concentrations greater than or equal to 0.01 mol kg^{-1}. Two vessels were started at 0.01 mol kg^{-1} Na_2CO_3, one with each solid. These initial solid phases were chosen based on preliminary thermodynamic modeling of the solubility of Np(V) in K_2CO_3 media [1].

$Na_3NpO_2(CO_3)_2(s)$ was prepared by adding 1 mol dm^{-3} Na_2CO_3 to the Np(V) stock solution to obtain a final carbonate concentration of about 0.5 mol dm^{-3}. A white precipitate was formed. A duplicate precipitate was prepared for X-ray analysis to verify the structure of this initial solid used to start the experiments. Purity of the Np(V) stock solution, including oxidation state purity, was verified as reported previously [1].

For routine analysis, a sample from each vessel was collected, filtered, and analyzed for Np concentration. The pH was measured using a Ross combination glass electrode that had been calibrated in each of the corresponding K-Cl and Na-K-Cl solutions to

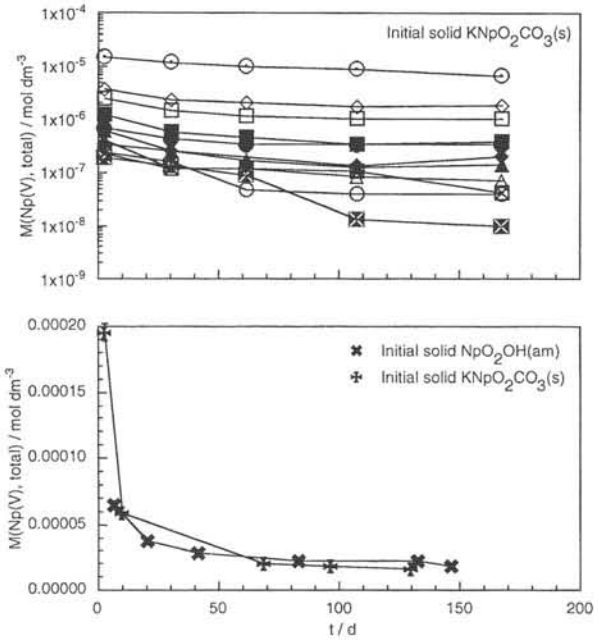


Fig. 1. Approach to steady-state for the K-Cl-CO_3 series of experiments, with concentrations (a): (■ 0.001 mol kg^{-1} K_2CO_3 + 0.0032 mol kg^{-1} KCl), ● 0.01 + 0.0032, ▲ 0.001 + 0.032, ◆ 0.01 + 0.032, □ 0.1 + 0.032, ○ 0.001 + 0.32, △ 0.01 + 0.32, ◇ 0.1 + 0.32, ⊠ 0.001 + 3.2, ⊠ 0.01 + 3.2, ⊙ 0.1 + 3.2. Note that (b), (1 mol kg^{-1} K_2CO_3 + 1.0 mol kg^{-1} KCl), is shown on a linear scale.

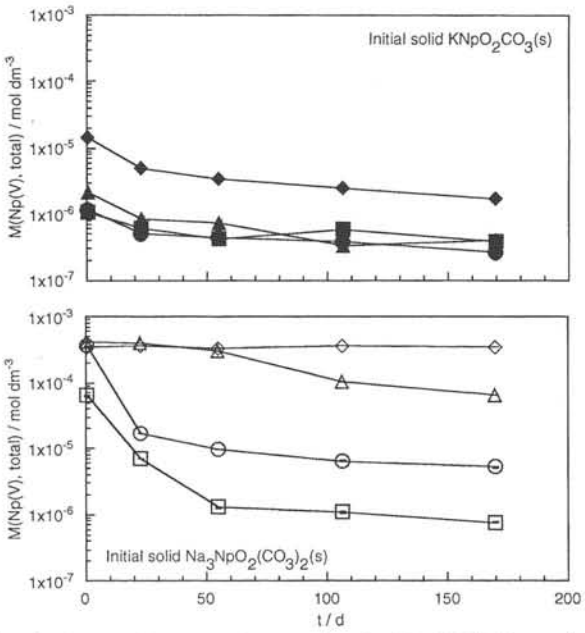


Fig. 2. Approach to steady-state for the Na-K-Cl-CO_3 series of experiments. Symbols represent (5 mol kg^{-1} NaCl + 0.1 mol kg^{-1} KCl) plus: ■ 0.0004 mol kg^{-1} Na_2CO_3, ● 0.001, ▲ 0.003, ◆ 0.01, □ 0.01, ○ 0.05, △ 0.2, ◇ 1.0.

account for liquid junction potential. The total inorganic carbon content was monitored using a Shimadzu TOC-5050 carbon analyzer to detect any large changes. No significant loss or gain of total inorganic carbon was noted, likely because these solutions had large carbonate concentrations, were highly basic, and were in tightly sealed vessels under an argon atmosphere.

Results

The K-Cl-CO_3 series of experiments was allowed to react for 168 days, with steady state being achieved within 107 days of reaction time; see Fig. 1. At carbonate concentrations less than 0.01 mol kg^{-1}, total dissolved Np(V) decreases as the KCl molalities increases, reflecting the dominant equilibrium

$$KNpO_2CO_3(s) \leftrightarrow K^+ + NpO_2CO_3^- . \quad (1)$$

At carbonate concentrations greater than 0.01 mol kg^{-1}, total dissolved Np(V) increases as the KCl molality increases, which is counter to the dominant equilibrium

$$KNpO_2CO_3(s) + 2\,CO_3^{2-} \leftrightarrow K^+ + NpO_2(CO_3)_3^{5-} . \quad (2)$$

Here, the large potassium ion molalities and high ionic strengths stabilize the highly negatively-charged neptunyl triscarbonato ion, which results in the opposite trend than would be obtained by simply applying Le Chatlier's Principle.

X-ray powder diffraction analysis of the final solid phases in the K-Cl-CO_3 series produced patterns identical to those of the initial $KNpO_2CO_3(s)$ in all but the most concentrated solutions. In solutions of (1.0 mol kg^{-1} KCl + 1.0 mol kg^{-1} K_2CO_3), both $KNpO_2CO_3(s)$ and $NpO_2OH(am)$ were converted to $K_3NpO_2(CO_3)_2(s)$. The powder pattern for these final solids are the same as those reported in [1]. Several representative patterns are given in Al Mahamid *et al.* [6].

The Na-K-Cl-CO_3 series of experiments was allowed to react for 170 days. Comparison of the aqueous Np(V) measurements for day 107 and day 170 in Fig. 2 suggest that these experiments were at steady state conditions.

X-ray powder diffraction analyses for the Na-K-Cl-CO_3 series, reported in [6], indicate that the original solid phases remained unchanged for all but the most concentrated solution. That is, $KNpO_2CO_3(s)$ remained present in solutions with less than 0.01 mol kg^{-1} carbonate ion, and $Na_3NpO_2(CO_3)_2(s)$ remained in solutions with between 0.01 and 0.2 mol kg^{-1} carbonate ion. Both initial solids remained unchanged in the 0.01 mol kg^{-1} carbonate solution, suggesting either that one of the solids is metastable or that both solids are approximated saturated in this solution. The X-ray powder diffraction pattern for the solid from the most concentrated solution (7.0 mol kg^{-1} Na^+, 0.1 mol kg^{-1} K^+, 5.1 mol kg^{-1} Cl^-, 1 mol kg^{-1} CO_3^{2-}), given in Table 3, does not match any of the patterns for sodium or potassium neptunyl(V) carbonate solids found in the literature.

Table 3. X-ray diffraction pattern, with *d*-spacings in Angstroms, for the unidentified solid from the 5.0 mol kg^{-1} NaCl + 0.1 mol kg^{-1} KCl + 1.0 mol kg^{-1} Na_2CO_3 solution. Relative intensities on a scale from 1 to 10 are given in parentheses

Unidentified Np(V) solid
7.39(1)
6.24(1)
5.24(1)
4.14(6)
3.34(2)
3.03(3)
2.82(2)
2.54(2)
2.27(2)
1.99(10)
1.73(3)
1.24(2)

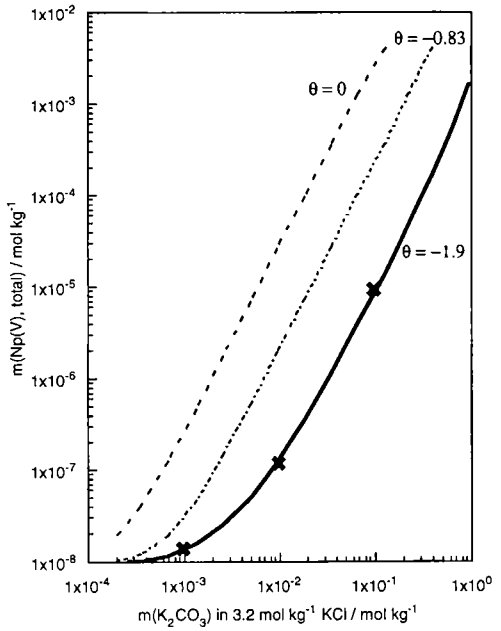


Fig. 3. Comparison of solubility measurements, ×, and thermodynamic predictions of the solubility of $KNpO_2CO_3(s)$ in 3.2 mol kg^{-1} KCl solutions as a function of K_2CO_3, for the three different values of $\theta_{CO_3NpO_2(CO_3)_3}$ in Novak *et al.* [1].

Comparison with thermodynamic model

Thermodynamic calculations were performed using the Np(V) solubility data base from Novak *et al.* [1] and references therein. The Np(V) data base is an extension of the Harvie *et al.* [2] and Felmy and Weare [3] data bases for predicting the solubilities of evaporite minerals in the "sea water" system Na-K-Mg-Ca-Cl-SO_4-CO_3. We have considered slight differences in temperatures, e.g., 22°C vs. 25°C, to be unimportant for our environmental applications, and thus all thermodynamic calculations were performed at 25°C. Thermodynamic calculations were conducted using the FMT v2.2 solubility and speciation computer code [7].

Table 4. Thermodynamic equilibrium constants at zero ionic strength for the Np(V) species in the data base. Uncertainties are reported as 2 σ

Species	log β^0 or log K_s	Reference
$NpO_2CO_3^-$	5.03 ± 0.06	[8]
$NpO_2(CO_3)_2^{3-}$	6.47 ± 0.14	[8]
$NpO_2(CO_3)_3^{5-}$	5.37 ± 0.36	[8]
$NaNpO_2CO_3 \cdot 3.5\ H_2O(s)$	−11.09 ± 0.11	[8]
$Na_3NpO_2(CO_3)_2(s)$	−14.8 ± 0.13	[8]
$KNpO_2CO_3(s)$	−13.6 ± 0.1	[1]
$K_3NpO_2(CO_3)_2(s)$	−15.9 ± 0.1	[1]

Table 5. Thermodynamic parameter values for Np(V) species in Na-K-Cl-CO_3 media, as discussed in Novak *et al.* [1] and references therein. Parameters not explicitly listed are zero. Parameters for the other species needed to make predictions are given in Harvie *et al.* [2]

Single electrolyte solution parameters for Np(V) species

i/j	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	$\beta_{ij}^{(2)}$	C_{ij}^{φ}	Reference
Na/NpO_2CO_3	0.10	0.34	0	0	[8]
$Na/NpO_2(CO_3)_2$	0.48	4.4	0	0	[8]
$Na/NpO_2(CO_3)_3$	1.80	22.7	0	0	[8]
K/NpO_2CO_3	0.10*	0.34*	0	0	[1]
$K/NpO_2(CO_3)_2$	0.48*	4.4*	0	0	[1]
$K/NpO_2(CO_3)_3$	2.34	22.7	−96	−0.22	[1]
NpO_2/Cl	0.1415	0.281	0	0	[8]

Common-ion two electrolyte parameter values for Np(V) species

a	*a'*	$\theta_{aa'}$	$\psi_{aa'Na}$	$\psi_{aa'K}$	Reference
Cl	NpO_2CO_3	−0.21	0	0*	[8]
Cl	$NpO_2(CO_3)_2$	−0.26	0	0*	[8]
Cl	$NpO_2(CO_3)_3$	−0.26	0	0*	[8]
CO_3	$NpO_2(CO_3)_3$	−1.9	0*	0*	[1]

* These values were assigned by analogy with Na or are included for completeness.

Comparisons between measurements and the predictions of the thermodynamic data base are made below for three systems of increasing complexity: K-Cl-CO_3 solutions, Na-K-Cl-CO_3 solutions, and Na-K-Mg-Ca-Cl-CO_3-SO_4-B-Br brines.

K-Cl-CO_3 solutions

A recently proposed set of thermodynamic parameters for Np(V) in Na-K-Cl-CO_3 media [1] contained a redundancy in ion interaction parameters expressed by the relationship $2\beta_{KX}^{(0)} + \theta_{CO_3X} = 2.80$, where X = $NpO_2(CO_3)_3^{5-}$. The redundancy occurred because the system was parameterized using data were the K^+ and CO_3^{2-} concentrations did not vary independently, and thus the effects of each could not be separated. The parameters were shown to describe Np(V) solubility data in K_2CO_3 media equally well for $-1.9 \leq \theta_{CO_3X} \leq 0$ with corresponding $\beta^{(0)}$ values [1]. The experi-

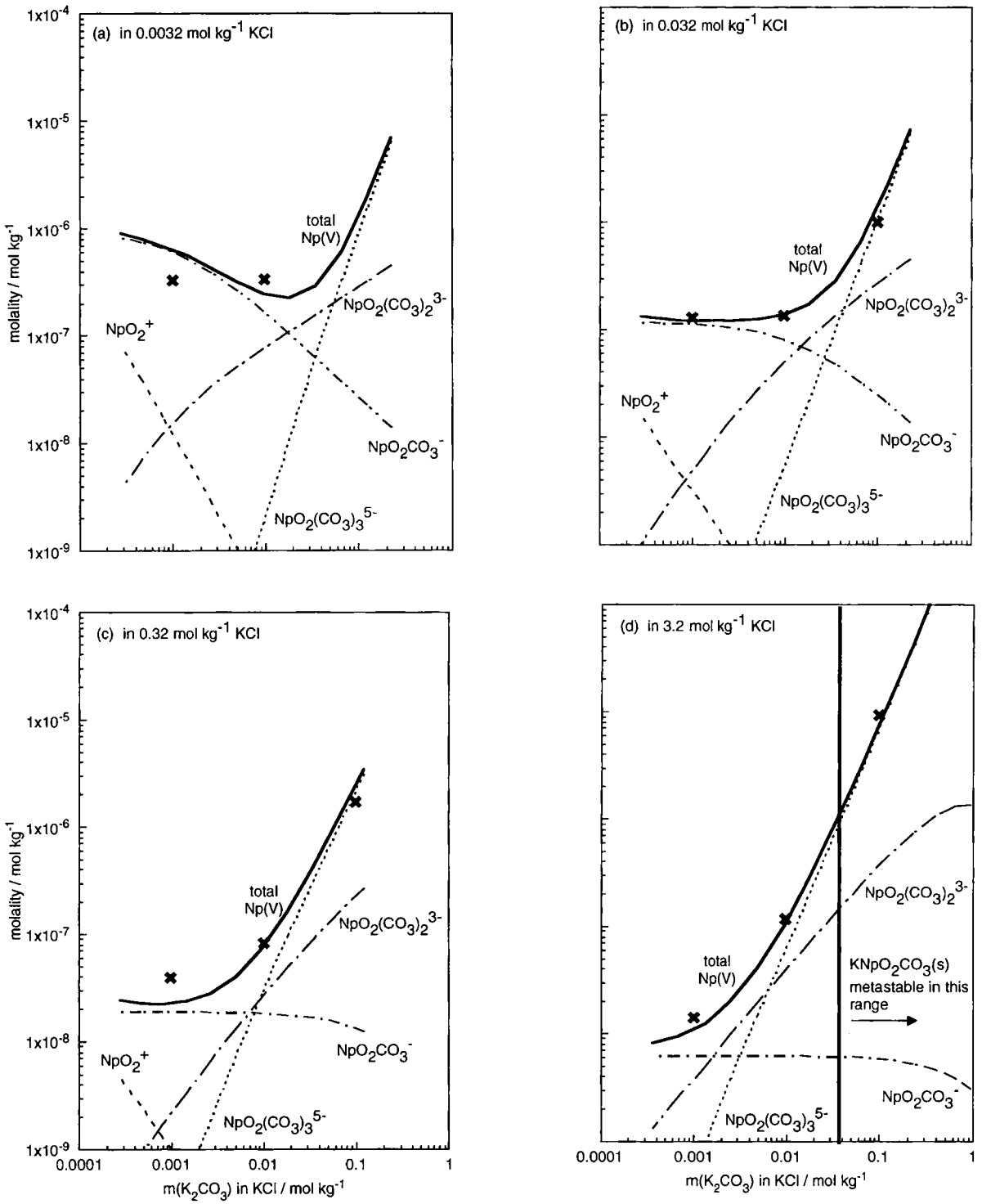


Fig. 4. Calculated solubility of $KNpO_2CO_3$(s) in KCl solutions as a function of K_2CO_3, and comparison with measurements, ×. KCl molalities are: (a) 0.0032 mol kg^{-1}, (b) 0.032 mol kg^{-1}, (c) 0.32 mol kg^{-1} and (d) 3.2 mol kg^{-1}. The vertical line in (d) denotes the K_2CO_3 molality at which $KNpO_2CO_3$(s) is predicted to become metastable with respect to $K_3NpO_2(CO_3)_2$(s) in this system.

ments in K-Cl-CO_3 media can be used to separate the effects of potassium ion interactions with the neptunyl triscarbonato ion from the effects of carbonate ion interactions. Most of the K-Cl-CO_3 experiments have neptunyl triscarbonato ion as the dominant Np(V) species, and both Cl^- and CO_3^{2-} are present in large concentrations.

A comparison of the results from the K-Cl-CO_3 experiments with 3.2 mol kg^{-1} KCl and model calculations with $\theta_{CO_3X} = 0$, -0.83, and -1.9 ($\beta^{(0)} = 1.40$, 1.81, and 2.34, respectively) is given in Fig. 3. The parameter sets with $\theta_{CO_3X} = 0$ and $\theta_{CO_3X} = -0.83$ significantly overpredict the solubility of $KNpO_2CO_3$(s) under these conditions by more than one and two

orders of magnitude, respectively. The parameter set with $\theta_{CO_3X} = -1.9$ provides excellent agreement with these data, leading us to select this parameter set as the best. In these solutions, the larger value of $\beta^{(0)}$ increases the activity coefficient of $NpO_2(CO_3)_3^{5-}$ and thus suppresses the solution concentration of $NpO_2(CO_3)_3^{5-}$. This effect dominates over the decrease in activity coefficient caused by CO_3^{2-}-$NpO_2(CO_3)_3^{5-}$ interactions. A similar though less pronounced trend in the predictions occurs in the 0.32 mol kg^{-1} KCl solutions, where the difference is less than 0.25 log units at 0.1 mol kg^{-1} CO_3^{2-}. The comparison in Fig. 3 confirms the selection of the thermodynamic parameter set with $\theta_{CO_3X} = -1.9$ recommended in [1]. Table 4 gives the thermodynamic stability and solubility constants for the Np(V) species included in the data base. Table 5 lists the ion interactions parameters for the Np(V) species with Na^+, K^+, Cl^-, and CO_3^{2-}.

The solubility data and the speciation calculations, both as a function of K_2CO_3 molality, are summarized for the 0.0032, 0.032, 0.32, and 3.2 mol kg^{-1} KCl solutions in Fig. 4. The speciation curves in the 0.0032, 0.032, and 0.32 mol kg^{-1} KCl are plotted up to the approximate molality where $K_3NpO_2(CO_3)_2(s)$ becomes the thermodynamically predicted stable phase. The precipitation of $K_3NpO_2(CO_3)_2(s)$ was suppressed in the predictions for 3.2 mol kg^{-1} KCl to facilitate comparison with the solid phase observed in the experiments. The bold vertical line of Fig. 4d indicates the approximate molality where $K_3NpO_2(CO_3)_2(s)$ would become the more stable phase. Thus, the data point at (0.1 mol kg^{-1} K_2CO_3 + 3.2 mol kg^{-1} KCl) represents a metastable equilibrium of $KNpO_2CO_3(s)$, consistent with observations of Novak *et al.* [1].

All of the data in Fig. 4 test the solubility product value for $KNpO_2CO_3(s)$. At the lower concentrations, the data test the thermodynamic parameters for the $NpO_2CO_3^-$ species. At the higher concentrations, the data test the parameters for the $NpO_2(CO_3)_3^{5-}$ species. The $NpO_2(CO_3)_2^{3-}$ species is predicted to be dominant only under narrow ranges of the conditions studied here, and its behavior in these ranges was not examined sufficiently to draw comparisons with the data base predictions. The calculations agree with the data within 0.3 log units at low concentrations and within 0.1 log units at high concentrations, reflecting the predominance of high concentration data for determining model parameters. The agreement at low concentrations suggests that the assignment of Na^+-$NpO_2CO_3^-$ parameters to K^+-$NpO_2CO_3^-$ [1] is a reasonable approximation.

Only for the solutions of (1.0 mol kg^{-1} K_2CO_3 + 1.0 mol kg^{-1} KCl) was the $K_3NpO_2(CO_3)_2(s)$ phase observed. The separate reaction vessels, started with either $NpO_2OH(am)$ or $KNpO_2CO_3(s)$, yielded $10^{-4.71}$ and $10^{-4.74}$ mol kg^{-1} total aqueous Np(V), respectively. The solubility of $K_3NpO_2(CO_3)_2(s)$ is predicted to yield a total Np(V) molality of $10^{-4.75}$ mol kg^{-1} under these conditions. Although additional data are required

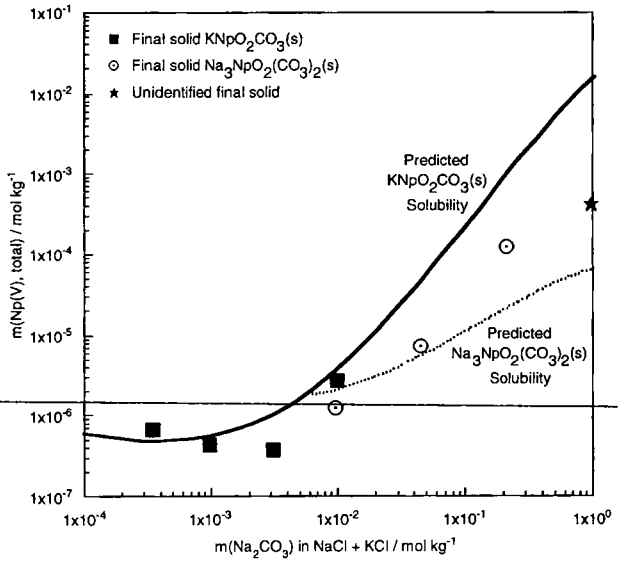


Fig. 5. Comparison between experiments and predictions for the solubility of Np(V) in (5.0 mol kg^{-1} NaCl + 0.10 mol kg^{-1} KCl) solutions as a function of added Na_2CO_3.

to test the utility of the data base for calculating the solubility of this potassium neptunyl carbonato solid, the reproducibility of the data and the agreement between the predictions and data suggest that the solubility product value is reliable.

In summary for the K-Cl-CO_3 solutions, the thermodynamic parameters of Novak *et al.* [1] provide excellent predictions of all Np(V) solubility measurements made over wide ranges of K-Cl-CO_3 solution compositions.

Na-K-Cl-CO_3 solutions

A comparison of the data in Na-K-Cl-CO_3 solutions and the predicted solubility and speciation from the thermodynamic data base is given in Fig. 5. The $KNpO_2CO_3(s)$ solid is predicted to be stable below about 0.006 mol kg^{-1} total carbonate concentration under these conditions, in agreement with the experimental observations. The predicted total Np(V) molalities are within 0.5 log units. The prediction of $KNpO_2CO_3(s)$ solubility at 0.01 mol kg^{-1} total carbonate concentration agrees well with the measured value even though it is not the most stable solid phase under these conditions. The lack of conversion from the monopotassium to the trissodium solid under these conditions may reflect a kinetic barrier to solid phase conversion consistent with that observed between the monopotassium and trispotassium neptunyl carbonato solids [1].

The $Na_3NpO_2(CO_3)_2(s)$ solid is predicted to be stable above about 0.006 mol kg^{-1} total carbonate molality in (5 mol kg^{-1} NaCl + 0.1 mol kg^{-1} KCl) solutions, as shown in Fig. 5. The predictions agree well with measurements for 0.01 and 0.045 mol kg^{-1} carbonate ion, but deviate in the 0.22 mol kg^{-1} total carbonate solutions by 0.8 log units. Little can be

Table 6. Solution compositions for Np(V) solubility experiments in synthetic predominantly Na-Cl and Na-Mg-K-Cl brines [5]. Brine compositions are based on those collected at the WIPP Site

	0.86 mol kg^{-1} "AlSinR" Brine		3.0 mol kg^{-1} "H17" Brine		7.8 mol kg^{-1} "SPC" Brine	
	mol kg^{-1}	(mol dm^{-3})	mol kg^{-1}	(mol dm^{-3})	mol kg^{-1}	(mol dm^{-3})
Na	0.656	(0.646)	2.54	(2.40)	2.06	(1.84)
K	0.00828	(0.00816)	0.0324	(0.0307)	0.859	(0.766)
Mg	0.0218	(0.0215)	0.0784	(0.0741)	1.61	(1.43)
Ca	0.0174	(0.0171)	0.0306	(0.0289)	0.0167	(0.0149)
Cl	0.577	(0.568)	2.63	(2.48)	6.05	(5.39)
S (as SO_4)	0.0808	(0.0796)	0.0794	(0.0750)	0.0489	(0.0436)
B	0.00283	(0.00279)	0.00421	(0.00398)	0.0229	(0.0204)
Br	0	(0)	0.00100	(0.000950)	0.00566	(0.00504)
Total Inorganic Carbon*	0.00347	(0.00342)	0.00274	(0.00260)	0.00152	(0.00135)
$p_{CO_2}(g)$	$10^{-2.71}$		$10^{-2.56}$		$10^{-3.95}$	
estimated density, g cm^{-3}	1.03		1.10		1.20	
$\frac{m}{M}$, $dm^3\ kg^{-1}$	1.01		1.06		1.12	
Ionic Strength, mol kg^{-1}	0.862		2.98		7.82	
pmH $\equiv -\log(m_{H^+})$	7.67		7.65		8.56	
Total Dissolved Solids, mg dm^{-3}	44,600		155,000		305,000	

* Total Inorganic Carbon concentration was calculated by assuming the fugacity was equal to the partial pressure for $CO_2(g)$.

concluded from the comparison between the model and the data point in the most concentrated solution because the solid has not been identified.

These experiments provide an additional test of the solubility product for $KNpO_2CO_3(s)$ and $Na_3NpO_2(CO_3)_2(s)$, and demonstrate that the potassium solid forms even when the sodium molality is fifty times greater than the potassium molality. Note that these experiments primarily test the ion interaction parameter values between the neptunyl carbonato species and the sodium ion, not with the potassium ion, because the sodium molality is much larger. The good agreement between predictions and experiment below 0.1 mol kg^{-1} carbonate indicates that the Na^+-$NpO_2(CO_3)_n^{1-2n}$, n = 1, 2, 3 parameters are reliable under these conditions. The deviation between predictions and experiment at higher carbonate concentrations suggests that the ion interaction parameter values between the sodium and neptunyl triscarbonato ion could be improved, perhaps with the addition of a C^{Φ}_{NaX} parameter. However, it must be recognized that these highly concentrated solutions represent an extrapolation of the Fanghänel *et al.* [8] data base beyond the sodium concentrations that were used to fit the ion interaction parameters.

In summary for the Na-K-Cl-CO_3 solutions, the thermodynamic parameters of Novak *et al.* [1] provide excellent predictions of the Np(V) solubility measurements made in concentrated Na-K-Cl-CO_3 solutions when the carbonate concentration is less than about 0.1 mol kg^{-1}, which includes most environmentally relevant conditions. Under conditions where carbonate ion concentrations are greater than about 0.1 mol kg^{-1}, the predictions from the $KNpO_2CO_3(s)$ and $Na_3NpO_2(CO_3)_2(s)$ solids can be considered to provide solubility estimates that may bound the actual value.

Complex synthetic brines

The thermodynamic data base [1] can also be tested through comparisons with solubility measurements in complex synthetic brines. Two such experiments were performed in predominantly Na-Cl brines, ionic strengths 0.86 and 3.0 mol kg^{-1}, containing small amounts of Mg, Ca, and K. Another such experiment was performed in a predominantly Na-Mg-K-Cl brine with ionic strength 7.8 mol kg^{-1}. These experiments, in which $CO_2(g)$ partial pressures and the pH meter reading were held constant, are reported in Novak *et al.* [5]. The solution compositions are reproduced in Table 6.

Operational pH measurements were taken with Ross electrodes calibrated to standard low ionic strength buffer solutions [5]. However, calibrations to determine the corrections for liquid junction potentials were not performed. To develop the correspondence between the meter reading and the hydrogen ion concentration, the operational pH values, pH_{op}, were converted to hydrogen ion molalities using the electrode calibration correlation

$$\text{pmH} \equiv -\log m_{H^+} = \text{pH}_{op} + 0.159\, m_{NaCl} + \log\left(\frac{m}{M}\right) \quad (3)$$

[9]. The ratio of molality to molarity, $\frac{m}{M}$, is given in Table 6 for the brines of concern here.

The meter readings $pH_{op} = 7.5 \pm 0.1$ and 7.1 ± 0.1 for the two predominantly NaCl brines were converted to $pmH = -\log(m_{H^+}) = 7.6 \pm 0.25$ and 7.6 ± 0.25 using the ionic strength of the solutions to approximate m_{NaCl}. Because of the uncertainty associated with this estimation, the error was arbitrarily increased from ± 0.1 to ± 0.25 units to reflect the lack of precise knowledge of the pmH. The meter reading for the Na-Mg-K-Cl brine, $pH_{op} = 7.3 \pm 0.1$ was converted to pmH = 8.6 ± 0.5, again using the ionic strength to approximate m_{NaCl}. However, because this brine is very different from NaCl, having $m_{Mg^{2+}} = 1.6$ mol kg^{-1} and $m_{K^+} = 0.8$ mol kg^{-1}, we have arbitrarily increased the uncertainty from ± 0.1 to ± 0.5 units. The minimum and maximum dissolved Np(V) concentrations given below correspond to the highest and lowest concentrations predicted over the pmH ranges given above.

In the simulations below, several carbonate solids in the data base [2] were prevented from precipitating, including aragonite and calcite, both $CaCO_3$(s), dolomite, $CaMg(CO_3)_2$(s), gaylussite, $CaNa_2(CO_3)_2 \cdot 5\,H_2O$(s), magnesite, $MgCO_3$(s), magnesium oxychloride, $Mg_2Cl(OH)_3 \cdot 4\,H_2O$(s), nesquehonite, $MgCO_3 \cdot 3\,H_2O$(s), and pirssonite, $Na_2Ca(CO_3)_2 \cdot 2\,H_2O$(s). None of the characteristic X-ray diffraction patterns for these solids were identified in the Np(V) experiments [5].

The solubility of Np(V) in the 0.86 and 3.0 mol kg^{-1} ionic strength brines was reported to be $(1.94 \pm 0.58) \times 10^{-6}$ mol dm^{-3} and $(8.2 \pm 3.9) \times 10^{-7}$ mol dm^{-3} [5], or $\log(m_{Np(V)}) = -5.73 \pm 0.13$ and -6.12 ± 0.22, respectively. The solid phases isolated from the brine experiments were identified as $KNpO_2CO_3$(s). The thermodynamic parameter set [1], reproduced for Np(V) species in Tables 4 and 5, predicts total dissolved Np(V) concentrations of $\log(m_{Np(V)}) = -5.1$ to -5.8 for the 0.86 mol kg^{-1} ionic strength brine, and $\log(m_{Np(V)}) = -5.3$ to -6.0 in the 3.0 mol kg^{-1} ionic strength brine. Graphical comparisons can be found in [6]. $KNpO_2CO_3$(s) is predicted to be the most stable solid phase, that is, the solutions is undersaturated with respect to all other Np(V) solids in the data base, including NpO_2OH(aged), $NaNpO_2CO_3 \cdot 3.5\,H_2O$(s), $Na_3NpO_2(CO_3)_2$(s), and $K_3NpO_2(CO_3)_2$(s). The thermodynamic model thus predicts both the correct solid phase and the total Np(V) concentrations within the uncertainty associated with the calculations and measurements.

The solubility of Np(V) in the 7.8 mol kg^{-1} ionic strength brine was reported to be $(2.38 \pm 0.80) \times 10^{-7}$ mol dm^{-3} [5], or $\log(m_{Np(V)}) = -6.60 \pm 0.15$. The solid phase was also identified as $KNpO_2CO_3$(s). Np(V) solubility predictions in this brine using the data base [1] yield the observed solid, $KNpO_2CO_3$(s), but give a solubility 4 to 5 orders of magnitude higher than that measured. This difference is probably because the thermodynamic data base was not parameterized for Mg^{2+} interactions and does not include ion interaction parameters between Mg^{2+} and the neptunyl carbonato ions. We can approximate the ion interaction parameters for Mg^{2+} and the neptunyl carbonato ions as the average of the parameter values for Na^+ and K^+, that is, $\beta^{(0)}_{MgNpO_2CO_3} = 0.10$, $\beta^{(1)}_{MgNpO_2CO_3} = 0.34$, $\beta^{(0)}_{MgNpO_2(CO_3)_2} = 0.48$, $\beta^{(1)}_{MgNpO_2(CO_3)_2} = 4.4$, $\beta^{(0)}_{MgX} = 2.07$, $\beta^{(1)}_{MgX} = 22.7$, $\beta^{(2)}_{MgX} = -48$, and $C^{\Phi}_{MgX} = -0.11$. This is a reasonable although arbitrary first approximation and no attempt was made to correlate between monovalent and divalent ions. Using these assignments, the data base predictions provide a remarkably good estimate of $\log(m_{Np(V)}) = -5.3$ to -6.6 for the 7.8 mol kg^{-1} ionic strength brine. A graphical comparison can be found in [6]. The assignment of parameter values for interactions between Mg^{2+} and the neptunyl carbonato anions effectively suppressed the formation of the neptunyl bis- and triscarbonato ions in this brine while having almost no effect on the neptunyl monocarbonato ion concentration. Obviously, more data in solutions with high magnesium content are necessary to support the use of the data base under these conditions.

The thermodynamic predictions for Np(V) solubility in the three synthetic brines are very satisfactory, agreeing with measured values to within less than an order of magnitude. These results demonstrate that reliable prediction of dissolved Np(V) concentrations in complex concentrated electrolyte solutions under environmentally relevant conditions is possible. In addition, this work demonstrates that combination of thermodynamic parameters determined in simpler media, in this case Np(V) in $NaClO_4$, NaCl, $NaClO_4$ with CO_2(g), NaCl with CO_2(g), Na_2CO_3, and K_2CO_3, can produce a reliable and robust data base for predicting solubilities in complex ionic media.

Conclusion

The thermodynamic data base for Np(V) species in Na-K-Cl-CO_3 solutions [1] has been shown to produce reliable independent predictions of measurements in the K-Cl-CO_3 and Na-K-Cl-CO_3 systems. It also provides good predictions of the limited data in complex Na-K-Mg-Ca-Cl-CO_3-SO_4-B-Br brines [5] when Na, K, and Cl are the dominant ions. The success of the data base in predicting a wide variety of solubility data provides confidence that the thermodynamic model can produce good estimates of Np(V) solubilities in environmentally-relevant systems such as those associated with nuclear waste repositories.

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