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**Systems Prioritization Method - Iteration 2  
Baseline Position Paper:**

**Actinide Source Term**

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## ACRONYMS

<b>BIR</b>	<b>Baseline Inventory Report</b>
<b>FSU</b>	<b>Florida State University</b>
<b>INEL</b>	<b>Idaho National Engineering Laboratory</b>
<b>LANL</b>	<b>Los Alamos National Laboratory</b>
<b>LBL</b>	<b>Lawrence Berkeley Laboratory</b>
<b>LLNL</b>	<b>Lawrence Livermore National Laboratory</b>
<b>PA</b>	<b>Performance Assessment</b>
<b>PNL</b>	<b>Battelle-Pacific Northwest Laboratory</b>
<b>SNL</b>	<b>Sandia National Laboratories</b>
<b>TRU</b>	<b>transuranic</b>
<b>WIPP</b>	<b>Waste Isolation Pilot Plant</b>
<b>WMCG</b>	<b>Waste Matrix Code Group</b>

## EXECUTIVE SUMMARY

The Actinide Source Term represents the quantity of actinides that could be mobilized, either as solutes in the WIPP brines or as colloidal particles, and could migrate with the brines away from the disposal room vicinity. This document presents alternative proposed methods for estimating this source term and evaluates the models for mobile dissolved and colloidal actinide concentrations. The main points in this document may be summarized as follows:

- (1) The 1992 Performance Assessment (PA) "Expert Panel" model for mobile actinide concentrations is no longer applicable as the sole model for actinide mobility. The model is not suitable for application by itself, but is used in combination with the "Inventory Limits" model in the "Inventory Limits Model with Realistically Conservative Maximum Concentrations" model.
- (2) The "Inventory Limits" model assumes that all actinides in the disposal rooms are mobile, up to an arbitrarily chosen value of 1 mole/liter. It is a worst case scenario for mobile actinide concentrations, and is unrealistically conservative. This model does not incorporate more recent or existing information for the chemical behavior of actinides in brines.
- (3) The "Inventory limits Model with Realistically Conservative Maximum Concentrations," a combination of the "Inventory Limits" and the "Expert Panel" models, is more judiciously conservative than the "Inventory Limits" model, and is the current baseline model for the WIPP Actinide Source Term.
- (4) The "Chemical Model for Mobile Actinide Concentrations," based on information published during the past fifteen years, and laboratory and modeling efforts in progress, is a realistic description of the important chemical phenomena that could mobilize actinides in the WIPP disposal rooms. When it becomes available, the model is intended to supplant the "Inventory limits Model with Realistically Conservative Maximum Concentrations." The "Chemical Model for Mobile Actinide Concentrations" follows established thermodynamic chemical theory for both dissolved and colloidal species, and some of its features have been verified experimentally in other contexts. At present, the model is only partially developed.

The Actinide Source Term program is the newest WIPP experimental program, and is now generating reliable data. The volume of recently developed data is such that the models presented here will be revised in the future, to incorporate more of the published literature on actinide mobility as well as different baseline concentrations.

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## 1. Role of Mobile Actinide Concentrations in Performance Assessment Calculations and Compliance

WIPP performance assessment calculations require information about the chemical behavior of the transuranic (TRU) waste elements Americium (Am), Thorium (Th), Uranium (U), Plutonium (Pu), and Neptunium (Np) in the WIPP disposal environment. Transuranic elements, technically those elements with atomic numbers greater than 92, are a subset of the *actinide* series that begins with Actinium, element number 89. The five elements of the actinide series most important to transuranic (TRU) waste are given in Table 1. Because thorium and uranium are not transuranic elements, but are actinides important in transuranic waste, we use the term *actinide* in this document, rather than *transuranic element*. The actinides important in TRU waste disposal are also a subset of *radionuclides*. The actinide elements have a similar atomic structure and exhibit similar chemical behavior; chemical behavior is independent of radioactivity, so that two isotopes of the same element, like Pu-238 and Pu-239, will exhibit essentially identical chemical behavior. Mass numbers, which distinguish isotopes of the same element, are not used in this position paper.

Table 1. The Five Elements of the Actinide Series That Are Important To TRU Waste. (Atomic numbers are given in the upper left corners.)

90 Th Thorium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium
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The inventory of actinides expected to be placed in the WIPP is given in the Baseline Inventory Report (BIR) (Department of Energy, 1994a). The BIR lists the types of waste substrates, e.g., cellulosic material, sludges, soils, metals, and the quantities of actinide isotopes associated with these substrates. The BIR is updated periodically to reflect new information from the waste generator sites. The basis for Actinide Source Term models is the chemical behavior of actinides, so that accurate knowledge of the quantities of these actinides, while needed for performance assessment, is not necessary to model development. As used for the WIPP, the Actinide Source Term identifies the potential mobile actinide concentrations as a function of chemical and physical properties of actinides in brines. The actinide inventory that is used in conjunction with Actinide Source Term models is specified independently.

This position paper discusses the bases for estimated concentrations of mobile actinides that may be released from the disposal room environment, as discussed in the Scenario Development Position Paper and in WIPP Performance Assessment Department (1992-1993). A narrative description of the essential features of the WIPP is given in Lappin et al. (1989).

Human intrusion into the repository, and deep drilling into other parts of the controlled area, can cause hydraulic connections to be formed between the WIPP disposal rooms, the Castile Formation, and the Culebra Dolomite, the most transmissive water-saturated unit within the Rustler Formation overlying the WIPP Site (see, e.g., Lappin et al., 1989, Chapters 5 and 7; and the Non-Salado Flow and Transport Position Paper). These connections may permit brines and accompanying materials to move from the repository horizon in the Salado Formation up to the land surface or to the Culebra, where they may move with the natural groundwater flow in the Culebra to the WIPP Land Withdrawal (i.e., regulatory) Boundary. Reviews and summaries of brine compositions in and around the WIPP Site are given in Siegel et al. (1991), Brush (1990), Novak (1992), and Molecke (1983).

If the moving brine contains dissolved actinides or carries colloidal particles on which actinides are adsorbed, these actinides could reach the accessible environment. 40 CFR 191.13 determines the allowed cumulative integrated release limit for the radioactive TRU actinides. The mobile concentrations of actinides that may leave the disposal environment will determine the maximum actinide concentrations that could cross the regulatory boundary through transport in brines. Therefore, definition of potential mobile actinide concentrations under various breach scenarios is central to determining whether any potential integrated release of radioactivity from the WIPP will exceed the release limits of 40 CFR 191.13. Mobile actinide concentrations will also determine whether the radiation dose to the maximally exposed individual and the groundwater concentration of actinides will be less than what is allowed by 40 CFR 191.15 and 40 CFR 191.24, the individual and groundwater protection standards, respectively.



## 2. CONCEPTUAL MODELS FOR MOBILE ACTINIDE CONCENTRATIONS

The conceptual models for movement of brine from the disposal room environment to the accessible environment are documented in WIPP Performance Assessment Department, Volume 2 (1992) and in other Project position papers, including the Salado Flow and Transport paper and the Non-Salado Flow and Transport paper; these are not reproduced here. The present discussion does not include brine movement, but examines only the conceptual models for the concentrations of mobile actinides, both dissolved and colloidal, that may occur in WIPP brines.

The term "mobile actinides" refers to all actinides that can move with the aqueous (brine) phase. Actinides are usually present in TRU waste as oxides (e.g.,  $\text{UO}_2$ ), but will be referred to throughout as "actinides" because the actinide itself has regulatory importance. Mobile actinides are made up of dissolved actinides (in true solution) and colloidal particles that contain actinides or have sorbed actinides. The present publication is the first to apply the terms "mobile", "dissolved," and "colloidal" actinides consistently to the WIPP actinide source term. Previously the term "soluble" was used in place of "mobile", because the formation and transport of colloidal actinides within the WIPP system were not considered. The change in nomenclature was necessary to include both true solution species and colloidal suspensions.

From a regulatory perspective, it is irrelevant whether actinides that cross the regulatory boundary are dissolved or in colloidal form. However, the transport of actinides (movement with the brine phase) from disposal rooms to the accessible environment is different for dissolved species and colloidal species, because the physical mechanisms that control colloidal and solute species transport are different. Transport of dissolved and colloidal actinides must be treated separately and differently.

Inorganic compounds that dissolve in an aqueous (polar) solvent are present in solution as ions, either ions of an element (like  $\text{Mg}^{2+}$ ) or complex ions (like  $\text{CO}_3^{2-}$ ). An aqueous system is saturated with a dissolved species when the concentration of the solute (the dissolved species) is at its maximum in that system. This maximum capacity of an aqueous system for a particular dissolved species is called the solubility of the species in that system. The maximum capacity, or solubility, is a function of the composition of the solution. When a system is saturated (at its maximum capacity for solute), one or more solids containing the dissolved species are also present. The solids that are most favored under the chemical conditions, i.e., the concentrations of all elements in the aqueous phase, may be said to govern the dissolved concentration of the

species. The solids that form are often called the “solubility-controlling solid(s).” Aqueous concentrations of a dissolved species can be described by the solubility product.

In an ideal solution, the solubility product is the product of the molalities of the positive and negative ions into which the species dissociates on dissolution. In a non-ideal solution (such as a very concentrated solution), the dissolved amount is proportional to the molality rather than equal to it; the proportionality constant  $\gamma$  is called the activity coefficient. In very dilute solution, the activity coefficient approaches unity. Solubility is then defined by an equilibrium constant called the solubility product. For example, magnesium carbonate in water dissociates as:



and the solubility product is

$$K_{\text{sp}} = (\gamma_{\text{Mg}^{2+}} m_{\text{Mg}^{2+}}) (\gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}) = (a_{\text{Mg}^{2+}}) (a_{\text{CO}_3^{2-}})$$

where  $m$  is molality and  $a$  is a parameter called the activity. The molar concentration of an ion is often referred to inaccurately as its “solubility”; the “solubility” of  $\text{Mg}^{2+}$  in the equation given above is, more correctly, its activity, which in very dilute solution, approaches the molal concentration (or molality). The chemical nature of the dissolved species depends on other ions and dissolved species present, so that one cannot say, for example, “the solubility of thorium in brine is ...” but, if thorium forms an amorphous stable hydroxyl complex in brine, “the solubility of thorium in the presence of solid  $\text{Th}(\text{OH})_4(\text{am})$ , in a brine with composition ... is ....” Solubility is heavily dependent on brine composition and acidity or alkalinity (pH), as well as temperature. The temperature in the WIPP is not expected to vary enough to cause a significant change in solubility; solubility is considerably more dependent on the other parameters.

Dissolution of actinides is influenced by chemical reactions of actinides with other species dissolved in the aqueous phase. These complexation reactions can increase the total amount of a dissolved actinide, because the actinide can combine with inorganic and organic species present in the aqueous phase. There are several different complexation reactions possible, including hydrolysis, acid-base reaction, ion pairing, ion association, and chelation.

If a sufficient quantity of a solubility-controlling solid is present, and the quantity of aqueous solvent is limited, the equilibrium dissolved concentration (at the particular temperature)

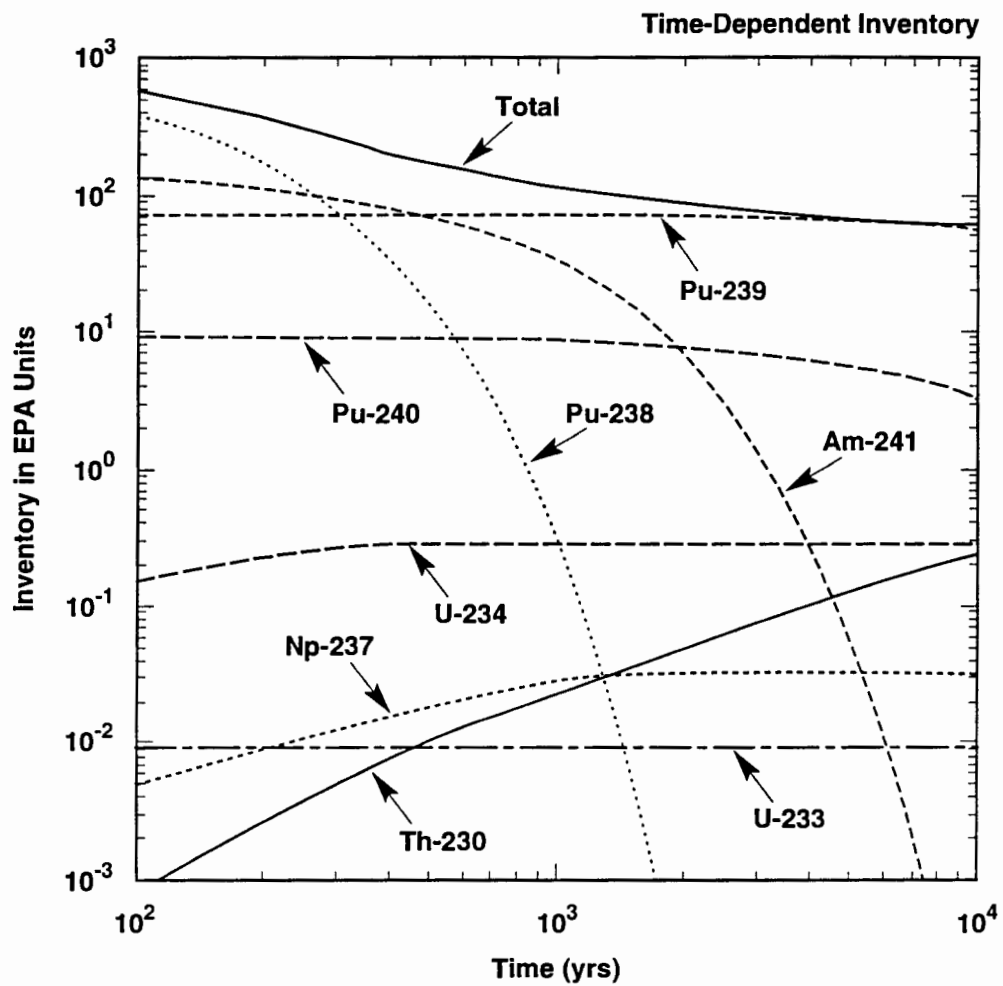
will be reached. On the other hand, if there is enough aqueous solvent (brine) to dissolve all available solid, the concentration of solute could be less than the equilibrium concentration. For relatively insoluble compounds (like the actinide oxides present in TRU wastes), the total amount of material mobilized could be greater in the latter case than in the former. (For very soluble compounds, like CsCl, or almost infinitely soluble ones, like CsNO<sub>3</sub>, the amount of aqueous solvent is rarely enough to reach equilibrium.) Given the amount of brine potentially available if the entire available void volume were filled, postulating that all solid actinide compounds present would dissolve leads to a more conservative estimate of mobilized actinides than postulating equilibrium concentrations. The postulate that all solid actinide compounds present (the entire actinide inventory) would dissolve is the basis for an "inventory concentration." Such an inventory concentration of each significant isotope of each actinide is defined as the mass (or moles) of the isotope divided by the available brine volume. Both the mass and the volume are based on the repository control volume used in the calculation, e.g., total repository, panel, or room.

Helton et al. (1992) identified eight isotopes as dominating the radioactive material that could cross the WIPP regulatory boundary under breach scenarios: <sup>239</sup>Pu, <sup>241</sup>Am, <sup>238</sup>Pu, <sup>240</sup>Pu, <sup>237</sup>Np, <sup>234</sup>U, <sup>233</sup>U, and <sup>230</sup>Th are considered to be important for WIPP performance assessment. <sup>234</sup>U, <sup>233</sup>U, and <sup>230</sup>Th are not strictly speaking "transuranic," but are included here because they are long-lived daughters of the transuranic radionuclides, and are expected to be present in TRU waste in non-negligible amounts. Figure 1 shows the expected WIPP radioisotope inventory, as estimated in 1990, as a function of time after waste emplacement (Helton et al., 1992). Early in the life of the repository, most of the activity comes from <sup>238</sup>Pu, <sup>239</sup>Pu, and <sup>241</sup>Am. However, other actinide isotopes become important during the 10,000 year post-operational phase. The inventories of <sup>234</sup>U and <sup>230</sup>Th increase as <sup>238</sup>Pu decays (99.95% conversion to <sup>234</sup>U after 1000 years), and significant quantities of <sup>237</sup>Np result from alpha-decay of <sup>241</sup>Am (~75% complete after 1000 years). Therefore, to ascertain compliance with 40 CFR Part 191 Subpart B, WIPP Performance Assessment requires estimates of the concentrations of Th, U, Np, Pu, and Am in Salado and Castile brines in contact with TRU waste under disposal room conditions. The radioisotopes of interest in release scenarios include those present in TRU waste and their decay products (daughter isotopes).

The wastes emplaced determine the actinide inventory. The estimated projected inventories for the most significant actinide isotopes are given in Table 2 (Department of Energy, 1994a). The brine volumes, an input parameter for calculating inventory concentrations, are based on the disposal room model and Salado brine inflow assumptions described in the position papers on those topics. The brine volumes will be different depending on the particular disposal room and brine inflow models used.

Table 2. Subset of Table 5-3 of the Baseline Inventory Report (Department of Energy, 1994a) Showing the Integrated Data Base (Department of Energy, 1994b) Totals for Selected Actinides. Inventory estimates for contact-handled waste were scaled by a factor of 1.4, discussed in detail in section 5.4 of the Baseline Inventory Report (Department of Energy, 1994a). Inventory estimates for remote-handled waste were not scaled.

Radionuclide	Contact-Handled Curies	Remote-Handled Curies
Pu-238	$8.12 \times 10^5$	$6.17 \times 10^4$
Pu-239	$1.72 \times 10^5$	$4.08 \times 10^4$
Pu-240	$2.28 \times 10^4$	$9.98 \times 10^3$
Pu-241	$4.54 \times 10^5$	$1.78 \times 10^5$
Pu-242	$6.89 \times 10^2$	0.948
U-233	$3.00 \times 10^2$	$1.04 \times 10^3$
U-235	1.39	$3.67 \times 10^2$
U-238	8.51	2.30
Am-241	$5.78 \times 10^4$	$8.98 \times 10^4$
Np-237	23.5	0.766
Th-232	0.141	0.333
Cf-252	$1.53 \times 10^2$	$1.10 \times 10^1$



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Figure 1. Expected WIPP radioisotope inventory as a function of time after waste emplacement (from Helton et al., 1992).

The chemical behavior of actinides, including both dissolved and colloidal behavior, depends on the actinide oxidation state. The local micro-environment in WIPP disposal rooms could be oxidizing or reducing, acidic or basic (Brush, 1990), and thus the actinides may have any of the oxidation states listed in Table 3. WIPP gas generation studies have indicated that the repository will likely be completely anoxic, i.e., without oxygen, within tens of decades after closure (see the Gas Generation position paper). The large amounts of metallic, i.e., reduced, iron in design-basis wastes may be sufficient to reduce most of the actinides to the lower oxidation states. However, there are apparently no measurements of the partitioning of actinides among oxidation states in chemical systems as potentially complex as the WIPP disposal rooms. Actual determinations of oxidation state distributions, especially for Pu and U, may indicate that not all of the oxidation states are important.

Table 3. Elements and Oxidation States Important to WIPP Performance Assessment. Elements/oxidation states in the same column exhibit similar chemical behavior.

Element	+III Oxidation State	+IV Oxidation State	+V Oxidation State	+VI Oxidation State
Plutonium	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
Uranium		U(IV)		U(VI)
Neptunium		Np(IV)	Np(V)	Np(VI)
Americium	Am(III)		Am(V)	
Thorium		Th(IV)		

## 2.1 Disposal Room Description Common to All Actinide Source Term Conceptual Models

WIPP performance assessment calculations require estimates for actinide concentrations that could be mobilized under different performance scenarios. There are several different ways that the mobile concentrations can be quantified, but all rely on the same underlying description of the system, as presented here.

WIPP design basis waste is a complex heterogeneous mixture of metals, cellulose, sludges, resins, pyrochemical salts, and other materials. The WIPP design basis indicates that wastes will be placed in the WIPP using the iron-based containers in which the wastes are currently stored. The rooms may be backfilled with crushed salt or a combination of salt and an engineered backfill material (although use of backfill is not part of the current baseline

assumptions). After sealing, natural creep closure in the Salado Formation will compress and crush the room contents, possibly rupturing some of the waste containers. Brines from the Salado and/or Castile Formations, with different compositions, may seep into the disposal rooms and contact the waste, converting actinides to dissolved or colloidal forms. Knowledge of brine composition, and how this composition changes through contact with the waste and backfill, is essential. If the brine migrates from the disposal rooms, it could carry actinides with it. The potential or likely concentrations of dissolved and colloidal actinides are the parameters called the "Actinide Source Term" for performance assessment calculations.

The chemical reactions that could occur in WIPP disposal rooms and impact mobile actinide concentrations can be divided into the following categories:

- (1) actinide dissolution reactions
- (2) reactions between brines and organic waste constituents (reactions that introduce organic ligands into the brines)
- (3) reactions between brines and cementitious waste or backfill materials like calcium oxide
- (4) reactions that produce gases, and reactions of gases dissolving in the brines
- (5) reactions between actinides and dissolved ligands, both inorganic and organic
- (6) reactions that produce non-radioactive carrier colloids, such as from clays and corroded materials
- (7) reactions among actinides, and possibly other species, to form actinide-intrinsic colloids
- (8) reactions between actinides and carrier colloids to form radioactive associative colloids (actinide sorption onto mobile substrates)
- (9) actinide sorption onto immobile substrates
- (10) precipitation of actinides
- (11) conversion of actinides among oxidation states (oxidation-reduction reactions)

The list of reactions is not intended to be exhaustive, but to illustrate essential features of the system. The reaction types are not listed in any particular order of importance. All of the listed reaction types can produce order-of-magnitude changes in mobile actinide concentrations. The task for the Actinide Source Term is to develop options for simplifying the system so it becomes tractable and amenable to a numerical description for use in WIPP Performance Assessment. Obviously, the effort required to quantify all of the reactions, extents of reactions, and reaction rates would be formidable. Several options for reducing the system to a mathematical description are given below as "Specific Conceptual Models."

## 2.2 Specific Conceptual Models for the Actinide Source Term

Six relevant conceptual models for describing mobile actinide concentrations in WIPP Performance Assessment scenarios have been identified. These include the "Inventory Limits" model (Section 2.2.1), the "Inventory Limits with Sorption" model (Section 2.2.2), the "Expert Panel" model, used as the 92 PA mobile actinide concentration data base (Section 2.2.3), the "Inventory Limits Model with Realistically Conservative Maximum Concentrations" (Section 2.2.4), the "Fresh Water Estimates" model (Section 2.2.5), and the "Chemical Model for Mobile Actinide Concentrations" (Section 2.2.6).

These models represent various methods for simplifying the detailed description of disposal room chemistry governing mobile actinide concentrations, usually by focusing on one or several types of reactions listed above and ignoring the others. The model used in the baseline is the "Inventory Limits Model with Realistically Conservative Maximum Concentrations." The "Chemical Model for Mobile Actinide Concentrations" is potentially the most reasonable and realistic. Although much information is available to support this model, the information has not yet been interpreted for use in WIPP Performance Assessment.

### 2.2.1 The "Inventory Limits" Model

The "Inventory Limits" model essentially assumes that nothing is known about the chemical behavior of actinides in the disposal room, and that all actinides are mobile. A calculation of actinide concentrations using the inventory of Table 2 and a brine volume of  $2.60 \times 10^8$  liters, and assuming that all actinides dissolve, yields the concentrations given in Table 4. The brine volume of  $2.60 \times 10^8$  liters was arrived at as follows:

Section 3.1.1 of WIPP PA Department, 1992, volume 3, gives the total excavated volume in the disposal region as  $4.36 \times 10^5 \text{ m}^3$ , or  $4.36 \times 10^8$  liters and a disposal volume (the volume occupied by waste) of  $1.76 \times 10^8$  liters. The difference between these is  $2.60 \times 10^8$  liters, which was used as the brine volume. This is a very rough estimate. In the interests of conservatism, other spaces that could be filled with brine were not included.



Table 4. Concentrations of Actinides, In Moles/Liter, Using the Inventory of Table 2 and a Brine Volume of  $2.66 \times 10^8$  Liters.

Nuclide	Total Curies	Moles	Moles/dm <sup>3</sup> (M)
Pu-238	$8.74 \times 10^5$	214	$8.24 \times 10^{-7}$
Pu-239	$2.13 \times 10^5$	$1.43 \times 10^4$	$5.51 \times 10^{-5}$
Pu-240	$3.28 \times 10^4$	601	$2.31 \times 10^{-6}$
Pu-241	$6.32 \times 10^5$	25.5	$9.79 \times 10^{-8}$
Pu-242	690	726	$2.79 \times 10^{-6}$
U-233	1340	596	$2.29 \times 10^{-6}$
U-235	368	$7.25 \times 10^5$	0.00279
U-238	10.8	$1.35 \times 10^5$	0.000520
Am-241	$1.48 \times 10^5$	178	$6.86 \times 10^{-7}$
Np-237	24.3	145	$5.57 \times 10^{-7}$
Th-232	0.474	$1.87 \times 10^4$	$7.19 \times 10^{-5}$
Cf-252	164	0.00121	$4.66 \times 10^{-12}$

The concentrations in Table 4 could be less than saturation equilibrium (by an undeterminable amount), if no undissolved actinides are present. Because saturation equilibrium of the important actinides has not yet been determined reliably for WIPP conditions, the "Inventory Limits" model added the following conservatism: the model postulated that a much smaller volume of brine, even though it did not fill a disposal panel, could come into contact with and dissolve all the actinides in that disposal panel. Very small volumes could result in absurdly high concentrations, so the total mobile concentration of each actinide was capped at the arbitrarily large value of 1 mole/dm<sup>3</sup> (mole/liter). Very little data exist showing actinide concentrations this large in aqueous solution.

The "Inventory Limits" model does not distinguish between the dissolved and colloidal forms of the mobile actinides or describe their relative proportions. Moreover, the model does not take advantage of any scientific knowledge of actinide behavior in brines. However, knowledge of the partitioning of the actinides among dissolved and colloidal forms is required for performance assessment calculations because of the dependence of radionuclide transport

on actinide form (see the Non-Salado Flow and Transport position paper). Currently, there is no technical basis from which to estimate relative proportions of dissolved and colloidal actinides. Specifying that all actinides are colloidal in form, although scientifically unrealistic, will lead to conservative, i.e., larger, calculated releases of radioactivity, because some types of colloids can be transported in the Culebra at speeds greater than the average groundwater speed. Therefore, if performance assessment assumes that all actinides are colloidal in form, mobile actinide concentrations far higher than could actually occur would be predicted.

The "Inventory Limits" model requires as input the identities and quantities of actinides in the wastes and the volumes of brines in the disposal rooms.

### **2.2.2 The "Inventory Limits with Sorption" Model**

The "Inventory Limits" model can be coupled with reversible sorption of actinides on fixed substrates and destabilized (i.e., immobile) colloids to produce the "Inventory Limits with Sorption" model. This model assumes that the only information known about actinide chemical behavior in the disposal room is that of sorption and that such reactions can be well described by equations for reversible sorption. Sorption on fixed substrates (reaction 9 above), including immobilized colloidal particles, can potentially reduce the concentration of dissolved actinides by several orders of magnitude, depending on the partitioning of actinides between the aqueous and solid phases under the specific physicochemical conditions in the disposal room environment. This model assumes that sorption is the only important mechanism affecting mobile actinide concentrations. However, data to quantify actinide sorption on the various substrates under WIPP-specific physicochemical conditions are not available; neither are data available to justify the assumption that only sorption is important.

If the "Inventory Limit with Sorption" model were to be used, the most likely candidates for sorption are iron hydroxides (from corrosion of waste containers and constituents), vermiculite (a waste constituent), cellulosic materials, and various proposed backfill materials like bentonite. All are known cation adsorbents, but little work has been done to quantify adsorption of actinides on these types of substrates. The "Inventory Limit with Sorption" model is very dependent on the substrate form and behavior; for example, the current reference backfill for WIPP does not include bentonite, which would significantly affect sorption. Because of the quantitative studies needed and the very large uncertainties in their outcomes, predicting sorption under WIPP-specific conditions is not feasible, and the "Inventory Limit with Sorption" model is not being considered further.

The "Inventory Limits with Sorption" model would require as input the identities and quantities of actinides in the wastes, brine volumes, brine compositions, sorbing materials, and the sorption capacity for each actinide on each sorbing substrate as a function of brine composition.

### 2.2.3 The "Expert Panel" Model

The "Expert Panel" model uses actinide concentration ranges that were developed by an expert panel for the 1992 WIPP Performance Assessment calculations (WIPP Performance Assessment Department, 1992). The expert panel considered the chemical behavior in WIPP disposal rooms and provided estimates of actinide concentrations, given the following information:

1. Aqueous solution speciation diagrams were constructed and key actinide species identified.
2. Equilibrium with solubility-controlling solids was assumed in order to calculate ranges of activities in dilute solutions.
3. An extensive literature on actinide solubilities was consulted.
4. Activities were corrected to high-ionic-strength brine conditions (WIPP Brine-A and its evaporation products) using the Pitzer equations (Pitzer, 1991).
5. The pH range considered was between pH 2 and pH 12, and complexation reactions were considered.

This process is documented in Chapters 3 and 4 of Trauth et al. (1992).

The panel of experts generated probability distribution functions indicating the likely concentrations of some actinides in specific oxidation states, reproduced in Table 5 (p. 4-5 of Trauth et al., 1992). Because Performance Assessment requires total actinide concentrations, the concentrations for individual oxidation states of each element were summed based on the relative sizes of oxidation state stability fields in Eh-pH space, as described in Chapter 3, pp. 3-38 to 3-41, of WIPP Performance Assessment Department (1992).

The solubility expert panel stated that they did not have enough information from which to estimate the importance of colloids, and thus gave no specific recommendations for colloid concentrations.

Table 5. "Expert Panel" Model Information From Trauth et al. (1992).

"Element"	"Solution Species"	"Solid Species Maximum and Minimum"	"Minimum Concentration"	"Maximum Concentration"
Actinide, Oxidation State	Dominant Solution Species	Solids that Control Solubility	log(Molar)	log(Molar)
Am(III)	AmCl	Am(OH) <sub>3</sub> (s), AmOHCO <sub>3</sub> (s)	-13.3	0.1
Pu(III)	no info given	no info given	no info given	no info given
Th(IV)	Th(OH)	Th(OH) <sub>4</sub> (s), ThO <sub>2</sub> (s)	-15.3	-5.7
U(IV)	U(OH)	UO <sub>2</sub> (am), U <sub>3</sub> O <sub>8</sub> (s)	-15.0	-1.3
Pu(IV)	Pu(OH)	Pu(OH) <sub>4</sub> (s), PuO <sub>2</sub> (s)	-15.7	-5.4
Np(IV)	Np(OH)	Np(OH) <sub>4</sub> (s), NpO <sub>2</sub> (s)	-15.5	-4.7
Pu(V)	PuO	Pu(OH) <sub>4</sub> (s), PuO <sub>2</sub> (s)	-16.6	-3.3
Np(V)	NpO <sub>2</sub> CO	NpO <sub>2</sub> OH(am), NaNpO <sub>2</sub> CO <sub>3</sub> •3.5H <sub>2</sub> O(s)	-10.5	-1.9
Am(V)	no info given	no info given	no info given	no info given
U(VI)	UO <sub>2</sub> (CO <sub>3</sub> )	UO <sub>2</sub> •2H <sub>2</sub> O(2), UO <sub>2</sub> (s)	-7.0	0.0
Pu(VI)	no info given	no info given	no info given	no info given

Although the expert panel model is based on published experimental data, it represents the analysis and reduction of that data by the scientific judgment of four individual experts. The following assumptions by the panel may explain some of the apparent inconsistencies in Table 5. Phosphate and fluoride ions were assumed not to exist in significant concentrations in the brines, and organic ligands from the WIPP waste were assumed to be insignificant compared to inorganic ligands present in the brine. Chloride rather than carbonate was assumed to control solubility, because of the high Mg<sup>++</sup> concentration and the assumption of magnesium carbonate formation. Pu(III), Am(V), and Pu(VI) were neglected because they occupy limited fields in the Eh-pH diagrams constructed in the elicitation. The panel members agreed on 100th percentile values that were higher than could be achieved in reality. All of these simplifying assumptions could be superseded by data and information from the experimental programs now underway.

The expert panel model for mobile actinide concentrations also does not distinguish between mobile actinides in dissolved form and in colloidal form. While this distinction is not important within the Performance Assessment models for actinide release from the disposal room

environment, it is important in models for Culebra transport. For this reason, the "Expert Panel" model does not provide sufficient information for Culebra transport modeling.

The "Expert Panel" model requires no input parameters.

#### **2.2.4 The "Inventory Limits Model with Realistically Conservative Maximum Concentrations"**

The "Inventory Limits Model with Realistically Conservative Maximum Concentrations" is a synthesis of the "Inventory Limits" model, the "Expert Panel" model, and scientific reasoning for mobile colloid concentrations. This model specifies more realistic but still markedly conservative maximum concentrations for both dissolved and colloidal actinides, and uses these concentrations in place of the 1 mole/liter arbitrary upper limit for all actinides in the "Inventory Limits" model. Although neither the "Inventory Limits" model nor the "Expert Panel" model are based directly on experimental data, the assumptions of both models are based on the known and documented physical and chemical behavior of the actinides in question, though not on the particular behavior of actinides under disposal room conditions. The "Inventory Limits" model can immediately be recognized as unrealistically conservative, and the only information available at the present time to modify that conservatism is from the "Expert Panel" model.

Table 6 gives the maximum concentrations for dissolved and colloidal actinides in this model. The reasoning used to arrive at the values in Table 6 is documented in Sections 2.2.4.1 and 2.2.4.2. It is interesting to note that, according to this model, colloidal thorium will always dominate over dissolved thorium, the contributions of colloidal and dissolved plutonium to mobile plutonium concentration are about the same, and the dissolved concentrations of uranium, neptunium, and americium will always dominate over colloidal concentrations of these elements.

This model is intended to be applied as follows. Calculate the total mass of each actinide in the computational domain, and calculate the volume of brine that contacts the waste in the computational domain. (The computational domain may be a waste room, a waste panel, or the entire repository.) The "inventory concentration" for each actinide is calculated as the ratio of actinide mass to brine volume in moles/liter. These calculated inventory limit concentrations are to be used as the actinide concentrations unless these concentrations exceed the upper bound concentrations given in Table 6, in which case the upper bound concentrations are used. When there is not enough actinide present to fully populate both the colloidal and dissolved

contributions, the colloids are populated first in the interest of conservatism because colloidal actinides are potentially retarded less than dissolved actinides.

The “Inventory Limits Model with Realistically Conservative Maximum Concentrations” requires as input the identities and quantities of actinides in the wastes, and the volumes of brines in the disposal rooms.

Table 6. Maximum Mobile Actinide Concentration for the “Inventory Limits Model with Realistically Conservative Maximum Concentrations.”

Actinide	Maximum Dissolved Concentration, moles/liter	Maximum Colloidal Concentration, moles/liter	Maximum Mobile Concentration, moles/liter
Th	$2.5 \times 10^{-6}$	$3.0 \times 10^{-4}$	$3.03 \times 10^{-4}$
U	1.0	$3.0 \times 10^{-4}$	1.00
Np	$1.0 \times 10^{-2}$	$3.0 \times 10^{-4}$	$1.03 \times 10^{-2}$
Pu	$4.0 \times 10^{-4}$	$3.0 \times 10^{-4}$	$7.0 \times 10^{-4}$
Am	1.0	$3.0 \times 10^{-4}$	1.00

#### 2.2.4.1 REALISTICALLY CONSERVATIVE MAXIMUM CONCENTRATIONS FOR DISSOLVED ACTINIDES

The “Inventory Limits Model with Realistically Conservative Maximum Concentrations” is a modification of the “Inventory Limits” model. This model combines a description of disposal room chemistry that is equivalent to the “Inventory Limits” model with a “reasonably likely” upper bound dissolved concentration for each actinide. These upper bound values are taken directly from Table 3.3-4 of Volume 3, WIPP Performance Assessment Department (1992), which in turn were taken from Trauth et al. (1992), as discussed above in the “Expert Panel” model. This resulted in the maximum dissolved concentrations for the five actinides listed above in Table 6.

#### 2.2.4.2 REALISTICALLY CONSERVATIVE MAXIMUM CONCENTRATIONS FOR COLLOIDAL ACTINIDES

This section briefly describes the rationale used to develop realistically conservative maximum concentrations for colloidal actinides. Mobile colloidal particles are particles with diameters between 0.001 and 1  $\mu\text{m}$  suspended by Brownian motion. The three types of colloids potentially important for the WIPP are “soft-sphere” carrier colloids (humic materials), sterically stabilized carrier colloids (microbes) and “hard-sphere” carrier and actinide-intrinsic colloids.

Table 7. Realistically Conservative Maximum Concentrations for Colloidal Actinides.

Colloidal Particle	Colloid Type	Plutonium Conc. (moles/dm <sup>3</sup> )	Uranium Conc. (moles/dm <sup>3</sup> )	Thorium Conc. (moles/dm <sup>3</sup> )	Neptunium Conc. (moles/dm <sup>3</sup> )	Americium Conc. (moles/dm <sup>3</sup> )
mineral fragments	"hard-sphere" carrier colloid	0.0	0.0	0.0	0.0	0.0
microbacteria	sterically stabilized carrier colloid	1.0x10 <sup>-4</sup>	1.0x10 <sup>-4</sup>	1.0x10 <sup>-4</sup>	1.0x10 <sup>-4</sup>	1.0x10 <sup>-4</sup>
high-molecular weight organic matter	"soft-sphere" carrier colloid	2.0x10 <sup>-4</sup>	2.0x10 <sup>-4</sup>	2.0x10 <sup>-4</sup>	2.0x10 <sup>-4</sup>	2.0x10 <sup>-4</sup>
actinide macromolecules	actinide intrinsic colloid	0.0	0.0	0.0	0.0	0.0

Of these, "hard-sphere" carrier and actinide-intrinsic colloids have been eliminated in this model because they would most likely not be kinetically stable in WIPP brines. For the two remaining types of mobile colloidal particles potentially important to the WIPP, the likely reasonable maximum concentrations of mobile colloidal actinides were bounded by calculations. These upper bound concentrations are summarized in Table 7.

The maximum concentrations for colloidal actinides shown in Table 7 are based on the following:

- "Hard-sphere" carrier colloids are not kinetically stable in brines associated with the WIPP (they are not mobile), and thus do not contribute to the actinide source term or to transport in the Culebra.
- "Soft-sphere" carrier colloids (i.e., humic materials) are stable in brines, and contribute to the mobile actinide concentrations defined by the Actinide Source Term. Humic materials are capable of sorbing significant quantities of metal cations, including actinides. Because humic materials are smaller than the pore throats in the Culebra, the transport of these sorbed actinides will be retarded by diffusion into matrix.
- Microbes (categorized as a sterically stabilized carrier colloids) are stable in brines and contribute to the mobile actinide concentrations defined by the Actinide Source Term. Microbes may act as substrates for sorption of actinides through passive bioaccumulation, or they may actively bioaccumulate actinides into or through their cell walls. The sizes of microbes prevent them from entering the pore throats in the Culebra.

- Actinide-intrinsic colloids age from a dissolved macromolecule (actinide polymer) to a crystalline or amorphous solid "hard-sphere" type colloid. Because "hard-sphere" colloids are not kinetically stable in the brines associated with the WIPP (they are not mobile), actinide-intrinsic colloids are not considered to contribute to the Actinide Source Term or to transport in the Culebra.
- The quantity of actinide-bearing colloidal particles generated in the far-field environment (i.e., the Culebra) will be negligible compared to colloidal particles generated in the disposal room environment (described by the actinide source term). The only potential colloid types that could be generated within the Culebra are microbes and humic materials. The microbe population in the disposal room environment will be greater than in the Culebra because of the presence of nutrients associated with WIPP wastes. The concentration of humic materials in the disposal room may also be greater than in the Culebra because of soils in WIPP waste. Mixing of disposal room brines with Culebra brines may result in precipitation of solids, and some may be colloidal in size. Those colloidal particles, however, will be "hard-sphere" type and will not be mobile.

High-molecular weight organic matter, which consists primarily of humic and fulvic materials, are generated by degradation of naturally occurring organic matter. High-molecular weight organic matter is commonly found in soils, surface waters, sea water, and in groundwaters present in shallow subsurface environments. In the WIPP disposal room environment, high-molecular weight organic matter is likely to be present in the soil component of WIPP wastes, which is likely to contain humic and fulvic materials of colloidal size.

An estimate of the total amount of soil that is expected to be buried in the repository is described in the Baseline Inventory Report (BIR) (Department of Energy, 1994a). The total volume of wastes (scaled to fill the repository) that primarily consist of soil (BIR, Table 1-2, Waste Matrix Codes 4000, 4100, 4200, and 4900) is  $1.1 \times 10^4 \text{ m}^3$  (BIR, Table 5-2). The source of that waste stream is the Idaho National Engineering Laboratory (INEL) and the Richland (Hanford) Site (BIR, Figure 5-8). It is important to note, however, that a significant amount of the soil Waste Matrix Code Group (WMCG) consists of non-soil materials (BIR, Figure 5-8). In fact, the average mass of soil in the soil WMCG is estimated to be only  $64.90 \text{ kg/m}^3$  (BIR, Figure 5-8). Table 6-2 in the BIR provides an estimate of the average concentration ( $5.3 \text{ kg/m}^3$ ) of soil in all waste streams scheduled and anticipated to be buried at the WIPP. Multiplying that estimated value by the total volume of the repository ( $1.756 \times 10^5 \text{ m}^3$ ) provides an estimate of the total average inventory of soil at the WIPP.



The concentrations of actinides sorbed to high-molecular weight organic matter in WIPP soils were estimated in bounding calculations using estimates of the maximum concentrations of organic material in soils, the maximum concentrations of kinetically stable high-molecular weight organic material in those soils, the concentrations of binding sites in high-molecular weight organic material, and the fluid volume of the repository. Using this approach, the realistically conservative maximum concentrations for colloidal actinides mobilized by high-molecular weight organic materials is  $2 \times 10^{-4}$  moles/dm<sup>3</sup>. There is insufficient information from which to propose a proportioning scheme among the five actinides of interest (Th, U, Am, Np, Pu) because  $K_d$  values for high-molecular weight organic matter under WIPP conditions are not known. Consequently, each of the five is assigned a concentration of  $2 \times 10^{-4}$  moles/dm<sup>3</sup> for this type of colloidal particle.

A broad base of knowledge has been gained about microbial activity in WIPP brines (see Francis and Gillow, 1994, and references therein) as part of the research conducted over the past several years supporting the disposal room gas generation program. Some of that information can be used to bound the concentration of actinides that could be transported by microbes. These calculations are done in two different ways in the following paragraphs.

The maximum concentration of actinides sorbed on or contained within an individual microbe is limited by geometrical constraints such as the size and surface area of the microbe and its sorption site density. Extrapolation of that maximum concentration to a microbe colony obviously depends on the concentration of cells in disposal room brine. However, the total concentration of bioaccumulated actinides must not produce so much radiation that growth of the microbe colonies is hindered or stopped. For example, Francis (1985) showed experimentally that radiation levels on the order of  $3 \times 10^7$  pCi/liter began to inhibit the growth of bacteria. These microbes were cultured from samples collected at the Maxey Flats, Kentucky, disposal site.

Currently, the relative uptake of different actinide elements due to bioaccumulation cannot be estimated so it is not possible to determine the maximum actinide concentrations that could be bioaccumulated without producing enough radiation to inhibit growth. However, estimates can be made assuming that uptake of the five actinides of particular importance to the WIPP occurs proportionately. Information on the WIPP waste inventory tabulated in the Baseline Inventory Report (Department of Energy, 1994a) was used to calculate a mean radiation level of Am, Np, Pu, Th, and U. That value,  $2.2 \times 10^{12}$  pCi/mole of actinides, coupled with the threshold survivability value of  $3 \times 10^7$  pCi/liter, indicates that the upper bound on concentrations of actinides that can be bioaccumulated by microbes is on the order of  $10^{-5}$  moles/liter ( $3 \times 10^7$  pCi/liter  $\div$   $2.2 \times 10^{12}$  pCi/mole). That estimated threshold value,  $10^{-5}$

moles/liter, is not dissimilar to values determined with the alternative bounding calculations given below.

Measured concentrations of halophilic bacteria in disposal room (G-Seep) brine range from  $7 \times 10^7$  to  $3 \times 10^9$  cells/liter (Francis and Gillow, 1994). Concentrations in brines at the surface near the WIPP Site are greater, and range from  $6 \times 10^9$  to  $1 \times 10^{10}$  cells/liter (Francis and Gillow, 1994). A concentration of  $1 \times 10^{10}$  cells/liter was used for the bounding calculations. Microbes are spherical or rod-shaped with dimensions on the order of 1 to  $2 \times 10^{-6}$  m. Geometric surface area and cell volumes do not vary substantially among those morphologies so the calculations assumed that the microbes are  $2 \times 10^{-6}$  m diameter spherical particles. Adsorption site density of mineral substrates is typically on the order of 0.1 to 1 site/ $10^{-18}$  m<sup>2</sup>, although density may be as high as 10 sites/nm<sup>2</sup> in some particularly strong-sorbing minerals, e.g., goethite. No equivalent information is available for microbes but 1 site/ $10^{-18}$  m<sup>2</sup> is a reasonable density considering that the effective site density will be reduced by competition from other metal cations for extracellular sorption sites.

The parameter values given above provide a value of  $1 \times 10^{-4}$  moles/liter to be used for the realistically conservative maximum concentration of actinides bioaccumulated by microbes through both extracellular and intracellular processes. That value reflects consideration of the threshold level of radiation in which microbes may thrive and the upper bounding estimate of actinides that could be bioaccumulated intracellularly and extracellularly. As for the colloidal high-molecular weight organic materials described above, each of the five actinides of particular importance to the WIPP should be assigned a concentration value of  $1 \times 10^{-4}$  moles/liter for this type of colloidal particle.

### 2.2.5 The "Fresh Water Estimates" Model

The "Fresh Water Estimates" model proposes to use values from fresh (not saline or brackish) groundwaters to estimate the mobile concentrations of actinides in the WIPP system. The model assumes that the behavior of the chemical reaction types listed in Section 2 is known in dilute groundwaters but not in brines, and that the differences in actinide chemical behavior between dilute and brine groundwaters are not large enough to be significant within the Performance Assessment calculations, or that actinide concentrations in brines will not exceed those anticipated for "fresh" water. The model assumptions probably do not apply to the WIPP for the following reasons. First, knowledge of actinide chemical behavior in dilute groundwaters is not demonstrably better than that for brines. Second, colloid behavior is not the same in fresh and briny waters: stability of some colloid types is strongly influenced by both the ionic strength

and composition of groundwaters, with colloids tending to be less stable in brines, resulting in rapid agglomeration and settling by gravity (Gregory, 1978, p. 93; van Olphen, 1977, p. 24). Third, fresh water values are not necessarily conservative, i.e., dissolved actinide concentrations are not necessarily higher in dilute groundwaters than in brines.

If a "Fresh Water Estimates" model for dissolved actinide concentrations existed, it might be acceptable for application to WIPP brines; data would be required only to support the assertion that the dilute model predicts higher actinide concentrations than would actually be in the brines. However, apparently no models adequate to predict dissolved actinides concentrations in dilute solutions exist. Uncertainties about the outcome of development of this model, and its inherent immediate inapplicability to the WIPP, suggest that its development would be less productive than development of the "Chemical Model for Mobile Actinide Concentrations" discussed below. Moreover, the latter model, when developed, can probably include solubilities in non-brackish aqueous media.

It is not clear what the "Fresh Water Estimates" model would require as input. The assumptions required to develop this model seem contradictory to the chemical situation in the disposal room. Extensive investigation would be necessary to examine the implications of the assumptions and the data required to support the assumptions, and thus to determine input parameters for this model.

#### **2.2.6 The "Chemical Model for Mobile Actinide Concentrations"**

The "Chemical Model for Mobile Actinide Concentrations" uses chemical principles to provide reasonable descriptions for the important chemical phenomena affecting mobile actinide concentrations. The 10 reaction types from Section 2.1 are examined, with supported assumptions about each being used to simplify the system. Then the chemical model quantifies the effects that dominate the chemical behavior, and provides numerical estimates for mobile actinide concentrations.

The most important assumptions in the chemical model for mobile actinide concentrations are the following:

- all reactions except gas generation and oxidation-reduction reactions can be described with equilibrium chemistry;
- gas generation reactions can be described with kinetic rate expressions;

- actinide sorption onto immobile substrates can be ignored.

The heterogeneous nature of the waste and the uncertainty associated with the chemical form of the actinides in the wastes make assessment of the kinetics of actinide dissolution an insurmountable problem. The assumption of thermodynamic equilibrium obviates the need for kinetic information and, neglecting any supersaturation effects, yields higher concentrations than under non-equilibrium conditions, and is therefore conservative from a regulatory standpoint. The assumption of equilibrium for complexation reactions occurring entirely within the aqueous phase is valid because these reactions are rapid. The assumption of equilibrium for precipitation of actinide solid phases is also valid, provided that the information on the identities of solid phases is obtained from the laboratory under similar conditions. Experiments using approximately the same temperature as the WIPP disposal rooms and having durations of several years or less can yield information that can be used to approximate instantaneous equilibrium conditions within the WIPP regulatory time frame of 10,000 years. Justification of a kinetic model for gas generation rates is given in the Gas Generation position paper, which also presents arguments as to why equilibrium cannot be assumed for oxidation-reduction reactions. Neglecting actinide sorption on immobile substrates is conservative, because sorption on immobile substrates might reduce, but would never increase, mobile actinide concentrations.

The following sections present the major features of the chemical model for mobile actinide concentrations: a model for dissolved actinides and a model for colloidal actinides. The models for dissolved and colloidal concentrations of actinides are being developed directly from experimental data relevant to the WIPP. Comparison of these models with the results of tests with real waste will challenge the model's ability to predict mobile dissolved and mobile colloidal actinide concentrations under conditions that may occur in the disposal room environment.

#### 2.2.6.1 THERMODYNAMIC MODEL FOR DISSOLVED ACTINIDES

The "Thermodynamic Model for Dissolved Actinides" is both reasonable and conservative. The model predicts dissolved actinide concentrations as controlled by actinide-bearing solid phases. The thermodynamic basis for this model is presented in general detail in Pitzer (1991), Harvie et al. (1984), and Felmy and Weare (1986). Details for dissolved concentration models for +III actinides are given for Pu(III) in Felmy et al. (1989), for Am(III) in Felmy et al. (1990) and Rai et al. (1994), and for Nd(III) in Rao et al. (1994). The above four papers demonstrate that the chemical properties of Pu(III), Am(III), and Nd(III) are

effectively identical. Similar details for Th(IV) and Np(V) dissolved concentration models are given in Felmy and Rai (1992) and Novak and Roberts (1994), respectively.

Different parts of the model are used to describe the individual important oxidation states of the significant actinides, i.e., for Am(III) and Pu(III), for Th(IV), Np(IV), U(IV), and Pu(IV), for Np(V) and Pu(V), and for U(VI) and Pu(VI). A preliminary model for the +III actinides, including inorganic ligands (but not possibly important organic ligands), is available but has not yet been interpreted for impact on WIPP Performance Assessment. The models for the other oxidation states are less developed.

Each oxidation state is considered separately because actinide (and lanthanide) elements in the same oxidation state have very similar chemical properties. For example, Am(III) and Pu(III), and the lanthanide Nd(III), form the same aqueous species and isostructural solid phases. Thus, the detailed chemical measurements required to parameterize the model are only necessary for one of these elements, for example Nd(III), but the resulting model is applicable to Am(III) and Pu(III) as well as Nd(III). This so-called oxidation state analogy allows a significant reduction in the number of experimental systems that must be examined to develop model parameters. Elements and oxidation states important to WIPP Performance Assessment and the development of the WIPP dissolved actinide concentration submodel are shown in Table 3. Unequivocal demonstration that a thermodynamic model for lanthanides, e.g., Nd(III), is applicable to actinides like Am(III) and Pu(III) is straightforward and part of this conceptual model. There is less total data on the chemical analogy for the +V actinides ( $\text{PuO}_2^+$ ,  $\text{NpO}_2^+$ , and  $\text{AmO}_2^+$ ) and the +VI actinides ( $\text{PuO}_2^{2+}$ ,  $\text{UO}_2^{2+}$ , and  $\text{NpO}_2^{2+}$ ), but existing evidence suggests that the chemical analogy also holds for these systems. In contrast to the +III, +V, and +VI oxidation states, the chemical analogy for the +IV actinides  $\text{Pu}^{4+}$ ,  $\text{U}^{4+}$ ,  $\text{Np}^{4+}$ , and  $\text{Th}^{4+}$  is not quantitative in all respects, but nevertheless can serve as a good indicator for the chemical behavior of a system and can result in a conservative approximation for actinides in the +IV oxidation state.

The thermodynamic approach to modeling dissolved actinide concentrations is fully supported by the international actinide chemistry community. The vast majority of chemical measurements made in support of nuclear waste repositories throughout the world are interpreted using thermodynamic formalism.

A degree of conservatism is inherent in the choice of a thermodynamic framework to describe the concentrations of mobile dissolved actinides. Laboratory information on actinide-bearing solid phases is usually generated over a time scale of weeks to tens of

months, which can be considered instantaneous when compared to the WIPP regulatory time scale of 10,000 years. After the precipitation of some mineral phases, it is not uncommon for the crystallinity of the mineral to mature with time. Along with the improved crystallinity, the solubility of the solid phase is typically decreased (Neck et al., 1992). Consequently, the dissolved actinide concentrations are likely to decrease as the solids age. Laboratory experiments will thus provide an upper bound on the expected dissolved concentrations, because conversion to more soluble forms than observed in the laboratory is improbable. The only plausible mechanism for this conversion is radiolysis within the solid phase, which would be evident in the laboratory.

Additional conservatism is built into the dissolved actinide concentration model because the effects of adsorption on immobile substrates in the disposal room are not included. Actinide adsorption, which is dependent on the dissolved concentrations of actinides, the identities of the dissolved actinide species, and the chemical properties of the solid phases to which the actinides absorb, will serve to reduce mobile dissolved actinide concentrations under some conditions but can never increase the mobile dissolved actinide concentrations. The model is therefore made more conservative from a regulatory standpoint by not including this mechanism. However, although the effort required to include adsorption phenomena in this model is significant, work can begin to incorporate adsorption at any time should it be deemed necessary.

Although sorption is not being included in this conceptual model for the Actinide Source Term, adsorption on Culebra materials is central to Culebra transport conceptual models for chemical retardation (Non-Salado Flow and Transport position paper). Sorption is the primary chemical retardation mechanism in the Culebra, but does not dominate mobile actinide behavior in the disposal room. Equilibrium chemical conditions in the Culebra have developed over very long periods of time, significantly longer than the performance period of the repository. In contrast, the disposal room environment is anthropogenic, with emplaced sorption substrates and with brine capacity to mobilize actinides as the expected dominant phenomenon. The states and forms of the heterogeneous mixture of emplaced materials in the disposal rooms are relatively difficult to predict over a 10,000-year time period, while it is inherently reasonable to assume the Culebra substrates will remain more or less as they are for an additional 10,000 years. By comparison with the expected disposal room substrates, the Culebra appears homogeneous with only two dominant substrates for sorption.

The thermodynamic model couples the dissolved actinide concentrations to brine compositions. In particular, this model can assess the influence of disposal room conditions on dissolved actinide concentrations. For example, this model can calculate the potential

increase in dissolved actinide concentrations that could be caused should large carbon dioxide gas pressures exist in the disposal rooms (Novak, 1993). Also, an evaluation could be made of the impact of calcium oxide (CaO) in the backfill (to remove  $\text{CO}_2(\text{g})$ ) versus the possible increase in dissolved actinide concentrations caused by very basic conditions and potentially high carbonate concentrations. In this manner, the thermodynamic model represents a powerful tool for evaluating mobile dissolved actinide concentrations for expected disposal room conditions as well as for evaluating engineering modifications for their impact on dissolved actinide concentrations.

Actinide oxidation state distributions, if governed by equilibrium processes within the WIPP disposal rooms, could be determined using a thermodynamic model for dissolved actinides. However, as discussed in detail in the Gas Generation position paper, oxidation-reduction (redox) couples are generally not in equilibrium in low temperature geologic systems. Oxidation states of the actinides will have to be ascertained based on information from source term tests with actual transuranic waste; information from gas generation studies; and statistical sampling over potential oxidation state distributions. The disposal rooms are expected to be anoxic within 100 years of decommissioning, and large amounts of metallic iron are expected to be present. Thus, it is reasonable to expect that the actinides will occur in their reduced oxidation states. However, alpha radiolysis has been shown to oxidize Am(III) to Am(V) (Magirus et al., 1985), and plutonium(VI) is stabilized in this oxidation state in the presence of carbonate (Reed et al., 1994). Existing information cannot assure that actinides will occur solely in their reduced oxidation states in the disposal room environment.

Little WIPP-specific information on actinide oxidation states is available from the source term tests and existing information from the gas generation studies has not been assimilated into the dissolved actinide concentration model. Presently, the preferred approach to incorporating oxidation states into performance assessment is statistical sampling over the potential oxidation state distributions. Unlike the sampling over probability distributions for actinide "solubilities," statistical sampling for oxidation state distribution would be highly constrained and the variables would irrefutably cover the entire possible range of conditions. The percentages of an isotope in each oxidation state must sum to 100%, and the abundance of each oxidation state for a given isotope must fall between 0% and 100%. For example, the total  $^{239}\text{Pu}$  concentration is the sum of the concentrations of  $^{239}\text{Pu}(\text{III})$ ,  $^{239}\text{Pu}(\text{IV})$ ,  $^{239}\text{Pu}(\text{V})$ , and  $^{239}\text{Pu}(\text{VI})$ , where percentages can be calculated from the ratio of  $^{239}\text{Pu}$  in a particular oxidation state to the total  $^{239}\text{Pu}$ . It is likely that information from the source term tests and the gas generation program will further constrain the ranges for these variables.

## 2.2.6.2 CHEMICAL MODEL FOR COLLOIDAL ACTINIDES

The "Chemical Model for Colloidal Actinides" describes the concentration of actinides sorbed on or contained in mobile colloidal particles in the WIPP disposal room and defines the stable colloids that must be quantified by transport modeling in the Culebra. The model is also a component of the conceptual models for colloid-facilitated radionuclide transport in the Culebra, in which the concentration of actinides reaching the accessible environment must be quantified or bounded. To adequately evaluate transport of colloids in the Culebra, the characteristics and concentrations of colloids produced in the disposal room must be quantified. The potential for additional actinide-bearing colloids forming in the Culebra is discussed in the Non-Salado Flow and Transport position paper.

Transport of colloids in the Culebra has not been addressed with rigorous numerical modeling because of the complexities of coupling hydrogeology, geochemistry, and colloid chemistry (Bennett et al., 1993). The potential for colloid-facilitated radionuclide transport has only been addressed for a little over a decade (Avogadro and de Marsily, 1983), and rigorous transport models and computer codes suitable for the WIPP environment are not yet available. For the WIPP environment, evaluation of the impacts of colloids on repository performance was begun a few years ago.

Several types of colloidal particles are potentially important at a geologic repository such as the WIPP, and identification of these colloid types is necessary to quantify the impact of colloids on transport of actinides (the colloid types are described briefly in Section 2.2.4.2, above). In the conceptual model, the colloid issue is simplified as much as possible based on the stability behavior of different colloid types. The WIPP environment is unique among proposed nuclear waste repositories in that both the near-field (i.e., the disposal room) and the far-field (i.e., the Culebra) environments contain high ionic strength brines (Brush, 1990; Siegel et al., 1991). The concentrations of actinides contained in colloids and the potential for transport of colloids in the Culebra are strong functions of ionic strength. Some types of colloids are not kinetically stable in high ionic strength electrolytes and quickly agglomerate to form clusters. The resulting agglomerated particles are sufficiently large ( $> 1 \mu\text{m}$ ) to settle due to gravitational forces. Preliminary experiments have confirmed that at least some colloidal particles possible in the disposal room environment and the Culebra are quickly destabilized in WIPP brine simulants and form large agglomerates that settle by gravity from within hours to days.

The two main types of colloids that must be addressed for the WIPP are called actinide intrinsic colloids and carrier colloids. Carrier colloids, which are ordinarily non-



radioactive, are colloidal-sized particles that may act as substrates for sorption of actinides and other metals ions. Carrier colloids with sorbed actinides are also known as pseudocolloids, Type II colloids, and Fremdkolloide (Lieser et al., 1986a, 1986b, 1990; Buddemeier and Hunt, 1988; Kim, 1991). The carrier colloid category has been further subdivided on the basis of known physico-chemical behavior.

“Hard-sphere” carrier colloids, usually called hydrophobic colloids in colloid chemistry, have discrete well-defined particle-fluid boundaries and are stabilized in very low ionic strength solutions by electrostatic effects caused by the electric double layer surrounding the particles (Heimenz, 1986). At high ionic strengths, however, the electric double layer surrounding the “hard-sphere” colloids collapses and virtually eliminates electrostatic repulsion between particles (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948; Matijeviloć, 1973). Van der Waals forces of attraction between the particles cause agglomeration, forming particles large enough to settle by gravity. This phenomenon has been known empirically for well over a century (see, e.g., Hardy, 1900) and was theoretically explained in the middle of this century (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Experiments conducted at Sandia National Laboratories (SNL) have demonstrated that dispersions of “hard-sphere” carrier colloids are not kinetically stable in Culebra brine simulants (hydrochemical facies “A” and “C;” Siegel et al., 1991), Salado Formation-like brine simulants (Brine A; Brush, 1990), and Castile Formation brine simulants (ERDA-6; Brush, 1990). Thus, “hard-sphere” carrier colloids can be eliminated from further consideration in quantifying transport of actinides. This group of colloids includes many of the colloids identified at other sites (see, e.g., the compilation in McCarthy and Degueudre, 1993, their Table 6). Colloidal particles that can be eliminated from consideration in transport of actinides at the WIPP include iron(III)-oxides and hydroxides, clay minerals, and mineral constituents of the host rock. Furthermore, colloidal particles produced from drilling (i.e., cuttings) and mineral precipitates formed from brine mixing will not be kinetically stable.

Sterically stabilized “hard-sphere” carrier colloids are coated with compounds capable of modifying the colloids’ surface behavior so that electrostatic attraction and repulsion forces are overcome, rendering them kinetically stable. Perhaps the best examples of these are particles stabilized by organic compounds in sea water (Honeyman, 1991; Honeyman and Santschi, 1992). However, no definite conclusions are available regarding the impact of these colloids on mobile actinide concentrations and actinide transport.

“Soft-sphere” carrier colloids are flexible particles with rather indistinct particle-fluid boundaries and are actually dissolved macromolecules. They are not affected by ionic

strength in the same way as "hard-sphere" carrier colloids. "Soft-sphere" carrier colloids are closest in form and behavior to particles referred to as hydrophilic colloids in the traditional colloid chemistry literature (Lyklema, 1978; Heimez, 1986); examples include humic and fulvic acids (Choppin, 1988; Tiller and O'Melia, 1993). Because this type of colloid is not destabilized by high ionic strengths, "soft-sphere" carrier colloids may be important in transport of actinides at the WIPP. Humic and fulvic materials (high-molecular weight organic macromolecules that occur in near-surface environments) are of particular concern because of their well-known capability of complexing with metal cations, including actinides (Choppin, 1988, Dearlove et al., 1990; Vlassopoulos et al., 1990; Tipping, 1993; van der Lee et al., 1993). However, no definite conclusions are available regarding the impact of these colloids on mobile actinide concentrations and actinide transport.

Actinide intrinsic colloids (also known as true colloids, Type I colloids, and Eigenkolloide) are thought to form by condensation reactions of hydrolyzed actinide ions to form macromolecules, or "polymers," of colloidal size (Maiti et al., 1989). It is believed that the actinide ions are bridged by hydroxyl groups or oxygen ions (Kim, 1991). Following the oxidation state analogy described earlier in this paper, the tendency of actinides to hydrolyze and to form intrinsic colloids follows the order:  $M^{4+} > M(VI)O > M^{3+} > M(V)O$  (Choppin, 1983; Kim, 1991). The tendency for formation of the Pu(IV)-polymer is enhanced by increased Pu(IV) concentrations, temperature, and basic conditions (Toth et al., 1981). The literature contains examples of polymeric species of most of the actinides of importance to the WIPP (see e.g., Baes and Mesmer, 1976; Kim, 1991). It is important, however, to note the sizes of polymers described in the literature. It is well known that as polyvalent metals, the actinides can form lower polymers such as dimers, trimers, tetramers, and hexamers. However, in terms of transport, the lower polymers behave the same as the dissolved species described above. In contrast, the higher polymers, such as the Pu(IV)-polymer, may reach colloidal sizes (1 nm to 1  $\mu$ m) and will have different hydrodynamic properties than the sub-colloidal-sized dissolved species as discussed in the Non-Salado Flow and Transport position paper.

The most well-known and well-studied actinide intrinsic colloid is the Pu(IV)-polymer. Most of the knowledge about the Pu(IV)-polymer comes from research at relatively high Pu concentrations in highly acidic solutions conducted to improve processing techniques (e.g., Kraus, 1956; Costanzo et al., 1973; Bell et al., 1973a; 1973b; Lloyd and Haire, 1978; Toth et al., 1981). Investigations focusing on chemical conditions relevant to environmental concerns have been conducted more recently (Cleveland, 1979; Rai and Swanson, 1981; Kim and Kanellakopulos, 1989; Nitsche et al., 1992). A conclusive demonstration of the mechanisms of formation of the Pu(IV)-polymer has not yet been made,

but there is a preponderance of evidence that shows that polymerization is strongly linked to hydrolysis (see e.g., Kim, 1991) and that the initial polymerization produces an amorphous macromolecule that becomes crystalline with time (see Cleveland, 1979, and references therein). Lloyd and Haire (1978) showed that the aged polymer actually consists of nanometer-sized mineral crystallites. Rundberg et al. (1988) and Triay et al. (1991) used different analytical methods to confirm the particulate nature of the Pu(IV)-polymer, and also estimated that the size was on the order of nanometers.

In terms of implications for transport at the WIPP, if the Pu(IV)-polymer is indeed a crystalline colloidal particle rather than a "soft-sphere"-like (hydrophilic) colloid, it would behave like a "hard-sphere" (hydrophobic) colloid. As such, it would be destabilized by high ionic strength solutions, such as WIPP brines. The observation that some Pu(IV)-polymer solutions have remained stable for years is not inconsistent with the notion that the Pu(IV)-polymer is a "hard-sphere" type colloid. For example, Overbeek (1982) reported that some of the gold sols (dispersions of 3 nm diameter colloidal metallic gold, a "hard-sphere" type colloid) used in historically important experiments by Michael Faraday in the mid-1800s are still in existence. Experiments are in progress to evaluate the formation and behavior of actinide intrinsic colloids. However, there are no definitive conclusions regarding the formation and stability properties of actinide intrinsic colloids and statements regarding their impact on actinide transport cannot yet be defended.

The colloid submodel relies on the demonstration that, under the range of conditions expected to be present in the WIPP disposal room and in the Culebra Dolomite, many of the potential colloids are not kinetically or chemically stable or that the actinide concentrations contained by stable colloids are negligible. As described above, "hard-sphere" carrier colloids likely can be eliminated from further consideration but no definitive statements about the behaviors and impacts of the other types of colloids are currently possible. As mentioned above in this section, however, it is highly likely that many of the potential colloids at the WIPP Site may be eliminated from further consideration solely based on their kinetic and chemical behaviors.

### 2.3 Summary of Conceptual Models for the Actinide Source Term

- The "Expert Panel" model, as used in the 1992 PA Data Base, provides values for expected dissolved actinide concentrations but does not provide values for colloidal actinide concentrations. The information represents the technical judgment of an expert panel and is not based directly on experimental data. The model is not suitable

for application by itself, but is used in combination with the "Inventory Limits" model in the "Inventory Limits Model with Realistically Conservative Maximum Concentrations" model

- The "Inventory Limits" model assumes that all actinides in the disposal rooms are mobile, up to an arbitrarily chosen value of 1 mole/liter. It is a worst case scenario for mobile actinide concentrations, and is unrealistically conservative. --
- The "Inventory Limits with Sorption" model combines the "Inventory Limits" model with reversible sorption on immobile substrates. This model is not sufficiently developed to evaluate the potential for use in WIPP Performance Assessment, would be difficult to implement, and is not considered further.
- The "Fresh Water Estimates" model is essentially undeveloped. Existing knowledge about aqueous actinide chemistry has demonstrated that some assumptions of this model are wrong. This model is not suitable for use in WIPP Performance Assessment.
- The "Inventory Limits Model with Realistically Conservative Maximum Concentrations" is a combination of the "Inventory Limits" model, the "Expert Panel" model, and scientific reasoning for mobile colloid concentrations. This model is very conservative, but more realistically so than the "Inventory Limits" model. The maximum concentrations, not probabilistic ranges of concentrations, are taken from the "Expert Panel" model.
- The "Chemical Model for Mobile Actinide Concentrations" is a realistic description of the important chemical phenomena that could mobilize actinides in the WIPP disposal rooms. This model follows established thermodynamic chemical theory for both dissolved and colloidal species, and some of its features have been verified experimentally in other contexts. At present, the model is only partially developed and is not ready to be used to estimate mobile actinide concentrations for WIPP Performance Assessment calculations.

The "Inventory Limits with Realistically Conservative Maximum Concentrations" model is used as the Actinide Source Term baseline model in Systems Prioritization Method-2 calculations.

### 3. DATA AVAILABLE FOR SUPPORTING CONCEPTUAL MODELS

The data available for directly supporting conceptual models for the actinide source term are given or referenced for each conceptual model in Section 2.2. Much additional information about chemical behavior in WIPP disposal rooms has not yet been published or evaluated for quantitative application. This information is called "available uninterpreted data." The discussion below is presented in terms of supporting the phenomena that mobilize actinides and most readily supports the "Chemical Model for Mobile Actinide Concentrations." However, analysis of this information with specific application to WIPP is required to support any conceptual model.

Active research programs in dissolved and colloidal actinide behavior exist to support the WIPP and other proposed nuclear waste repositories throughout the world. While chemical information pertinent to the WIPP is constantly being generated, this information must be published and interpreted before it can be used for WIPP. The following sections discuss some of this information available to support the conceptual models for the Actinide Source Term. In addition, proposed experiments with actual transuranic waste are documented in Phillips and Molecke (1993) and Villarreal and Phillips (1993).

#### 3.1 Available Uninterpreted Data for Dissolved Actinide Concentrations

The experimental work necessary to develop the models for mobile dissolved actinide concentrations is being performed to support the WIPP under five separate contracts. As of 21 March 1995, these contracts are AF-3339 with Andrew R. Felmy and Dhanpat Rai of Battelle-Pacific Northwest Laboratory (PNL), AF-3341 with Cynthia E.A. Palmer and Robert J. Silva of Lawrence Livermore National Laboratory (LLNL), AH-5592 with Ilham al-Mahamid of Lawrence Berkeley Laboratory (LBL), AH-5590 with Gregory R. Choppin of Florida State University (FSU), and AN-1756 with Wolfgang Runde of Los Alamos National Laboratory (LANL).

Felmy and Rai are developing the solubility models for the +III actinides Pu(III) and Am(III), and the +IV actinides Pu(IV), Th(IV), Np(IV), and U(IV). Palmer and Silva are measuring solubility data for the +VI actinides U(VI) and Pu(VI) and are developing solubility models in conjunction with Craig F. Novak, the Sandia Principal Investigator for the actinide dissolved concentration model. Al-Mahamid is measuring solubility data for the +V actinides Np(V) and Pu(V), and is developing solubility models, also in conjunction with

Novak. Choppin is measuring the complexation between organic ligands and actinides and is working with Novak to model these data. Runde is demonstrating the oxidation state analogy for +V actinides. These researchers will achieve a complete dissolved concentration model for each important actinide in each important oxidation state. These actinide dissolved concentration models are a synthesis of results from the contractors and existing information in the literature. Interpretation of this information will determine the impact on repository performance. This interpreted information will then be combined with information from the model for mobile actinide colloid concentrations and substantiated with information from the source term tests with actual transuranic wastes.

Data being generated by these studies will be published when the technical work and quality reviews are complete. However, these data shape the WIPP understanding of actinide behavior as they are generated and thus guide work well before the results are published. Additional data that may be useful for WIPP may be found in the open literature. These data are routinely assessed to determine whether they are reliable, useful, and pertinent to the WIPP. Several compilations of literature data for actinide chemical properties serve as starting points for locating pertinent research. These reviews include Clark et al. (1995); Fuger et al. (1992); Grenthe et al. (1992); and Newton and Sullivan (1985).

An initial submodel for the solubility of Np(V) in Na-Cl-CO<sub>3</sub> media has been developed in Novak and Roberts (1994). This submodel is primarily a synthesis and reinterpretation of data in the literature (Inoue and Tochiyama, 1985; Kim et al. 1991; Lierse et al., 1985; Maya, 1983; Neck et al., 1992, 1994, and 1995; Ueno and Saito, 1975; Vasudeva Rao et al., 1979) along with WIPP specific data from LBL. Predicted Np(V) dissolved concentrations from this model compare favorably to measured Np(V) solubility in two WIPP Culebra brines at specific chemical conditions.

An initial submodel for the solubility of the +III actinides as a function of major inorganic constituents of WIPP brines exists in the form of several journal publications (Felmy et al., 1989; Felmy et al., 1990; Rai et al., 1992a; 1992b; 1994; Rao et al., 1994). Similarly, an initial submodel for the solubility of the +IV actinides as a function of some of the major inorganic constituents of WIPP brines exists in the form of several journal publications (Felmy and Rai, 1992; Felmy et al., 1991; Roy et al., 1992). However, these have yet to be used for WIPP analyses.

The process of data interpretation for dissolved actinide concentration models is discussed in great detail in publications such as Felmy and Weare (1986), Felmy et al., (1990), Felmy and Rai (1992), Harvie et al. (1984), and Novak and Roberts (1994).

Data for the dissolved concentration model are being interpreted in a consistent manner. The influence of brine species concentrations on dissolved actinide concentrations is systematically examined and interpreted through chemical reaction equilibria using a thermodynamic model. The data sets developed under the auspices of WIPP are designed to examine binary interactions, e.g., the influence of carbonate concentration on total dissolved neptunyl concentration. To conserve resources and expedite work, data sets are taken from the literature as they exist; such studies were not designed explicitly to support WIPP. Through systematic examination and study, these separate data sets are synthesized into a single, integrated model that both makes chemical sense and describes all of the available reliable data.

### 3.2 Available Uninterpreted Data for Colloidal Actinide Concentrations

The laboratory program to investigate actinide concentrations contained by mobile colloids as well as evaluation of colloid-facilitated radionuclide transport in the Culebra Dolomite have been organized following the two major types of colloidal particles that may be important at the WIPP Site. Actinide intrinsic colloids are being investigated under contract AG-4965 at Lawrence Livermore National Laboratory (LLNL). Carrier colloids, which form by sorption of actinides onto otherwise non-radioactive colloidal particles, are being investigated at Sandia National Laboratories (SNL). Both programs use initial stability screening experiments to attempt to simplify the problem by eliminating kinetically or chemically unstable colloids from further consideration. Quantification of actinide masses sorbed on carrier colloids or within actinide intrinsic colloids will be conducted only for mobile, i.e., kinetically stable colloids.

Experiments with carrier colloids were initiated at SNL in September 1993. Based on results from these experiments and the published literature (see Section 2.2.6.2), the "hard-sphere" carrier colloid category has been eliminated from further consideration on the basis of kinetic stability behavior in Culebra Dolomite brine simulants (hydrochemical facies "A" and "C;" Siegel et al., 1991), Salado Formation-like brine simulants (Brine A; Brush, 1990), and Castile Formation brine simulants (ERDA-6; Brush, 1990).

Experiments with actinide intrinsic colloids were initiated at LLNL in January 1994. Methods development experiments and initial scoping experiments with Pu(IV) and U(VI) have been completed. Observations are consistent with the review presented in "Chemical Model for Colloidal Actinides" (Section 2.2.6.2).

Results from actual transuranic waste experiments will be used to evaluate results of the colloid characterization and transport program. Order of magnitude agreement between the STTP experimental results and ASTP model predictions will confirm the predictive capability of the model.



#### 4. FORM FOR DATA TRANSFER TO PERFORMANCE ASSESSMENT

Information on mobile actinide concentrations will be transferred to Performance Assessment in the form of a look-up table. This table represents a distillation of the dissolved concentration and colloid models and presents mobile actinide concentrations as a function of the most important variables determining these concentrations. These variables are expected to include such things as hydrogen ion concentration (pH), brine composition (e.g., from the Salado, Castile, and Rustler Formations), types of gases present and gas pressure (e.g., carbon dioxide), and type of backfill materials (e.g., bentonite, CaO). The table(s) will be generated from detailed models for the actinide source term and then transferred to Performance Assessment. This process will require no modifications to the existing Performance Assessment codes but would require some small amount of work in data structuring.



## 5. REFERENCES

- Avogadro, A., and G. de Marsily. 1983. "The Role of Colloids in Nuclear Waste Disposal," *Scientific Basis for Nuclear Waste Management VII, Materials Research Society Symposia Proceedings, Boston, MA, November 14-17, 1983*. Ed. G.L. McVay. New York, NY: North-Holland. Vol. 26, 495-505.
- Baes, C. F., Jr., and R.E. Mesmer. 1976. *The Hydrolysis of Cations*. New York, NY: John Wiley & Sons.
- Bell, J.T., C.F. Coleman, D.A. Costanzo, and R.E. Biggers. 1973a. "Plutonium Polymerization—III. The Nitrate Precipitation of Pu(IV) Polymer," *Journal of Inorganic and Nuclear Chemistry*. Vol. 35, no. 2, 629-632.
- Bell, J.T., D.A. Costanzo, and R.E. Biggers. 1973b. "Plutonium Polymerization—II. Kinetics of the Plutonium Polymerization," *Journal of Inorganic and Nuclear Chemistry*. Vol. 35, no. 2, 623-628.
- Bennett, D.G., S.K. Liew, L. Nanu, D. Read, and J.B. Thomas. 1993. "Modeling Colloidal Transport of Radionuclides Through Porous Media," *High Level Radioactive Waste Management, Proceedings of the Fourth Annual International Conference, Las Vegas, NV, April 26-30, 1993*. New York, NY: American Society of Civil Engineers. 638-645.
- Brush, L.H. 1990. *Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant*. SAND90-0266. Albuquerque, NM: Sandia National Laboratories.
- Buddemeier, R.W., and J.R. Hunt. 1988. "Transport of Colloidal Contaminants in Groundwater: Radionuclide Migration at the Nevada Test Site," *Applied Geochemistry*. Vol. 3, no. 5, 535-548.
- Choppin, G.R. 1983. "Solution Chemistry of the Actinides," *Radiochimica Acta*. Vol. 32, no. 1-3, 43-53.

- Choppin, G.R. 1988. "Humics and Radionuclide Migration," *Radiochimica Acta*. Vol. 44/45, pt. 1, 23-28.
- Clark, D.L., D.E. Hobart, and M.P. Neu. 1995. "Actinide Carbonate Complexes and Implications for Actinide Environmental Chemistry," *Chemical Reviews*. Vol. 95, no. 1, 25-48.
- Cleveland, J.M. 1979. "Critical Review of Plutonium Equilibria of Environmental Concern," *Chemical Modeling in Aqueous Systems: Speciation, Solubility and Kinetics, 176th Meeting of the American Chemical Society, Miami Beach, FL, September 11-13, 1978*. Ed. E.A. Jenne. ACS Symposium Series 93. Washington, DC: American Chemical Society. 321-338.
- Costanzo, D.A., R.E. Biggers, and J.T. Bell. 1973. "Plutonium Polymerization—I. A Spectrophotometric Study of the Polymerization of Plutonium(IV)," *Journal of Inorganic and Nuclear Chemistry*. Vol. 35, no. 2, 609-622.
- Dearlove, J.P.L., G. Longworth, M. Ivanovich, J.I. Kim, B. Delakowitz, and P. Zeh. 1990. "Organic Colloid Transport of Radionuclides at Gorleben, West Germany," *Waste Management '90, Proceedings of the Symposium, Tucson, AZ, February 25-March 1, 1990*. Ed. R.G. Post. Tucson, AZ: University of Arizona. Vol. 2, 565-569.
- Department of Energy. 1994a. *Waste Isolation Pilot Plant Transuranic Waste Baseline Inventory Report*. CAO-94-1005, Revision 0. Carlsbad, NM: Carlsbad Area Office.
- Department of Energy. 1994b. *Integrated Data Base for 1993: U.S. Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics*. DOE/RW-00006, Rev. 9. Washington, DC: U.S. Department of Energy, Office of Civilian Radioactive Waste Management.
- Derjaguin, B.V., and L. Landau. 1941. "A Theory of the Stability of Strongly Charged Lyophobic Sols and the Coalescence of Strongly Charged Particles in Electrolytic Solutions," *Acta Phys.-Chim. USSR*. Vol. 14, 633.
- Felmy, A.R., and D. Rai. 1992. "An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte  $\text{Th}^{4+}$ -SO in the System  $\text{Na}^+$ - $\text{K}^+$ - $\text{Li}^+$ -NH-SO-HSO- $\text{H}_2\text{O}$  to High Concentration." *Journal of Solution Chemistry* vol. 21 #5: 407-423.

- Felmy, A.R., and J.H. Weare. 1986. "The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California," *Geochimica et Cosmochimica Acta*. Vol. 50, no. 12, 2771-2783.
- Felmy, A.R., D. Rai, J.A. Schramke, and J.L. Ryan. 1989. "The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines," *Radiochimica Acta*. Vol. 48, no. 1/2, 29-35.
- Felmy, A.R., D. Rai, and R.W. Fulton. 1990. "The Solubility of  $\text{AmOHCO}_3(\text{c})$  and the Aqueous Thermodynamics of the System  $\text{Na}^+ - \text{Am}^{3+} - \text{HCO}^- - \text{OH}^- - \text{H}_2\text{O}$ ." *Radiochimica Acta* vol. 50: 193-240.
- Felmy, A.R., D. Rai, and M.J. Mason. 1991. "The Solubility of Hydrrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model," *Radiochimica Acta*. Vol. 55, no. 4, 177-185.
- Francis, A. J. (1985) Low-level radioactive wastes in subsurface soils, in *Soil Reclamation Processes: Microbiological Analyses and Applications* (eds. R. L. Tate III, and D. A. Klein), 279-331, Marcel Dekker, Inc., New York, New York.
- Francis, A. J., and Gillow, J. B. (1994) Effects of microbial processes on gas generation under expected Waste Isolation Pilot Plant repository conditions. Progress report through 1992. Sandia National Laboratories, SAND93-7036, Albuquerque, New Mexico.
- Fuger, J., I.L. Khodakovsky, E.I. Sergeyeva, V.A. Medvedev, and J.D. Navratil. 1992. *The Chemical Thermodynamics of Actinide Elements and Compounds: Part 12: The Actinide Aqueous Inorganic Complexes*. Vienna, Austria: International Atomic Energy Agency.
- Gregory, J. 1978. "Flocculation by Inorganic Salts," *The Scientific Basis of Flocculation*. Ed. K.J. Ives. Alphen aan den Rijn: Sijthoff & Noordhoff. 89-99.
- Grenthe, I., J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. 1992. *Chemical Thermodynamics of Uranium*. Eds. H. Wanner and I. Forest. New York: NY: Elsevier Science Publishers.

- Hardy, W.B. 1900. "A Preliminary Investigation of the Conditions Which Determine the Stability of Irreversible Hydrosols," *Proceedings of the Royal Society of London*. Vol. 66, 110-125.
- Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O System to High Ionic Strength at 25°C," *Geochimica et Cosmochimica Acta*. Vol. 48, no. 4, 723-751.
- Helton, J.C., J.W. Garner, R.P. Rechard, D.K. Rudeen, and P.N. Swift. 1992. *Preliminary Comparison with 40 CFR 191, Subpart B for the Waste Isolation Pilot Plant, December 1991. Volume 4: Uncertainty and Sensitivity Analysis Results*. SAND91-0893/4. Albuquerque, NM: Sandia National Laboratories.
- Hiemenz, P.C. 1986. *Principles of Colloid and Surface Chemistry*. New York, NY: Marcel Dekker, Inc.
- Honeyman, B.D. 1991. "Surface Chemistry, Colloids and Trace-Element Scavenging," *Marine Particles: Analysis and Characterization*. Eds. D.C. Hurd and D.W. Spencer. Geophysical Monograph 63. Washington, DC: American Geophysical Union. 437-451.
- Honeyman, B.D., and P.H. Santschi. 1992. "The Role of Particles and Colloids in the Transport of Radionuclides and Trace Metals in the Oceans," *Environmental Particles*. Eds. J. Buffle and H.P. van Leeuwen. Chelsea, MI: Lewis Publishers, Inc. Vol. 1, 379-423.
- Inoue, Y. and O. Tochiyama. 1985. "Studies of the Complexes of Np(V) with Inorganic Ligands by Solvent Extraction with Thenoyltrifluoroacetone and 1,10-Phenanthroline. I. Carbonate Complexes," *Bulletin of the Chemical Society of Japan*. Vol. 58, no. 2, 588-591.
- Kim, J.I. 1991. "Actinide Colloid Generation in Groundwater," *Radiochimica Acta*. Vol. 52/53, pt. 1, 71-81.
- Kim, J.I., and B. Kanellakopulos. 1989. "Solubility Products of Plutonium(IV) Oxide and Hydroxide," *Radiochimica Acta*. Vol. 48, no. 3-4, 145-150.

- Kim, J.I., R. Klenze, V. Neck, T. Sekine, and B. Kanellakopoulos. 1991. *Np(V) Hydrolysis, Carbonate, and Humate Complexation*. Translated from *Hydrolyse, Carbonat- und Humat-Komplexierung von Np(V)*. RCM 01091. Institut für Radiochemie der Technischen Universität München. (Available from Office of Scientific and Technical Information, Oak Ridge, TN.)
- Kraus, K.A. 1956. "Hydrolytic Behavior of the Heavy Elements," *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, August 8-20, 1955*. New York, NY: United Nations. Vol. 7, 245-257.
- Lappin, A.R., R.L. Hunter, D.P. Garber, P.B. Davies, R.L. Beauheim, D.J. Borns, L.H. Brush, B.M. Butcher, T. Cauffman, M.S.Y. Chu, L.S. Gomez, R.V. Guzowski, H.J. Iuzzolino, V. Kelley, S.J. Lambert, M.G. Marietta, J.W. Mercer, E.J. Nowak, J. Pickens, R.P. Rechar, M. Reeves, K.L. Robinson, and M.D. Siegel. 1989. *Systems Analysis, Long-Term Radionuclide Transport, and Dose Assessments, Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico; March 1989*. SAND89-0462. Albuquerque, NM: Sandia National Laboratories.
- Lierse, Ch., W. Treiber, and J.I. Kim. 1985. "Hydrolysis Reactions of Neptunium(V)," *Radiochimica Acta*. Vol. 38, no. 1, 27-28.
- Lieser, K.H., B. Gleitsmann, S. Peschke, and T. Steinkopff. 1986a. "Colloid Formation and Sorption of Radionuclides in Natural Systems," *Radiochimica Acta*. Vol. 40, no. 1, 39-47.
- Lieser, K.H., B. Gleitsmann, and T. Steinkopff. 1986b. "Sorption of Trace Elements or Radionuclides in Natural Systems Containing Groundwater and Sediments," *Radiochimica Acta*. Vol. 40, no. 1, 33-37.
- Lieser, K.H., A. Ament, R. Hill, R.N. Singh, U. Stingl, and B. Thybusch. 1990. "Colloids in Groundwater and Their Influence on Migration of Trace Elements and Radionuclides," *Radiochimica Acta*. Vol. 49, no. 2, 83-100.
- Lloyd, M.H., and R.G. Haire. 1978. "The Chemistry of Plutonium in Sol-Gel Processes," *Radiochimica Acta*. Vol. 25, no. 3-4, 139-148.

- Lyklema, J. 1978. "Surface Chemistry of Colloids in Connection with Stability," *The Scientific Basis of Flocculation*. Eds. K.J. Ives. Alphen aan den Rijn: Sijthoff & Noordhoff. 3-36.
- Magirius, S., W.T. Carnall, and J.I. Kim. 1985. "Radiolytic Oxidation of Am(III) to Am(V) in NaCl Solutions," *Radiochimica Acta*. Vol. 38, no. 1, 29-32.
- Maiti, T.C., M.R. Smith, and J.C. Laul. 1989. "Colloid Formation Study of U, Th, Ra, Pb, Po, Sr, Rb, and Cs in Briny (High Ionic Strength) Groundwaters: Analog Study for Waste Disposal," *Nuclear Technology*. Vol. 84, no. 1, 82-87.
- Matijević, E. 1973. "Colloid Stability and Complex Chemistry," *Journal of Colloid and Interface Science*. Vol. 43, no. 2, 217-245.
- Maya, L. 1983. "Hydrolysis and Carbonate Complexation of Dioxoneptunium(V) in 1.0 M HClO<sub>4</sub> at 25°C," *Inorganic Chemistry*. Vol. 22, no. 14, 2093-2095.
- McCarthy, J.F., and C. Degueudre. 1993. "Sampling and Characterization of Colloids and Particles in Ground Water for Studying Their Role in Contaminant Transport," *Environmental Particles*. Eds. J. Buffle and H.P. van Leeuwen. IUPAC Environmental Analytical and Physical Science Series Vol. 2. Chelsea, MI: Lewis Publishers, Inc. 247-315.
- Molecke, M.A. 1983. *A Comparison of Brines Relevant to Nuclear Waste Experimentation*. SAND83-0516. Albuquerque, NM: Sandia National Laboratories.
- Neck, V., J.I. Kim, and B. Kanellakopoulos. 1992. "Solubility and Hydrolysis Behaviour of Neptunium(V)," *Radiochimica Acta*. Vol. 56, no. 1, 25-30.
- Neck, V., J.I. Kim, and B. Kanellakopoulos. 1994. *Thermodynamic Behavior of Neptunium(V) in Concentrated NaCl and NaClO<sub>4</sub> Solutions*. Translated from *Thermodynamisches Verhalten von Neptunium(V) in Konzentrierten NaCl- und NaClO<sub>4</sub> Lösungen*. KfK 5301. Kernforschungszentrum Karlsruhe: Institut für Nukleare Entsorgungstechnik, Institut für Heiße Chemie.
- Newton, T.W., and J.C. Sullivan. 1985. "Actinide Carbonate Complexes in Aqueous Solution," *Handbook on the Physics and Chemistry of the Actinides*. Eds. A.J. Freeman and C. Keller. New York, NY: North-Holland. Vol. 3, 387-406.



- Nitsche, H., K. Roberts, R.C. Gatti, T. Prussin, K. Becraft, S.C. Leung, S.A. Carpenter, and C.F. Novak. 1992. *Plutonium Solubility and Speciation Studies in a Simulant of Air Intake Shaft Water from the Culebra Dolomite at the Waste Isolation Pilot Plant*. SAND92-0659. Albuquerque, NM: Sandia National Laboratories.
- Novak, C.F. 1992. *An Evaluation of Radionuclide Batch Sorption Data on Culebra Dolomite for Aqueous Compositions Relevant to the Human Intrusion Scenario for the Waste Isolation Pilot Plant (WIPP)*. SAND91-1299. Albuquerque, NM: Sandia National Laboratories.
- Novak, C.F. 1993. "Modeling of the Chemical Alteration of SPC Brine as a Function of CO<sub>2</sub>(g) Fugacity, and Modeling the Fugacity of Pure CO<sub>2</sub>(g) as a Function of Pressure." Appendix B in: Phillips, M.L.F., and M.A. Molecke. 1993. *Technical Requirements for the Actinide Source-Term Waste Test Program*. SAND91-2111. Albuquerque, New Mexico: Sandia National Laboratories
- Novak, C.F., and K.E. Roberts. 1994. *Thermodynamic Modeling of Neptunium(V) Solubility in Na-CO<sub>3</sub>-HCO<sub>3</sub>-Cl-CIO<sub>4</sub>-H-OH-H<sub>2</sub>O Electrolytes*. SAND94-0805C. Albuquerque, New Mexico: Sandia National Laboratories.
- Novak, C.F., and K.E. Roberts. 1995. "Thermodynamic Modeling of Neptunium(V) Solubility in Na-CO<sub>3</sub>-HCO<sub>3</sub>-Cl-CIO<sub>4</sub>-H-OH-H<sub>2</sub>O Electrolytes," *Scientific Basis for Nuclear Waste Management, Kyoto, Japan, October 23-27, 1994*. SAND94-0805C. Albuquerque, NM: Sandia National Laboratories.
- Overbeek, J.T.G. 1982. "Colloids, A Fascinating Subject: Introductory Lecture," *Colloidal Dispersions*. J.W. Goodwin. Special Publication No. 43. London: Royal Society of Chemistry. 1-21.
- Phillips, M.L.F., and M.A. Molecke. 1993. *Technical Requirements for the Actinide Source-Term Waste Test Program*. SAND91-2111. Albuquerque, NM: Sandia National Laboratories.
- Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*. 2nd ed. Boca Raton, FL: CRC Press.
- Rai, D., and J.L. Swanson. 1981. "Properties of Plutonium (IV) Polymer of Environmental Importance," *Nuclear Technology*. Vol. 54, no. 1, 107-112.

- Rai, D., A.R. Felmy, and R.W. Fulton. In press. "The  $\text{Nd}^{3+}$  and  $\text{Am}^{3+}$  Ion Interactions with  $\text{SO}_4^{2-}$  and Their Influence on  $\text{NdPO}_4(\text{c})$  Solubility," *Journal of Solution Chemistry*. (Copy on file in Sandia WIPP Central Files, Sandia National Laboratories, Albuquerque, NM.)
- Rao, L., D. Rai, A.R. Felmy, and R.W. Fulton. 1994. "Solubility of  $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$  in Concentrated Sodium Carbonate and Sodium Bicarbonate Solutions," *Radiochimica Acta*. SAND94-1948J. Albuquerque, NM: Sandia National Laboratories.
- Reed, D.T., S. Okajima, and M.K. Richmann. 1994. *Stability of Plutonium(VI) in Selected WIPP Brines*. SAND93-7114C. Albuquerque, NM: Sandia National Laboratories.
- 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. 1992. "Activity Coefficients in Electrolyte Mixtures:  $\text{HCl} + \text{ThCl}_4 + \text{H}_2\text{O}$  for  $5^\circ\text{-}55^\circ\text{C}$ ," *Journal of Physical Chemistry*. Vol. 96, no. 26, 11065-11072.
- Rundberg, R.S., A.J. Mitchell, I.R. Triay, and N.B. Torstenfelt. 1988. "Size and Density of a  $^{242}\text{Pu}$  Colloid," *Scientific Basis for Nuclear Waste Management XI, Materials Research Society Symposia Proceedings, Boston, MA, November 30-December 3, 1987*. Eds. M.J. Apter and R.E. Westerman. Pittsburgh, PA: Materials Research Society. Vol. 112, 243-248.
- Sandia WIPP Project. 1992. *Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992*. SAND92-0700/3. Albuquerque, NM: Sandia National Laboratories.
- Siegel, M.D., K.L. Robinson, and J. Myers. 1991. "Chapter 2: Solute Relationships in Groundwaters from the Culebra Dolomite and Related Rocks in the Waste Isolation Pilot Plant Area, Southeastern New Mexico," *Hydrogeochemical Studies of the Rustler Formation and Related Rocks in the Waste Isolation Pilot Plant Area, Southeastern New Mexico*. Eds. M.D. Siegel, S.J. Lambert, and K.L. Robinson. SAND88-0196. Albuquerque, NM: Sandia National Laboratories. 2-1 through 2-164.

- Tiller, C.L., and C.R. O'Melia. 1993. "Natural Organic Matter and Colloidal Stability: Models and Measurements," *Colloids in the Aquatic Environment. Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Eds. T.F. Tadros and J. Gregory. London: Elsevier Applied Science. Vol. 73, 89-102.
- Tipping, E. 1993. "Modeling Ion Binding by Humic Acids," *Colloids in the Aquatic Environment. Colloids and Surfaces A: Physicochemical and Engineering Aspects*. Eds. T.F. Tadros and J. Gregory. London: Elsevier Applied Science. Vol. 73, 117-131.
- Toth, L.M., H.A. Friedman, and M.M. Osborne. 1981. "Polymerization of Pu(IV) in Aqueous Nitric Acid Solutions," *Journal of Inorganic and Nuclear Chemistry*. Vol. 43, no. 11, 2929-2934.
- Trauth, K.M., S.C. Hora, R.P. Rechar, and D.R. Anderson. 1992. *The Use of Expert Judgment to Quantify Uncertainty in Solubility and Sorption Parameters for Waste Isolation Pilot Plant Performance Assessment*. SAND92-0479. Albuquerque, NM: Sandia National Laboratories.
- Triay, I.R., D.E. Hobart, A.J. Mitchell, T.W. Newton, M.A. Ott, P.D. Palmer, R.S. Rundberg, and J.L. Thompson. 1991. "Size Determinations of Plutonium Colloids Using Autocorrelation Photon Spectroscopy," *Radiochimica Acta*. Vol. 52/53, pt. 1, 127-131.
- Ueno, K., and A. Saito. 1975. "Solubility and Absorption Spectra of a Carbonato Complex of Pentavalent Neptunium," *Radiochemical and Radioanalytical Letters*. Vol. 22, no. 2, 127-133.
- van der Lee, J., G. de Marsily, and E. Ledoux. 1993. "Are Colloids Important for Transport Rate Assessment of Radionuclides?" *High Level Radioactive Waste Management, Proceedings of the Fourth Annual International Conference, Las Vegas, NV, April 26-30, 1993*. New York, NY: American Society of Civil Engineers. 646-652.
- van Olphen, H. 1977. *Introduction to Clay Colloid Chemistry*. 2nd ed. New York, NY: John Wiley & Sons.

- Vasudeva Rao, P.R., N.M. Gudi, S.V. Bagawde, and S.K. Patil. 1979. "The Complexing of Np(V) by Some Inorganic Ligands," *Journal of Inorganic and Nuclear Chemistry*. Vol. 41, 235-239.
- Verwey, E.J.W., and J.T.G. Overbeek. 1948. *Theory of the Stability of Lyophobic Colloids. The Interaction of Sol Particles Having an Electric Double Layer*. New York, NY: Elsevier Publishing Company, Inc.
- Villarreal, R., and M.L.F. Phillips. 1993. "Test Plan for Actinide Source-Term Waste Test Program (STTP)." CL21-STP-SOP5-012/0. Los Alamos, NM: Los Alamos National Laboratory.
- Vlassopoulos, D., S.A. Wood, and A. Mucci. 1990. "Gold Speciation in Natural Waters: II. The Importance of Organic Complexing—Experiments with Some Simple Model Ligands," *Geochimica et Cosmochimica Acta*. Vol. 54, no. 6, 1575-1586.
- WIPP Performance Assessment Department. 1992-1993. *Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992*. SAND92-0700. Albuquerque, New Mexico: Sandia National Laboratories. Vols. 1-5.