

Speciation and Solubility Modeling of Actinides in the Waste Isolation Pilot Plant

Donald E. Wall¹, Nathalie A. Wall¹, and Laurence H. Brush¹

¹Sandia National Laboratories, Carlsbad Programs Group
Carlsbad, NM

The WIPP geochemical model uses the Pitzer equations coupled with a thermodynamic database to carry out speciation and solubility calculations for the actinides in the +III, +IV, and +V oxidation states in aqueous systems composed of Na⁺—K⁺—Mg²⁺—Ca²⁺—SO₄²⁻—OH⁻—CO₃²⁻—HCO₃⁻—H₂O—acetate—citrate—oxalate—EDTA. The WIPP database incorporates results for actinide speciation and complexation work carried out primarily at Pacific Northwest National Laboratory, Forschungszentrum Karlsruhe (Germany) and Florida State University. Calculations are performed at Sandia National Laboratories with the code FMT, using the Harvie-Møller-Weare database, and parameters that were developed specifically for actinides in high ionic strength aqueous solutions. This paper described derivation of the thermodynamic database, and provides normalized standard chemical potentials and Pitzer parameters for modeling An(III, IV, and V) speciation and solubility in brines.

The Waste Isolation Pilot Plant, located 42 km east of Carlsbad, New Mexico has been accepting defense related transuranic waste since March 1999. The repository is located approximately 655 meters below the surface in the Salado Formation, a bedded salt formation. The salt formation is primarily halite (NaCl), but also contains clay seams, anhydrite (CaSO₄), gypsum (CaSO₄•2H₂O), polyhalite (K₂MgCa₂(SO₄)₄•2H₂O) and magnesite (MgCO₃). In the undisturbed state, reconsolidation of the host rock will establish a post-closure environment that will prevent the movement of radionuclides due to the low porosity and permeability of the halite of the Salado Formation. Brine from the Salado or underlying Castile Formation may enter the repository if exploratory drilling for natural resources intersects a disposal area. Radionuclides may move to the accessible environment as dissolved, suspended, or colloidal material, with the magnitude of a direct brine release (DBR) proportional to the radionuclide solubility. Brine solution chemistry will be controlled by emplacement of MgO, which will buffer the brines at mildly basic pH about 9 and act as a sink for CO₃²⁻ that could form as a result of CO₂ production by microbes that act upon the cellulosic, plastic, and rubber materials in the waste.

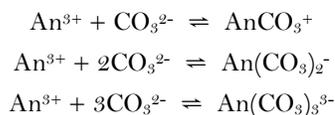
The radionuclides of greatest concern in the WIPP are ^{239,240}Pu and ²⁴¹Am, which account for more than 99% of the total radioactivity for most of the 10,000 year regulatory period. Iron will be emplaced within the repository as part of the waste and waste drums, and will maintain a chemically reducing condition. As a result, Pu is expected to exist as Pu(III) or Pu(IV) and Am as Am(III). U is modeled as U(IV) in half of the performance assessment vectors and as U(VI) in the other half; likewise, Np is modeled as Np(IV) in half of the vectors as Np(V) in the other half. Speciation and solubility calculations are carried out for three oxidation states, An(III, IV, and V) but not for An(VI) due to the propensity of U(VI) to form polynuclear species, for which there is not a sufficient thermodynamic database for modeling at high ionic strengths. The solubility values for U(VI) have been determined based upon a literature survey of the most relevant solubility studies (Hobart et al. 1996).

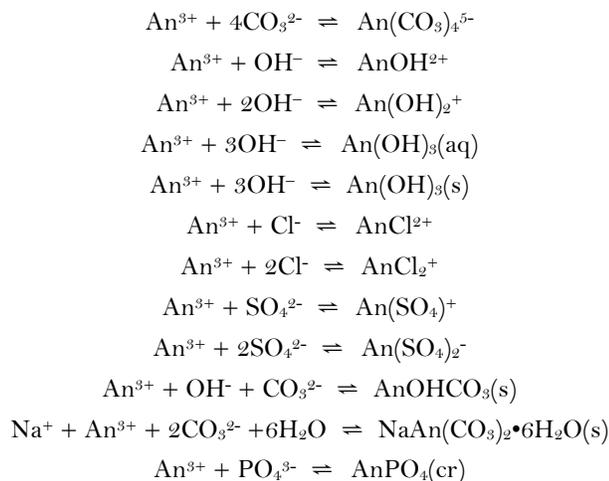
Ions of importance in Salado and Castile brines are H⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, OH⁻, Cl⁻, CO₃²⁻, and SO₄²⁻. Representative compositions of the Salado and Castile brines are given in Table I (Snider 2003 and Popielak 1983). Actinide solubilities may also be influenced by the predominant organic ligands present in the waste: acetate, citrate, oxalate, and EDTA.

The semi-empirical Pitzer equations are used to calculate the ionic activity coefficients for the actinides, and inorganic and organic complexing agents in the WIPP inventory. Solubilities are calculated with the Fracture Matrix Transport (FMT) code, which determines the minimum Gibbs free energy for an input array of possible system components. The speciation and solubility of each oxidation state are determined separately, without accounting for redox interchanges among the available oxidation states. The Pitzer parameters that describe the ionic activity coefficients were either taken directly from the literature or calculated with the code NONLIN, which was developed by A. Felmy at PNNL.

Much of the FMT database, including standard chemical potentials and Pitzer parameters, was developed during the 1990's to carry out speciation and solubility calculations for actinides in high NaCl content brines. Most of the early work focused on the influence of inorganic ligands, such as CO₃²⁻, OH⁻, and SO₄²⁻, with additional focus on organic ligands as more data became available on the composition of the wastes destined for the WIPP. Compilation of the database is described in a series of SNL memoranda written by C.F. Novak and E.R. Giambalvo; the memoranda are available from the WIPP records center (Novak 1996, Novak and Moore 1996, Giambalvo 2002a, 2002b, 2002c, 2002d). This paper lists the normalized standard chemical potentials (μ⁰/RT) and the Pitzer parameters for the species used in speciation and solubility calculations for the WIPP. The μ⁰/RT values for the WIPP modeling were based upon a review of relevant literature reports, and research programs funded by the WIPP project. Some values from the NEA database were incorporated in the WIPP calculations, and are also included in the present data tables (Mompean et al. 2003). Implementation of the Pitzer parameters in the FMT database used for the WIPP speciation and solubility calculations has been described in a set of Sandia National Laboratories memoranda that are available through the WIPP records center at the SNL/Carlsbad Programs Group (Giambalvo 2002a, 2002b, 2002c, 2002d).

The An(III) model. Most of the work carried out on An(III) complexation has been performed with Am(III) or Cm(III), and have been used to generate a model for An(III) speciation and solubility. Due to the similarity of the chemical behavior of Pu(III), Am(III), and Cm(III), the chemical potentials, stability constants, and Pitzer parameters that were determined for Am(III) and Cm(III) have been applied to modeling of the Pu(III) solution behavior. The reactions that are used to model the speciation and solubility for Am(III) and Pu(III) are given below.





Fanghänel et al. (1999) used peak deconvolution of laser fluorescence spectra (TRLFS) to measure the stability constants of formation of the carbonate complexes $\text{Cm}(\text{CO}_3)_n^{3-2n}$ in 0–6 m NaCl solution at 25 °C. The stability constants for the carbonate complexes and standard chemical potentials are listed in Table II, while the Pitzer parameters are given in Tables III through V. Fanghänel et al. (1999) reported standard state complexation constants at zero ionic strength of $\log \beta_{101}^0 = 8.1 \pm 0.3$, $\log \beta_{102}^0 = 13.0 \pm 0.6$, $\log \beta_{103}^0 = 15.2 \pm 0.4$, $\log \beta_{104}^0 = 13.0 \pm 0.5$; a description of the derivation of error limits was not provided. The authors also noted that there was no indication of formation of mixed hydroxide-carbonate complexes. Finally, the authors compared published solubility data to model predictions using their stability constant values, Pitzer parameters, and a $\log K_{\text{sp}}^0 = -22.7$ for $\text{AmOHCO}_3(\text{s})$. The fit of the model to the experimental data of Felmy et al. (1990), Bernhopf (1984) and Giffaut (1994) was good, especially in the $\log [\text{CO}_3^{2-}]$ range of 10^{-6} to 10^{-7} M, which is particularly relevant for WIPP conditions.

Fanghänel and Kim (1998) published a review of Cm(III) complexation with Cl^- , SO_4^{2-} , CO_3^{2-} and OH^- . The authors describe examination of the fluorescence of Cm(III) with various SO_4^{2-} concentrations, and plot the variation in the $\log \beta_{101}$ and $\log \beta_{102}$ values as a function of NaCl concentration over a range of 0 to 6 m. The authors state that the data were used for parameterization of the ion interaction model. The An(III)– SO_4^{2-} stability constant and Pitzer parameters used in WIPP modeling are based on work with Cm(III), presented in Table 1 in Fanghänel and Kim (1998), which references unpublished data from their laboratory as the source of the parameter values. As of the date of this writing, detailed results of the study describing the measurement of the Cm(III) sulfate stability constants and Pitzer parameter data have not been published. As a result, we have not attempted to evaluate the uncertainty associated with the An(III)– SO_4^{2-} parameters.

Pitzer parameters and stability constants of formation for the An(III) hydroxides were reported by Fanghänel et al. (1994). The stability constants were determined in 1, 2, and 4 m NaCl solutions by examination of the Cm spectra using TRLFS. Varying the pH range over 4 to 10, the investigators observed three Cm species: Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, and $\text{Cm}(\text{OH})_2^+$. The authors used the data to determine the binary Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^\square for the Cm(III) hydrolysis species, and using the Pitzer equations, they extrapolated the stability constants to zero ionic strength, and determined $\log \beta_{101}^0 = 6.44 \pm 0.09$ and $\log \beta_{102}^0 = 12.3 \pm 0.2$; a description of the derivation of error limits was not provided. As a test of the suitability of the parameters, the authors compared the predicted values with experimental solubilities of $\text{Am}(\text{OH})_3$ in 5.61 m NaCl solution over a pH range of 5 to 12, and found good agreement. Additionally, the authors note that the thermodynamic model predicts a solubility for $\text{Am}(\text{OH})_3$ at pH = 9 to be about four orders of magnitude greater in saturated NaCl solution than in deionized water. The reported stability constants were used to calculate the standard chemical potentials of formation of the hydroxide complexes. The standard chemical potentials and Pitzer parameters are listed in Tables II, III and IV.

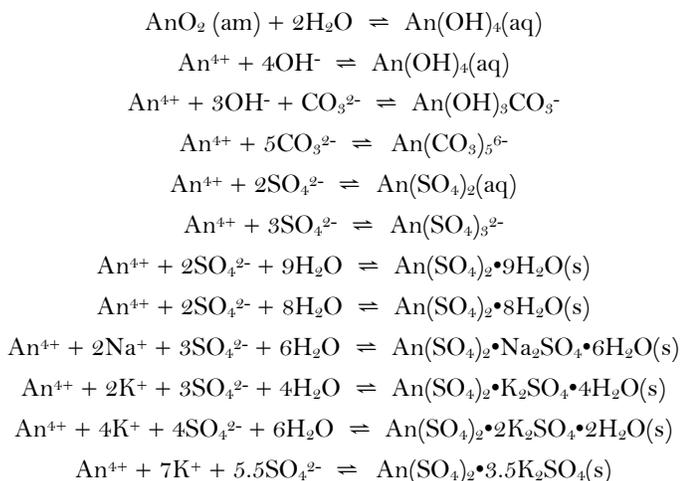
Fanghänel et al. reported results of a study of inner sphere Cl^- complexation of Cm(III) in a $\text{pH} \cong 2$ solution, varying the Cl^- concentration from $2 < m_{\text{CaCl}_2} < 6.5$ m by addition of CaCl_2 . The authors reported difficulty extrapolating to zero ionic strength due to a lack of data at lower Cl^- concentrations, although a further analysis reported later by the same group (Könnecke et al. (1997)) provides the Pitzer parameters and values of

$\log \beta_{101}^0 = 0.24 \pm 0.03$ and $\beta_{102}^0 = -0.74 \pm 0.05$, for 25 °C and zero ionic strength; a description of the derivation of error limits was not provided. Harvie et al. (1984) stated that the behavior of complexes of the metal ion of interest with the anion in the bulk electrolyte is sufficiently described in the $\beta^{(0)}$, $\beta^{(1)}$, and C^\square parameters as ionic strength effects when complexation constants are less than $\log \beta \cong 1.3$ in dilute solution. Complexation by Cl^- of An(III) has much less effect on the solubility under WIPP conditions than the ionic strength effect exerted by the presence of large amounts of Cl^- .

The anions PO_4^{3-} and ClO_4^- are not important components in the WIPP inventory, but were included in the database to accommodate possible future changes. Neither component is currently included in the WIPP geochemical model. The NEA database provides a chemical potential for $\text{AmPO}_4(\text{am,hyd})$, while a similar value is quoted by Rai et al. (1992) for a crystalline phase. Both values are reproduced in Table II.

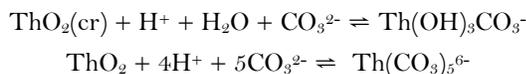
The solubility-limiting solid phase that is used in WIPP speciation and solubility calculations for trivalent actinides is $\text{Am}(\text{OH})_3$ with a $\log K_{\text{sp}}^0 = -27.5$ at zero ionic strength. Consequently, $\text{Am}(\text{OH})_3$ is less soluble under WIPP conditions than $\text{AmCO}_3\text{OH}(\text{cr})$, as described in Fanghänel et al. (1999), based on Felmy et al. (1990). The $\log K_{\text{sp}}^0$ and standard chemical potential values for $\text{AmCO}_3\text{OH}(\text{cr})$ are -22.7 and -570.34 , respectively. The NEA database does not provide data for $\text{AmCO}_3\text{OH}(\text{cr})$, but includes values for $\text{AmCO}_3\text{OH}\cdot 0.5\text{H}_2\text{O}(\text{cr})$ and $\text{AmCO}_3\text{OH}(\text{am,hyd})$. The K_{sp} and chemical potential data are provided in Table II.

The An(IV) Model The actinides that can exist in the +IV oxidation state that are also in the WIPP inventory include Th(IV), U(IV), Np(IV) and Pu(IV). Much of the data used as input into the An(IV) model was developed using Th as the An(IV) analog, with application of the results to U(IV), Np(IV) and Pu(IV). Th is considered to be a conservative analog in WIPP solubility calculations because, even though it forms weaker complexes with ligands than the other An(IV) ions, the solubility-limiting solid phases of U(IV), Np(IV) +or Pu(IV) are less soluble than the analogous Th phase, and performance assessment calculations seek to establish boundary conditions rather than more accurately representative but less easily defensible sets of conditions (Neck and Kim, 2001). The reactions that are used in the modeling of Th(IV), U(IV), Np(IV) and Pu(IV) are given below:



The hydrolysis species, $\text{An}(\text{OH})_{4n-1}$ ($n=1,2,3$) are not considered because they will not be predominant at the $\text{pH} \approx 9$ expected to exist within the repository. The chemical potentials and Pitzer parameters for the complexes of An(IV) with inorganic anions are given in Tables VI through IX.

Ostholts et al. (1994) reported stability for the reactions



The respective $\log \beta$ values are 6.11 ± 0.19 and 42.12 ± 0.32 at in 0.5 M NaClO_4 at 25 °C; the uncertainties are given as three standard deviations. The authors used the specific ion interaction theory (SIT) to calculate the

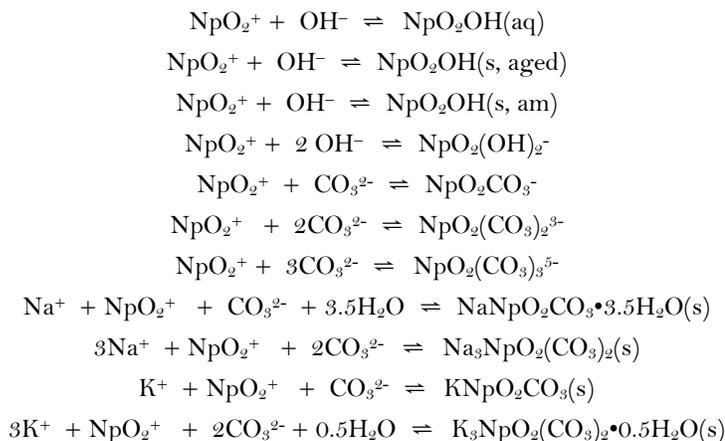
standard state stability constants at zero ionic strength, resulting in $\log \beta \pm 3\sigma$ values of 6.78 ± 0.3 and 39.64 ± 0.4 , respectively. Rai et al. (1995) reported results of a study of the solubility of Th(IV) and U(IV) hydrous oxides in concentrated NaHCO_3 and Na_2CO_3 solutions. The study was not carried out with either NaClO_4 or NaCl background electrolytes. The data in Osthols et al. (1994) and Rai et al. (1995) were later interpreted by Felmy et al. (1997), who calculated the standard state $\log \beta^0$ of 6.78 and 37.6, respectively. Felmy et al. (1997) also reported binary Pitzer parameters for the interaction of the $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$ complexes with Na^+ , although this was based on the data published by Osthols et al. for a single ionic strength, 0.5 M NaClO_4 solution. Felmy et al. (1997) state that, due to the high charge on the $\text{Th}(\text{CO}_3)_5^{6-}$ anion, stability constants may exhibit large variations depending upon the identity of the electrolyte, and that it is impossible to extrapolate unambiguous standard-state thermodynamic quantities for such highly charged species from solution data in different electrolyte media. The WIPP model for carbonate complexation of tetravalent actinides is based on the work of Felmy et al. (1997).

The thermodynamic and Pitzer parameters for the An(IV)— SO_4^{2-} species that have been incorporated into the WIPP PA database are for $\text{An}(\text{SO}_4)_2(\text{aq})$ and $\text{An}(\text{SO}_4)_3^{2-}$, based on a study of the thermodynamics of Th^{4+} — SO_4^{2-} interactions in the Na^+ — K^+ — Li^+ — NH_4^+ — Th^{4+} — SO_4^{2-} — HSO_4^- — H_2O system, published by Felmy and Rai (1992).

Formation of complexes of An(IV) with chloride is not specifically modeled with values of μ^0/RT , although it is known that ion pairing occurs in concentrated chloride systems, and is accounted for as an ionic strength effect by the inclusion of a large negative value for $\beta^{(2)}$ in the binary interaction parameters for Th^{4+} with Cl^- , which is given in Table VII. Roy et al. describe the basis for inclusion of the large negative $\beta^{(2)}$ as due to the impact of chloride complexation, and note that the solubility of $\text{Th}(\text{OH})_4$ in Cl^- solutions exceeds that in comparable ClO_4^- solutions by a factor of about 1000.

The solubility-limiting solid phase for the tetravalent actinides in the WIPP geochemical model is $\text{AnO}_2(\text{am})$, with $\text{ThO}_2(\text{am})$ used as the model for $\text{UO}_2(\text{am})$, $\text{NpO}_2(\text{am})$, and $\text{PuO}_2(\text{am})$. Th is the most soluble of the four actinides, making it a conservative analog for the others. Felmy et al. (1991) measured the solubility of $\text{ThO}_2(\text{am})$ in NaCl solutions from 0.6 to 3.0 M and in 0.6 M KCl over a pcH range of 3 to 11, using equilibration times extending beyond one year. The authors reported solubilities of $\text{ThO}_2(\text{am})$ that were up to three orders of magnitude greater in NaCl than in NaClO_4 solutions, with solubilities increasing with NaCl ionic strength, illustrating the large chemical behavior differences of actinides in chloride and perchlorate solutions, and the impossibility of adequately accounting for the differences without experimental data. The authors found that, under carefully controlled conditions, Th exhibited a solubility of approximately 3×10^{-8} M over at $\text{pH} = 9$ in 3 M NaCl solution in the absence of carbonate and other complexing ligands, thus, since the presence of sulfate, carbonate, and other ligands may be expected to increase solubility, this may be regarded as an approximate lower limit of solubility when using Th as a model for An(IV) behavior in mildly basic NaCl brines.

The An(V) Model The pentavalent actinide solubility model for WIPP includes only Np(V) . The reactions that are included in the WIPP geochemical model are given below:



Fanghänel et al. (1995 and references therein) reported Pitzer parameters for OH^- and CO_3^{2-} complexes of NpO_2^+ in NaClO_4 and NaCl solutions, based upon an evaluation of previously published experimental data for

solubility studies on NpO_2^+ in 0.1 – 3 M NaClO_4 and 5 M NaCl . In the cases of the interaction of Na^+ with $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{OH})_2^-$, insufficient data was available at low ionic strengths to calculate the $\beta^{(1)}$ parameter. The authors estimated the value of $\beta^{(1)} = 0.34$ for $\text{Na}^+/\text{NpO}_2\text{CO}_3^-$, and set $\beta^{(1)} = 0$ for $\text{Na}^+/\text{NpO}_2(\text{OH})_2^-$. A subsequent report by Novak et al. (1997), describing thermodynamic modeling of Np(V) in K_2CO_3 solutions, features the adoption of the Pitzer parameters that characterize the interaction of Na^+ with $\text{NpO}_2(\text{OH})_n^{1-n}$ and $\text{NpO}_2(\text{CO}_3)_n^{1-2n}$ species as reasonable estimates for the interaction of K^+ with the same species. As a result, the DOE has elected to adopt the same approach, assigning the interaction parameters for K^+ with the neptunyl hydroxides and carbonates to be the same as the respective parameters for Na^+ . Likewise, the interaction parameters for Mg^{2+} with the various neptunyl species have been set equal to those used for Na^+ . The $\text{NpO}_2(\text{OH})_2^-$ moiety will not exist at $\text{pH} \cong 9$, therefore the interaction parameters have been set to zero. Further experimental work would be required if it becomes necessary to extend WIPP geochemical modeling to $\text{pH} > 10$ values. The normalized standard chemical potentials and Pitzer parameters used for modeling speciation and solubility of Np(V) are provided in Tables X through XIII.

Organic Ligands. The experimental work of measuring stability constants for actinide-organic ligand interactions at various ionic strengths was carried out at Florida State University by Choppin and coworkers (Choppin et al., 2001). Stability constants of acetate, citrate, oxalate, and EDTA with Th(IV) , Np(V) and Am(III) were determined by solvent extraction; Mg^{2+} stability constants with the same ligands were measured by potentiometric titration. Interactions of the organic ligands with Mg^{2+} were added to the database to account for the competitive effect of Mg^{2+} in WIPP brines, especially the Salado brine. The normalized standard chemical potentials for the species that are included in the WIPP geochemical model are reproduced in Tables XV through XVIII. The Pitzer parameters are presented in Tables XV to XXI.

Additional Modeling Considerations. Normalized standard chemical potentials for the WIPP brine components H_2O , H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HSO_4^- , OH^- , HCO_3^- and CO_3^{2-} are provided in Table XIV. During the course of a speciation and solubility calculation, the FMT code adjusts brine composition to account for changes in chemistry, such as depletion of Mg^{2+} content in Salado brine as a result of increasing pH due to reaction of MgO with water. Binary and ternary ion interaction parameters for Mg^{2+} with anionic actinide complexes are not included in the WIPP geochemical model. In general, the impact of the ternary parameters is small, but not negligible. Omission of the binary and ternary parameters for Mg^{2+} has not been viewed as a significant issue due to precipitation of Mg^{2+} at the mildly basic pH of the repository brines.

The inclusion of organic ligands does not have a significant effect on the solubility of the An(III) and An(IV) under WIPP conditions, due to the extensive competition with hydrolysis and carbonate complexation. However, due to the absence of hydrolysis of Np(V) and Pu(V) at $\text{pH} \cong 9$, it may be anticipated that organic ligand complexation will both enhance the solubility of these species, and enlarge the stability field for the An(V) oxidation state with respect to both pH and Eh.

A speciation and solubility model for An(VI) has not been explicitly developed as it has for An(III) , An(IV) and An(V) . The only two radionuclides that could reasonably be expected to exist in the hexavalent oxidation state are U and Pu. The current solubility model for U(VI) is based upon a literature survey by Hobart et al. (1996). Studies designed to elucidate thermodynamics of interactions between U(VI) and both inorganic and organic ligands are considerably complicated by the tendency of U(VI) to form polynuclear species. Fortunately, the radioactive inventory of U in the WIPP is small, and U is not an important component in calculating releases from the repository. Additionally, Pu is not expected to persist as Pu(V) or Pu(VI) due to the large amount of metallic Fe that will be present within the WIPP, mitigating the necessity to develop a speciation and solubility model for Pu(VI) . However, regulatory intervention by the EPA could force the DOE to consider Pu(VI) in some of the PA determinations, which could require reassessment of the An(VI) model.

Conclusions

Normalized standard chemical potentials and Pitzer parameters for the FMT database used in the WIPP geochemical model have been taken from a literature review or programs funded by the WIPP project. The database used in An(III,IV, and V) speciation and solubility calculations have been reproduced in the present work.

Acknowledgments

Compilation of the WIPP thermodynamic database is the result of a long term effort with the involvement of numerous individuals; however, two people deserve special recognition: Craig Novak and Emily Giambalvo, both formerly of Sandia National Laboratories carried out a great deal of the work on the database compilation. This research is funded by WIPP programs administered by the U.S. Department of Energy. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin

Company, for the United States Department of Energy supported this research under contract DE-AC04-94AL85000.

Table I. Composition of the Brines

<i>Component</i>	<i>Castile Fm. (mM) (b)</i>	<i>Salado Fm.(mM) (c)</i>
B(III) (a)	63	156
Br ⁻	11	27
Ca ²⁺	12	14
Cl ⁻	4800	5610
K ⁺	97	467
Mg ²⁺	19	1020
Na ⁺	4870	3570
SO ₄ ²⁻	170	178

(a) B is added to the synthetic brines as Na₂B₄O₇ · 10H₂O

(b) Described by Popielak et al. (1983)

(c) Described by Snider (2003)

Table II. Normalized Standard Chemical Potentials for An(III)

<i>Species</i>	μ°/RT (a)	μ°/RT (b)	$\log \beta$ or K_p	<i>Reference</i>
Am ³⁺	-241.511 ± 1.918	-241.694		Fuger and Oetting (1976)
AmCO ₃ ⁺	-472.882 ± 2.134	-473.29 ± 0.69	8.1 ± 0.3	Fanghänel et al. (1999)
Am(CO ₃) ₂ ⁻	-697.116 ± 2.384	-697.52 ± 1.38	13.0 ± 0.6	Fanghänel et al. (1999)
Am(CO ₃) ₃ ³⁻	-914.903 ± 3.034	-915.53 ± 0.92	15.2 ± 0.4	Fanghänel et al. (1999)
Am(CO ₃) ₄ ⁵⁻	Not available	-1123.40 ± 1.15	13.0 ± 0.5	Fanghänel et al. (1999)
AmSO ₄ ⁺	-549.235 ± 1.956	-549.56	3.25 (c)	Fanghänel and Kim (1998)
Am(SO ₄) ₂ ⁻	-850.282 ± 1.978	-850.99	3.70 (c)	Fanghänel and Kim (1998)
AmOH ²⁺	-320.593 ± 2.237	-319.96 ± 0.21	6.44 ± 0.09	Fanghänel et al. (1994)
Am(OH) ₂ ⁺	-398.063 ± 2.505	-396.89 ± 0.46	12.3 ± 0.2	Fanghänel et al. (1994)
Am(OH) ₃ (aq)	-468.165 ± 2.238	-469.53	16.3	Könnecke et al. (1997), from Silva et al. (1995)
AmCl ₂ ⁺	-294.995 ± 1.920	-295.20 ± 0.07	0.24 ± 0.03	Könnecke et al. (1997)
AmCl ₂ ⁺	-345.671 ± 1.924	-345.90 ± 0.12	-0.74 ± 0.05	Könnecke et al. (1997)
AmCO ₃ OH(cr)	N/A	-570.34	-22.5	Fanghänel et al. (1999), based on Felmy et al. (1990)
AmCO ₃ OH•0.5H ₂ O(cr)	-617.291 ± 5.560	N/A	N/A	N/A
AmCO ₃ OH(am,hyd)	-564.396	N/A	N/A	N/A
Am(OH) ₃ (s)	-492.572 ± 2.364	-495.32	-27.5	Könnecke et al. (1997) from Morse and Williams (1994)
NaAm(CO ₃) ₂ •6H ₂ O	N/A	-1396.468		Rao et al. (1996)
AmPO ₄ (cr)		-709.75		Rai et al. (1992)
AmPO ₄ (am, hyd)	-712.268 ± 1.382			NEA

(a) NEA database values; the uncertainties are at the 95% confidence limit (Mompean, 2003)

(b) WIPP values based on referenced work, derivation of the uncertainties are not described in the references

(c) based on non-published work that was cited in the reference

Table III. Binary Pitzer Parameters for An(III)

<i>Cation</i>	<i>Anion</i>	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^c	<i>Reference</i>
Na ⁺	Am(CO ₃) ₂ ⁻	-0.24	0.224	0	0.0284	Fanghänel et al. (1999)
Na ⁺	Am(CO ₃) ₃ ³⁻	0.125	4.73	0	0.0007	Fanghänel et al. (1999)
Na ⁺	Am(CO ₃) ₄ ⁵⁻	2.022	19.22	0	-0.305	Fanghänel et al. (1999)
AmCO ₃ ⁺	Cl ⁻	-0.072	0.403	0	0.0388	Fanghänel et al. (1999)
Am ³⁺	SO ₄ ²⁻	1.792	15.04	0	0.600	Fanghänel and Kim (1998)
AmSO ₄ ⁺	Cl ⁻	-0.091	-0.39	0	0.048	Fanghänel and Kim (1998)
Na ⁺	Am(SO ₄) ₂ ⁻	-0.354	0.4	0	0.051	Fanghänel and Kim (1998)
Am ³⁺	H ₂ PO ₄ ²⁻	0	0	-92.9	0	Rai et al. (1995)
Am ³⁺	ClO ₄ ⁻	0.8	5.35	0	-0.0048	Felmy et al. (1990)
Am ³⁺	Cl ⁻	0.5856	5.60	0	-0.016	Könnecke et al. (1997)
AmOH ²⁺	Cl ⁻	-0.055	1.60	0	0.050	Könnecke et al. (1997)
Am(OH) ₂ ⁺	Cl ⁻	-0.616	-0.45	0	0.050	Könnecke et al. (1997)
AmCl ²⁺	Cl ⁻	0.593	3.15	0	-0.006	Könnecke et al. (1997)
AmCl ₂ ⁺	Cl ⁻	0.516	1.75	0	0.010	Könnecke et al. (1997)

Table IV. Neutral Ion Interaction Parameters for An(III)

<i>Species</i>	<i>Ion</i>	β	<i>Reference</i>
Am(OH) ₃ (aq)	Na ⁺	-0.2	Könnecke et al. (1997)
Am(OH) ₃ (aq)	Cl ⁻	-0.2	Könnecke et al. (1997)

Table V. Ternary Interaction Parameters (β, β) for An(III)

<i>Ion i</i>	<i>Ion j</i>	<i>Ion k</i>	β_{ij}	β_{jk}	<i>Reference</i>
Ca ²⁺	Am ³⁺	Cl ⁻	0.2	0	Könnecke et al. (1997)
Ca ²⁺	AmCl ²⁺	Cl ⁻	-0.014	0	Könnecke et al. (1997)
Ca ²⁺	AmCl ₂ ⁺	Cl ⁻	-0.196	0	Könnecke et al. (1997)
Na ⁺	Am ³⁺	Cl ⁻	0.1	0	Könnecke et al. (1997)
Cl ⁻	Am(CO ₃) ₃ ³⁻	Na ⁺	0	0	Fanghänel et al. (1999)
SO ₄ ²⁻	ClO ₄ ⁻	Na ⁺	0	0	Rai et al. (1995)

Table VI. Normalized Standard Chemical Potentials for An(IV)

<i>Species</i>	μ^0/RT	<i>Reference</i>
Th ⁴⁺	-284.227	Fuger and Oetting (1976)
Th(CO ₃) ₅ ⁶⁻	-1411.378	Felmy et al. (1997)
Th(OH) ₃ (CO ₃) ⁻	-775.627	Felmy et al. (1997)
Th(OH) ₄ (aq)	-622.47	Ryan and Rai (1987)
Th(SO ₄) ₂ (aq)	-911.69	Felmy and Rai (1992)
Th(SO ₄) ₃ ²⁻	-1214	Felmy and Rai (1992)
ThO ₂ (am)	-451.408	Felmy et al. (1991)
Th(SO ₄) ₂ •9H ₂ O(s)	-1775.9	Felmy and Rai (1992)
Th(SO ₄) ₂ •8H ₂ O(s)	-1680	Felmy and Rai (1992)
Th(SO ₄) ₂ •Na ₂ SO ₄ •6H ₂ O(s)	-2011.29	Felmy and Rai (1992)
Th(SO ₄) ₂ •K ₂ SO ₄ •4H ₂ O(s)	-1837.57	Felmy and Rai (1992)
Th(SO ₄) ₂ •2K ₂ SO ₄ •2H ₂ O(s)	-2181.81	Felmy and Rai (1992)
Th(SO ₄) ₂ •3.5K ₂ SO ₄ (s)	-2790.83	Felmy and Rai (1992)

Table VII. Binary Pitzer Parameters for An(IV)

<i>Cation</i>	<i>Anion</i>	β^0	β^1	β^2	C^1	<i>Reference</i>
Na ⁺	Th(SO ₄) ₃ ²⁻	0.12	0	0	0	Felmy and Rai (1992)
Na ⁺	Th(OH) ₃ (CO ₃) ⁻	0	0	0	0	Felmy et al. (1997)
Na ⁺	Th(CO ₃) ₅ ⁶⁻	1.31	30	0	0	Felmy et al. (1997)
K ⁺	Th(SO ₄) ₃ ²⁻	0.9	0	0	0	Felmy and Rai (1992)
H ⁺	Th(SO ₄) ₃ ²⁻	0.84	0	0	0	Felmy and Rai (1992)
Th ⁴⁺	Cl ⁻	1.092	13.7	-160	-0.112	Roy et al. (1992)
Th ⁴⁺	SO ₄ ²⁻	1.56	0	0	0	Felmy and Rai (1992)
Th ⁴⁺	HSO ₄ ⁻	1.44	0	0	0	Felmy and Rai (1992)

Table VIII. Neutral Ion Interaction Parameters (λ) for An(IV)

<i>Neutral</i>	<i>Ion</i>	λ	<i>Reference</i>
Th(SO ₄) ₂ (aq)	Cl ⁻	0.29	Felmy and Rai (1992)
Th(SO ₄) ₂ (aq)	HSO ₄ ⁻	0.68	Felmy and Rai (1992)

Table IX. Ternary Ion Interaction Parameters (\square, \square) for An(IV)

<i>ion i</i>	<i>ion j</i>	<i>ion k</i>	\square_{ij}	\square_{ik}	<i>Reference</i>
Na ⁺	Th ⁴⁺	Cl ⁻	0.42	0.21	Rai et al. (1997)
Mg ²⁺	Th ⁴⁺	Cl ⁻	0.60	0.21	Rai et al. (1997)
H ⁺	Th ⁴⁺	Cl ⁻	0.60	0.37	Roy et al. (1992)
Th(CO ₃) ₅ ⁶⁻	Cl ⁻	Na ⁺	2.0	-0.08	Felmy and Rai (1999)
Th(CO ₃) ₅ ⁶⁻	ClO ₄ ⁻	Na ⁺	5.5	0	Felmy et al. (1997)

Table X. Normalized Standard Chemical Potentials for Np(V)

<i>Species</i>	μ^0/RT (a)	μ^0/RT (b)	<i>Reference</i>
NpO ₂ ⁺	-366.186 ± 2.270	-369.105	Fuger and Oetting (1976)
NpO ₂ CO ₃ ⁻	-590.563 ± 2.280	-593.601	Fanghänel et al. (1995)
NpO ₂ (CO ₃) ₂ ³⁻	-807.134 ± 2.293	-809.832	Fanghänel et al. (1995)
NpO ₂ (CO ₃) ₃ ⁵⁻	-1017.704 ± 2.313	-1020.214	Fanghänel et al. (1995)
NpO ₂ OH(aq)	-435.828 ± 2.784	-438.730	Fanghänel et al. (1995)
NpO ₂ (OH) ₂ ⁻	-503.167 ± 2.546	-506.238	Fanghänel et al. (1995)
NpO ₂ OH(am,aged)	-451.025 ± 2.545	-454.369	Neck et al. (1995)
NpO ₂ OH(am)	-449.643 ± 2.317	-452.757	Neck et al. (1995)
NaNpO ₂ CO ₃ · 3.5H ₂ O	-1044.948 ± 2.343	-1048.058	Neck et al. (1995)
Na ₃ NpO ₂ (CO ₃) ₂ (s)	-1141.841 ± 2.568	-1144.597	Neck et al. (1995)
KNpO ₂ CO ₃ (s)	-723.379 ± 2.318	-727.330	Novak et al. (1997)
K ₃ NpO ₂ (CO ₃) ₂ (s)	-1169.574 ± 2.326	-1173.546	Novak et al. (1997)

(a) NEA database values; the uncertainties are at the 95% confidence limit (Mompean 2003)

(b) WIPP values based on referenced work

Table XI. Binary Pitzer Parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^\square for Np(V)

<i>Cation</i>	<i>Anion</i>	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^\square	<i>Reference</i>
Na ⁺	NpO ₂ (OH) ₂ ⁻	0	0	0	0	Fanghänel et al. (1995)
Na ⁺	NpO ₂ CO 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 ₂ CO 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 ₂ CO 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)

Table XII. Neutral Ion Interaction Parameter (λ) for Np(V)

<i>Neutral Species</i>	<i>Ion</i>	λ	<i>Reference</i>
NpO ₂ OH(aq)	Na ⁺	0	Fanghänel et al. (1995)
NpO ₂ OH(aq)	ClO ₄ ⁻	0	Fanghänel et al. (1995)
NpO ₂ OH(aq)	Cl ⁻	-0.19	Fanghänel et al. (1995)

Table XIII. Ternary Interaction Parameters for Np(V)

<i>ion i</i>	<i>ion j</i>	<i>ion k</i>	\square_{ij}	\square_{jk}	<i>Reference</i>
Cl ⁻	NpO ₂ (OH) ₂ ⁻	Na ⁺	-0.24	0	Fanghänel et al. (1995)
Cl ⁻	NpO ₂ CO 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	Al Mahamid et al. (1998)

Table XIV. Normalized Standard Chemical Potentials for Components in WIPP Brines

<i>Species</i>	μ°/RT (a)	ΔG_m° (b)	μ°/RT
H ₂ O	-95.6635	-237.140 ± 0.041	-95.6606 ± 0.017
H ⁺	0	0	0
Na ⁺	-105.651	-261.953 ± 0.096	-105.670 ± 0.039
K ⁺	-113.957	-282.510 ± 0.116	-113.963 ± 0.047
Mg ²⁺	-183.468	-455.375 ± 1.335	-183.695 ± 0.539
Ca ²⁺	-223.30	-552.806 ± 1.050	-222.998 ± 0.424
Cl ⁻	-52.955	-131.217 ± 0.117	-52.932 ± 0.047
SO ₄ ²⁻	-300.386	-744.004 ± 0.418	-300.126 ± 0.169
HSO ₄ ⁻	-304.942	-755.315 ± 1.342	-304.689 ± 0.541
OH ⁻	-63.435	-157.220 ± 0.072	-63.422 ± 0.029
HCO ₃ ⁻	-236.751	-586.845 ± 0.251	-236.729 ± 0.101
CO ₃ ²⁻	-212.944	-527.900 ± 0.390	-212.951 ± 0.157

(a) Harvie et al. (1984)

(b) NEA database values; the uncertainties are at the 95% confidence limit (Mompean 2003)

Table XV. Acetate

<i>Species</i>	μ°/RT	<i>Reference</i>
HAc(aq)	-158.300	Choppin et al. (2001)
Ac ⁻	-147.347	Choppin et al. (2001)
AmAc ²⁺	-395.356	Giambalvo (2002d)
ThAc ³⁺	-448.525	Choppin et al. (2001)
ThAc ₂ ²⁺	-604.800	Moore et al. (1999)
NpAc(aq)	-526.061	Choppin et al. (2001)
MgAc ⁺	-333.346	Giambalvo (2002d)

Table XVI. Citrate

<i>Species</i>	μ°/RT	<i>Reference</i>
H ₃ Cit(aq)	0	Choppin et al. (2001), Mizera et al. (1999)
H ₂ Cit ⁻	7.476	Choppin et al. (2001), Mizera et al. (1999)
HCit ²⁻	18.620	Choppin et al. (2001), Mizera et al. (1999)
Cit ³⁻	33.410	Choppin et al. (2001), Mizera et al. (1999)
AmCit(aq)	-228.687	Choppin et al. (2001)
ThCit ⁺	-285.898	Choppin et al. (2001)
NpO ₂ Cit ²⁻	-343.747	Choppin et al. (2001)
MgCit ⁻	-162.261	Giambalvo (2002d)

Table XVII. Oxalate

<i>Species</i>	μ°/RT	<i>Reference</i>
H ₂ Ox(aq)	0	Choppin et al. (2001), Mizera et al. (1999)
HOx ⁻	3.209	Choppin et al. (2001), Mizera et al. (1999)
Ox ²⁻	13.017	Choppin et al. (2001), Mizera et al. (1999)
AmOx ⁻	-242.853	Choppin et al. (2001), Borkowski et al. (2001)
ThOx ²⁺	-297.428	Choppin (2001), Borkowski et al. (2001)
NpO ₂ Ox ⁻	-365.851	Choppin (2001), Borkowski et al. (2001)
MgOx(aq)	-179.185	Giambalvo (2002d)

Table XVIII. EDTA

<i>Species</i>	μ°/RT	<i>Reference</i>
H ₄ EDTA(aq)	0	Choppin et al. (2001), Mizera (1999)
H ₃ EDTA ⁻	5.761	Choppin et al. (2001), Mizera (1999)
H ₂ EDTA ²⁻	12.870	Choppin et al. (2001), Mizera (1999)
HEDTA ³⁻	28.710	Choppin et al. (2001), Mizera (1999)
EDTA ⁴⁻	53.050	Choppin et al. (2001), Mizera (1999)
AmEDTA ⁻	-232.977	Choppin et al. (2001)
ThEDTA(aq)	-285.419	Giambalvo (2002d)
NpO ₂ EDTA ³⁻	-335.708	Choppin et al. (2001), Pokrovsky et al. (1998)
MgEDTA ²⁻	-153.734	Giambalvo 2002d
NpO ₂ HEDTA ²⁻	-351.852	Choppin 2001, Pokrovsky 1998
NpO ₂ H ₂ EDTA ⁻	-364.098	Choppin 2001, Pokrovsky 1998

Table XIX. Binary Pitzer Parameters for Actinides and Organic Ligands

<i>Cation</i>	<i>Anion</i>	β^0	β^1	β^2	C^3	<i>Reference</i>
Na ⁺	Ac ⁻	0.1426	0.22	0	-0.00629	Choppin 2001, Novak et al. (1996)
K ⁺	Ac ⁻	0.1587	0.3251	0	-0.0066	Pitzer (1991)
H ⁺	Ac ⁻	0	0	0	0	Novak et al. (1996)
MgAc ⁺	Cl ⁻	-0.0833	0.29	0	0.0987	Giambalvo 2002d
ThAc ₂ ²⁺	Cl ⁻	0.4671	1.74	0	0.143	Moore et al (1999)
AmAc ₂ ²⁺	Cl ⁻	0.309	1.74	0	-0.132	Giambalvo (2002d)
Na ⁺	H ₂ Cit ⁻	-0.1296	0.29	0	0.013	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	HCit ²⁻	-0.0989	1.74	0	0.027	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	Cit ³⁻	0.0887	5.22	0	0.047	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	MgCit ⁻	0.1742	0.29	0	-0.06923	Giambalvo (2002d)
ThCit ⁺	Cl ⁻	-0.7467	0.29	0	0.319	Choppin et al. (2001)
Na ⁺	NpO ₂ Cit ²⁻	-0.4226	1.75	0	0.142	Choppin et al. (2001)
Na ⁺	HOx ⁻	-0.2448	0.29	0	0.068	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	Ox ²⁻	-0.2176	1.74	0	0.122	Choppin et al. (2001), Mizera et al. (1999)
ThOx ²⁺	Cl ⁻	-0.343	1.74	0	0.5	Choppin (2001), Borkowski et al. (2001)
AmOx ⁺	Cl ⁻	-0.9374	0.29	0	0.248	Choppin (2001), Borkowski et al. (2001)
Na ⁺	NpO ₂ Ox ⁻	-0.5418	0.29	0	0.095	Choppin (2001), Borkowski et al. (2001)
Na ⁺	H ₃ EDTA ⁻	-0.2345	0.29	0	0.059	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	H ₂ EDTA ²⁻	-0.1262	1.74	0	0.054	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	HEDTA ³⁻	0.5458	5.22	0	-0.048	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	EDTA ⁴⁻	1.016	11.6	0	0.001	Choppin et al. (2001), Mizera et al. (1999)
Na ⁺	MgEDTA ²⁻	0.2134	1.74	0	0.00869	Giambalvo (2002d)
Na ⁺	NpO ₂ EDTA ³⁻	0.683	5.911	0	0	Choppin et al. (2001), Pokrovsky et al. (1998)
Na ⁺	NpO ₂ HEDTA ²⁻	0.4733	-1.504	0	0	Pokrovsky et al. (1998)
Na ⁺	NpO ₂ H ₂ EDTA ⁻	-0.8285	0.2575	0	0.256	Pokrovsky et al. (1998)
Na ⁺	AmEDTA ⁻	-0.2239	0.29	0	0.002	Choppin et al. (2001)

Table XX. Neutral-Ion Interaction Parameter (λ)

<i>Neutral Species (a)</i>	<i>Ion</i>	λ	<i>Reference</i>
HAc	Cl ⁻	0	Choppin et al. (2001), Novak et al. (1996)
H ₃ Cit	Cl ⁻	0	Choppin et al. (2001); Mizera et al. (1999)
H ₄ EDTA	Cl ⁻	0	Choppin et al. (2001); Mizera et al. (1999)
H ₂ Ox	Cl ⁻	0	Choppin et al. (2001); Mizera et al. (1999)
AmCit	Cl ⁻	-0.406	Choppin et al. (2001)
ThEDTA	Cl ⁻	0.1111	Giambalvo (2002d)
NpO ₂ Ac	Cl ⁻	0	Choppin et al. (2001), Novak et al. (1996)
MgOx	Cl ⁻	0.0189	Giambalvo (2002d)

(a) all species are aqueous solution species

Table XXI. Ternary Pitzer Parameters

Anion <i>i</i>	Anion <i>j</i>	Cation <i>k</i>	β_{ij}	β_{ijk}	Reference
Ac ⁻	Cl ⁻	Na ⁺	-0.09	0.01029	Novak et al. (1996); Moore et al. (1999)

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