

WPO 43072

11/9/97 KH < FINAL - Revised w/reference

PREDICTION OF DISSOLVED ACTINIDE CONCENTRATIONS IN CONCENTRATED ELECTROLYTE SOLUTIONS: A CONCEPTUAL MODEL AND MODEL RESULTS FOR THE WASTE ISOLATION PILOT PLANT (WIPP) *changes made 12/3/96*

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ABSTRACT

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy facility intended to store transuranic nuclear wastes. The conceptual model for WIPP dissolved concentrations is a description of the complex natural and artificial chemical conditions expected to influence dissolved actinide concentrations in the repository. By a set of physical and chemical assumptions regarding chemical kinetics, sorption substrates, and waste-brine interactions, the system was simplified to be amenable to mathematical description. The analysis indicated that an equilibrium thermodynamic model for describing actinide solubilities in brines would be tractable and scientifically supportable. This paper summarizes the conceptualization and modeling approach and the computational results as used in the WIPP application for certification of compliance with relevant regulations for nuclear waste repositories.

The WIPP Site contains complex natural brines ranging from about sea water concentration to about ten times more concentrated than sea water. Data bases for predicting the solubility of Am(III) (as well as Pu(III) and Nd(III)), Th(IV), and Np(V) in these brines under potential repository conditions have been developed, focusing on chemical interactions with Na, K, Mg, Cl, SO₄, and CO₃ ions, and the organic acid anions acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate. The laboratory and modeling effort augmented the Harvie et al. [1] parameterization of the Pitzer [2] activity coefficient model so that it could be applied to the actinides and oxidation states important to the WIPP system.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy facility located in southeastern New Mexico. The WIPP is intended to store defense-generated transuranic wastes, a category that may include such items as protective clothing, glove boxes, and machining equipment contaminated with actinides, as well as process waste streams containing actinide residues such as pyrochemical salts and solidified sludges [3]. The wastes are typically a highly heterogeneous assortment of these and other materials stored in steel drums or standard waste boxes. The WIPP design basis involves emplacing the waste into the disposal rooms in its existing forms without reprocessing. A magnesium oxide backfill may be interspersed among the waste to control the chemical environment in the repository. After emplacement, creep closure of the bedded salt is expected to envelop the waste and isolate it from the environment.

The WIPP disposal horizon is located within a natural bedded salt formation approximately 655 meters below ground surface in the Salado Formation (Fm) [4]. The salt is predominantly halite, NaCl(s), but also contains accessory evaporite minerals such as anhydrite, CaSO₄(s), gypsum, CaSO₄•2H₂O(s), polyhalite, K₂MgCa₂(SO₄)₄•2H₂O(s), and magnesite, MgCO₃(s), as well as fractured anhydrite marker beds and clay seams [5]. The inter- and intragranular brines associated with the salt at the repository horizon are highly concentrated solutions (about 10 times that of sea water) of predominantly Na-Mg-K-Cl-SO₄ containing smaller amounts of Ca, CO₃, and B. The brine has been in contact with the evaporite salts for geologic time and is saturated with respect to the evaporate minerals. As such, it holds little potential for dissolving Salado minerals. The compositional variations in Salado brine from

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point to point and between intra- and intergranular brines are less than about 20%. The Castile Formation is a bedded anhydrite formation underlying the Salado Fm. Brines associated with the Castile Fm are predominantly saturated sodium chloride solutions containing calcium, sulfate, and small concentrations of other elements, and are about eight times more concentrated than sea water. The major difference between the brines is magnesium concentration, about 0.02m in Castile brines and about 1.0m in Salado brines.

A CONCEPTUAL MODEL FOR WIPP DISSOLVED ACTINIDE CONCENTRATIONS

WIPP disposal scenarios assume that brine from the Salado Fm could seep into disposal rooms and contact the wastes after waste containers have been crushed by creep closure of the surrounding salt. Should this occur, actinides could dissolve or form colloids in these brines. WIPP Performance Assessment scenarios suggest that brines originating in either the Salado Fm or the Castile Fm, or both, could contact wastes if the repository is inadvertently intersected by one or more boreholes during future prospecting for natural resources.

The compositions of brines are a primary determining factor for the chemical behavior of actinides in the aqueous and solid phases. There are two native, approximately uniform, brine compositions from the Salado and Castile Formations that may be chemically altered through contact with the disposal system. The potential inclusion of MgO as a backfill material would be intended to control the hydrogen ion concentration and to consume CO₂(g) that may be generated by microbial decay of cellulosic waste material. Also influencing the chemical environment are portlandite and calcite, which are introduced into the repository both as cement in some of the waste forms and from the seal material used to close the shafts. In addition, organic ligands in the waste could promote the dissolution and stabilization of actinides in solution, and iron corrosion products could form colloids that sorb actinides. All of these potential brine/waste/backfill interactions can have a significant impact on brine compositions and thus on mobile actinide concentrations.

The mobile actinide concentration needed for evaluation of the WIPP with respect to regulatory requirements is the sum of dissolved and colloidal actinides. Dissolved actinides include hydrated ions, hydrolysis species, complexes with inorganic ligands, and complexes with inorganic and organic ligands. Colloids are particles small enough to remain suspended in solution by Brownian motion, and are stable if they do not coagulate and/or settle out of solution by gravity. The processes governing the concentrations of mobile actinides include dissolution/precipitation, complexation with inorganic and organic ligands, formation and persistence of actinide-bearing colloids, and actinide adsorption. All of these mechanisms have a fundamental dependence on brine compositions. Colloid formation and persistence have in addition a dependence on kinetics and particle size. Adsorption in addition has a dependence on the chemical nature of the substrate, regardless of whether the substrate is mobile (colloidal) or immobile. Because of their inherent differences in nature and properties, dissolved species and colloids are two separate study areas in support of the WIPP. Investigations of colloids pertinent to the WIPP are discussed elsewhere [6].

The chemical situation expected in WIPP disposal rooms is too complex to be described exactly. Thus, several key assumptions were employed to make the problem tractable and to provide a measure of conservatism to the description. For estimating dissolved concentrations, these assumptions are (1) complexation and precipitation/dissolution (nonredox) reactions can be described with equilibrium thermodynamics, (2) actinides do not sorb on immobile substrates, and (3) actinide conversion among oxidation states (redox reactions) is not an equilibrium process.

The assumption of equilibrium for all nonredox reactions provides a great simplification in the description of the system and an additional measure of conservatism in the conceptual model. Implicit in this assumption is the corollary: "actinides in the waste dissolve immediately when contacted with brine." Certainly actinides will not dissolve immediately, and the time required for dissolution could be significant given the relative insolubility of the expected forms.

e.g., $\text{PuO}_2(\text{s})$. However, determination of the kinetics of actinide dissolution for the actinides in WIPP wastes would require location and characterization of the actinides in the heterogeneous waste mixture, an exceptionally challenging task. The assumption of instantaneous dissolution obviates this problem, and potentially yields higher concentrations of mobile actinides, particularly in the early years of repository life, which is conservative with respect to regulatory requirements.

The assumption of instantaneous equilibrium for nonredox reactions also means that actinide solid phases will precipitate immediately when the brine is oversaturated. This corollary appears to be nonconservative, but this concern is mitigated by further considerations. The formation of actinide precipitates in the laboratory is typically examined over a time scale of days to months, a period that can be considered instantaneous compared with the 10,000 year regulatory lifetime of the WIPP. The actinide solid phases included in the model are only those that have formed within the laboratory time frame. These solid precipitates may be metastable and could convert to more stable forms as they age [7], with a corresponding decrease in solubility. Therefore, using laboratory-determined, possibly metastable, solids for the precipitated actinide phases potentially adds conservatism. Intraaqueous complexing reactions occur rapidly at WIPP temperatures, so the assumption is acceptable in this regard.

The assumption of no sorption also simplifies and adds a measure of conservatism to the conceptual model. Certainly actinides will sorb to solids. However, quantitative models describing actinide sorption in highly heterogeneous natural or manmade systems do not yet have reliable predictive capabilities. Thus, an attempt to quantify adsorption in the WIPP disposal room environment would not appear to have a high potential for success given the current state of knowledge and the complexity of the chemical conditions. Assuming no sorption is conservative in that the mobility of actinides is potentially overestimated.

Finally, the dissolved actinide conceptual model assumes that oxidation-reduction reactions are not considered to be at thermodynamic equilibrium. Oxidation-reduction equilibrium is often not attained in low temperature geochemical systems like the WIPP, even over geologic time [8]. The kinetics can be very slow, and conversion among oxidation states is strongly influenced by other factors. The WIPP disposal room environment will likely contain regions in which radiolysis would produce oxidizing conditions, regions in which large quantities of metallic iron will produce reducing environments, and regions where microbes may catalyze conversion among actinide oxidation states [5]. The distribution of actinide oxidation states in the WIPP is considered elsewhere [9].

The above assumptions indicate that the solubility of actinides in the WIPP can be estimated from thermodynamic models. The models must describe the brine compositions resulting from interactions between WIPP Salado and Castile brines with the wastes and any backfills, including the solubility and complexation behavior of the actinides as influenced by species concentrations.

THERMODYNAMIC DATA BASE AND ACTIVITY COEFFICIENT MODEL

Reference Data Base

The thermodynamic model of Harvie et al. [1] and Felmy and Weare [10] (HMW-FW) is capable of modeling most of the important chemical interactions in WIPP brines, including evaporite salt solubilities, potential waste or backfill additives such as calcium or magnesium oxides or hydroxides, and the carbon dioxide gas that may be generated within the disposal rooms. The HMW-FW data base has numerous applications for modeling and explaining chemical interactions in brines, including the formation of borate mineral deposits [11], the determination of the compositions of Permian-age sea water [11], and the evaporation of sea water [12].

The HMW-FW data base calculates aqueous species activity coefficients using the Pitzer activity coefficient formalism to account for deviations from ideal solution behavior [2]. The mathematics are based on a virial expansion of ion interactions in solutions as determined through chemical statistical mechanics theories of electrolytes and incorporate the Debye-Hückel limiting law for dilute solutions. The Pitzer formalism was developed for and has been shown to be applicable to electrolytes as concentrated as those in the WIPP system, with an ionic strength range from 0.8 to 8 molal. The Pitzer equations for activity coefficients account for ion interaction effects that become important in concentrated salt solutions. Summaries of the Pitzer formalism and various applications are given in Pitzer [2]; the parameterization of this formalism for evaporite systems is documented in [1, 11].

Extension to Actinides

The WIPP Project has extended the HMW-FW data base with the addition of thermodynamic parameters for Am(III), Th(IV), and Np(V). The actinide parameters were developed for interactions with the species expected to be the most important in the WIPP system, including Na^+ , K^+ , Mg^{2+} , Cl^- , $\text{HCO}_3^-/\text{CO}_3^{2-}$, acetate, citrate, EDTA, oxalate, and hydrogen ion concentration. These extensions are summarized below. The complete thermodynamic data base, including Am(III), Th(IV), Np(V) species, actinide solid phases, and organic ligand complexes is documented in Novak [13; 14]. A similar data base for U(VI) is under development but is not yet ready for application.

The Am(III) data base is based on the work documented in [15, 16, 17, 18, 19, 20]. This data base was extended to mixed $\text{NaCl}/\text{NaHCO}_3$ and $\text{NaCl}/\text{Na}_2\text{CO}_3$ media based on solubility measurements for $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{c})$, and the predictive ability of the resulting model was verified both in complex synthetic WIPP brines and with data for the solubility of $\text{Na}^{241}\text{Am}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ in 5.6m NaCl with a constant $\text{CO}_2(\text{g})$ overpressure [21]. The data base includes the species Am^{3+} , AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$, $\text{Am}(\text{CO}_3)_3^{3-}$, AmOH^{2+} , $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{OH})_3(\text{aq})$, $\text{AmOHCO}_3(\text{s})$, $\text{Am}(\text{OH})_3(\text{s})$, and $\text{NaNAm}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{c})$, and associated ion interaction parameters, and is applicable to $\text{Na-Cl-SO}_4\text{-CO}_3$ media.

The Th(IV) data base is a compilation of the thermodynamic data in [22, 23, 24, 25] extended to include an interpretation of the solubility data for $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in concentrated NaCl , MgCl_2 , NaHCO_3 , and Na_2CO_3 media [26, 23]. The model includes the species Th^{4+} , $\text{Th}(\text{OH})_3\text{CO}_3^-$, $\text{Th}(\text{CO}_3)_5^{6-}$, $\text{Th}(\text{OH})_4(\text{aq})$, $\text{Th}(\text{SO}_4)_2(\text{aq})$, $\text{Th}(\text{SO}_4)_3^{2-}$, and $\text{ThO}_2 \cdot x\text{H}_2\text{O}(\text{am})$, and associated ion interaction parameters, and is applicable to $\text{Na-Mg-K-Cl-ClO}_4\text{-SO}_4\text{-CO}_3$ media. Measurements of the solubility of Th(IV) in complex synthetic WIPP brines as a function of hydrogen ion concentration are in progress; when available, these data will be compared with the thermodynamic model summarized here.

The primary reference for the +V data base is Fanghänel et al. [27], which provides parameters for the Np(V) system in aqueous NaCl and NaClO_4 media, including the species NpO_2^+ , $\text{NpO}_2\text{OH}(\text{aq})$, $\text{NpO}_2(\text{OH})_2^-$, $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, $\text{NpO}_2\text{OH}(\text{am})$, $\text{NpO}_2\text{OH}(\text{aged})$, $\text{NaNpO}_2\text{CO}_3(\text{s})$, $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s})$, and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$. We have extended this data base to aqueous KCl and K_2CO_3 media by including the solids $\text{KNpO}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ and $\text{K}_3\text{NpO}_2(\text{CO}_3)_2 \cdot 0.5\text{H}_2\text{O}(\text{s})$ and the necessary K^+ and CO_3^{2-} ion

interaction parameters. Documentation of this parameter set and the predictive ability of the resulting Np(V) solubility model in K-Cl-CO₃ and Na-K-Cl-CO₃ media is in progress.

The deprotonation behavior of the organic ligands acetate (Ac⁻), citrate (Cit³⁻), EDTA⁴⁻, and oxalate (Ox²⁻) was measured as a function of NaCl concentration using potentiometric titration techniques [28]. The formation of the 1 to 1 actinide-ligand complexes as a function of NaCl concentration was measured by solvent extraction [28, 29]. The standard chemical potentials of the actinide-ligand complexes were determined for AmAc²⁺, AmCit(aq), AmEDTA⁻, AmOx⁺, ThAc³⁺, ThCit⁺, ThEDTA(aq), ThOx²⁺, NpO₂Ac(aq), NpO₂Cit²⁻, NpO₂EDTA³⁻, and NpO₂Ox⁻, along with the necessary ion interaction parameters required to describe the observed behavior in NaCl media. The formation and behavior of MgAc⁺, MgCit⁻, MgEDTA²⁻, and MgOx(aq) in NaCl media were also measured and modeled [30].

CALCULATION OF DISSOLVED +III, +IV, AND +V ACTINIDE CONCENTRATIONS

Estimates of the dissolved concentrations of +III, +IV, and +V actinides were made in a series of equilibrium calculations beginning with reported compositions of SPC Brine or "Brine A" and ERDA6 Brine, for the Salado and Castile Fms, respectively [5]. These brines were brought into equilibrium with the halite and anhydrite to reflect the ubiquitous presence of these minerals in the WIPP disposal system. The actinides Am(III), Th(IV), and Np(V) were added to the halite+anhydrite equilibrated brines until an actinide-bearing solid phase precipitated for each. Brines were maintained at saturation with a solubility-controlling solid for each actinide, although the particular solubility-controlling solid for each actinide was allowed to change as dictated by the thermodynamic data base as the composition of the brines change.

The brine compositions in the WIPP disposal rooms are expected to be in chemical equilibrium with brucite, Mg(OH)₂(s), and magnesite, MgCO₃(s), or with portlandite, Ca(OH)₂(s), and calcite, CaCO₃(s) [31]. Accordingly, the brine compositions were modified by addition of brucite+magnesite, or portlandite+calcite, until saturation with the added minerals was achieved. In the final modification of the brine compositions, the organic ligands acetate, citrate, EDTA, and oxalate are added to the brines at the maximum total concentrations expected of Ac=1.2×10⁻³m, Cit=5.4×10⁻⁴m, EDTA=4.8×10⁻⁶m, and Ox=8.5×10⁻³m [32]. The brines contained the organic ligands at the above specified concentrations except when precipitation of the ligand was indicated by the thermodynamic data. However, only oxalate solids are included in the data base.

RESULTS

Calculated Actinide Concentrations

Results of the calculations are summarized in Table 1 for ERDA6 and SPC Brines at brucite+magnesite saturation with and without organic ligands, and at portlandite+calcite saturation with and without organic ligands. The total element concentrations are given along with the equilibrium solid phases. The solubility controlling solid phases for the actinides are calculated to be Am(OH)₃(s) and ThO₂(am) under all conditions, while KNpO₂CO₃•2H₂O(s) controls in the brucite+magnesite cases and NpO₂OH(aged) controls in the portlandite+calcite cases. The very low concentrations predicted under some of the conditions, e.g., less than 10⁻⁸

of 10^{-9} m, are extrapolations below analytical detection limits and thus should probably be replaced with detection limit values. All solids in the Harvie et al. [1] data base were allowed to form except for dolomite. In addition to solids mentioned above, glauberite, $\text{Na}_2\text{Ca}(\text{SO}_4)_2(\text{s})$, magnesium oxychloride, $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}(\text{s})$, calcium oxychloride A, $\text{Ca}_4\text{Cl}_2(\text{OH})_6 \cdot 13\text{H}_2\text{O}(\text{s})$, and $\text{Na}_2\text{Ox}(\text{s})$ were calculated to form.

Castile Brine at Brucite+Magnesite Saturation. The dissolved Am(III) concentration in ERDA6 at brucite+magnesite saturation is increased by about 40 times to 3×10^{-6} m with the addition of the organic ligands. The total Th(IV) concentration is effectively unchanged when organic ligands are added. The total Np(V) concentration increases by a factor of about 33 with the addition of organic ligands. Because of the low concentration of divalent cations available to sequester the organic ligands, these ligands are expected to have the largest influence on actinide concentrations in ERDA6 brine at brucite+magnesite saturation. Magnesium, with a concentration of 0.04m in this case, is calculated to sequester 27% of total acetate, 56% of total citrate, 41% of total EDTA, and 90% of total oxalate.

Castile Brine at Portlandite+Calcite Saturation. In ERDA6 at portlandite+calcite saturation, the calculated solubility of Am(III) and Th(IV) are slightly lower than at brucite+magnesite saturation. That of Np(V) is slightly higher because of the increased importance of the hydrolysis species $\text{NpO}_2\text{OH}(\text{aq})$ and $\text{NpO}_2(\text{OH})_2^-$. The increase in dissolved actinide concentrations caused by the organic ligands is small for all three actinides, a factor of 1.2 or less, because hydroxide ion effectively outcompetes the organic ligands for complexing the actinides. The model calculates that $\text{Na}_2\text{Ox}(\text{s})$ will precipitate under these conditions, reducing the total dissolved oxalate concentration to about 54% of its original value. Magnesium, with a concentration of 4×10^{-7} m in this case, does not complex with the organic ligands to any significant extent. The high concentration of calcium ion may cause sequestering of the organic ligands, but model parameters for such reactions are currently unavailable.

Salado Brine at Brucite+Magnesite Saturation. The total dissolved concentrations of Am(III), Th(IV), and Np(V) in SPC Brine at brucite+magnesite saturation are calculated to be increased by factors of 2.1, 1.0, and 3.3, respectively, with the addition of organic ligands. The addition of the organic ligands causes only a minor increase because of the complexation of the organic ligands by Mg^{2+} . Magnesium, with a concentration of 0.5m in this case, is calculated to tie up 74% of total acetate, 65% of total citrate, 88% of total EDTA, and 98% of total oxalate. Dissolved Am(III) concentrations increase because of the formation of AmEDTA^- and AmOx^+ ; dissolved Np(V) concentrations increase because of the formation of NpO_2Ox^- .

Salado Brine at Portlandite+Calcite Saturation. In SPC at portlandite+calcite saturation, the calculated solubilities of Am(III) and Th(IV) are much lower than at brucite+magnesite saturation and that of Np(V) is slightly higher. The Am(III) concentration is controlled by the second and third hydrolysis species. The Th(IV) concentration decreases because the carbonate concentration is no longer sufficient to stabilize thorium as the $\text{Th}(\text{CO}_3)_5^{6-}$ ion. For Np(V), the concentrations of the hydrolysis products increase while the neptunyl ion concentration decreases. Under these conditions, the addition of organic ligands is predicted to increase the dissolved concentrations of Am(III) by a factor of 2.1, while the Th(IV) concentration is unchanged. The dissolved concentration of Np(V) increases by a factor of 1.7 from the

formation of NpO_2Ox^- . As for the ERDA6 case at portlandite+calcite saturation, the low concentration of Mg^{2+} , $2 \times 10^{-6}\text{m}$ in this case, does not significantly complex with the organic ligands.

Influence of Potential Backfills on Brine Compositions

The potential backfill additives can have little or great effect on brine compositions. For Castile brines like ERDA6, the primary influence of the addition of brucite+magnesite is to change the hydrogen ion concentration and reduce the carbonate ion concentration. The addition of portlandite+calcite to ERDA6 decreases the relatively low total magnesium content of the brine and reduces the carbonate ion concentration as the major effect. For Salado brines like SPC, both backfill options have a more pronounced effect. The addition of brucite+magnesite to SPC doubles sodium ion concentration and reduces magnesium ion concentration to a third of the initial value, while the addition of portlandite+calcite replaces magnesium ion almost stoichiometrically with calcium ion. Thus, addition of the calcium-containing backfill would change Salado brines from predominantly Na-Mg-Cl to predominantly Na-Ca-Cl brines.

Anticipated Model Accuracy

The actinide dissolved concentration models were targeted to be accurate within one order of magnitude for solubility predictions. The models have been shown to be more accurate than this when compared with solubility measurements in complex synthetic brines in the absence of organic ligands [19]. However, confirmatory studies of the accuracy of predictions in the presence of organic ligands are not yet completed. Therefore, we adopt the order of magnitude targeted accuracy for providing the best estimates of dissolved +III, +IV, and +V actinides under anticipated WIPP disposal room conditions.

SUMMARY

Actinide solubility in the WIPP disposal rooms can be determined by approximating the chemical conditions with equilibrium thermodynamics. A data base for calculating the solubility of Am(III)/Pu(III)/Nd(III), Th(IV), and Np(V) in concentrated electrolytes using aqueous thermodynamics and the Pitzer formalism has been developed. The major chemical effects accounted for in the data base are interactions with Na, K, Mg, Cl, SO_4 , CO_3 , H, and OH ions, and the organic ligands acetate, citrate, EDTA, and oxalate. The data base has been used to estimate potential dissolved concentrations of actinides under WIPP conditions.

REFERENCES

- [1] HARVIE, C.E., N. MØLLER, AND J.H. WEARE, "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl- SO_4 -OH- HCO_3 - CO_3 - CO_2 - H_2O System to High Ionic Strengths at 25°C," *Geochimica et Cosmochimica Acta*, 48, 723-751, 1984.
- [2] PITZER, K.S. "Ion Interaction Approach: Theory and Data Correlation." Chapter 3, pp. 75-153 in Activity Coefficients in Electrolyte Solutions, CRC Press, Boca Raton, Florida 1991.
- [3] DEPARTMENT OF ENERGY, Waste Isolation Pilot Plant Transuranic Waste Baseline Inventory Report, CAO-94-1005, Revision 0, 1994. DOE Carlsbad Area Office, Carlsbad, NM.

- [4] LAPPIN, A.R., R.L. HUNTER, D.P. GARBER, P.B. DAVIES, R.L. BEAUHEIM, D.J. BORNIS, L.H. BRUSH, B.M. BUTCHER, T. CAUFFMAN, M.S.Y. CHU, L.S. GOMEZ, R.V. GUZOWSKI, H.J. IZZOLINO, V. KELLEY, S.J. LAMBERT, M.G. MARIETTA, J.W. MERCER, E.J. NOWAK, J. PICKENS, R.P. RECHARD, M. REEVES, K.L. ROBINSON, AND M.D. SIEGEL, Systems Analysis, Long-Term Radionuclide Transport, and Dose Assessments, Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico; March 1989, SAND89-0462, Sandia National Laboratories, Albuquerque, New Mexico, 1989.
- [5] BRUSH, L.H., Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant, SAND90-0266, Sandia National Laboratories, Albuquerque, New Mexico, 1990.
- [6] PAPENGUTH, H.W., AND Y. BEHL. Test Plan : For Evaluation of Colloid Facilitated Actinide Transport at the WIPP, TP 96-01, Sandia WIPP Central Files, 1996.
- [7] NECK, V., W. RUNDE, J.I. KIM, AND B. KANELLAKOPULOS, "Solid-Liquid Equilibrium Reactions of Neptunium(V) in Carbonate Solution at Different Ionic Strength," *Radiochimica Acta*, 65, 29-37, 1994.
- [8] LINDBERG, R.D., AND D.D. RUNNELLS, "Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling," *Science*, 225, 925-927, 1984.
- [9] CLARK, D.L., Oxidation State Distribution in STTP Test Plan, WIPP Document CST-OSD-TST-002/0, Sandia National Laboratories, Albuquerque, New Mexico, 1995.
- [10] FELMY, A.R., AND J.H. WEARE, "The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California," *Geochimica et Cosmochimica Acta*, 50, 2771-2783, 1986.
- [11] HORITA, J., T.J. FRIEDMAN, B. LAZAR, AND H.D. HOLLAND, "The Composition of Permian Seawater," *Geochimica et Cosmochimica Acta*, 55, 417-432, 1991.
- [12] MCCAFFREY, M.A., B. LAZAR, AND H.D. HOLLAND, "The Evaporation Path of Seawater and the Coprecipitation of Br⁻ and K⁺ with Halite," *Journal of Sedimentary Petrology*, 57, 5, 928-937, 1987.
- [13] NOVAK, C.F. 1996. "Release of FMT Data Base File HMW_3456_960312.CHEMDAT." Sandia National Laboratories internal memorandum. On file under SWCF-RC-110110. WPO#35376. 13 March 1996.
- [14] NOVAK, C.F. 1996. "Parameter Values for +III Actinide Hydrolysis Species." Sandia National Laboratories internal memorandum. On file under SWCF-RC-QA-1.1.10.1.1. WPO#40692. 11 June 1996.
- [15] FELMY, A.R., D. RAI, J.A. SCHRAMKE, AND J.L. RYAN, "The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines," *Radiochimica Acta*, 48, 29-35, 1989.
- [16] FELMY, A.R., D. RAI, AND R.W. FULTON, "The Solubility of AmOHCO₃(c) and the Aqueous Thermodynamics of the System Na⁺-Am³⁺-HCO₃⁻-OH⁻-H₂O," *Radiochimica Acta*, 50, 193-204, 1990.
- [17] RAI, D., A.R. FELMY, R.W. FULTON, AND J.L. RYAN, "Aqueous Chemistry of Nd in Borosilicate-Glass/Water Systems," *Radiochimica Acta*, 58/59, 9-16, 1992.
- [18] RAI, D., A.R. FELMY, AND R.W. FULTON, "The Nd³⁺ and Am³⁺ Ion Interactions with Sulfate Ion and their Influence on NdPO₄(c) Solubility," *Journal of Solution Chemistry*, 24, 9, 879-895, 1995.
- [19] RAO, L., D. RAI, A.R. FELMY, AND R.W. FULTON, "Solubility of NaNd(CO₃)₂•6H₂O in Concentrated Sodium Carbonate and Sodium Bicarbonate Solutions," *Radiochimica Acta*, revised and resubmitted, 1996.
- [20] FANGHANEL, TH., J.I. KIM, P. PAVIET, R. KLENZE, AND W. HAUSER, "Thermodynamics of Radioactive Trace Elements in Concentrated Electrolyte Solutions: Hydrolysis of Cm³⁺ in NaCl Solutions," *Radiochimica Acta*, 66/67, 91-97, 1994.
- [21] RUNDE, W., AND J.I. KIM, Chemical Behavior of Trivalent and Pentavalent Americium in Saline NaCl Solutions, RCM 01094, Institute for Radiochemistry,

- Technical University of Munich. Munich, Germany, copy of the original (in German) and the English translation on file in the Sandia WIPP Central Files, 1995.
- [22] FELMY, A.R., D. RAI, AND M.J. MASON, "The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model," *Radiochimica Acta*, 55, 177-185, 1991.
- [23] ROY, R.N., K.M. VOGEL, C.E. GOOD, W.B. DAVIS, L.N. ROY, D.A. JOHNSON, A.R. FELMY, AND K.S. PITZER, "Activity Coefficients in Electrolyte Mixtures: HCl + ThCl₄ + H₂O for 5°-55°C," *Journal of Physical Chemistry*, 96, 11065-11072, 1992.
- [24] FELMY, A.R., D. RAI, S.M. STERNER, M.J. MASON, N.J. HESS, AND S.D. CONRADSON, "Thermodynamic Models for Highly Charged Aqueous Species: The Solubility of Th(IV) Hydrous Oxide in Concentrated NaHCO₃ and Na₂CO₃ Solutions," manuscript submitted to *Journal of Solution Chemistry*, 1996.
- [25] FELMY, A.R., AND D. RAI, "An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte Th⁴⁺-SO₄²⁻ in the System Na⁺-K⁺-Li⁺-NH₄⁺-Th⁴⁺-SO₄²⁻-HSO₄⁻-H₂O to High Concentration.," *Journal of Solution Chemistry*, 21, 5, 407-423, 1992.
- [26] RAI, D., A.R. FELMY, D.A. MOORE, AND M.J. MASON, "The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaHCO₃ and Na₂CO₃ Solutions." *Materials Research Society Symposium Proceedings. Volume 353. Scientific Basis for Nuclear Waste Management XVIII.* T. Murakami and R.C. Ewing, editors, Materials Research Society, Pittsburgh, Pennsylvania, 1143-1150, 1995.
- [27] FANGHÄNEL, TH., V. NECK, AND J.I. KIM, "Thermodynamics of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes," *Radiochimica Acta*, 69, 169-173, 1995.
- [28] MOORE, R.C., "Revision 1. Final Model Parameters for Deprotonation of Lactic Acid, Citric Acid, Oxalic Acid, and EDTA and Complexation of Acetate, Lactate, Citrate, Oxalate, and EDTA with NpO₂⁺, Am³⁺, Th⁴⁺, and UO₂²⁺ in NaCl Media," Internal Sandia memorandum to C.F. Novak, 14 March 1996.
- [29] NOVAK, C.F., M. BORKOWSKI, AND G.R. CHOPPIN, "Thermodynamic Modeling of Neptunium(V)-Acetate Complexation in Concentrated NaCl Media," *Radiochimica Acta* vol. 74: 111-116, 1996.
- [30] MOORE, R.C., "Model Parameters for Magnesium Complexation Acetate, Citrate, Oxalate, and EDTA in NaCl Media." Internal Sandia memorandum to C.F. Novak, 17 March 1996.
- [31] WANG, Y. , "Define Chemical Conditions for FMT Actinide Solubility Calculations," Internal Sandia memorandum to M.D. Siegel, 18 March 1996.
- [32] WEINER, R.F., "Dissolved Ligand Concentrations," Internal Sandia memorandum to C.F. Novak, 27 March 1996.

This work was supported by the United States Department of Energy under contract DE-AC0494AL85000.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Table 1. Calculated equilibrium concentrations (molal) in prototypical WIPP Castile and Salado brines containing organic ligands (+OL), in equilibrium, at brucite+magnesite saturation (@Mg), and at portlandite+calcite (@Ca) saturation.

	ERDA6 (Castile) Brine				SPC (Salado) Brine			
	@Mg	+OL@Mg	@Ca	+OL@Ca	@Mg	+OL@Mg	@Ca	+OL@Ca
Hydrogen	111.287	111.287	111.335	111.334	111.123	111.123	111.128	111.128
Oxygen	56.5444	56.5445	56.3567	56.3231	55.8554	55.8555	55.6272	55.6272
Sodium	6.199	6.198	6.228	6.222	4.693	4.691	3.495	3.481
Potassium	0.1091	0.1091	0.11011	0.1101	1.047	1.046	1.060	1.059
Magnesium	0.04429	0.05406	3.01E-07	4.54E-07	0.5088	0.5196	5.98E-06	6.71E-06
Calcium	0.01330	0.01333	0.02003	0.02136	0.03305	0.03308	1.307	1.320
Chlorine	5.967	5.966	5.9956	5.997	6.665	6.664	7.116	7.107
Sulfur	0.1908	0.1909	0.1326	0.1245	0.06024	0.06026	0.00197	0.00197
Carbon	3.15E-05	3.10E-05	1.43E-05	1.38E-05	4.08E-05	4.10E-05	5.87E-06	5.88E-06
Boron	0.07085	0.07082	0.07085	0.07082	0.02719	0.02717	0.02438	0.02434
Bromine	0.01237	0.01237	0.01237	0.01237	0.01359	0.01359	0.01219	0.01217
Am(III)	7.41E-08	2.95E-06	1.05E-09	1.18E-09	6.67E-07	1.43E-06	3.09E-09	3.06E-09
Th(IV)	6.78E-09	6.50E-09	1.29E-09	1.29E-09	4.98E-06	5.03E-06	1.16E-09	1.16E-09
Np(V)	2.53E-06	8.40E-05	1.30E-05	1.52E-05	2.64E-06	8.75E-06	4.85E-06	8.20E-06
Acetate	0	0.0012	0	0.0012	0	0.0012	0	0.0012
Citrate	0	0.00054	0	0.00054	0	0.00054	0	0.00054
EDTA	0	4.8E-06	0	4.8E-06	0	4.8E-06	0	4.8E-06
Oxalate	0	0.0085	0	0.0046	0	0.0085	0	0.0085
log[m _{H+}]	9.89	9.88	13.06	13.04	9.36	9.36	12.12	12.12
log[a _{H+}]	9.24	9.23	12.40	12.39	8.69	8.69	11.47	11.47
Ionic Strength	6.66	6.66	6.52	6.52	7.40	7.40	8.44	8.47
Am(OH) ₃ (s)	present	present	present	present	present	present	present	present
ThO ₂ (am)	present	present	present	present	present	present	present	present
NpO ₂ OH (aged)	-	-	present	present	-	-	present	present
K ₂ NpO ₂ CO ₃ ·2H ₂ O(s)	present	present	-	-	present	present	-	-
Anhydrite	present	present	present	present	present	present	present	present
Halite	present	present	present	present	present	present	present	present
Brucite	present	present	present	present	present	present	present	present
Magnesite	present	present	-	-	present	present	-	-
Portlandite	-	-	present	present	-	-	present	present
Calcite	-	-	present	present	-	-	present	present
Glauberite	present	present	-	-	-	-	-	-
MgOxyCl	-	-	-	-	present	present	-	-
CaOxyCl A	-	-	-	-	-	-	present	present
Na ₂ Ox(s)	-	-	-	present	-	-	-	-