DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Actinide Source Term Program Position Paper .......................................................... 1

### Executive Summary ......................................................................................... 1

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

#### 2. Conceptual Models for Mobile Actinide Concentrations ............................... 3

##### 2.1 1992 Performance Assessment Data Base ................................................. 7

##### 2.2 Adequacy of 92 PA Data Base ............................................................... 7

##### 2.3 Relevant Conceptual Models ..................................................................... 8

###### 2.3.1 Inventory Limits .................................................................................. 9

###### 2.3.2 Inventory Limits with Sorption ............................................................ 9

###### 2.3.3 Fresh Water Estimates ......................................................................... 10

###### 2.3.4 Chemical Modeling of Mobile Actinide Concentrations ....................... 10

###### 2.3.4.1 Thermodynamic Modeling of Dissolved Actinides ............................ 11

###### 2.3.4.2 Modeling of Colloidal Actinides ..................................................... 16

###### 2.3.4.3 Determination of Mobile Actinide Concentrations using Actual Waste ................................................................. 20

##### 2.4 Utility of Other Conceptual Models ......................................................... 23

##### 2.5 Currently Defensible Model for PA/Compliance ....................................... 24

#### 3. Data Available for Compliance .................................................................... 24

##### 3.1 92 PA Data Base ..................................................................................... 25

##### 3.2 Available Uninterpreted Data .................................................................. 25

###### 3.2.1 Available Uninterpreted Data for Dissolved Actinide Concentrations 25

###### 3.2.2 Available Uninterpreted Data for Colloidal Actinide Concentrations .... 25

#### 4. 92 Form for Data Transfer to PA (PA CDFs Adequacy) ............................... 28

##### 4.1 92 PA Data Base Documentation ........................................................... 28

##### 4.2 Recommended Changes ......................................................................... 29

#### 5. Nonparametric and Calculational Requirements ........................................... 29

##### 5.1 Assumptions and Limitations ................................................................. 29

#### 6. Summary of Position on the Actinide Source Term ........................................ 30

#### 7. References ................................................................................................. 30
Actinide Source Term Program Position Paper

Executive Summary

The Actinide Source Term represents the quantity of actinides that could be mobilized within WIPP brines and could migrate with the brines away from the disposal room vicinity. This document presents the various proposed methods for estimating this source term, with a particular focus on defining these methods and evaluating the defensibility of the models for mobile actinide concentrations. The conclusions reached in this document are: the 92 PA "expert panel" model for mobile actinide concentrations is not defensible; and, although it is extremely conservative, the "inventory limits" model is the only existing defensible model for the actinide source term. The model effort in progress, "chemical modeling of mobile actinide concentrations," supported by a laboratory effort that is also in progress, is designed to provide a reasonable description of the system and be scientifically realistic and supplant the "inventory limits" model.

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

Long term isolation of the transuranic (TRU) waste elements (e.g., Am, Th, U, Pu, and Np) from the accessible environment is a primary technical objective for WIPP. Transuranic element, technically those elements with atomic numbers greater than 92, are a subset of the actinide series, the lower row of elements usually placed off to the bottom of the periodic table. Atomic number indicates the number of protons in the nucleus. The beginning of the actinide series is given in Table 1. The actinide elements in general exhibit chemical behavior distinct from most other elements, but similar to each other. Because thorium is not a transuranic element, but is an actinide, we use the more general term actinide in this document. The term radionuclide is still more general, indicating elements that decay spontaneously and emit radiation. An isotope is a particular version of an element, e.g., $^{238}$Pu and $^{239}$Pu are two different isotopes of plutonium, both with atomic number 92 (the difference is in the number of neutrons in the nucleus). The chemical behavior of an element depends primarily on the charge of the nucleus and the number of electrons associated with that nucleus, i.e., the oxidation state, while radioactive decay properties depend primarily on the number of protons and neutrons in the nucleus (thus the term nuclear decay). Therefore, the isotope number, i.e., 238 versus 239 in the above example, is not important for the chemical properties.
Table 1. The first six elements of the actinide series, with atomic number given in the upper left corners. Transuranic elements are those elements with atomic numbers greater than 92, i.e., atoms heavier than uranium.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>91</td>
<td>92</td>
<td>93</td>
<td>94</td>
<td>95</td>
</tr>
<tr>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
</tr>
<tr>
<td>Thorium</td>
<td>Protactinium</td>
<td>Uranium</td>
<td>Neptunium</td>
<td>Plutonium</td>
<td>Americium</td>
</tr>
</tbody>
</table>

Actinides that are mobilized in brines may migrate from the repository site. This document focuses on the current knowledge base for estimating the concentrations of mobile actinides that may be released from the disposal room environment under repository breach scenarios, as discussed in the Scenarios White Paper and in WIPP Performance Assessment Department (1992). For a narrative description of the essential features of the WIPP, see Lappin et al. (1989).

Human intrusion scenarios provide hydraulic connections between the WIPP disposal rooms and the Culebra Dolomite, a low grade aquatard within the Rustler Formation overlying the WIPP Site (see e.g., Lappin et al., 1989, Chapters 5 and 7; and the non-Salado Position Paper). These connections may permit brines and accompanying materials to move from the repository horizon in the Salado up to the Culebra and from there move with the natural groundwater flow in the Culebra and WIPP Land Withdrawal (i.e., regulatory) Boundary. The term "mobile actinides" means the amounts of actinides that can move with these brines. A review of brine compositions in and around the WIPP Site is given by Molecke (1983).

The inventory of actinides expected to be emplaced in the WIPP is given in the Baseline Inventory Report (BIR) (Department of Energy, 1994). 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 cumulative integrated release of actinides across a regulatory boundary is one of the primary standards against which the performance of WIPP will be judged. 40 CFR 191 contains specific upper limits on releases of radioactivity. The mobile concentrations of actinides that may leave the disposal panel environment dictate 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 the potential integrated release of radioactivity from the WIPP.
2. **Conceptual Models for Mobile Actinide Concentrations**

The term "mobile actinides" refers to all actinides that can move with the aqueous (brine) phase. Mobile actinides are made up of two broad categories: dissolved actinides and colloidal particles that contain actinides or have sorbed actinides. From a regulatory perspective, it is irrelevant whether actinides that cross the regulatory boundary are in dissolved or colloidal form. However, the physical and chemical behavior of the actinides during transport (movement with the brine phase) from disposal rooms to the accessible environment would be very different for dissolved and colloidal species because the physical and chemical mechanisms that control colloidal and solute species transport are very different. Therefore, dissolved and colloidal actinides must be considered, including the different chemical and physical mechanisms governing each form.

The terms "mobile", "dissolved", and "colloidal" actinides were first rigorously applied to the WIPP beginning in November 1993. Before that, the term "solubility" was used in place of "mobile," and the formation and transport of colloidal actinides within the WIPP system were not considered. This change in nomenclature was necessary to reflect the system more realistically. However, special consideration of the meaning of the word "solubility" is appropriate here.

In an aqueous system at equilibrium, the maximum concentration of a dissolved element will be governed by the formation of one or more solids containing the element. The solid phase or phases that form are the most favored under the chemical conditions, e.g., the concentrations of all elements in the aqueous phase, of the system. Thermodynamic formalism describes the aqueous concentrations associated with the element in the solid phase(s) through a solubility product expression. The solids that form are often called the "solubility-controlling solid(s)." Thus, one cannot say, e.g., "the solubility of thorium is...." Rather, one must say "the solubility of thorium in a brine with composition ... is ..."

Dissolved concentrations, e.g., of actinides, are influenced by chemical reactions with other species dissolved in the aqueous phase. These **complexation** reactions can increase the total amount of, e.g., a dissolved actinide, by combination with inorganic and organic species that may be present in the aqueous phase. The various types of complexation reactions have specific individual names, such as hydrolysis, ion pairing, ion association, and chelation. Although they differ in details, all such reactions fall under the general category of complexation.

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 Salado Flow and Transport, and non-Salado...
Flow and Transport; these are not reproduced here. Rather, the following discussion examines the conceptual models for the concentrations of mobile actinides, both dissolved and colloidal, that may occur in WIPP brines.

The concentration of a particular radionuclide in brine within the disposal rooms will be limited either by the amount present in the disposal rooms or by its maximum possible concentration in brine. The maximum possible concentration is determined by the waste inventory, and is defined as the mass (or moles) of each isotope divided by the available brine volume, where both quantities are based on the repository control volume used in the calculation. e.g., total repository, panel, or room. The amounts of actinides depends on the wastes emplaced, see for example the Baseline Inventory Report (Department of Energy, 1994). The brine volumes are calculated based on the disposal room model, and Salado brine inflow assumptions, described in the position papers on those topics. The radioisotopes of interest in release scenarios are those present in TRU waste and their daughters (decay products). Some of these decay products, e.g., 226Ra will be present in such small quantities that their release will be controlled by the amounts in the inventory alone, i.e., all of the radioisotope is assumed to dissolve because there is not enough to exceed the solubility limit and thus cause precipitation of a solid phase containing radium.

For the eight actinide isotopes that dominate the radioactivity of TRU waste, the potential for the actinides to cross the regulatory boundary under breach scenarios will be controlled by the degree to which they can be mobilized by dissolution or colloid formation. Helton et al. (1992) identified the isotopes 239Pu, 241Am, 238Pu, 240Pu, 237Np, 234U, 233U, and 230Th as important for WIPP performance assessment. At early times, the bulk of the activity comes from 238Pu, 239Pu, and 241Am. However, other actinide isotopes come into play during the 10,000 year post-operational phase. The inventories of 234U and 230Th increase as 238Pu decays (99.95% conversion to 234U after 1000 years), and significant quantities of 237Np result from alpha-decay of 241Am (~75% complete after 1000 years). Therefore, to ascertain compliance with 40CFR191B, WIPP PA 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.
Table 2. Radioisotopes expected to be important in the evaluation of WIPP performance (from Helton et al., 1992).

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>$t_{1/2}$ (yr)</th>
<th>Curies</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-238</td>
<td>$8.77 \times 10^1$</td>
<td>$9.26 \times 10^6$</td>
<td>$5.41 \times 10^5$</td>
</tr>
<tr>
<td>Pu-239</td>
<td>$2.41 \times 10^4$</td>
<td>$8.45 \times 10^5$</td>
<td>$1.36 \times 10^7$</td>
</tr>
<tr>
<td>Pu-240</td>
<td>$6.53 \times 10^3$</td>
<td>$1.07 \times 10^5$</td>
<td>$4.69 \times 10^5$</td>
</tr>
<tr>
<td>Pu-242</td>
<td>$3.76 \times 10^5$</td>
<td>$2.16 \times 10^6$</td>
<td>$5.50 \times 10^2$</td>
</tr>
<tr>
<td>U-233</td>
<td>$1.59 \times 10^5$</td>
<td>$1.037 \times 10^2$</td>
<td>$1.07 \times 10^4$</td>
</tr>
<tr>
<td>U-234</td>
<td>$2.44 \times 10^5$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>U-236</td>
<td>$2.34 \times 10^7$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Am-241</td>
<td>$4.32 \times 10^2$</td>
<td>$1.64 \times 10^6$</td>
<td>$4.79 \times 10^5$</td>
</tr>
<tr>
<td>Np-237</td>
<td>$2.14 \times 10^6$</td>
<td>$2.14$</td>
<td>$3.04 \times 10^3$</td>
</tr>
<tr>
<td>Th-229</td>
<td>$7.43 \times 10^3$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Th-230</td>
<td>$7.70 \times 10^4$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ra-226</td>
<td>$1.60 \times 10^3$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.4-3. Simplified radionuclide decay chains used for transport calculations in the Culebra Dolomite (from Ch. 6 of Vol. 2)

(1) Pu-240
(2) Am-241 → Np-237 → U-233
(3) U-234 → Th-230
(4) Pu-239
Figure 1. Expected WIPP radioisotope inventory as a function of time after waste emplacement (from Helton et al., 1992).
2.1 1992 Performance Assessment Data Base

The 1992 Performance Assessment data base was derived from expert judgment to "quantify uncertainty in solubility [old definition] parameters" for the WIPP. This 92 PA "Solubility" Data Base is also called the "expert panel" model because it was obtained through a process of expert judgment, as documented in Chapters 3 and 4 of Trauth et al. (1992). However, this documentation does not include the scientific reasoning behind the judgments used to arrive at the parameter values. The panel of experts generated probability functions indicating their technical experience and expertise of the likely concentrations of some actinides, reported in tabular form (p. 4-5 of Trauth et al., 1992) and in graphical form in Chapter 3, pp. 3-38 to 3-41, of WIPP Performance Assessment Department (1992). This is the data base used for dissolved actinide concentrations in the 12/92 PA calculations. This "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.

2.2 Adequacy of 92 PA Data Base

The mobile actinide concentration model in the 1992 PA is indirectly based on experimental data, but primarily represents the intuition and impressions of four individual experts. The scientific rationale behind the experts' values have not yet been published, making peer review of their reasoning difficult. However, examination of Table 4-1 of Trauth et al. (1992) elicits technical questions such as:

Why wasn’t Pu(VI) considered?

Why is only the neptunyl monocarbonato species considered for Np(V), and not the bis- and triscarbonato species?

Why is only the uncomplexed plutonyl species considered for Pu(V), and not the same carbonato species as needed for Np(V)?

Why is Pu(V) aqueous concentration controlled by Pu(IV) solids?

These questions represent internal inconsistencies in this data set, inconsistencies with the expected conditions in the WIPP disposal room environment such as elevated gaseous carbon dioxide, CO₂(g), pressure, and inconsistencies with current understanding of actinide aqueous chemistry.
The experts' estimates of mobile actinide concentrations was intended to be a stop-gap expedient while laboratory measurement of the chemical properties of actinides in brines were being performed. These parameter values cannot compared directly with data, and so the reasonableness of these values for quantifying the actinide concentrations that could occur in the WIPP cannot be determined. It is not clear that these values can be considered conservative, i.e., that actual values would be lower than those given by the expert panel, and it does not appear likely that the actinide chemistry community would consider these values to be "reasonable."

The 1992 PA model for mobile actinide concentrations also suffers from the inability to distinguish between mobile actinides in dissolved form and mobile actinides in colloidal form. While this issue is not important within the Performance Assessment models for actinide release from the disposal room environment, it is of paramount importance in models for Culebra transport. The form of the actinides, i.e., whether dissolved or colloidal, is central to calculating the degree of physical retardation and chemical retardation that the actinides could experience during transport through the Culebra. Because the 92 PA model can only give the total amount of mobile actinides, not the amounts of dissolved and colloidal actinides, the "expert panel" model serves as poor source of information for Culebra transport modeling.

2.3 Relevant Conceptual Models

Five relevant conceptual models for mobile actinide concentrations in WIPP PA scenarios have been identified. These include the "expert panel" model, used as the 92 PA mobile actinide concentration data base (Sec. 2.1, 2.2), the "inventory limits" model (Sec. 2.3.1), the "inventory limits with sorption" model (Sec. 2.3.2), the "fresh water estimates" model (Sec. 2.3.4), and the "chemical modeling of mobile actinide concentrations" model (Sec. 2.3.5). Of these five models, only one is completely developed in terms of parameter values and the rationale behind the model: the "inventory limits" model. The "expert panel" model is complete in terms of parameter values but not in documentation of the rationale behind it. Of the three remaining models, the "chemical modeling of mobile actinide concentrations" has been selected as most likely to meet the requirements of a reasonable, defensible model within the Disposal Decision Plan. For this reason, work supporting the chemical modeling of mobile actinide concentrations" is discussed in detail below. Although much information is available to support this model, the information has not yet been interpreted for use in PA. The other two conceptual models, "inventory limits with sorption" and "fresh water estimates" are included for completeness, but do not appear to represent reasonable and/or attainable descriptions of the chemical behavior or actinides in the disposal room environment.
2.3.1 Inventory Limits

The "Inventory Limit" model assumes that all actinides contained in the waste are mobile. Under this model, all actinides from the waste could be released from the sampled repository volume, e.g., a panel, if human intrusion were to occur. The Inventory Limit model places no constraint on the capacity of the aqueous phase to contain actinides. Thus, the aqueous phase can contain actinides in concentrations anywhere from zero to a maximum given as the mass of radionuclides in the samples volume divided by the volume of brine in the samples volume under the particular scenario. The "inventory limits" model includes no information about the form of these actinides, whether dissolved or colloidal. This model is the worst case for mobile actinide concentrations, i.e., it allows the maximum release of radioactivity, and as such is entirely and utterly defensible. Although this is one reasonable endpoint description of the system, it is exceedingly conservative. Actinides are relatively insoluble; thus, unlimited aqueous actinide concentrations are not expected to occur under any of the WIPP performance scenarios.

2.3.2 Inventory Limits with Sorption

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. Sorption on fixed substrates and 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. Although this conceptual model is technically reasonable, data are not available describing the sorption capacities for the various substrates under WIPP-specific physicochemical conditions. If the "Inventory Limit with Sorption" model is to be considered, the most likely candidates for sorption are iron (hydr)oxides (from corrosion of waste containers and constituents), vermiculite (a constituent of the waste), and bentonite (a proposed backfill material) present as either immobilized colloids or fixed substrates. Both have been fairly well characterized with respect to adsorption of non-actinide brine cations such as sodium and potassium. However, little work has been done to specifically quantify adsorption of actinides. This model also is very dependent on the waste form and backfill. If iron drums are eliminated from the design, iron (hydr)oxides would be less pervasive in the disposal rooms. The reference backfill for WIPP does not include bentonite. Because of the difficulties in predicting sorption over ranges of chemical conditions, this model would be difficult to implement and may remain non-defensible.
The Acute Toxic Source Term Program (ATSP) was begun in late 1992 to develop a credible alternative for the WIPP.

Existing fresh water data base is incomplete and indeterminable, and does not provide a viable alternative. Much more useful than the expert panel numbers discussed above. However, the model would certainly be a useful estimate for behavior at available for fresh water systems, such a model would certainly be a useful estimate for behavior at

If all the necessary information about dissolved and colloidal behavior were

carbonatable.

The Fresh Water model proposes to use values from fresh water to...
a model describing mobile actinide colloid concentrations, and studies with actual transuranic waste, each of which are functions of brine composition. The overall program has been examined by approximately 10 technical experts in the fields of actinide chemistry, geochemistry, and colloid chemistry.

The following sections present the major features of the three components of the ASTP: a model for dissolved actinides, a model for colloidal actinides, and the tests with actual waste. These components were developed together, and each relies on information from the other two for meeting project objectives. This work is in progress, with each part being performed simultaneously. The three parts of the ASTP, called "thermodynamic modeling of dissolved actinides," "modeling of colloidal actinides," and "determination of mobile actinide concentrations using actual waste" are addressed in the following three subsections.

The models for dissolved and colloidal concentrations of actinides are being developed directly from experimental data relevant to the WIPP. Therefore, these models should be highly defensible in the scientific venue. Comparison of these models with the actual waste tests should generate a high degree of confidence in the ability of the model to predict mobile dissolved and mobile colloidal actinide concentration. This high degree of confidence will allow the model to be used to predict mobile actinide concentrations under conditions that may occur in the disposal room environment that were not amenable to measurement within the actual waste tests.

2.3.4.1 Thermodynamic Modeling of Dissolved Actinides

"Thermodynamic Modeling of Dissolved Actinides" is both a conservative and is a reasonable description of mobile dissolved actinide concentrations. It is the subset of the ASTP involving development of a thermodynamic model for dissolved actinide concentrations. Briefly, this work involves development of a model for dissolved actinide concentrations as controlled by actinide-bearing solid phases. The experimental work in progress is measuring dissolved actinide concentrations as a function of brine composition. These data are being interpreted with the thermodynamic formalism presented in general detail in Pitzer (1991), Harvie et al. (1984), and Felmy and Weare (1986). Details for developing 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 the chemical properties of Pu(III), Am(III), and Nd(III) are effectively identical. Similar details for Th(IV) dissolved concentration models are given in Felmy and Rai (1992). This process is also extensively outlined for Np(V) in Novak and Roberts (1994), included as an appendix to this document.
Different models are being developed for the individual important oxidation states of the important 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). The preliminary model for the +III actinides, including inorganic ligands (but not possibly important organic ligands), has been completed as of 15 July 1994. However, the interpretation of this model for impact on WIPP Performance Assessment has not yet begun. The models for the other oxidation states are progressing.

Work is divided by oxidation state 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 need to 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. The program includes provisions to demonstrate that a model developed from, e.g., Nd(III), is applicable to Am(III) and Pu(III). Unequivocal demonstration is straightforward and requires fewer resources and less time than the model development itself. There is less total data on the chemical analogy for the +V actinides (PuO$_2^+$, NpO$_2^+$, and AmO$_2^+$) and the +VI actinides (PuO$_2^{2+}$, UO$_2^{2+}$, and NpO$_2^{2+}$). However, it is believed that the chemical analogy holds for these systems. In contrast to the +III, +IV, and +VI oxidation states, the chemical analogy for the +IV actinides Pu$^{4+}$, U$^{4+}$, Np$^{4+}$, and Th$^{4+}$ is not quantitative, but nevertheless can serve as a good indicator for the chemical behavior of a system, and can result in a conservative approximation for An(IV) behavior.
Table 3. Elements and oxidation states important to WIPP Performance Assessment and WIPP solubility submodel development. Elements/oxidation states in the same column exhibit similar chemical behavior.

<table>
<thead>
<tr>
<th>Element</th>
<th>+III Oxidation State</th>
<th>+IV Oxidation State</th>
<th>+V Oxidation State</th>
<th>+VI Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plutonium</td>
<td>Pu(III)</td>
<td>Pu(IV)</td>
<td>Pu(V)</td>
<td>Pu(VI)</td>
</tr>
<tr>
<td>(actinide)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(actinide)</td>
<td>U(IV)</td>
<td></td>
<td>U(VI)</td>
<td></td>
</tr>
<tr>
<td>Neptunium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(actinide)</td>
<td>Np(IV)</td>
<td>Np(V)</td>
<td>Np(VI)</td>
<td></td>
</tr>
<tr>
<td>Americium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(actinide)</td>
<td>Am(III)</td>
<td></td>
<td>Am(V)</td>
<td></td>
</tr>
<tr>
<td>Thorium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(actinide)</td>
<td>Th(IV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neodymium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(lanthanide)</td>
<td>Nd(III)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The primary variables influencing chemical behavior in aqueous systems are ionic radius, $r$, ionic charge, $z$, and the ratio of charge to radius cubed, $z/r^3$. Actinides and lanthanides, the f-elements, have approximately the same ionic radius when in the same oxidation state because the f electron shell is inside the s electron shell, and it is the s electron shell that determines the ionic radius. There is a small variation in ionic radius among f-elements with the same oxidation state, but this variation typically provides a difference in chemical properties of only several percent. The oxidation state analogy is supported by data throughout the literature. However, although chemical principles provide convincing arguments for the validity of the analogy, experimental verification is still necessary. Such verification is a part of the experimental program.

Thermodynamics is the key feature of this modeling approach. Thermodynamics is one of the primary tools in the science of chemistry, is extremely well documented, and is well recognized as an accurate and useful description for aqueous chemistry. 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. In addition, dissolution kinetics may not be important over the 10,000 year regulated life of the repository.
A degree of conservatism is inherent in the choice of a thermodynamic framework to describe the concentrations of mobile dissolved actinides. The experimental work in progress for this program provides information on actinide-bearing solid phases that form over a laboratory time scale, i.e., weeks to tens of months, in contrast 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. Consequently, the dissolved actinide concentrations are likely to decrease as the solids age. The laboratory experiments will thus provide an upper bound on the expected dissolved concentrations. Conversion to less stable, i.e., 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 it is not being included in the ASTP, adsorption on Culebra materials is being examined to support chemical retardation. The difference in importance of adsorption between the disposal room environment and the Culebra is due to several factors. Equilibrium chemical conditions in the Culebra have developed over very long periods of time, substantially longer than the performance period of the repository. In contrast, the disposal room environment is manmade, with sorption substrates that were emplaced by man, with brine capacity to mobilize actinides as the expected dominant phenomena. The states and forms of the heterogeneous mixture of man-emplaced materials in the disposal rooms are relatively difficult to predict and defend over a 10,000 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 is designed to link the mobile dissolved concentrations of actinides to brine compositions, and thus the chemical environment. In particular, this model will enable assessment of the influence of disposal room conditions on mobile dissolved actinide
concentrations. For example, this model will be able to calculate the potential increase in dissolved actinide concentrations that could be caused should large gaseous carbon dioxide (CO$_2$(g)) pressures exist in the disposal rooms. Also, an evaluation could be made about the impact of calcium oxide (CaO) in the backfill (to remove CO$_2$(g)), versus the possible increase in mobile actinide concentrations caused by very basic conditions and potentially high carbonate concentrations. In this manner, the thermodynamic model represents a very 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.

The thermodynamic modeling of dissolved actinides could provide information on the actinide oxidation state distributions if these were governed by equilibrium processes within the WIPP disposal rooms. However, as discussed in detail in the Gas Generation Position Paper, oxidation-reduction (redox) couples are generally not in equilibrium in geologic systems, and thus such an assumption is not reasonable. Therefore, the oxidation states of the actinides will have to be ascertained based on other information. Several possibilities exist in this regard: information from the source term tests with actual transuranic waste, information from studies of gas generation, 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) (Magirius et al., 1985), and plutonium(VI) is stabilized in this oxidation state in the presence of carbonate (Reed et al., 1994). Existing information thus cannot assure that actinides will occur solely in their reduced oxidation states in the disposal room environment.

As of 15 July 1994, no information on oxidation states was available from the source term tests, and existing information from the gas generation studies had not been assimilated into the mobile dissolved actinide concentration model. Presently, the only possibility is statistical sampling as part of the numerical performance assessment codes over the potential oxidation state distributions. Unlike the sampling over probability distributions for actinide "solubilities," this sampling would be bounded by physics.

Physical and mathematical principles dictate that 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 $^{239}\text{Pu(III)}$, $^{239}\text{Pu(IV)}$, $^{239}\text{Pu(V)}$, and $^{239}\text{Pu(VI)}$, where percentages can be calculated from the ratio of $^{239}\text{Pu}$ in a particular oxidation state to the total $^{239}\text{Pu}$. Although the thermodynamic modeling of dissolved actinides in its current state of development must rely on
statistical sampling, the sampled variables are highly constrained and these variables absolutely, irrefutably cover the entire possible range of conditions. It is likely that information from the source term tests and the gas generation program will further constrain the ranges for these variables.

2.3.4.2 Modeling of Colloidal Actinides

"Modeling of Colloidal Actinides" is the subset of the ASTP that involves laboratory work and development of a model describing the concentration of actinides sorbed on or contained in mobile colloidal particles (defined as particles suspended by Brownian motion with diameters between 0.001 and 1 μm) in the WIPP disposal room. It is also a component of the research effort evaluating the potential for colloid-facilitated radionuclide transport in the Culebra Dolomite, 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 are being investigated under a separate program (refer to the non-Salado position paper).

Work completed to date has focused on defining stable colloids that must be quantified by transport modeling in the Culebra. 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 (see, e.g., 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 Site are not yet available. For the WIPP Site, evaluation of the impacts of colloids on repository performance was begun a few years ago.

It is important to distinguish between the several types of colloidal particles that could potentially be important at a geologic repository such as the WIPP. Prior to attempting to quantify the impact of colloids on transport of actinides, one must first have a clear idea of what types of colloids must be evaluated. For the WIPP colloid laboratory and modeling program, we have elected to simplify the colloid issue as much as possible on the basis of the stability behavior of different colloid types. The WIPP Site 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 (refer to Brush, 1990; Siegel et al., 1991). As will be discussed below, it has been known for well over a century that some types of colloids are not kinetically stable in high ionic strength electrolytes. That is, those colloidal particles quickly agglomerate to
form clusters; the resulting agglomerated particles are sufficiently large (>1 \(\mu m\)) to be influenced by gravitational forces, and will settle. Results from preliminary experiments have confirmed that at least some colloidal particles that could be present in the disposal room environment and the Culebra are quickly (on the order of hours to days) destabilized in WIPP brine simulants and form large agglomerates which settle by gravity.

The laboratory programs implemented to quantify the concentrations of actinides contained by colloids (i.e., the ASTP colloid subprogram) and the potential for transport of colloids in the Culebra are both designed to evaluate the potential effects of the high ionic strength WIPP brine simulants on colloids. Different types of colloids, however, are affected differently by high ionic strength electrolytes. Separate laboratory efforts are underway investigating actinide intrinsic colloids and carrier colloids, the two main types of colloids that must be addressed for the WIPP. Those laboratory programs are described in more detail in Section 2.6.2.

Carrier colloids, which are ordinarily non-radioactive, are colloidal-sized particles which may act as substrates for sorption of actinides as well as other metals (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, traditionally 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 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; Matijeviç, 1973). Forces of attraction between the particles (i.e., van der Waals forces) cause agglomeration to form 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 Degueldre, 1993, their Table 6). Colloidal particles that can be eliminated from consideration in transport of actinides
at the WIPP include iron(III)-(hydr)oxides, clay minerals, and mineral constituents of the host rock. Further, 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). This type of colloid is currently being investigated in the laboratory at SNL, but no definite conclusions have yet been reached regarding their impact on 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; Heimenz, 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) 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). This type of colloid is currently being investigated in the laboratory at SNL, but no definite conclusions have yet been reached regarding their impact on 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 (Maiti et al., 1989), to form macromolecules, or "polymers," of colloidal size. 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: $M^{4+} > M(VI)O_2^{2+} > M^{3+} > M(VI)O_2^{2+}$ (Choppin, 1983; Kim, 1991). The tendency for formation of one particular actinide intrinsic colloid, the Pu(IV)-polymer, is enhanced by increased concentrations of Pu(IV), temperature, and basic conditions (Toth et al., 1981). Examples can be found the literature of polymeric species of most of the actinides of importance to 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 behavior, the lower polymers will behave no differently than the dissolved species.
described above in Section 2.3.4.1. In contrast, the higher polymers, such as the Pu(IV)-polymer, may reach colloidal sizes (1 nm to 1 μm) and will have different hydrodynamic properties than the sub-colloidal-sized dissolved species (refer to the non-Salado 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 (e.g., Kraus, 1956; Costanzo et al., 1973; Bell et al., 1973a, b; Lloyd and Haire, 1978; Toth et al., 1981), which was conducted to help improve processing techniques. Investigations focusing on chemical conditions relevant to environmental concerns have been conducted more recently (Cleveland, 1979; Rai, 1981; Kim, 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. Critics may point out that they are familiar with Pu(IV)-polymer solutions that have remained stable for years. That observation is not necessarily 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-1800's are still in existence. Experiments are in progress to evaluate the formation and behavior of actinide intrinsic colloids, including the Pu(IV)-polymer, at Lawrence Livermore National Laboratory (LLNL). However, we have not reached definite conclusions regarding the formation and stability properties of actinide intrinsic colloids, and cannot yet defend statements regarding their impact on actinide transport.

The anticipated colloid submodel and the design and sequence of the supporting laboratory program are closely coupled. Both the actinide intrinsic colloid program (LLNL) and carrier colloid laboratory program (SNL) have been designed to permit 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 in this section, we
can eliminate the "hard-sphere" carrier colloids from further consideration, but cannot yet make
definitive statements about the behaviors and impacts of the other types of colloids.

At the most fundamental level, the model that will be produced from the colloid laboratory
work is expected to consist of a binary decision tree, in which for each colloid type, given the
environmental conditions (e.g., pH, ionic strength, brine composition, potential colloid or actinide
element, etc.), will screen that particular colloid for further consideration. In other words, if that
particular colloid is not kinetically or chemically stable under the given conditions, and cannot
contribute a significant concentration of mobile actinides, it is not evaluated further.

The next step in the actinide colloid model is to predict, for any colloids that persist, the
steady state concentration of actinides per unit volume. The later steps in the model for both carrier
colloids and actinide intrinsic colloids are substantially more complicated to evaluate both
analytically and numerically. 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.

As was stated above in Section 2.3.1, the "inventory limits" model does not describe the
relative proportions of dissolved actinides and colloidal actinides. However, in order for the
Systems Prioritization Methodology (SPM) process to evaluate the potential value gained in
investigating colloids and in investigating transport properties of colloids in the Culebra Dolomite
(refer to the non-Salado position paper), the dissolved and colloidal portions of the actinide source
term must be defined. As was described above in this Section, the types of mobile colloidal
particles that may be important components of the actinide source term are: "soft-sphere" carrier
colloids (e.g., humic materials), sterically stabilized "hard-sphere" carrier colloids, and actinide
intrinsic colloids. "Hard-sphere" carrier colloids have been eliminated from consideration.
Currently, we have no technical basis on which to estimate relative proportions of dissolved and
colloidal actinides. For the SPM Baseline calculations, we recommend that the inventory-limited
concentrations of actinides be sampled probabilistically, so that the sum of the colloidal actinides
and the dissolved actinides equals the inventory limits.

2.3.4.3 Determination of Mobile Actinide Concentrations using Actual Waste

The Actinide Source-Term Waste Test Program (STTP) is a set of experiments designed to
measure mobile actinide concentrations in experiments with actual waste. Technical requirements
for these tests are set forth in "Technical Requirements for the Actinide Source-Term Waste Test
Program" (Phillips and Molecke, 1993); the test plan for these experiments is "Test Plan for
Actinide Source-term Waste Test Program (STTP)" (Villarreal and Phillips, 1993). While all
possible waste types and potential repository conditions cannot be examined in the laboratory, these tests are intended to simulate some of the expected repository conditions, and thus allow measurement of actinide concentrations mobilized from TRU waste under these conditions.

The STTP complements the laboratory studies of radionuclide chemistry. STTP results will be used to gain confidence in the mobile actinide concentration model, and will provide information on actinide oxidation state distributions. The STTP by itself cannot cover the large ranges of potential conditions in WIPP disposal rooms, however it can provide some confidence that the model for mobile concentrations works for the conditions sampled in the STTP, and thus is likely to be realistic for other conditions. The goals of both the laboratory program and the STTP are to develop and evaluate a defensible actinide source-term model that will provide a narrower uncertainty range of actinide concentration data to WIPP PA than is currently available from expert judgment. To the extent that they are available, the dissolved actinide and colloid actinide models will be able to predict the results of the STTP studies.

Briefly, the test concept for the STTP involves filling test containers with a variety of actual CH TRU wastes and completely saturating the containers with brines. The brines will be a mixture of natural and synthetic brines with compositions chemically similar to those of intergranular brines found in the Salado and Castile Formations. Experiment vessels were engineered based on the size of waste objects and on waste homogeneity; heterogeneous waste types such as combustibles will use "drum scale" vessels of approximately 250 L volume, while more homogeneous types such as sludges will use "liter scale" test containers of 2-5 L volume.

The containers will permit regular sampling of brine and head space gas. (The head space gas is sampled only as an indicator of the anoxic/oxic condition within the containers. No information on gas generation rates will be obtained.) The wastes will be intentionally fortified or "spiked" with actinides to a level that will ensure that concentration measurements will reflect equilibrium conditions and will not be limited by the quantity of actinide in the waste sample. In addition, certain wastes will be spiked with waste constituents that are expected to increase dissolved concentrations, e.g., complexing agents, in order to measure the sensitivity of actinide concentration to these waste-matrix components. The test vessels will also be inoculated with halophilic and halotolerant microbes found in the WIPP underground and in saline environments on the surface near the WIPP Site. This may identify effects of microbial activity on the mobilization of actinides. Prior to test initiation, the containers will be purged with argon or helium to remove much of oxygen. This will accelerate the approach to anoxic conditions, in an attempt to simulate the environment predicted for the WIPP disposal rooms after they have been filled and sealed.
During operation, the test environment will be held at constant temperature to simulate the expected post-closure conditions of WIPP disposal rooms. The test containers will be agitated to promote thorough mixing of the TRU waste with the brine, and to keep brine compositions homogeneous. Brine samples (called leachate) will be withdrawn at regular intervals throughout the experiment. The leachate samples will be analyzed to ascertain the chemical and physical form and concentration of actinides dissolved or dispersed in the brine. These experiments are expected to operate for approximately 2-3 years, though individual tests may run longer if trends in the measured actinide concentrations warrant.

The test criteria reflect the intent of the program to analyze the effects of various waste constituents on actinide concentrations in brines. Three independent processes are cumulatively responsible for the quantity of actinides that can be supported in the aqueous phase and thus that can be mobilized. These processes are dissolution/precipitation, sorption/desorption and colloid formation/destruction reactions. The test matrix is intended to identify influences or factors within the wastes that can participate in or influence these reactions. In order to adequately test a chemical model of the disposal room based on data obtained in the laboratory, it will be necessary to sample test conditions that represent all major influences on actinide mobilization. Note that given a matrix of reasonable scope and a finite test duration, it may not be possible to access all chemical environments that can be tested in the laboratory. However, this is not essential to testing a laboratory data-based model, which is the principal goal of the source-term test program.

The principal objective of the STTP is to test the predictive ability of a numeric model using concentration data obtained from actual TRU wastes subjected to conditions anticipated in the disposal rooms. The STTP is designed to complement the laboratory studies by supplying actinide concentration data along with information about chemical conditions present in the wastes, and will test the numeric model using actual wastes under conditions similar to those expected in the post-disposal phase. Ultimately, the concentration of each actinide should have a unique value at a given set of conditions once the disposal rooms reach chemical equilibrium. It is not possible to guarantee, however, that the waste-brine system will reach equilibrium within the life of the STTP experiments. To account for perturbations to equilibrium such as high levels of radiolysis (which can increase Eh) and the chemical state of actinides in the waste (which can either increase or decrease dissolved concentrations), the test matrix provides experimental controls that either isolate the perturbation or cause the system to reach a steady-state within the duration of the STTP.

An important caveat in this strategy is that although the STTP will sample actinide concentrations in subsets of parameter space that ought to resemble conditions of the disposal rooms, it is not possible to measure concentrations under truly authentic repository conditions.
These conditions will evolve over hundreds of years, and it is not possible to authoritatively predict a set of conditions at any given time in the post-disposal phase. This is why the source-term tests will be more useful for testing a source-term model than for directly predicting disposal room actinide concentrations.

The laboratory studies of radionuclide chemistry and the source-term tests are complementary. It is useful to illustrate how they differ technically and programmatically by discussing tradeoffs between the two programs. The advantages of the laboratory program (vs. the STTP) are that test conditions are subject to greater control, allowing actinide mobilization mechanisms to be tested individually, and that actinide concentrations may be measured over a wide range of test conditions. These features allow one to construct a numerical model from laboratory data. In addition, these data will be far less expensive than those collected by the STTP. However, the laboratory program is limited by its inability to test the numeric model with data from actual wastes, which is scientifically desirable and significantly enhances the credibility of the model.

2.4 Utility of Other Conceptual Models

Extensive discussion of the utility of other conceptual models is included in section 2.3; a summary is provided here.

- The "expert panel" model, as used in the 92 PA Data Base is complete and has been used in performance assessment calculations. However, this model represents expert judgment about chemical properties that are measurable and are being measured, so the defensibility of using this information is questionable. (Also see Section 2.2 Adequacy of 92 PA Data Base, for more discussion.) This model is not demonstrably conservative. The "expert panel" model is available for use, however, the documentation used to develop it has not been completed, issued, or peer-reviewed.

- The "inventory limits" model is a worst case scenario for mobile actinide concentrations, and is exceedingly conservative. However, this model is the only complete, defensible model for mobile actinide concentrations within the WIPP disposal room environment at present.

- The "inventory limits with sorption" model is less unrealistic than the "inventory limits" model, but it is not sufficiently developed to evaluate. Because of the difficulties in demonstrating sorption on anthropogenic materials (e.g., bentonite and iron corrosion products) that have not equilibrated with the environment over geologic time, and the
sensitivity of sorption to the wide range of chemical conditions possible in the disposal room, this model would be difficult to implement and may remain non-defensible.

- The "fresh water estimates" model is essentially undeveloped, so the conservatism and defensibility of this model cannot be evaluated.

- The "chemical modeling of mobile actinide concentrations" model, currently under development as the Actinide Source Term Program, is designed to be realistically conservative following established formalism for both dissolved and colloidal species.

In summary, the only existing defensible model for mobile actinide concentration is the "inventory limits" model.

2.5 Currently Defensible Model for PA/Compliance

Five models for mobile actinide concentrations have been presented: the "expert panel" model, the "inventory limits" model, the "inventory limits with sorption" model, the "fresh water estimates" model, and the "chemical model for mobile actinide concentrations." The "inventory limits" model is completed. The "chemical model for mobile actinide concentrations" is under development, i.e., work is in progress. The "inventory limits with sorption" and "fresh water estimates" models are undeveloped, i.e., not available for use and not being pursued.

Interpreting "currently defensible model" to mean the credibility of a conceptual model and the data set that is used by the conceptual model, only the "inventory limits" is currently defensible. The "expert panel" model (the model used in the 92 PA) is not defensible for the reasons described in Sections 2.1 and 2.2. The data necessary to defend the other models are not currently available.

While the "inventory limits" model, as discussed in Section 2.3.1, is ultraconservative and unrealistic, it is defensible. It appears necessary to use the inventory limits model until adequate further work is completed to enable the chemical model approach to be implemented and defended.

3. Data Available for Compliance

The existing data sets that have been interpreted with respect to compliance are the expert panel "data" and the inventory limits. Additional data are available, notably the model for dissolved concentrations of +III actinides as influenced by inorganic ligands. The interpretation of these data is in progress.
3.1 92 PA Data Base

The 92 PA Data Base is also called the "expert panel" model. The process of expert judgment is documented in Chapters 3 and 4 of Trauth et al. (1992), as are the resulting "solubility" parameters; however, this documentation does not include the scientific reasoning behind the judgments used to arrive at the parameter values. The panel of experts generated probability curves indicating their ideas of the likely concentrations of some actinides, reported in tabular form on p. 4-5 of Trauth et al. (1992), and in graphical form in Volume 3, pp. 3-38 to 3-41 of WIPP Performance Assessment Department (1992). As discussed in Section 2.2, this model is neither conservative nor defensible. The basis for this data set would need to be compiled and published to enable its use for compliance analysis.

3.2 Available Uninterpreted Data

Active research programs are in place for examining both dissolved actinide concentrations and colloid actinide concentrations in WIPP brines. In addition, there is an active program for measuring dissolved and colloidal actinide concentrations in tests with actual transuranic waste. Most of this work is being interpreted and checked for adherence to quality assurance requirements. As such, it falls within the category of "available uninterpreted data," and is discussed below.

3.2.1 Available Uninterpreted Data for Dissolved Actinide Concentrations

The experimental work necessary to develop the models for mobile dissolved actinide concentrations is being performed under four separate contracts. As of 9 August 1994, 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 David E. Hobart of Lawrence Berkeley Laboratory (LBL), and AH-5590 with Gregory R. Choppin of Florida State University (FSU).

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. Hobart is measuring solubility data for the +V actinides Np(V) and Pu(V), and is developing solubility models again in conjunction with Novak. Choppin is measuring the complexation between organic ligands and actinides, and is working with Novak to model these data. These contractors and their efforts will achieve a complete dissolved
concentration model for each important actinide in each important oxidation state. The final actinide dissolved concentrations model is a synthesis of results from the contractors and existing information in the literature, with an interpretation of this information to determine the impact on repository performance. This interpreted information will then be combined with information from the model for mobile actinide colloid concentrations, and compared with information from the source-term tests with actual transuranic wastes.

Large amounts of uninterpreted data exist. Some of these data are in the laboratory notebooks of the contractors measuring actinide properties, some are published in the open literature. These include information being generated in support of nuclear waste repositories throughout the world. Data being generated by the contractors will be published when technical 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 are scattered throughout the open literature. We are in the process of gathering and assessing these data 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-CI-CO₃ 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; Ueno and Saito, 1975; Vasudeva Rao et al., 1979) along with WIPP specific data from LBL.

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., 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 scenarios.

Data for the dissolved concentration model, whether discovered in the literature or measured by a contractor, are being interpreted in the same consistent way. 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 under our control 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.

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).

3.2.2 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, has 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 are utilizing an initial stability screening experimental approach to attempt to simplify the problem by eliminating kinetically or chemically unstable colloids from further consideration. Quantification of masses of actinides sorbed on carrier colloids or within actinide intrinsic colloids will be conducted only for those that are mobile (i.e., kinetically stable).

Experiments with carrier colloids were initiated at SNL in September 1993. Based on our experimental results and the published literature (see section 2.3.4.2), 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). We expect to publish the experimental results soon, pending checks for adherence to quality assurance requirements.

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 "Modeling of Colloidal Actinides" (section 2.3.4.2). We expect to publish the experimental results soon, pending checks for adherence to quality assurance requirements.
As described above in Section 2.3.4.2, the laboratory programs and the modeling programs for the colloid subset of the ASTP are designed to closely track one another in strategy. If stable colloids are found, additional laboratory work is planned to quantify aggregation kinetics, sorption capacity, and persistence in complex environments, as necessary.

These laboratory activities are closely tied to the colloid work being conducted to address colloid-facilitated radionuclide transport in the Culebra Dolomite. To minimize duplication of effort and to optimize utilization of resources, experiments for both the carrier colloid and actinide intrinsic colloid laboratory programs are done with brine simulants from the Culebra Dolomite as well as the Salado and Castile Formations, as described above.

Results from actual transuranic waste experiments being conducted in the source term test program subset (STTP) of the ASTP 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. 92 Form for Data Transfer to PA (PA CDFs Adequacy)

Information on mobile actinide concentrations is 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 type (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 the models developed within the ASTP, and then forwarded to PA. This process will require no modifications to the existing PA codes, but would require some small amount of work in data structuring.

4.1 92 PA Data Base Documentation

The 92 PA Data Base documentation, specifically Volume 3, pp. 3-38 to 3-41, of WIPP Performance Assessment Department (1992), is adequate to explain what numbers were used in the calculations. A supporting document, Trauth et al. (1992), is adequate to explain the expert elicitation process used to generate the "expert panel" model. However, no document exists to explain the technical reasoning of the experts and explain why particular numerical values were
assigned. There can be no technical credibility for the 92 PA model in the absence of such a document. However, such a document will not guarantee technical credibility.

4.2 Recommended Changes

The mobile actinide concentration data base used in the 92 PA Data Base is not technically defensible, and thus should not be used in future performance assessment calculations. However, should it be deemed necessary to use this data set in the absence of measured data or with the mechanistic model discussed above, the following points should be addressed:

- It is necessary to have a technical document explaining the thought processes used by the experts to generate their predictions if PA is intending to use the expert panel numbers in their calculations for compliance.

- The detection limit for dissolved or colloidal actinides is on the order of $10^{-10}$ moles/dm$^3$. Thus, although the "true" concentration of an actinide may be $10^{-15}$ moles/dm$^3$ or less, as given by the expert panel for some elements, concentrations below analytical detection limit can never be supported by measurements. Therefore, the lowest actinide concentration that should be used is $10^{-10}$ moles/dm$^3$.

5. Nonparametric and Calculational Requirements

It is expected that information about mobile actinide concentrations will be passed to PA through a look-up table as a function of several variables. Important variables for dissolved actinide concentrations are likely to include hydrogen ion concentration (pH), gas phase composition and pressure, changes in brine composition caused by the waste, and backfill additives. These variables and several others may be important for calculating colloidal actinide concentrations. As model development continues, this list of parameters will likely be shortened to three or four critical factors.

5.1 Assumptions and Limitations

This program requires information about brine compositions that exist in the WIPP environment, information about gas partial pressures, information about waste type, and information about backfill materials. These data determine how brine compositions will change as a result of contact with these materials. This, in turn, governs the equilibrium concentrations of actinides in various oxidation states within the disposal room environment.
6. Summary of Position on the Actinide Source Term

Although reasonable models for mobile actinide concentrations in the WIPP disposal room environment are in development, these models have not yet been exercised to estimate mobile actinide concentrations. Therefore, they are unavailable for use in WIPP Systems Prioritization Management (SPM) activities. The "inventory limits" model, Section 2.3.1, thus must be used as the baseline for the SPM.

7. References


Distribution for Position Paper

**SNL WIPP Managers**

| MS 1334 | W. Weart | 6303 |
| MS 1335 | S. Goldstein | 6305 |
| MS 1341 | A. Stevens | 6306 |
| MS 1345 | P. Davis | 6307 |
| MS 1341 | R. Lincoln | 6308 |
| MS 1328 | D. R. Anderson | 6342 |
| MS 1341 | D. Schafer | 6347 |
| MS 1341 | J. Holmes | 6348 |
| MS 1324 | P. Davies | 6115 |
| MS 0751 | W. Wawersik | 6117 |
| MS 1320 | J. Nowak | 6119 |
| MS 1322 | J. Tillerson | 6121 |
| MS 1395 | V. Harper-Slaboszewicz | 6743 |

**SNL 6307 Staff, MS 1345**

<table>
<thead>
<tr>
<th>NAME</th>
<th>PHONE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Bertram</td>
<td>6345</td>
</tr>
<tr>
<td>S. Bigger</td>
<td>6308</td>
</tr>
<tr>
<td>T. Corbet</td>
<td>6308</td>
</tr>
<tr>
<td>L. Hill</td>
<td>6308</td>
</tr>
<tr>
<td>A. Lappin</td>
<td>6308</td>
</tr>
<tr>
<td>P. Swift</td>
<td>6308</td>
</tr>
<tr>
<td>T. Steinborn</td>
<td>6308</td>
</tr>
<tr>
<td>J. Tollison</td>
<td>6308</td>
</tr>
<tr>
<td>M. Wallace</td>
<td>6308</td>
</tr>
<tr>
<td>M. Glora</td>
<td>6308</td>
</tr>
</tbody>
</table>

**SNL 6700 Staff, WIPP Site, MS 1395**

<table>
<thead>
<tr>
<th>NAME</th>
<th>PHONE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Pickering</td>
<td>6308</td>
</tr>
<tr>
<td>P. Sanchez</td>
<td>6308</td>
</tr>
</tbody>
</table>

**SNL PTB Position Paper Working Group Chairs**

| MS 1324 | R. Beauheim | 6115 |
| MS 1324 | S. Howarth | 6115 |
| MS 1341 | N. Dhooge | 6348 |
| MS 1322 | F. Hansen | 6121 |
| MS 1341 | B. Butcher | 6348 |
| MS 1328 | M. Marietta | 6342 |
| MS 1322 | D. Munson | 6121 |
| MS 1328 | M. Fewell | 6342 |
| MS 1341 | L. Brush | 6348 |

**Others**

| MS 1328 | J. Helton | 6341 |
| MS 1328 | M. Tierney | 6241 |
| J. Berglund | NMERI |
| Galson Sciences (3) | |
| D. Powers | |
| P. Drez | |
| CAO (R. Bills, J. Mewhinney, R. Batra, R. Wise, M. McFadden, R. Lark, V. Bynum) | |
| WID (R. Kehrman) | |
| MS 1330 | SWCF-A: 1.1.1.4; AST: Actinide Source Term Program | Org. 6352 |