

517373

RESPONSE TO EEG-77,  
PLUTONIUM CHEMISTRY UNDER CONDITIONS RELEVANT  
FOR WIPP PERFORMANCE ASSESSMENT:  
REVIEW OF EXPERIMENTAL RESULTS AND  
RECOMMENDATIONS FOR FUTURE WORK,  
BY V. M. OVERSBY

L. H. Brush,<sup>1</sup> R. C. Moore,<sup>2</sup> and N. A. Wall<sup>1</sup>

1. Repository Performance and Certification Dept. 6822  
Sandia National Laboratories  
Carlsbad, NM 88220

2. Program Development and Environmental Decisions Dept. 6849  
Sandia National Laboratories  
Albuquerque, NM 87185-0779

March 15, 2001

INTRODUCTION

This response addresses several issues reiterated by Oversby (2000). These issues all pertain to the solubilities of actinide elements, especially Pu, in brines that could be present in the Waste Isolation Pilot Plant (WIPP), a US Department of Energy (DOE) repository in southeastern New Mexico for defense-related transuranic (TRU) waste. Oversby (1997), Neill (1997), and Neill et al. (1998) discussed these issues in detail prior to Oversby (2000). The DOE has responded to these issues several times previously (see, for example, US DOE, 1997; US DOE, 1998; Brush, 2000a, 2000b; Brush and Moore, 2000a, 2000b; Brush and Wang, 2000; Moore, 1999; Moore et al., 1999).

To respond to Oversby (2000), we have organized her comments into seven major issues: (1) predictions of Pu oxidation states in the WIPP; (2) use of experimental data for Am(III), and especially Th(IV), and the oxidation-state analogy to predict the speciation and solubilities of Pu(III) and Pu(IV), respectively; (3) the effects of organic ligands on actinide solubilities, especially the effect of citrate on Pu(IV) solubility; (4) the effects of MgO backfill on actinide solubilities, especially the effect of the MgO reaction product nesquehonite; (5) the effects of the heterogeneity of TRU waste and other waste characteristics on actinide solubilities; (6) the use of the speciation-solubility code Fracture Mass Transport (FMT) to predict actinide solubilities; (7) the uncertainty ranges assigned to the solubilities. This list and the responses below do not attempt to prioritize these issues.

## BACKGROUND

The solubilities of actinide elements under conditions expected in brines present in WIPP disposal rooms after filling and sealing (high-ionic-strength brines, reducing Eh, mildly basic pH) were among the most important chemical parameters required for the performance assessment (PA) calculations for the Compliance Certification Application (CCA). (Distribution coefficients, or  $K_d$ s, for dissolved actinides under conditions expected during transport in the Culebra Dolomite Member of the Rustler Formation are much less important than solubilities for long-term WIPP PA. This is because transport through the Culebra will not be a significant release path relative to direct releases up a borehole after inadvertent human intrusion into the repository during exploratory drilling for resources such as oil and gas, and potash.) The former DOE Carlsbad Area Office (CAO), now the Carlsbad Field Office (CBFO), submitted the CCA to the US Environmental Protection Agency (EPA) in October 1996 to demonstrate compliance with EPA regulations for non-mixed TRU waste (see US DOE, 1996b). (In this response, we refer to the CAO and the CBFO as the "DOE.") Sensitivity analyses of the CCA PA calculations by Helton et al. (1998) have shown that Pu and Am are the most important actinides in TRU waste from the standpoint of their potential effects on the long-term performance of the WIPP. U and Th are less important, but could also affect the long-term performance of the repository. Np is much less important, but the DOE included Np in its laboratory and modeling studies for completeness. Actinide solubilities would also be among the most important chemical parameters for any PA calculations required for re-certification of the WIPP.

### ISSUE 1: PREDICTIONS OF ACTINIDE OXIDATION STATES

Predictions of the oxidation states of the important, multivalent WIPP actinides under expected repository conditions are important for PA because the oxidized species of these actinides, Pu(V), Pu(VI), U(VI), Np(V), and Np(VI), generally have higher solubilities than the reduced species, Pu(III), Pu(IV), U(IV), and Np(IV). (The oxidized species also have lower  $K_d$ s than the reduced species, but  $K_d$ s for dissolved actinides under conditions expected during transport in the Culebra are much less important than solubilities for long-term WIPP PA because transport through the Culebra will not be a significant release path relative to direct releases.) Therefore, oxidized species of these elements, if present, would be more likely to be released than reduced species.

In the CCA PA, the DOE asserted that Pu, Am, U, Th, and Np will speciate as Pu(III) or Pu(IV), Am(III), U(IV) or U(VI), Th(IV), and Np(IV) or Np(V) in any brines present in WIPP disposal rooms (see US DOE, 1996b, Appendix SOTERM). (The DOE also asserted that, because conditions in WIPP disposal rooms will be strongly reducing and because the Culebra is mildly reducing, these elements will also speciate as Pu(III) or Pu(IV), Am(III), U(IV) or U(VI), Th(IV), and Np(IV) or Np(V) in the Culebra.) The DOE acknowledged that Pu(V) and Pu(VI) could occur in isolated microenvironments in

WIPP disposal rooms. However, the DOE asserted that Pu(V) and Pu(VI) would not persist in significant quantities because diffusive and, especially in the event of human intrusion, advective transport (see Issue 5, Effects of Heterogeneity and Other Waste Characteristics below) would expose any oxidized Pu to the reductants that will be present in the repository (see below). The DOE did not base its predictions of actinide oxidation states on thermodynamic and/or kinetic redox models. Instead, it based them on experimental studies of reduction of Pu(V) and Pu(VI) by metallic Fe, which will be present in large quantities as steel waste containers (drums and boxes) and in the waste itself; and/or by Fe corrosion products (see Granbow et al., 1996; Xia et al., 1996; Slater et al., 1997; Felmy et al., 2000; Reed et al., 2000). Microbial degradation of cellulose, or of cellulose, plastics, and rubbers, assumed to have a probability of 0.5 in the CCA PA, would also create reducing conditions in the WIPP. Oxidizing species, such as hypochlorite (ClO<sup>-</sup>) and O<sub>2</sub>, created by α radiolysis of H<sub>2</sub>O in WIPP brines, could continuously oxidize Pu(III) or Pu(IV) to Pu(V) and/or Pu(VI). (Hydrogen peroxide, also produced by α radiolysis of H<sub>2</sub>O in brines, is a reducing agent under the mildly basic conditions expected in the WIPP; see Morgenstern and Choppin, 1999). However, metallic Fe, Fe(II)- or Fe(II, III)-bearing corrosion products, dissolved Fe(II) species, metallic Al, and/or microbial activity would continuously reduce Pu(V) and Pu(VI) to Pu(III) or Pu(IV). In contact-handled (CH) TRU waste, the quantities of reductants to be emplaced in the WIPP greatly exceed the quantity of Pu. For example, there will be, on average, about 60 kg of metallic Fe (including steel waste containers and Fe-base metals in the waste), 4 kg of metallic Al, 10 kg of cellulose, 10 kg of plastics, and 2 kg of rubbers per 208-L drum, but only about 20 g of Pu per drum. Therefore, reduction of oxidized Pu would generally occur rapidly relative to oxidation of reduced Pu. However, isolated microenvironments with solid or dissolved Pu concentrations high enough for oxidation to outpace reduction could exist.

Since the CCA PA, some of the results from the WIPP Source Term Test Program, or STTP (see Villarreal et al., 2000) led Oversby and the EEG to assert that significant quantities of Pu will speciate as Pu(V) or Pu(VI) in WIPP brines, contrary to the DOE assertion that Pu(V) and Pu(VI), if formed, would not persist in significant quantities (see, for example, Oversby, 2000, pp. 12-18). The STTP is a series of 15 drum-scale and 39 liter-scale experiments with actual CH TRU waste carried out at Los Alamos National Laboratory, or LANL (see LANL, 2000). In two of the 39 liter-scale containers (L-27 and L-36), LANL investigators observed detectable concentrations of Pu(V). In two of the other liter-scale containers (L-26 and L-28), they observed detectable quantities of Pu(VI). LANL did not observe oxidized Pu in any of the drum-scale containers.

The DOE continues to assert that Pu will speciate as Pu(III) or Pu(IV), and that significant quantities of Pu(V) and Pu(VI) will not persist (see, for example, Brush, 2000a, 2000b; Brush and Moore, 2000a, 2000b, Brush and Wang, 2000). There are at least four reasons for this assertion.

First, LANL observed Pu(V) or Pu(VI) in just four of the 54 STTP containers, and in only four of the 15 liter-scale containers containing pyrochemical salts (see

Villarreal et al., 2000). Although LANL did not analyze for Pu(V) and Pu(VI) in every container, most of the 54 STTP containers had low or very low concentrations of Pu, consistent with the presence of relatively insoluble Pu(III) and Pu(IV), but not with that of relatively soluble Pu(V) and Pu(VI).

Second, significant quantities of Pu(V) and Pu(VI) did not persist in L-26, L-27, L-28, and L-36 (see Villarreal et al., 2000). In all four of these containers, the concentrations of Pu(V) and Pu(VI) decreased to levels below the detection limits of the spectrophotometric technique used to detect Pu(V) and Pu(VI). This does not imply that no oxidized Pu was present in these containers, but it does imply that the process or processes that produced significant quantities of Pu(V) and Pu(VI) were transient. Furthermore, the total dissolved Pu concentration in these containers also decreased as the concentrations of Pu(V) and Pu(VI) decreased. In L-27 and L-36, the Pu concentrations decreased to levels significantly below their highest values. These observations are consistent with the expectation that the oxidized forms of these actinides are more soluble than the reduced forms.

Third, L-26, L-27, L-28, and L-36 contained pyrochemical salts, which have higher loadings of  $\alpha$ -emitting radionuclides than the average loading of the TRU waste to be emplaced in the WIPP. (In this report, we use the terms "loading" and "loadings" to specify the total, or solid- *and* aqueous-phase, concentrations of radioelements, radionuclides, or waste in these containers, in pyrochemical salts or other types of TRU waste, or in average TRU waste.) The  $^{239}\text{Pu}$  loadings of L-26, L-27, L-28, and L-36 were about four to 50 times higher than the average Pu content of WIPP waste (about 20 g of Pu per 208-L drum). Brush (2000b) calculated that the  $^{239}\text{Pu}$  loadings of L-26, L-27, L-28, and L-36 were 0.347, 1.13, 5.23, and 3.71 g/L, respectively. These loadings exceed the average (total) Pu loading of TRU waste (0.0960 g/L) by factors of about 4, 10, 50, and 40, respectively. Because the loadings of these containers were higher than that of average TRU waste, the specific  $\alpha$  activities in these containers were higher than that of average TRU waste. Therefore,  $\alpha$  radiolysis of  $\text{H}_2\text{O}$  in the brines in these containers produced oxidizing species faster than it will in brines in contact with average TRU waste, and oxidation of Pu(III) or Pu(IV) to Pu(V) and/or Pu(VI) proceeded faster. The (transient) occurrence of (detectable) Pu(V) in L-27 and L-36, and of Pu(VI) in L-26 and L-28 could reflect the (transient) failure of reductants such as metallic Fe, Fe(II)- or Fe(II, III)-bearing corrosion products, or dissolved Fe(II) species to reduce Pu(V) and/or Pu(VI) to Pu(III) or Pu(IV) as fast as radiolytically produced oxidants converted Pu(III) or Pu(IV) to Pu(V) and/or Pu(VI).

A comparison of the behavior of L-25 and L-26 (see Villarreal et al., 2000) supports this hypothesis. L-25 and L-26 had very similar loadings of comminuted pyrochemical salts (1,338 g in L-25, 1,315 g in L-26) and iron mesh (110 g each). Both contained Brine A, and both had an identical brine:solid ratio (2:1, units unspecified). However, the Pu and Am loadings and the specific activities of these containers were significantly different: L-25 contained 0.38 g of  $^{239}\text{Pu}$  and 0.4 mg of  $^{241}\text{Am}$ , or a total of 6.5 Ci of  $\alpha$ -emitting radionuclides; L-26 contained 1.04 g of  $^{239}\text{Pu}$  and 2.3 mg of  $^{241}\text{Am}$ , or a total of 17.8 Ci. This difference might be responsible for the significantly different

behavior of these two containers: L-26 yielded dissolved Pu concentrations significantly higher than L-25 and (transient) Pu(VI); L-25 had low dissolved Pu concentrations consistent with the presence of relatively insoluble Pu(III) and Pu(IV), but not with that of relatively soluble Pu(V) and Pu(VI).

It is also worth noting that L-25 had a specific activity, 2.17 Ci/L, higher than that required to oxidize *all* of the Pu(IV) to Pu(VI) in 5 M NaCl with pH > 7, about 1 Ci/L (see Kim et al., 1987). Apparently, the reductants in L-25 (metallic Fe, Fe(II)- or Fe(III)-bearing corrosion products, or dissolved Fe(II) species) were effective despite the fact that conditions were similar to those under which relatively high, steady-state concentrations of ClO<sup>-</sup> were produced and maintained (see Kelm et al., 1999).

Oversby (2000, p. 15) acknowledged that the pyrochemical salts contain a disproportionately high Pu content:

“The pyrochemical salt residues to be sent from Rocky Flats contain about 1 metric ton of plutonium contained in 14.9 metric tons of pyrochemical salts.”

She also pointed out that this is a significant fraction of the “13 to 16 metric tons” of Pu to be emplaced in the WIPP.

Fourth, pyrochemical salts constitute a very small (volumetric) fraction of the waste to be emplaced in the WIPP. The volume of pyrochemical salts is about 640 m<sup>3</sup>, or about 0.4 vol. % of the total CH and RH TRU inventory (US DOE, 1996a, Table 2-1). Therefore, as stated previously, the DOE asserts that the oxidized Pu that could be produced in microenvironments containing these pyrochemical salts would not persist in significant quantities in the repository. Oxidized Pu would not persist because brines from these volumetrically small oxidizing microenvironments would become well mixed with the significantly larger volumes of brines in the strongly reducing environments characteristic of typical TRU waste (see Issue 5, Effects of Heterogeneity and Other Waste Characteristics, below). Reactions between the oxidized brines and the reducing agents in the typical brine and TRU waste (metallic Fe and Al, solid Fe(II) or Fe(II, III)-bearing corrosion products, dissolved Fe(II) species, and possible microbial degradation of cellulose, plastics, and rubbers) would then reduce Pu(V) and Pu(VI) to Pu(III) or Pu(IV), thereby decreasing the Pu solubility. Furthermore, it is worth reiterating that LANL detected oxidized Pu in only four of the 15 liter-scale containers containing pyrochemical salts (L-26, L-27, L-28, and L-36), and that detectable quantities of Pu(V) and Pu(VI) did not persist in these containers (see above).

## ISSUE 2: USE OF OXIDATION-STATE ANALOGS

For the CCA PA, the DOE asserted that Pu, Am, U, Th, and Np will speciate as Pu(III) or Pu(IV), Am(III), U(IV) or U(VI), Th(IV), and Np(IV) or Np(V) in any brines

present in WIPP disposal rooms (see Issue 1, Predictions of Actinide Oxidation States, above). Because of the experimental difficulties involved in maintaining Pu, U, and Np in the +III or +IV oxidation states, the DOE used experimental data (Pitzer ion-interaction parameters) obtained with Am(III) and the oxidation-state analogy to predict the solubility of Pu(III), and experimental data for Th(IV) and the oxidation-state analogy to predict the solubilities of Pu(IV), U(IV), and Np(IV) (see US DOE, 1996b, Appendix SOTERM). The DOE used literature data to develop a Pitzer-based solubility model for Np(V), but did not use this model for elements other than Np because it maintained that none of the actinides that could affect the long-term performance of the WIPP would speciate in the +V oxidation state (see Issue 1 above). (The US DOE, 1996b, also used oxidation-state analogs to establish ranges and probability distributions of  $K_{ds}$  for the CCA PA but, as stated previously,  $K_{ds}$  are much less important than solubilities for long-term WIPP PA.) Since the CCA PA, the DOE also obtained preliminary experimental data for Pu(III) and Pu(IV) (see below).

Oversby (2000) criticized the DOE's use of experimental data for Am(III), and especially Th(IV), and the oxidation-state analogy to predict the speciation and solubilities of Pu(III) and Pu(IV), respectively. This report reiterated previous criticism by Oversby (1997), Neill (1997), and Neill et al. (1998) of the use of the oxidation-state analogy in the CCA PA.

The DOE has already provided a detailed response to this criticism (see US DOE, 1998, DOE Response to Issue #2). We quote from that response here:

“The oxidation state analogy, as used in the WIPP CCA, states that actinides in the same oxidation state exhibit similar trends and behaviors. SNL used this similarity along with theoretical and observed trends in behavior to establish bounding cases for the actinide solubility. The NAS in its WIPP Committee Report appropriately recognized that there are documented cases where the actinide oxidation state analogy is not an appropriate assumption. The key to the oxidation state analogy then lies in understanding the chemical conditions where it is and is not applicable, and also understanding the appropriate use, including limitations, as applied to a real problem.”

This response then described the chemical reasons for these “similar trends and behaviors” in considerable detail (US DOE, 1998, DOE Response to Issue #2), which we will not reiterate here. However, we summarize three important points.

First, actinides in the same oxidation state exhibit *similar behavior, not identical behavior*. For example, Th(IV), U(IV), Np(IV), Pu(IV) form highly insoluble (under reducing conditions), isostructural, crystalline solids with the composition  $AnO_2$ . (The “An” in  $AnO_2$  represents the actinides Th, U, Np, or Pu in this case.) These solids are so similar that Haschke (2000) reported the occurrence of excess oxygen in  $PuO_{2-x}$ , analogous to the well known occurrence of excess  $O_2$  in  $UO_2$ . The uptake of excess  $O_2$  by these An(IV) oxides results in nonstoichiometric  $PuO_{2+x}$ , analogous to  $UO_{2+x}$

(see Issue 5, Effects of Heterogeneity and Other Waste Characteristics, below). However, the solubility products of the amorphous An(IV) oxides (and, almost certainly, the crystalline An(IV) solids) decrease significantly as the atomic number of the actinide increases (compare Tables 1, 8, 9, and 10 in Rai et al., 1998).

Second, the solubility models for Am(III) and, especially, Th(IV) establish *upper bounds* for the solubilities of Pu(III), and for Pu(IV), U(IV), and Np(IV), respectively, *not exact predictions* of these solubilities. This is because the solubility products of these actinide-bearing solids, especially An(IV)-bearing solids, decrease much more as the atomic number increases than the stability constants for the analogous dissolved complexes increase (see, for example, Rai et al., 1998, Tables 1, 8, 9, and 10). Therefore, even though the speciation of dissolved Th(IV) differs somewhat from that of U(IV), Np(IV), and Pu(IV) (compare Tables 1, 2, 8, 9, and 10 in Rai et al., 1998), the solubility of Th(IV) is *significantly* greater than those of U(IV), Np(IV), and Pu(IV) under expected WIPP conditions.

Third, Am(III) is a better analog for Pu(III) and other trivalent actinides than is Th(IV) for Pu(IV) and other quadrivalent actinides (see Choppin, 1999). Therefore, Am(III) is *somewhat* more soluble than Pu(III) under comparable conditions, but Th(IV) is *significantly* more soluble than Pu(IV) under comparable conditions (see below). Preliminary results of efforts to develop solubility models for Pu(III) and Pu(IV) (see below) support this conclusion.

Furthermore, the DOE was developing models for the solubility of Pu(III) and Pu(IV) in WIPP brines at PNNL and SNL to provide additional validation of the approach used for the CCA PA. Investigators at PNNL were carrying out experiments with Pu(III) and Pu(IV), not analogs such as Am(III), Nd(III), or Th(IV), to obtain Pitzer ion-interaction parameters that could be used to calculate activity coefficients for Pu(III) and Pu(IV) species dissolved in WIPP brines. Upon completion of these experiments, SNL personnel planned to use the PNNL results to develop a database to calculate Pitzer activity coefficients in WIPP brines, incorporate the database into the speciation and solubility code FMT, analyze the results to ensure completeness and internal consistency, and use FMT to predict the speciation and solubilities of Pu(III) and Pu(IV) directly.

PNNL made significant progress toward the development of a solubility model for Pu(III). Although PNNL did not complete this model, preliminary results imply that both Am(III) and Nd(III) are good (conservative) analogs for Pu(III) because these elements are somewhat more soluble than Pu(III) under comparable conditions. PNNL started to develop a solubility model for Pu(IV), but did not make as much progress with this oxidation state as it did with Pu(III) because of the difficulties in maintaining dissolved Pu species in the +IV oxidation state. Nevertheless, based on compilations and reviews of previous work (see, for example, Rai et al., 1998), DOE believes that Th(IV) is significantly more soluble than Pu(IV). Therefore, Th(IV) is a very conservative analog for Pu(IV).

### ISSUE 3: EFFECTS OF ORGANIC LIGANDS

Predictions of the quantities of organic ligands in the TRU waste to be emplaced in the WIPP, the concentrations of these ligands in any brines present in WIPP disposal rooms after filling and sealing, and the extent to which these organics could form complexes with Pu, Am, U, Th, and Np are important for PA because organo-actinide complexes could increase the solubilities of these actinides significantly. (Organo-actinide complexes could also decrease the  $K_{ds}$  for these actinides, but  $K_{ds}$  are much less important than solubilities for long-term WIPP PA.)

For the CCA PA, the DOE estimated the quantities of acetate, citrate, ethylenediaminetetraacetic acid (EDTA), and oxalate in TRU waste (see US DOE, 1996a, Table 3-2). The DOE also estimated the concentrations of these organics in WIPP brines assuming an inundated repository (see US DOE, 1996b, Appendix SOTERM, Table SOTERM-4). Based on preliminary calculations using stability constants for organo-actinide complexes in aqueous solutions with ionic strengths lower than those of WIPP brines, US DOE (1996b, Appendix SOTERM, p. SOTERM-38) asserted that

“The calculations showed that under these [expected WIPP] conditions 99.8 percent of the EDTA was complexed by Ni, thus effectively rendering the EDTA unavailable for complexation with the actinides and rendering complexation of actinides by organic ligands inconsequential.”

Despite the preliminary nature of these calculations, US DOE (1996b, Appendix SOTERM, p. SOTERM-38) asserted that this conclusion was conservative because

“... the fact that a single metal cation could bind more than 99 percent of the EDTA strongly suggests that the full range of metals that will be present will readily overwhelm the complexation sites of the organic ligands,”

and

“Variation in ionic strength is not expected to change the complexation constants sufficiently to reduce this effect on the organics.”

All three of these statements have proven to be true (see below).

Since the CCA PA, the DOE carried out a comprehensive experimental study of the complexation of Am(III), U(VI), Th(IV), and Np(V) by acetate, citrate, EDTA, and oxalate at Florida State University (FSU). SNL investigators then used FSU's results to develop a database to calculate Pitzer activity coefficients, incorporated the database into the speciation and solubility code FMT, analyzed the results to ensure completeness and internal consistency, and used FMT to predict the effects of organo-actinide



complexation on the speciation and solubilities of Am(III) and Th(IV). Moore et al. (1999) presented the results of this multi-year effort to the National Academy of Sciences Committee on the WIPP in July 1999. Four of the viewgraphs in Moore et al. (1999) show the speciation of Am(III) in Brine A (a Salado-Fm. brine) as a function of pH, the speciation of Am(III) in ERDA-6 (a Castile-Fm. brine) as a function of pH, the speciation of Th(IV) in Brine A as a function of pH, and the speciation of Th(IV) in ERDA-6 as a function of pH, respectively. Moore (1999) also presented these results to the New Mexico Environmental Evaluation Group (EEG) in October 1999. (Moore, 1999, contains the same four speciation diagrams as Moore et al., 1999). Furthermore, it is perfectly reasonable to use the speciation predicted for Am(III) and the oxidation-state analogy to predict the speciation of Pu(III), and the speciation predicted for Th(IV) and the oxidation-state analogy to predict the speciation of Pu(IV), U(IV), and Np(IV) (see Issue 2 above).

The results presented by Moore et al. (1999) clearly support the DOE's (1996b) conclusion, quoted above, that divalent metals initially present in WIPP brines, especially Mg, or divalent metals dissolved from TRU waste, such as Fe, Ni, or Pb, will effectively prevent acetate, citrate, EDTA, and oxalate from increasing the solubilities of Am(III) and Th(IV) significantly and, by analogy, those of Pu(III), Pu(IV), U(IV), and Np(IV). The speciation diagrams in Moore et al. (1999), cited above, clearly show that: (1) Am-citrate, the organic Am complex with the highest concentration in Brine A between a pH of 8.5 and 9.0, has a concentration at least one order of magnitude lower than that of  $\text{Am}(\text{OH})_2^+$ , the dominant inorganic Am complex over this pH range; (2) Am-citrate, the organic Am complex with the highest concentration in ERDA-6 between a pH of 8.5 and 9.5, has a concentration about one order of magnitude lower than that of  $\text{Am}(\text{OH})_2^+$ , the dominant inorganic Am complex over most of this pH range; (3) Th-citrate, the organic Th complex with the highest concentration in Brine A between a pH of 8.5 and 9.0, has a concentration about five orders of magnitude lower than that of  $\text{Th}(\text{OH})_3\text{CO}_3^-$ , the dominant inorganic Th complex over this pH range; (4) Th-citrate, the organic Th complex with the highest concentration in ERDA-6 between a pH of 8.5 and 9.5, has a concentration from five to seven orders of magnitude lower than that of  $\text{Th}(\text{OH})_3\text{CO}_3^-$ , the dominant inorganic Th complex over this pH range. Therefore, Am-citrate increases the total dissolved concentration (solubility) of Am by about 10% in these brines under these conditions, and Th-citrate increases the solubility of Th(IV) by about 0.00001 to 0.001%.

There are at least five reasons why Neill et al. (1998, p. 43) and Oversby (2000, p. 4) were incorrect when they stated:

“In the solubility calculations, the CCA inappropriately discounts the role of organic ligands on plutonium solubility by arguing that EDTA is the strongest complexing agent. But citrate forms very strong complexes with actinides in the +4 [sic] oxidation state and very weak complexes with other cations. Thus, the solubility of a stable plutonium citrate complex in individual waste containers needs to be calculated.”

First, DOE *correctly* discounted the effects of acetate, citrate, EDTA, and oxalate on actinide solubilities (see above).

Second, EDTA *is* the strongest complexing agent of the four organic ligands discussed above (see, for example, US DOE, 1996b, Appendix SOTERM, Table SOTERM-5).

Third, An(IV)-citrate complexes *are* stronger than Mg-citrate complexes, as stated by Oversby (see above). As discussed above,  $\log \beta$  for Th-citrate in 3 m NaCl is 9.55 and  $\log \beta$  for Th-citrate in 5 m NaCl is 10.18 (Choppin et al., 1996, Table 3.B);  $\log \beta$  for Mg-citrate in 3 m NaCl is 2.02 (Bond and Mizera, 1996, third table; US DOE 1996b, Appendix SOTERM, Table SOTERM-6). However, *the Mg-citrate complex is strong enough*, given the relative concentrations of citrate and Mg in WIPP brines, to ensure that citrate increases the solubility of Th by no more than about 0.00001 to 0.001% (see above).

Fourth, “the solubility of a stable plutonium citrate complex” is inappropriate for use in PA. The solubility of Pu is the sum of *all* of the dissolved species of Pu. As shown by Moore et al. (1999), the concentration of Th-citrate and, by analogy, Pu(IV)-citrate is only about 0.001% of the solubility of Pu(IV) in Brine A at a pH of 8.5 to 9, and 0.00001 to 0.001% of the solubility of Pu(IV) in ERDA-6 at a pH of 8.5 to 9.5.

Fifth, it would be indefensible and inappropriate to calculate “the solubility of a stable plutonium citrate complex in individual waste containers” because the parameters required to calculate the concentration of the Pu(IV)-citrate complex, the concentrations of other organic Pu(IV) complexes, the concentrations of inorganic Pu(IV) complexes, and hence the solubility (sum of all the species) of Pu(IV) in individual waste containers are unknown (see Issue 5, Effects of Heterogeneity and Other Waste Characteristics, below). Clearly, one could assume *any* values of the (numerous) parameters required to calculate the speciation and solubility of Pu(IV) “in individual waste containers,” but such assumptions would be indefensible. Instead, the DOE has chosen to establish reasonable ranges and probability distributions of Pu(IV) (and other actinide) solubilities for various combinations of conditions expected in WIPP disposal rooms, and to sample these ranges (and those established for numerous other parameters) for its probabilistic PA calculations. For the actinide solubilities, the conditions considered include the compositions of representative WIPP brines after reaction with MgO backfill, including the concentrations of all major and several minor elements,  $P_{CO_2}$ , pH, and the *average* concentrations of acetate, citrate, EDTA, and oxalate in these brines. To predict the average concentrations of these organics, the DOE used estimates of the quantities of acetate, citrate, EDTA, and oxalate in TRU waste from US DOE (1996a, Table 3-2) and a *conservative* assumption of the quantity of brine that could be present.

#### ISSUE 4: EFFECTS OF MgO

Oversby (2000) criticized predictions of the behavior of the MgO backfill in US DOE (1996b). Oversby (2000, p. 4) stated:

“There are serious unanswered questions about the impact of magnesium oxide backfill on the solubility of the actinides. It is proposed that magnesium oxide will reduce the solubility of the actinides by controlling pH. But, it is not known how long the early reaction product, nesquehonite, will persist. The FMT model calculates that the presence of nesquehonite drives the solubility of the +4 [sic] actinides, such as plutonium, higher than in the no backfill case. This requires further investigation.”

This criticism reiterates previous criticism by the EEG and Oversby. However, most of the MgO-related criticism in Oversby (2000) derives from the apparent behavior of STTP liter-scale container L-28 after MgO was added in February 1997. According to Oversby (2000, p. 17), addition of MgO initially decreased the Pu concentration in this container from 91 to 18 ppm,

“but subsequent samplings showed increasing Pu concentrations, rising to 42 ppm in the next sampling and then to 174 and 198 ppm in the two final reported sampling points. ... Pu(VI) was positively identified in L-26 and L-28.”

Based on these results, Oversby (2000, p. 18, Conclusion 4) concluded:

“The addition of MgO to a test that contained a high concentration of both Pu(VI) and carbon dioxide gas did not produce a long-term decrease in plutonium concentration in the test system, provided a level of Pu(VI) that could be detected by spectroscopy, and appeared to raise questions about the arguments that MgO would lower Pu solubility.”

The DOE asserts that both the occurrence of nesquehonite in the preliminary experiments on the hydration and carbonation of MgO carried out by SNL, and the increased Pu concentrations in STTP liter-scale container L-28 after addition of MgO resulted from conditions that were not representative of those expected in WIPP disposal rooms after filling and sealing. SNL investigators used CO<sub>2</sub> partial pressures on the order of 0.1 to 1 atm, and LANL personnel used CO<sub>2</sub> partial pressures of 60 atm in STTP containers L-28, L-29, and L-30. In the repository, (possible) microbial degradation of cellulose, plastics, and rubbers will produce CO<sub>2</sub> at rates much lower than the rates of CO<sub>2</sub> consumption by Mg(OH)<sub>2</sub>, the hydration product of the MgO backfill. Therefore, the fugacity (essentially, the partial pressure) of CO<sub>2</sub> will not increase to values as high as those used by LANL and SNL.

These differences between the CO<sub>2</sub> partial pressures used in the studies described above and those expected in the repository are significant because the CO<sub>2</sub> fugacity determines which phase or phases result from the carbonation of Mg(OH)<sub>2</sub> (see the phase diagrams in Lippmann, 1973, Fig. 33; and Königsberger et al., 1999, Fig. 4).

Nevertheless, the DOE has initiated a study of MgO carbonation at much lower CO<sub>2</sub> partial pressures at SNL in Carlsbad. This study is simulating conditions expected in WIPP disposal rooms more closely than the previous study at SNL and the STTP, and will reduce or eliminate the tendency to nucleate and grow phases such as nesquehonite.

#### ISSUE 5: EFFECTS OF HETEROGENEITY AND OTHER WASTE CHARACTERISTICS

Oversby (2000) criticized the DOE's assertion that brines present in WIPP disposal rooms after filling and sealing will be well mixed with respect to the concentrations of organic ligands such as citrate (see US DOE, 1996b, Appendix SOTERM). For example, Oversby (2000, p. 5) stated:

"In evaluation of the effect of organic ligands on the mobilization of actinides, EPA considers only the case of homogeneous equilibrium [sic], in which the entire actinide inventory is well-mixed with a very large volume of brine that inundates the repository. This is an unrealistic and non-conservative model for evaluation of the effect of organics."

(Note that Oversby uses the terms "homogeneous equilibrium" and "heterogeneous equilibrium" differently than defined by geochemists; in this response, we assume "homogeneous equilibrium" and "heterogeneous equilibrium" in her report actually mean "homogeneous concentrations" and "heterogeneous concentrations" of chemical constituents such as organic ligands, or "homogeneous distributions" and "heterogeneous distributions" of these constituents.) Oversby (2000) repeated this criticism several times throughout her report (see, for example, pp. 8, 10, and 24). This report reiterated previous criticism by Neill (1997), Oversby (1997), and Neill et al. (1998). For example, Neill (1997, p. 3) stated:

"Moreover, the DOE and EPA have each assumed that the actinides and the brine would be evenly distributed and well mixed throughout the repository. The problem with this assumption is that the plutonium and the citrate are located within the same drums. These waste forms result from chemical separation of Pu and do not fit the classic description by DOE of TRU waste as contaminated tools, rags, gloves, booties, etc. The solubility of the plutonium for these waste forms must also be calculated as a very stable Pu citrate complex where other cations in the brine diffusing into the drum cannot compete effectively with the complexed actinides (IV)."

Oversby (1997, p. 8 and Appendix C, p. 1) stated:

“To model the behavior of Pu with citrate, we must also consider heterogeneous equilibria [sic] for organic complexation with the actinides. The main difficulty arises because the Pu in the waste is probably located in the same drums as the citrate, which is the dominant organic ligand. This is because these wastes arise from chemical separation of Pu and are not the type of waste described in the general description of TRU waste as contaminated equipment, clothing, etc. To get an accurate estimate of the effects of organic ligands on Pu solubility, one must calculate the concentration of Pu as citrate complex inside a waste drum that has been breached, but can still provide a hindrance to mixing of the brine inside the drum with a larger pool of brine outside the drum. This will give a high concentration of Pu in solution as the citrate complex.”

Neill et al. (1998) repeated this statement (see Appendix 8.4a, p. 8; Appendix 8.4, (sub)Appendix C, p. 1).

The DOE has already provided a detailed response justifying the assumption that brines will be well mixed for calculating the solubilities of actinides (see US DOE, 1997). We quote that response here:

“The assumption that brine within the waste is well mixed may not be realistic for conditions in which very little brine is present in the repository. However, conditions in which very little brine is present in the repository do not result in releases of contaminated brine from the controlled area because brine mobility is greatly reduced at low saturations. As discussed below, releases of radionuclides in brine require relatively large quantities of brine in the repository, and sufficiently long travel paths and residence times for this brine to be in the waste, that it is reasonable to assume that complete mixing occurs and that the assumption of equilibrium solubilities will result in the largest reasonable aqueous concentrations of actinides.

“For undisturbed performance, brine enters the entire repository by drainage from the DRZ and by long-term inflow from anhydrite interbeds, and by necessity must flow through a large volume of waste before reaching a potential exit point at the down-dip (southern) portion of the disposal region. No plausible mechanism exists by which large volumes of brine could enter and exit an undisturbed repository without long travel paths and residence times in the waste.

“For disturbed performance, the volume of brine that must be present in a single panel before a brine release occurs can be estimated from examination of performance assessment results. For long-term brine flow up an intrusion borehole to occur, the entire intruded panel must be filled, or nearly filled, with brine, starting from the bottom up. This volume of brine can be estimated by considering a panel volume of

approximately 46,000 cubic meters (from Figures 6-14 and 6-15 of the CCA) and a representative final porosity [as implemented in BRAGFLO] of approximately 15% (from Figure 7.1-18 of the Analysis Package for the Salado Flow Calculations, Task 1 of the Performance Assessment Analysis Supporting the Compliance Certification Application [previously transmitted to the EPA), yielding a panel pore volume of approximately 6900 cubic meters. Neglecting the extremely small quantity of liquid present in the waste initially and the much larger quantities of brine that may flow out into marker beds and be consumed by corrosion, a minimum of 6900 cubic meters of brine therefore must flow through the waste before flowing up an intrusion borehole. Nearly all pore surfaces within the waste will have been contacted by brine before flow up the borehole begins.

“The panel need not be completely filled for direct brine releases to occur at the surface during drilling, but the volume of brine required within the panel is still large. As shown in Appendix SA, Figure SA-17, no direct brine releases occur until brine saturation exceeds approximately 20%, and the largest volumes of direct brine release occur at brine saturations between approximately 50% and 80%. As discussed above, a single panel may have a pore volume of approximately 6900 cubic meters, and a brine saturation of 50% therefore requires the inflow of a minimum of approximately 3450 cubic meters of brine into a single panel, again neglecting brine outflow and consumption of brine during corrosion. For intrusions into a previously unintruded repository, brine will have entered the waste by drainage from the DRZ and by long-term flow from anhydrite interbeds. In either case, brine must flow from the floor and ceiling of the disposal region through the waste and backfill before it reaches the location of the future intrusion borehole. Before brine participates in a direct release, it therefore must have contacted a large volume of waste for a relatively long period of time, and therefore achieved chemical conditions representative of a large and well-mixed region of waste.

“Intrusions into a previously intruded repository are less likely to result in direct brine releases than those into an undisturbed repository, because pressures are generally lower following the first intrusion. However, in those realizations in which pressures do rise sufficiently after intrusion to allow direct brine releases, the previous borehole may provide an additional pathway for brine to flow into the repository. In this case, the brine entering from the previous borehole will flow outward radially into the repository, mixing with brine already present in the waste. The minimum distance any portion of this brine must travel through the waste to participate in a direct brine release from a later intrusion is the distance between the two intrusion holes. Other brine present near the second borehole at the time of intrusion will have traveled to that location by longer and more complex flow paths. It is reasonable, therefore, to

assume that flow will have resulted in a brine composition representative of a large volume of waste.”

The DOE asserts that brines will be well mixed because: (1) the flow rates of brines through WIPP disposal rooms are very low under both disturbed and undisturbed conditions, (2) the surface area of solids that brines will contact as they flow slowly through voids within the waste are very large; (3) the (panel-scale) volumes of brine into which brines from (possibly atypical) microenvironments will be mixed before they flow out of the repository through a marker bed or up a borehole to the Culebra or the surface are very large.

The statements by Oversby (2000) that citrate is present along with Pu in many of the waste containers to be emplaced in the WIPP are undoubtedly true, and concentrations of citrate in brines in and around many of these containers could be higher than the estimated average citrate concentration in WIPP brines (see US DOE, 1996b, Appendix SOTERM, Table SOTERM-4). However, because brines will be well mixed with respect to constituents such as organic ligands prior to release from WIPP disposal rooms, the use of an estimated, average citrate concentration is valid. Furthermore, prior to mixing, for every container with a (possibly) higher-than-average citrate concentration and (possibly) higher-than-predicted actinide solubilities, there would be a comparable container or containers with lower-than-average citrate concentration and lower-than-predicted actinide solubilities.

Moreover, it would be indefensible and inappropriate to calculate for PA

“the solubility of the plutonium for these [citrate-bearing] waste forms ... as a very stable Pu citrate complex where other cations in the brine diffusing into the drum cannot compete effectively with the complexed actinides,”

as requested by Neill (1997, p. 3). It would also be indefensible and inappropriate to calculate

“the solubility of a stable plutonium citrate complex in individual waste containers,”

as requested by Neill et al. (1998, p. 43) and Oversby (2000, p. 4); or

“... the concentration of Pu as citrate complex inside a waste drum that has been breached, but can still provide a hindrance to mixing of the brine inside the drum with a larger pool of brine outside the drum,”

as suggested by Oversby (1997, p. 8 and Appendix C, p. 1). Finally, it would be indefensible and inappropriate to use

“... bounding calculations ... [that] consider the type of waste that produces the largest amount of Pu and citrate together in a single waste container,”

as requested by (Oversby, 2000, p. 24). These calculations would be indefensible because it would be impossible to obtain sufficient information for such calculations (the actual quantities of citrate, and other organics, in individual containers; the extent to which corrosion of individual containers, and degradation of their plastic liners and any plastic bags within the containers, exposes the contents to the repository environment; the transport rates of brine and its constituents, especially Mg, into and out of partially corroded containers and their partially degraded plastic liners and bags; the effects of interactions with the contents of adjacent, subjacent, and superjacent containers, etc.) Clearly, any such calculations based on arbitrarily specified values of the parameters described above would not be defensible. Finally, the

“... bounding calculations ... [that] consider the type of waste that produces the largest amount of Pu and citrate together in a single waste container”

(Oversby, 2000, p. 24) would be inappropriate for the probabilistic PA methodology used by the DOE for the CCA (US DOE, 1996b).

Oversby (2000, pp. 19-23) devotes considerable attention to the results of Haschke et al. (2000), who described the occurrence of excess oxygen in the Pu(IV) oxide  $\text{PuO}_2$ . This results in nonstoichiometric  $\text{PuO}_{2+x}$ , in which  $x \leq 0.27$ . The occurrence of  $\text{PuO}_{2+x}$  should not be surprising in view of the extensive literature on  $\text{UO}_{2+x}$ , the fact that  $\text{UO}_{2+x}$  and  $\text{PuO}_{2+x}$  have the same crystal structure and form a continuous solid solution, and the applicability of the oxidation-state analogy for predicting the behavior of actinide elements in the same oxidation state (see Issue 2, Use of Oxidation-State Analogs, above).

The DOE asserts that the occurrence of  $\text{PuO}_{2+x}$  will not significantly affect its prediction of actinide oxidation states in WIPP disposal rooms after filling and sealing (see Issue 1, Predictions of Actinide Oxidation States, above). The DOE has never stated that the validity of these predictions depends on the emplacement of metallic Pu, Pu(III), or Pu(IV) in the repository. Instead, these predictions are based on experimental work such as studies of reduction of Pu(V) and Pu(VI) by metallic Fe, which will be present in large quantities as steel waste containers and in the waste itself, or by Fe corrosion products (see Granbow et al., 1996; Xia et al., 1996; Slater et al., 1997; Felmy et al., 2000; Reed et al., 2000). Microbial activity could also create reducing conditions in the WIPP. Of course, oxidizing species, such as  $\text{ClO}^-$  and  $\text{O}_2$ , created by  $\alpha$  radiolysis of  $\text{H}_2\text{O}$  in WIPP brines, could continuously oxidize Pu(III) or Pu(IV) to Pu(V) and/or Pu(VI). However, metallic Fe, Fe(II)- or Fe(II, III)-bearing corrosion products, dissolved Fe(II) species, metallic Al, and/or microbial activity would continuously reduce Pu(V) and Pu(VI) to Pu(III) or Pu(IV). Because the quantities of these reductants are so large relative to that of Pu (see Issue 1, Predictions of Actinide



Oxidation States), it probably wouldn't make much difference if *all* of the Pu were emplaced as Pu(VI).

Furthermore, any formation of  $\text{PuO}_{2+x}$  *after* filling and sealing WIPP disposal rooms would probably not affect the DOE's predictions of actinide oxidation states *at all*. This is because the incremental consumption of oxidants required to form  $\text{PuO}_{2+x}$  instead of  $\text{PuO}_2$  would reduce the extent to which other oxidation reactions would occur, and thus would not increase the overall quantity of reductants necessary to maintain Pu in its reduced oxidation states.

## ISSUE 6: USE OF FMT

Any groundwaters present in WIPP disposal rooms after filling and sealing will be high-ionic-strength brines; values of the ionic strength (I) calculated for typical WIPP brines range as high as 8.8 m (Du and Choppin, 1999). Therefore, the DOE had to consider approaches such as Hydration Theory, Specific Ion Interaction Theory, (SIT), and the Pitzer model to calculate activity coefficients for dissolved Pu, Am, U, Th, and Np species, and to predict the solubilities of these actinides in WIPP brines.

For solutions with ionic strengths less than about 1 M, speciation and solubility codes such as EQ3NR and FMT use the ion-association model to predict the speciation of solutes. This model explicitly recognizes the reaction of oppositely charged species to form complexes, and applies mass-action, mass-balance, and charge-balance equations to calculate the relative activities of the free (dissociated) ions, and complexes. Typically, speciation and solubility codes use the Debye-Hückel equation, or an extended Debye-Hückel equation such as the B-dot Equation of Helgeson (1969), to determine activity coefficients for solute species.

The ion-association model, in conjunction with extended Debye-Hückel equations such as the B-dot Equation, has proven very successful in modeling dilute aqueous solutions of geochemical interest. Furthermore, sufficient thermodynamic data now exist for modeling the behavior of several important radionuclides, including Pu, Am, U, Th, and Np, in these solutions. In solutions with ionic strengths above 1 M, however, these equations fail to predict activity coefficients accurately, and the ion-association model breaks down. These failures are especially apparent in the case of highly concentrated solutions such as WIPP brines.

For solutions with ionic strengths up to several molar, speciation and solubility codes require a mixed-electrolyte model for the speciation of solutes. Mixed-electrolyte models generally include fewer complexes than ion-association models, and treat activity coefficients of dissolved species more empirically than ion-association models. However, these models have the advantage that empirically fitted parameters obtained from complexation experiments, solubility experiments, or isopiestic measurements in

relatively simple solutions can be used to predict activity coefficients in more complex solutions such as WIPP brines.

Initially, the DOE considered hydration theory (Stokes and Robinson, 1948; Robinson and Stokes, 1965) because it appeared that this approach could be developed using physically meaningful parameters to calculate activity coefficients. However, these parameters began to look more and more empirical, and hence more and more like the Pitzer ion-interaction parameters, as work on this approach proceeded. A large database of Pitzer parameters already existed for the important dissolved species in brines, including  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$  (the so-called Harvie-Møller-Weare or HMW database of Harvie, Møller, and Weare, 1984). Furthermore, Eugster, Harvie, and Weare (1980), Harvie and Weare (1980), Harvie et al. (1980), Harvie, Møller, and Weare (1984), and Pabalan and Pitzer (1987) had already validated the mixed-electrolyte model, the Pitzer equations, and various ion-interaction parameters for brines and evaporite minerals. Unfortunately, no such database existed for hydration theory. Therefore, the DOE decided not to continue developing hydration theory.

Later, the DOE considered SIT because it is simpler than the Pitzer approach. However, it concluded that SIT would probably not work at ionic strengths higher than about 3 molar, and would certainly not work at ionic strengths as high as those of WIPP brines. Furthermore, there was no SIT database comparable to that available for the Pitzer for the important dissolved species in brines. Therefore, for FMT, the DOE chose the equations of Pitzer (1973, 1975, 1977, 1979, 1991) and Pitzer and Kim (1974) to calculate activity coefficients as a function of the composition of the solution. (Personnel at Lawrence Livermore National Laboratory and the US Geological Survey had also decided to use the Pitzer approach in EQ3/6 and PHREEQE, respectively.)

For the CCA PA, the DOE used the speciation and solubility portions of FMT, the HMW database (Harvie, Møller, and Weare, 1984), experimentally obtained Pitzer ion-interaction parameters for Am(III) and Th(IV), ion-interaction parameters obtained from literature data for Np(V), and the oxidation-state analogy to predict the solubilities of Pu, Am, U, Th, and Np in WIPP brines.

Oversby (2000, p. 4) criticized the use of FMT for the CCA PA. This report reiterates previous criticism by Neill (1997) and Neill et al. (1998, pp. 49-51). However, as US DOE (1998) pointed out:

“The FMT code has undergone extensive validation. This included a comparison of problem solutions by FMT with the solutions to the same problem as provided by PHRQPITZ and EQ3/6. The code PHRQPITZ was utilized instead of PHREEQE (the use of PHREEQE was suggested by EEG) since PHRQPITZ includes the Pitzer formalism (which is used by FMT) whereas PHREEQE does not. These validation efforts are extensively documented in FMT Version 2.0 Validation Document Version 1.0. This validation document was placed in the Sandia WIPP Central Files under WPO# 28121 on 11/17/95.”

Babb (1995) carried out and documented the validation of FMT for the WIPP Project.

Oversby (2000, p. 10) stated:

“Second, starting with a peer-reviewed database for plutonium and uranium, adjust solution species activity as a function of ionic strength using Specific Ion Interaction Theory, rather than try to determine Pitzer parameters, which can have very large uncertainties for highly charged species, for use in the FMT code.”

Oversby (2000, p. 31) reiterates these comments. However, as pointed out above, SIT probably would not work at ionic strengths higher than about 3 molar, and certainly would not work at ionic strengths as high as those of WIPP brines. Choppin and Du (1992, p. 104) identified this problem in their study of complexation of  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  by  $\text{Cl}^-$  and  $\text{NO}_3^-$  in 3.5, 6.5, 10.0 and 14.1 molal  $\text{NaClO}_4$  solutions:

*“As anticipated [our italics], the experimental values of  $\log \beta$  are significantly smaller than those predicted by SIT for  $I > 3$  m. However, for the systems studied, in the variation in  $\log \beta$  from  $I = 3$  m to  $I = 15$  m, a fairly linear correlation with  $I$  is observed. This suggests that an empirical relation similar to SIT but with different values of  $\Delta\epsilon$  may be applicable over this range of ionic strengths.”*

Rather than develop, parameterize, and validate a novel “empirical relation similar to SIT,” the DOE decided to obtain Pitzer ion-interaction parameters for Am(III), Th(IV), and Np(V). This decision was, in all likelihood, the only viable decision, given: (1) the difficulties encountered with hydration theory and SIT (see above); (2) the existence of the HMW database for  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$  (Harvie, Møller, and Weare, 1984); (3) the validation of the Pitzer ion-association model and this database for brines and evaporite minerals by Eugster, Harvie, and Weare (1980), Harvie and Weare (1980), Harvie et al. (1980), Harvie, Møller, and Weare (1984), and Pabalan and Pitzer (1987); (4) the previous, successful incorporation and validation of the Pitzer activity-coefficient option in EQ3/6 (see below) and PHREEQE; (5) the subsequent, successful incorporation and validation of the Pitzer equations in FMT (Babb, 1995).

Eventually, the DOE plans to replace FMT with the EQ3/6 software package (see Daveler and Wolery, 1992; Wolery, 1992a, 1992b; Wolery and Daveler, 1992) because: (1) the EQ3/6 software package contains a reaction-path code (EQ6), but FMT does not; (2) additional development of EQ3/6, funded by the US DOE’s Yucca Mountain Project, is currently under way, but there is no additional development of FMT under way or even planned; (3) EQ3/6 is easier to use than FMT; (4) EQ3/6 is an internationally recognized software package, but only the WIPP Project uses FMT. Jackson and Wolery (1985) and Jackson (1988) added the Pitzer activity-coefficient option and the HMW database to the EQ3/6 software package and validated EQ3/6 with the Pitzer activity-coefficient option. Therefore, EQ3/6 is already capable of predicting reactions among evaporite minerals and WIPP brines. SNL investigators have already made some minor coding changes in

EQ3/6, and have added the Pitzer ion-interaction parameters for Am(III), Th(IV), and Np(V) developed by the WIPP Project to the EQ3/6 thermodynamic database. SNL plans to qualify EQ3/6 for actinide speciation and solubility calculations according to the SNL/WIPP quality assurance (QA) procedures for software. This will consist mainly of verification of EQ3/6 predictions of actinide speciation and solubilities with the Pitzer option. However, even after qualification of EQ3/6 according to SNL/WIPP software QA procedures, the EPA must approve the use of EQ3/6 for any actinide speciation and solubility calculations used for compliance-related activities.

## ISSUE 7: UNCERTAINTY RANGES

Oversby (2000) criticized the DOE's (1996b) determination of a range of uncertainty for its predictions of Am(III), Th(IV), and Np(V) solubilities calculated with the speciation and solubility code FMT. For example, Oversby (2000, p. 4, Item 3) stated:

“EEG agrees with EPA's documentation of the shortcomings of the solubility ranges advanced by DOE. However, EPA has accepted the ranges as adequate based on a weak argument. EEG recommends that the uncertainty range needs to be determined with the appropriate plutonium data.”

Oversby (2000) reiterated this criticism several times throughout her report (see, for example, pp. 9, 11, and 29-31). This report reiterated previous criticism by Neill (1997), Oversby (1997), and Neill et al. (1998).

The DOE continues to assert that its range of uncertainty for the solubilities of Am(III), Th(IV), and Np(V) is valid (see US DOE, 1996b, Appendix SOTERM, pp. SOTERM-28 to SOTERM-33, and Figure SOTERM-6 and SOTERM-7). We reiterate that discussion here:

“Uncertainties in the solubility data and uncertainty in the NONLIN least squares refinement result in uncertainty in the model predictions. This is also evident when the data of Runde and Kim (1994) are compared with the FMT results. A measure of uncertainty was obtained by Bynum (1996) by examining the difference between the modeled solubilities for each oxidation state analog and comparing these to the experimental data used to generate the respective Pitzer parameters. The results of Bynum's analysis is [sic] given in Figure SOTERM-6. [We have not reproduced this figure or the following figure in this response.] These results were combined as shown in Figure SOTERM-7 for entry into the parameter database as a cumulative distribution. This distribution was sampled in performance assessment as discussed in Section SOTERM.7.1.3. Note that the median of this distribution is -0.09 and not

zero, indicating that slightly more experimental values were below the model prediction than above. Table 6-11 in Chapter 6.0 of this application reports the median values, which are  $10^{-9}$  [sic] (0.8128) times the model values shown in Table SOTERM-2, for those actinides assigned a distribution of solubilities rather than a single value.”

## REFERENCES

- Babb, S.C. 1995. “WIPP PA Validation Document for FMT (Version 2.0), Document Version 1.00.” Unpublished report, WPO #21821. Carlsbad, NM: Sandia National Laboratories. WPO #28121.
- Bond, A.H., and J. Mizera. 1996. Unpublished letter from A.H. Bond and J. Mizera to G.R. Choppin, March 15, 1996. Tallahassee, FL: Florida State University.
- Brush, L.H. 2000a. “Relevance of WIPP STTP Results to the WIPP.” Unpublished presentation to the DOE-EPA Information Exchange Meeting, April 12, 2000, Washington, DC. Carlsbad, NM: Sandia National Laboratories.
- Brush, L.H. 2000b. “Use of WIPP STTP Results in the WIPP CCA PA.” Unpublished presentation to the DOE-EPA Information Exchange Meeting, April 12, 2000, Washington, DC. Carlsbad, NM: Sandia National Laboratories.
- Brush, L.H., and R.C. Moore. 2000a. “Iron Corrosion.” Unpublished presentation to the DOE-EPA Information Exchange Meeting, June 29, 2000, Carlsbad, NM. Carlsbad, NM: Sandia National Laboratories.
- Brush, L.H., and R.C. Moore. 2000b. “Solidified Mass.” Unpublished presentation to the DOE-EPA Information Exchange Meeting, June 29, 2000, Carlsbad, NM. Carlsbad, NM: Sandia National Laboratories.
- Brush, L.H., and Y. Wang. 2000. “Bidegradation.” Unpublished presentation to the DOE-EPA Information Exchange Meeting, June 29, 2000, Carlsbad, NM. Carlsbad, NM: Sandia National Laboratories.
- Bynum, R.V. 1996. “Update of Uncertainty Range and Distribution for Actinide Solubilities to Be Used in CCA NUTS Calculation.” Unpublished memorandum to M.S. Tierney and C.T. Stockman. Carlsbad, NM: Sandia National Laboratories. WPO #38268.
- Choppin, G.R. 1999. “Utility of Oxidation State Analogs in the Study of Plutonium Behavior,” *Radiochimica Acta*. Vol. 85, 89-95.

- Choppin, G.R., and M. Du. 1992. "f-Element Complexation in Brine Solutions," *Radiochimica Acta*. Vol. 58/59, 101-104. WPO #44147.
- Choppin, G.R., H.N. Erten, and Y.-X. Xia. 1996. "Variation of Stability Constants of Thorium Citrate Complexes with Ionic Strength," *Radiochimica Acta*. Vol. 74, 123-127. WPO #44148.
- Daveler, S.A., and T.J. Wolery. 1992. *EQPT, A Data File Preprocessor for the EQ3/6 Software Package: User's Guide and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT II. Livermore, CA: Lawrence Livermore National Laboratory. WPO #41540.
- Du, M., and G.R. Choppin. 1999. "Correlation of Equilibrium Constants with Ionic Strength by SIT, Pitzer and Parabolic Models." In D.T. Reed, S.B. Clark, and L. Rao, Eds., *Actinide Speciation in High Ionic Strength Media: Experimental and Modeling Approaches to Predicting Actinide Speciation and Migration in the Subsurface*, 125-139. New York, NY: Kluwer Academic/Plenum Publishers.
- Eugster, H.P., C.E. Harvie, and J.H. Weare. 1980. "Mineral Equilibria in a Six-Component Seawater System, Na-K-Mg-Ca-SO<sub>4</sub>-H<sub>2</sub>O, at 25°C," *Geochimica Cosmochimica Acta*. Vol. 44, 1335-1347.
- Felmy, A.R., R.C. Moore, Z. Wang, D. Rai, and D.A. Dixon. 2000. "Understanding Actinide Oxidation/Reduction Reactions: Relevance to the WIPP Repository." Presentation to the American Chemical Society National Meeting, March 27-31, 2000, San Francisco, CA. SAND99-2805A. Albuquerque, NM: Sandia National Laboratories.
- Granbow, B., E. Smailos, H. Geckeis, R. Müller, and H. Hentschel. 1996. "Sorption and Reduction of U(VI) on Iron Corrosion Products under Reducing Saline Conditions," *Radiochimica Acta*. Vol. 74, 149-154.
- Harvie, C.E., N Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H<sub>2</sub>-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 Strengths at 25°C," *Geochimica Cosmochimica Acta*. Vol. 48, 723-751.
- Harvie, C.E., and J.H. Weare. 1980. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O System from Zero to High Concentrations at 25°C," *Geochimica Cosmochimica Acta*. Vol. 44, 981-997.
- Harvie, C.E., J.H. Weare, L.A. Hardie, and H.P. Eugster. 1980. "Evaporation of Seawater: Calculated Mineral Sequences," *Science*. Vol. 208, 498-500. WPO #41802.

- Haschke, J., T.H. Allen, and L.A. Morales. 2000. "Reaction of Plutonium Dioxide with Water: Formation and Properties of  $\text{PuO}_{2+x}$ ," *Science*. Vol. 287, 285-287.
- Helgeson, H.C. 1969. "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures," *American Journal of Science*. Vol. 267, 729-804. WPO #49091.
- Helton, J.C. J.E. Bean, J.W. Berglund, F.J. Davis, K. Economy, J.W. Garner, J.D. Johnson, R.J. MacKinnon, J. Miller, D.G. O'Brien, J.L. Ramsey, J.D. Schreiber, A. Shinta, L.N. Smith, D.M. Stoelzel, C. Stockman, and P. Vaughn. 1998. *Uncertainty and Sensitivity Analysis Results Obtained in the 1996 Performance Assessment for the Waste Isolation Pilot Plant*. SAND98-0365. Albuquerque, NM: Sandia National Laboratories. SNL WIPP Library.
- Jackson, K.J. 1988. *Verification and Validation Studies of the Addition of Pitzer's Equations to the EQ3/6 Brine Model*. UCRL 53841. Livermore, CA: Lawrence Livermore National Laboratory. WPO #43106.
- Jackson, K.J., and T.J. Wolery. 1985. "Extension of the EQ3/6 Computer Codes to Geochemical Modeling of Brines." *In Scientific Basis for Nuclear Waste Management VIII, Symposium Held November 26-29, 1984, Boston, Massachusetts, U.S.A. Materials Research Society Symposia Proceedings*. Eds. C. M. Jantzen, J.A. Stone, and R.C. Ewing. Pittsburgh, PA: Materials Research Society. Vol. 44, 507-514. SNL NWMP Library.
- Kelm, M., I. Pashalidis, and J.I. Kim. 1999. "Spectroscopic Investigation on the Formation of Hypochlorite by Alpha Radiolysis in Concentrated NaCl Solutions," *Applied Radiation and Isotopes*. Vol. 51, 637-642.
- Kim, J.I., C. Lierse, K. Büppelmann, and S. Magirius. 1987. "Radiolytically Induced Oxidation Reactions of Actinide Ions in Concentrated Salt Solutions," *Scientific Basis for Nuclear Waste Management X, Symposium Held December 1-4, 1986, Boston, Massachusetts, U.S.A. Materials Research Society Symposia Proceedings*. Eds. J.K. Bates and W.B. Seefeldt. Pittsburgh, PA: Materials Research Society. Vol. 44, 507-514.
- Königsberger, E., L.-C. Königsberger, and H. Gamsiöger. 1999. "Low-Temperature Thermodynamic Model for the System  $\text{Na}_2\text{CO}_3\text{-MgCO}_3\text{-CaCO}_3\text{-H}_2\text{O}$ ," *Geochimica Cosmochimica Acta*. Vol. 63, No. 19/20, 3105-3119.
- Lippmann, F. 1973. *Sedimentary Carbonate Minerals*. New York, NY: Springer-Verlag. SNL Tech Library.

- Los Alamos National Laboratory. 2000. "Los Alamos National Laboratory STTP Data Historical Compilation, Vol. I: Actinides w/pcH, Elemental Analyses, Radiochemistry and pcH, TIC/TOC, Particle Concentration." Unpublished report to the US Department of Energy Carlsbad Area Office, September 2000. Los Alamos, NM: Los Alamos National Laboratory.
- Morgenstern, A., and G.R. Choppin. 1999. "Kinetics of the Reduction of  $\text{Pu(V)O}_2^+$  by Hydrogen Peroxide," *Radiochimica Acta*. Vol. 86, 109-113.
- Moore, R.C. 1999. "Actinide Source Term Overview and Status." Unpublished presentation to the Environmental Evaluation Group, October 28, 1999, Albuquerque, NM: Carlsbad, NM: Sandia National Laboratories.
- Moore, R.C., H.W. Papenguth, E.J. Nowak, L.H. Brush, and S.J. Free. 1999. "Actinide Source Term: Solubility Model." Unpublished presentation to the National Academy of Sciences Committee on the WIPP, July 26, 1999, Albuquerque, NM. Carlsbad, NM: Sandia National Laboratories.
- Neill, R.H. 1997. Letter from R. Neill, EEG, to F. Marcinowski, EPA, December 31, 1997. In R.H. Neill, L. Chaturvedi, D.F. Rucker, M.K. Silva, B.A. Walker, J.K. Channell, and T.M. Clemo, *Evaluation of the WIPP Project's Compliance with the EPA Radiation Protection Standards for Disposal of Transuranic Waste*, Appendix 8.3. EEG-68. Albuquerque, NM: Environmental Evaluation Group. SNL WIPP Library.
- Neill, R.H., L. Chaturvedi, D.F. Rucker, M.K. Silva, B.A. Walker, J.K. Channell, and T.M. Clemo. 1998. *Evaluation of the WIPP Project's Compliance with the EPA Radiation Protection Standards for Disposal of Transuranic Waste*. EEG-68. Albuquerque, NM: Environmental Evaluation Group. SNL WIPP Library.
- Oversby, V.M. 1997. "The Solubility of Plutonium under Conditions Expected in the WIPP Repository." Report to EEG, October 31, 1997. In R.H. Neill, L. Chaturvedi, D.F. Rucker, M.K. Silva, B.A. Walker, J.K. Channell, and T.M. Clemo, *Evaluation of the WIPP Project's Compliance with the EPA Radiation Protection Standards for Disposal of Transuranic Waste*, Appendix 8.4a. EEG-68. Albuquerque, NM: Environmental Evaluation Group. SNL WIPP Library.
- Oversby, V.M. 2000. *Plutonium Chemistry under Conditions Relevant for WIPP Performance Assessment: Review of Experimental Results and Recommendations for Future Work*. EEG-77. Albuquerque, NM: Environmental Evaluation Group. SNL WIPP Library.



- Pabalan, R.T., and K.S. Pitzer. 1987. "Thermodynamics of Concentrated Electrolyte Mixtures and the Prediction of Mineral Solubilities to High Temperatures for Mixtures in the System Na-K-Mg-Cl-SO<sub>4</sub>-OH-H<sub>2</sub>O," *Geochimica Cosmochimica Acta*. Vol. 51, 2429-2443.
- Pitzer, K.S. 1973. "Thermodynamics of Electrolytes I. Theoretical Basis and General Equations," *Journal of Physical Chemistry*. Vol. 77, 268-277. WPO #42315.
- Pitzer, K.S. 1975. "Thermodynamics of Electrolytes, V. Effects of Higher-Order Electrostatic Terms," *Journal of Solution Chemistry*. Vol. 4, 249-265. ERMS #500454.
- Pitzer, K.S. 1977. "Electrolyte Theory - Improvements since Debye and Hückel," *Accounts of Chemical Research*. Vol. 10, 317-377.
- Pitzer, K.S. 1979. "Theory: Ion Interaction Approach." In *Activity Coefficients in Electrolyte Solutions*, R. M. Pytkowicz, Ed. Boca Raton, FL: CRC Press, 157-208. WPO #43909.
- Pitzer, K.S. 1991. "Ion Interaction Approach: Theory and Data Correlation." In *Activity Coefficients in Electrolyte Solutions, 2nd Ed.*, K.S. Pitzer, Ed. Boca Raton, FL: CRC Press, 75-153. WPO #40213.
- Pitzer, K.S., and J.J. Kim. 1974. "Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes," *Journal of the American Chemical Society*. Vol. 96, 5701-5707. ERMS #504521.
- Rai, D., L. Rao, H.T. Weger, A.R. Felmy, and G.R. Choppin. 1998. *Thermodynamic Data for Predicting Concentrations of Th(IV), U(IV), Np(IV), and Pu(IV) in Geologic Environments*. PNWD-2428, Rev. 1. Richland, WA: Pacific Northwest National Laboratory.
- Reed, D.T., S.B. Aase, R.C. Moore, and A.J. Kropf. 2000. "Reduction of Actinide(VI) Species in the Waste Isolation Pilot Plant." Unpublished report. Carlsbad, NM: Sandia National Laboratories.
- Robinson, R.A., and R.H. Stokes. 1965. *Electrolyte Solutions, 2nd Ed.* London, UK: Butterworth's. SNL Tech Library.
- Runde, W., and J.L. Kim. 1994. *Untersuchungen der Übertragbarkeit von Labordaten natürliche Verhältnisse: Chemisches Verhalten von drei- und fünfwertigem Americium in Salinen NaCl Lösungen*. RCM-01094. München, FRG: Institut für Radiochemie Technische Universität München.

- Slater, S.A., D.B. Chamberlain, S.A. Aase, B.D. Babcock, C. Conner, J. Sedlet, and G.F. Vandegrift. 1997. "Optimization of Magnetite Carrier Precipitation Process for Plutonium Waste Reduction," *Separation Science and Technology*. Vol. 32, 127-147.
- Stokes, R.H., and R.A. Robinson. 1948. "Ionic Hydration and Activity in Electrolyte Solutions," *Journal of the American Chemical Society*. Vol. 70, 1870-1878.
- US DOE. 1996a. *Transuranic Waste Baseline Inventory Report, Rev. 3*. DOE/CAO-95-1121. Carlsbad, NM: US Department of Energy Carlsbad Area Office. SNL WIPP Library.
- US DOE. 1996b. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Vol. 1-21*. Carlsbad, NM: US Department of Energy Carlsbad Area Office. SNL WIPP Library.
- US DOE. 1997. Unpublished letter from G. Dials to R. Trovato, May 2, 1997. Carlsbad, NM: US Department of Energy Carlsbad Area Office.
- US DOE. 1998. Unpublished letter from G. Dials to M. Kruger, February 24, 1998. Carlsbad, NM: US Department of Energy Carlsbad Area Office.
- Villarreal, B., A. Trujillo, C. Scherer, and A. Morzinski. 2000. "A Study of Pyrochemical Salt Tests and Results Featuring L25, 26, 27, and 28." Unpublished report to the US Department of Energy Carlsbad Area Office, January 2000. Los Alamos, NM: Los Alamos National Laboratory.
- Wolery, T.J. 1992a. *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0)*. UCRL-MA-110662 PT I. Livermore, CA: Lawrence Livermore National Laboratory. WPO #41375.
- Wolery, T.J. 1992b. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT III. Livermore, CA: Lawrence Livermore National Laboratory. WPO #41376.
- Wolery, T.J., and S.A. Daveler. 1992. *EQ6, A Computer Program for Reaction-Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT IV. Livermore, CA: Lawrence Livermore National Laboratory. WPO #41379.

Xia, Y., L. Rao, A.R. Felmy, and D. Rai. 1996. "Determining the Distribution of Pu, Np, and U Oxidation States in Dilute NaCl and Synthetic Brine Solutions." Presentation to the American Chemical Society National Meeting, August 26-28, 1996, Orlando, FL. Washington, DC: American Chemical Society.