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subject: Recommended Parameter Values for Modeling An(V) Solubility in WIPP Brines

1. Introduction

In preparation for the actinide solubility calculations that will be performed in support of the Compliance Recertification Application (CRA), I have been reviewing the geochemical parameters used in the Fracture-Matrix Transport (FMT) database. In previous memorandums addressed to you, I recommended changes to the parameter values used to simulate the solubilities of actinides in the +III and +IV oxidation states (Giambalvo, 2002a; 2002b) and to the parameter values used to simulate the interaction of organic ligands with metals (Giambalvo, 2002c).

The current memo recommends minor changes to normalized chemical potential (μ^0/RT, where R is the ideal gas constant and T is temperature in Kelvin) values in the FMT database. It does not recommend any other changes to the speciation and solubility model for actinides in the +V oxidation state (An(V)) implemented in the version of the FMT database used for compliance baseline performance assessment (PA) calculations (baseline database)*. The recommended model differs from the baseline (PAVT) model only in the precision of parameter conversion calculations, not in the fundamental model assumptions nor in parameter sources. Therefore, I have described only the baseline model.

2. An(V) Model in the Baseline Database

The An(V) speciation and solubility model in the current baseline database is essentially that described by Novak et al. (1997) and expanded by Al Mahamid et al. (1998). Additional parameters were calculated by Neck et al. (1995) and Fanghänel et al. (1995). Parameters are derived from Np solubility and speciation data collected in a variety of ionic media. The WIPP actinide solubility model assumes that Np(V) will be the only actinide that persists in the +V oxidation state in the repository (DOE, 1996).

* The baseline database is identical to the database used for the Performance Assessment Verification Test (PAVT), and is the most recent documented version of the database (Novak, 1997). It is stored in the CHEMDAT file FMT_970407.CHEMDAT in Sandia National Laboratories' Configuration Management System on the WIPP Alpha Cluster in the library WP$NONPA_CMSROOT:[FMT].

WIPP:1.3.5.1.2.1:PA:QA:FMT Database for the CRA

1. Pitzer parameters describing the interaction of NpO_2^+ with Cl^- and ClO_4^- are derived from measurements of Np speciation in 1-5 mol/L NaCl and $NaClO_4$ solutions (Neck et al., 1995).

2. Normalized chemical potentials (μ^0/RT, where R is the ideal gas constant and T is temperature in Kelvin) for hydrolysis species of NpO_2^+ and related Pitzer parameters are derived from solubility measurements of $NpO_2OH_{(aged)}$ and $NpO_2OH_{(am)}$ in 0.1-3 M $NaClO_4$ and 5 mol/L NaCl solutions (Fanghänel et al., 1995).

3. Normalized chemical potentials for NpO_2^+-carbonate complexes and Pitzer parameters describing their interaction with Na^+ ($\beta^{(0)}$, $\beta^{(1)}$, C^ϕ) and Cl^- (θ) are derived from solubility measurements of $Na_3NpO_2(CO_3)_{2(s)}$ and $NaNpO_2CO_{3(s)}$ in 0.1-6.5 mol/kg $NaClO_4$ and 1.02 and 5.6 mol/kg NaCl solutions (Fanghänel et al., 1995).

4. Pitzer parameters describing the interaction of NpO_2^+-carbonate complexes with K^+ are derived by analogy with the Na^+ system and from solubility measurements of $NpO_2OH_{(s)}$ and $KNpO_2CO_{3(s)}$ in 0.01-6.38 mol/kg K_2CO_3 solutions (Novak et al., 1997).

5. Pitzer parameters describing the interaction of NpO_2^+-carbonate complexes with Mg^{2+} are derived by analogy with the Na^+ and K^+ systems and verified by simulation of high-Mg brines, including SPC brine (Salado Primary Constituent brine) (Al Mahamid et al., 1998). In actinide solubility calculations completed for the Compliance Certification Application and the Performance Assessment Verification Test, the composition of Salado Formation brine is assumed to equal that of SPC brine (Novak et al., 1996; Novak, 1997).

6. Neptunium solid phases include $NpO_2OH_{(aged)}$, $NpO_2OH_{(am)}$, $NaNpO_2CO_3 \cdot 3.5H_2O_{(s)}$, $Na_3NpO_2(CO_3)_{2(s)}$ (Neck et al., 1995), $KNpO_2CO_{3(s)}$, and $K_3NpO_2(CO_3)_{2(s)}$ (Novak et al., 1997).

Tables 1-4 list the parameter values used in the An(V) model. Table 1 includes both baseline and recommended values of μ^0/RT.

3. References

Al Mahamid, I., C.F. Novak, K.A. Becraft, S.A. Carpenter and N. Hakem, 1998. Solubility of Np(V) in K-Cl-CO_3 and Na-K-Cl-CO_3 solutions to high concentrations: Measurements and thermodynamic model predictions, *Radiochimica Acta*, **81**:93-101.

DOE, 1996. Appendix SOTERM in *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant*, US Department of Energy, Carlsbad, NM.

Fanghänel, T., V. Neck and J.I. Kim, 1995. Thermodynamics of neptunium(V) in concentrated salt solutions: II. Ion interaction (Pitzer) parameters for Np(V) hydrolysis species and carbonate complexes, *Radiochimica Acta*, **69**:169-176.

Fuger, J. and F.L. Oetting, 1976. *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 2. The Actinide Aqueous Ions.*, Int. Atomic Energy Agency, Vienna, Austria.

Giambalvo, E.R., 2002a. "Recommended Parameter Values for Modeling An(III) Solubility in WIPP Brines," Memo to L. H. Brush, 25 July 2002, Carlsbad, NM: Sandia National Laboratories. (in WIPP Records Center)

Giambalvo, E.R., 2002b. "Recommended Parameter Values for Modeling An(IV) Solubility in WIPP Brines," Memo to L. H. Brush, 26 July 2002, Carlsbad, NM: Sandia National Laboratories. (in WIPP Records Center)

Giambalvo, E.R., 2002c. "Recommended Parameter Values for Modeling Organic Ligands in WIPP Brines," Memo to L. H. Brush, 25 July 2002, Carlsbad, NM: Sandia National Laboratories. (in WIPP Records Center)

Neck, V., T. Fanghänel, G. Rudolph and J.I. Kim, 1995. Thermodynamics of neptunium(V) in concentrated salt solutions: Chloride complexation and ion interaction (Pitzer) parameters for the NpO_2^+ ion, *Radiochimica Acta*, **69**:39-47.

Novak, C.F., 1997. "Calculation of actinide solubilities in WIPP SPC and ERDA6 brines under MgO backfill scenarios containing either nesquehonite or hydromagnesite as the Mg-CO_3 solubility-limiting phase," Memo to R. V. Bynum, April 21, 1997, Albuquerque, NM: Sandia National Laboratories. WPO 46124

Novak, C.F., I. Al Mahamid, K.A. Becraft, S.A. Carpenter, N. Hakem and T. Prussin, 1997. Measurement and thermodynamic modeling of Np(V) solubility in aqueous K_2CO_3 solutions to high concentrations, *Journal of Solution Chemistry*, **26**:681-697.

Novak, C.F., R.C. Moore and R.V. Bynum, 1996. "Prediction of dissolved actinide concentrations in concentrated electrolyte solutions: A conceptual model and model results for the Waste Isolation Pilot Plant (WIPP)," October 25, 1996, Sandia National Laboratories, Albuquerque, 10 pp. SAND96-2695C, WPO 38628.

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Table 1. Normalized Chemical Potential (μ^0/RT)

Species	Current Baseline	Recommended	
	μ^0/RT	μ^0/RT	Source
NpO_2^+	-369.109	-369.105	Fuger and Oetting (1976)[a]
$NpO_2CO_3^-$	-593.635	-593.601	Fanghänel et al. (1995)[a]
$NpO_2(CO_3)_2^{3-}$	-809.895	-809.832	Fanghänel et al. (1995)[a]
$NpO_2(CO_3)_3^{5-}$	-1020.306	-1020.214	Fanghänel et al. (1995)[a]
$NpO_2OH_{(aq)}$	-438.738	-438.730	Fanghänel et al. (1995)[a]
$NpO_2(OH)_2^-$	-506.249	-506.238	Fanghänel et al. (1995)[a]
NpO_2OH(aged)	-454.373	-454.369	Neck et al. (1995)[b]
$NpO_2OH_{(am)}$	-452.761	-452.757	Neck et al. (1995)[b]
$NaNpO_2CO_3 \cdot 3.5H_2O_{(s)}$	-1048.062	-1048.058	Neck et al. (1995)[b]
$Na_3NpO_2(CO_3)_{2(s)}$	-1144.601	-1144.597	Neck et al. (1995)[b]
$KNpO_2CO_{3(s)}$	-727.33	-727.330	Novak et al. (1997)
$K_3NpO_2(CO_3)_{2(s)}$	-1173.55	-1173.546	Novak et al. (1997)

[a]Fuger and Oettting (1976) and Fanghänel et al. (1995) report chemical potential (μ^0). Recommended values were calculated using R = 8.31451 J mol^{-1} K^{-1} and T = 298.15 K.

[b]Recommended values are calculated from log K_{sp} reported in Table 5 of Neck et al. (1995).

Table 2. Binary Pitzer Parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ})[a]

Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Source
Na^+	$NpO_2(OH)_2^-$	0	0	0	0	Fanghänel et al. (1995)
Na^+	$NpO_2CO_3^-$	0.1	0.34	0	0	Fanghänel et al. (1995)
Na^+	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0	0	Fanghänel et al. (1995)
Na^+	$NpO_2(CO_3)_3^{5-}$	1.8	22.7	0	0	Fanghänel et al. (1995)
K^+	$NpO_2(OH)_2^-$	0	0	0	0	
K^+	$NpO_2CO_3^-$	0.1	0.34	0	0	Novak et al. (1997)
K^+	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0	0	Novak et al. (1997)
K^+	$NpO_2(CO_3)_3^{5-}$	2.34	22.7	-96	-0.22	Novak et al. (1997)
Mg^{2+}	$NpO_2(OH)_2^-$	0	0	0	0	
Mg^{2+}	$NpO_2CO_3^-$	0.1	0.34	0	0	Al Mahamid et al. (1998)
Mg^{2+}	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0	0	Al Mahamid et al. (1998)
Mg^{2+}	$NpO_2(CO_3)_3^{5-}$	2.07	22.7	-48	-0.11	Al Mahamid et al. (1998)
NpO_2^+	Cl^-	0.1415	0.281	0	0	Neck et al. (1995)
NpO_2^+	ClO_4^-	0.257	0.18	0	0.0081	Neck et al. (1995)

[a]Recommended values are identical to current baseline values.

Table 3. Neutral-Ion Interaction Parameter (λ)[a]

Neutral	Ion	λ	Source
$NpO_2OH_{(aq)}$	Na^+	0	Fanghänel et al. (1995)
$NpO_2OH_{(aq)}$	ClO_4^-	0	Fanghänel et al. (1995)
$NpO_2OH_{(aq)}$	Cl^-	-0.19	Fanghänel et al. (1995)

[a]Recommended values are identical to current baseline values.

Table 4. Ternary Interaction Parameters (θ, ψ)[a]

ion *i*	ion *j*	ion *k*	θ_{ij}	ψ_{ijk}	Source
Cl^-	$NpO_2(OH)_2^-$	Na^+	-0.24	0	Fanghänel et al. (1995)
Cl^-	$NpO_2CO_3^-$	Na^+	-0.21	0	Fanghänel et al. (1995)
Cl^-	$NpO_2(CO_3)_2^{3-}$	Na^+	-0.26	0	Fanghänel et al. (1995)
Cl^-	$NpO_2(CO_3)_3^{5-}$	Na^+	-0.26	0	Fanghänel et al. (1995)
CO_3^{2-}	$NpO_2(CO_3)_3^{5-}$	K^+	-1.9	0	Novak et al. (1997); Al Mahamid et al. (1998)

[a]Recommended values are identical to current baseline values.