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Sandia National Laboratories  
Waste Isolation Pilot Plant

# Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Analysis Plan AP-098

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Author:	<u>L.H. Brush</u> Laurence H. (Larry) Brush, 6822	<u>3/19/03</u> Date
Author:	<u>Yongliang Xiong</u> Yongliang Xiong, 6822	<u>3/19/03</u> Date
Technical Reviewer:	<u>Yifeng Wang</u> Yifeng Wang, 6822	<u>3/20/03</u> Date
QA Reviewer:	<u>Mario J. Chavez</u> Mario J. Chavez, 6820	<u>3/20/03</u> Date
Management Reviewer:	<u>David S. Kessel</u> David S. Kessel, 6821	<u>3/20/03</u> Date

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## 1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1 defines the abbreviations, acronyms, and initialisms used in this analysis plan (AP).

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym or Initialism	Definition
Am	americium
am	amorphous
anhydrite	CaSO <sub>4</sub>
An(III)	actinide element(s) in the +III oxidation state
An(IV)	actinide(s) in the +IV oxidation state
An(V)	actinide(s) in the +V oxidation state
An(VI)	actinide(s) in the +VI oxidation state
AP	analysis plan
aq	aqueous
ASTP	(WIPP) Actinide Source Term Program
atm	atmosphere(s)
B, B(OH) <sub>x</sub> <sup>3-x</sup>	boron, boric acid/borate
Br, Br <sup>-</sup>	bromine, bromide (ion)
Brine A	a synthetic brine representative of intergranular Salado brines
brucite	Mg(OH) <sub>2</sub>
C	carbon
Ca, Ca <sup>2+</sup>	calcium, calcium ion
calcite	CaCO <sub>3</sub>
CCA	(WIPP) Compliance Certification Application
CH <sub>4</sub>	methane
Cl, Cl <sup>-</sup>	chlorine, chloride ion
Cm	curium
CMS	(SNL NWMP software) Configuration Management System
CO <sub>2</sub>	carbon dioxide
CO <sub>3</sub> <sup>2-</sup>	carbonate ion
CPR	cellulosics, plastics, and rubbers (in TRU waste)
Cr	chromium
CRA	(WIPP) Compliance Recertification Application
DOE	(U.S.) Department of Energy

Table 1. Abbreviations, Acronyms, and Initialisms (cont.).

Abbreviation, Acronym or Initialism	Definition
EDTA	ethylenediaminetetraacetate
EEG	(NM) Environmental Evaluation Group
Eh	oxidation potential
EPA	(U.S.) Environmental Protection Agency
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
$f_{\text{CO}_2}$	fugacity (similar to the partial pressure) of $\text{CO}_2$
Fe	iron
Fm.	Formation or formation, depending on usage
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
FSU	Florida State University
g	gaseous
glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
$\text{H}^+$	hydrogen ion
$\text{H}_2\text{O}$	water (aq or g)
halite	$\text{NaCl}$
$\text{HCO}_3^-$	bicarbonate ion
hydromagnesite	$\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
K, $\text{K}^+$	potassium, potassium ion
L	liter(s)
LANL	Los Alamos National Laboratory
M	molar
m	molal
magnesite	$\text{MgCO}_3$
Mg, $\text{Mg}^{2+}$	magnesium, magnesium ion
Mg	milligram(s)
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and ~5-10 wt % impurities
mM	millimolar
Mn	manganese

Table 1. Abbreviations, Acronyms, and Initialisms (cont.).

Abbreviation, Acronym or Initialism	Definition
Na, Na <sup>+</sup>	sodium, sodium ion
Nd	neodymium
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O
Ni	nickel
NP	(SNL NWMP) Nuclear Waste Management Procedure
Np	neptunium
NWMP	(SNL) Nuclear Waste Management Program
OH <sup>-</sup>	hydroxide ion
PA	performance assessment
PAB-1	Performance Assessment Brine 1, the original name for SB-1
PAVT	(WIPP) Performance Assessment Verification Test
Pb	lead
Periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
PH	the negative, common logarithm of the activity of H <sup>+</sup>
PNNL	Pacific Northwest National Laboratory
Pu	plutonium
U	uranium
SB-1	Standard Brine 1, a synthetic brine similar to GWB
SNL	Sandia National Laboratories
SO <sub>4</sub> <sup>2-</sup>	sulfate ion
SP	(SNL NWMP) Activity/Project Specific Procedure
sp gr	specific gravity
SPC	Salado Primary Constituents, a synthetic brine similar to Brine A
TDS	total dissolved solids
Th	thorium
TRU	transuranic waste
V	vanadium
VMS	virtual memory system
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
Wt	weight
μM	micromolar

## 2 REVISION HISTORY

This is the original version of this AP. The objectives and content of any revisions of this AP will be described in this section of subsequent versions. Changes to this AP, other than those defined as editorial changes by Sandia National Laboratories' (SNL's) Nuclear Waste Management Program (NWMP) Nuclear Waste Management Procedure (NP) 9-1 (see Section 9, Applicable Procedures), shall be reviewed and approved by the same organization(s) that carried out the original review and approval.

## 3 INTRODUCTION

This AP describes the calculation of revised actinide solubilities for the performance assessment (PA) calculations for the U.S. Department of Energy's (DOE's) first Waste Isolation Pilot Plant (WIPP) Compliance Recertification Application (CRA). These solubilities will replace the solubilities used for the U.S. Environmental Protection Agency's (EPA's) WIPP Performance Assessment Verification Test (PAVT) in 1997, the solubilities currently in the WIPP Project's technical baseline.

SNL coordinated the WIPP Actinide Source Term Program (ASTP), a collaborative program to establish the actinide source term (actinide solubilities and colloidal actinide concentrations) for the PA calculations for the WIPP Compliance Certification Application (CCA) (U.S. DOE, 1996b). The DOE submitted the CCA to the EPA in October 1996 to demonstrate compliance with the EPA's regulations for the radioactive constituents of transuranic (TRU) waste (U.S. EPA, 1993). The ASTP used the results of extensive laboratory studies carried out at Argonne National Laboratory, Florida State University (FSU), Lawrence Livermore National Laboratory, Los Alamos National Laboratory (LANL), and Pacific Northwest National Laboratory (PNNL) to develop thermodynamic models for the important actinide elements in TRU waste under conditions expected in the WIPP after filling and sealing (high-ionic-strength brines, strongly reducing Eh, mildly basic pH, and low  $f_{\text{CO}_2}$ ). U.S. DOE (1996b, Appendix SOTERM) described these lab studies and models in detail.

SNL used the speciation and solubility code EQ3NR and the reaction-path code EQ6, parts of the EQ3/6 geochemical software package (Daveler and Wolery, 1992; Wolery, 1992a, 1992b; and Wolery and Daveler, 1992), and the speciation and solubility code Fracture-Matrix Transport (FMT) to define chemical conditions (brine composition,  $f_{\text{CO}_2}$ , and pH) in the repository after filling and sealing. SNL used FMT to predict the speciation and solubilities of actinides in the +III, +IV, and +V oxidation states (An(III), An(IV), and An(V)) under the conditions defined using EQ3/6 and FMT (U.S. DOE, 1996b, Appendix SOTERM). The ASTP did not develop a model for the solubility of actinides in the +VI oxidation state (An(VI)). Instead, results from studies carried out for applications other than the WIPP were used to estimate the solubility of An(VI) (U.S. DOE, 1996b, Appendix SOTERM).

The EPA conducted a thorough review of the CCA, including a PAVT to verify the results of the CCA PA. The EPA's review of the CCA also included a detailed evaluation of the ASTP (U.S. EPA, 1998a, 1998b, 1998c, and 1998d). Based on its evaluation of the actinide-solubility calculations for the CCA PA, the EPA recalculated these solubilities for the PAVT. Novak (1997), Trovato (1997, Attachment 2), U.S. EPA (1998a, Table 5). U.S. EPA (1998b, Subsection 4.10.4, Tables 4.10-1, 4.10-3 and 4.10-4; and Subsection 12.4, Table 12.4-1), and U.S. EPA (1998c, Subsections 5.26–5.32 and Section 6.0, Table 6.4) described the recalculation of solubilities for the PAVT.

The EPA certified that the WIPP complies with its regulations in May 1998 (U.S. EPA, 1998e). However, the New Mexico Environmental Evaluation Group (EEG) and other review panels raised several issues regarding the actinide solubilities used for the CCA PA and the PAVT (e.g., Neill et al., 1998; Oversby, 2000). Additional lab and modeling studies of actinide chemistry were performed at FSU, PNNL, and SNL to address these concerns.

#### 4 OBJECTIVES

The objectives of this analysis are to incorporate the following new or modified features in the calculation of revised actinide solubilities for the WIPP CRA PA: (1) use of Generic Weep Brine (GWB), along with Brine A, to simulate brines from the Salado Formation; (2) redefinition of chemical conditions for those PA vectors without microbial activity; (3) use of a revised and updated FMT thermodynamic database; (4) inclusion of the effects of complexation by organic ligands. Subsection 5.3, CRA Solubilities, describes these features in detail.

We will not revise any of the conceptual models on which these solubilities are based because the EPA certified that they are adequate, and because additional studies carried out since the CCA PA and the PAVT do not imply that they require revision. Furthermore, we will not revise the estimates of An(VI) solubilities used in the CCA PA. Moreover, we will not revise the colloidal actinide source term because the EPA certified that this component of the actinide source term is adequate, and because a recently initiated study of the effects of the WIPP engineered barrier on colloids has not yielded any results yet.

Finally, we will not revise the ranges and probability distribution applied to the solubilities used in the CCA and the PAVT at this time. We believe that the proper way to update ranges and probability distributions for these solubilities is to: (1) compare Th solubilities calculated with FMT to the results of carefully designed and executed solubility experiments carried out with Th (see the discussion of oxidation-state analogs in Subsection 5.1, CCA Solubilities); (2) compare calculated Am solubilities to the results of experiments carried out with Nd and/or Am. Eventually, this study could be extended to include comparison of calculated Th and Am solubilities with experimentally determined solubilities of Pu(III) and Pu(IV), respectively. This work is being proposed

to the DOE for possible inclusion in its actinide chemistry program and would, if funded, take several months to a few years to plan, initiate, and complete.

## 5 APPROACH

This section describes the approaches used to establish actinide solubilities for the CCA in 1996 and the PAVT in 1997, and the approach we will use for the CRA PA.

### 5.1 CCA Solubilities

WIPP PA calculations require parameters that specify the actinide source term, the time-dependent concentrations of Th, U, Pu, and Am in brines under conditions expected in the repository after filling and sealing. From the standpoint of their potential effects on the long-term performance of the repository, the order of importance of these actinides is Pu > Am >> U > Th (Helton et al., 1998). The ASTP also included Np and other actinides because it was not known at the outset which actinides could significantly affect the long-term performance of the repository.

The solubility of an actinide (or any other element or compound) is the dissolved concentration of that actinide in equilibrium with the actinide-bearing solid(s) present. Because the solubility of an actinide is the sum of all of the dissolved actinide species in equilibrium with the solubility-controlling solid(s), it is necessary to predict the speciation of these elements to predict their solubilities.

The ASTP used two synthetic solutions to simulate brines that could be present in the WIPP after filling and sealing: (1) Brine A, representative of intergranular (grain-boundary) brines from the Salado Formation at or near the stratigraphic horizon of the repository (Molecke, 1983); and (2) ERDA-6, typical of fluids in brine reservoirs in the underlying Castile Fm. (Popielak et al., 1983). The ASTP used these brines to obtain data such as solubility products for actinide-bearing solids and stability constants for dissolved actinide species. Novak and Moore (1996), Novak et al. (1996), and Novak (1997) also used Salado Primary Constituents (SPC) brine, a modified formulation of Brine A, for modeling. In addition to their use by the ASTP, Brine A and ERDA-6 have been used extensively for other laboratory and modeling studies of WIPP chemistry. SPC, however, was only used by the ASTP just prior to and at the time of the CCA and the PAVT, and is no longer used for any studies of WIPP chemistry. Table 2 provides the compositions of Brine A and ERDA-6 prior to any reactions with the contents of WIPP disposal rooms. Because the ionic strengths of these brines are high, Pitzer activity-coefficient models were developed for the important actinides in TRU waste.



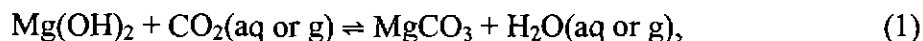
Table 2. Compositions of Brine A and ERDA-6 Prior to Reaction.

Element or Property	Brine A <sup>1</sup>	ERDA-6 <sup>2</sup>
$B(OH)_x^{3-x}$	20 mM	63 mM
$Na^+$	1.83 M	4.87 M
$Mg^{2+}$	1.44 M	19 mM
$K^+$	770 mM	97 mM
$Ca^{2+}$	20 mM	12 mM
$SO_4^{2-}$	40 mM	170 mM
$Cl^-$	5.35 M	4.8 M
$Br^-$	10 mM	11 mM
Total inorganic C (as $HCO_3^-$ )	10 mM	16 mM
pH	6.5	6.17
Specific gravity (sp gr)	1.2	1.216
Total dissolved solids (TDS)	306,000 mg/L	330,000 mg/L

1. From Molecke (1983).
2. From Popielak (1983).

Wang (1996a, 1996b) used EQ6 (Wolery and Daveler, 1992) to predict chemical conditions in WIPP disposal rooms after filling and sealing. He asserted that equilibria among Brine A or ERDA-6 and brucite ( $Mg(OH)_2$ ) and magnesite ( $MgCO_3$ ) will buffer (control) brine composition,  $f_{CO_2}$ , and pH in the WIPP. Brucite is the thermodynamically stable hydration product of periclase (pure, crystalline  $MgO$ , the primary constituent of the WIPP engineered barrier) under expected WIPP conditions; magnesite is the stable carbonation product of periclase and/or brucite. Brucite and magnesite could form after Brine A, ERDA-6, and  $CO_2$  generated from (possible) microbial degradation of cellulose, plastics, and rubbers (CPR) in TRU waste react with

periclase. (The possibility that carbonation of brucite could produce metastable Mg-carbonates is discussed in Subsection 5.2, PAVT Solubilities; and Subsection 5.3, CRA Solubilities.) Wang (1996a, 1996b) concluded that the reaction,



will buffer  $f_{\text{CO}_2}$ ; and the reaction,



will buffer pH. (In this and subsequent analyses, it has been assumed that the effects of possible substitution of  $\text{Fe}^{2+}$  for  $\text{Mg}^{2+}$  in Mg-bearing solids such as brucite and magnesite are insignificant.) Wang (1996a, 1996b) did not force SPC and ERDA-6 to remain in equilibrium with Salado minerals such as halite ( $\text{NaCl}$ ) and anhydrite ( $\text{CaSO}_4$ ). He obtained a pH of 9.2 for Brine A in equilibrium with brucite and magnesite, and a pH of 10 for ERDA-6 in equilibrium with brucite and magnesite. However, he did not report values for  $f_{\text{CO}_2}$ .

Novak et al. (1996) used FMT to predict chemical conditions in the repository. They agreed that the brucite-magnesite carbonation reaction (see Reaction 1 above) will buffer  $f_{\text{CO}_2}$ . However, they forced SPC and ERDA-6 to equilibrate with the major Salado minerals halite and anhydrite. Their equilibrium mineral assemblage calculated for SPC was halite, anhydrite, brucite,  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$ , and magnesite;  $f_{\text{CO}_2}$  and pH were  $10^{-6.9}$  atm and 8.69, respectively. (Because of the presence of  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$ ,  $f_{\text{CO}_2}$  was actually buffered by two reactions, the brucite-magnesite and the  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$ -magnesite carbonation reactions; and pH was buffered by two reactions, the brucite and the  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$  dissolution reactions.) For ERDA-6, the equilibrium mineral assemblage was halite, anhydrite, brucite, magnesite, and glauberite ( $\text{Na}_2\text{Ca(SO}_4)_2$ );  $f_{\text{CO}_2}$  and pH were  $10^{-6.9}$  atm and 9.24 (Novak et al., 1996; U.S. DOE, 1996, Appendix SOTERM, Table SOTERM-2).

Dissolved Th, U, Np, Pu, and Am will speciate essentially entirely as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III) under the strongly reducing conditions expected after reacting with metallic Fe (and other metals) in steel waste containers and/or the waste, Fe(II)-bearing solids produced by anoxic corrosion of these metals, and/or dissolved Fe(II) species; and after possible microbial activity (U.S. DOE, 1996b, Appendix SOTERM, SOTERM.4). Pu(V) and Pu(VI) could occur in isolated microenvironments in WIPP disposal rooms. However, Pu(V) and Pu(VI) would not persist in significant quantities because diffusive and, especially in the event of human intrusion, advective transport would expose any oxidized Pu to the reductants that will be present in the repository.

Because of the experimental difficulties involved in maintaining Pu in the +III oxidation state, laboratory studies with Nd(III), Am(III), and Cm(III) were used to develop a solubility model for An(III), and this model was used to predict the solubilities of Pu(III) and Am(III). Similarly, Th(IV) was used to develop an An(IV) solubility model, which was used for Th(IV), U(IV), Np(IV) and Pu(IV). Literature data for Np(V) were used to develop an An(V) solubility model, which was used only for Np(V). The An(V) model has not been used for other actinides because oxidized Pu would not persist in significant quantities in the WIPP. The use of the oxidation-state analogy to extend the An(III) and the An(IV) solubility models to Pu(III) and to U(IV), Np(IV) and Pu(IV), respectively, is valid because: (1) Nd, Am, and Cm speciate essentially entirely in the +III oxidation state, and Th occurs essentially entirely in the +IV oxidation state under typical laboratory conditions, thus making experiments with these actinides much easier to carry out and interpret than experiments with actinides that occur in more than one oxidation state, such as Pu; (2) the chemical behavior, especially the speciation and solubilities, of Nd(III), Pu(III), Am(III), and Cm(III) are very similar; (3) the chemical behavior of Th(IV), U(IV), Np(IV), and Pu(IV) are similar, although the solubility of Th(IV) is higher than that of U(IV), Np(IV), and especially Pu(IV).

G. R. Choppin and his students at FSU carried out extensive laboratory studies of the effects of acetate, citrate, EDTA, lactate, and oxalate on actinide speciation and solubilities prior to the CCA PA. Furthermore, the concentrations of these organic ligands were estimated prior to the CCA PA by assuming that all of these organics in the contact-handled and remote-handled TRU waste to be emplaced in the WIPP (U.S. DOE, 1996a) will dissolve in 29,841 m<sup>3</sup> of brine, the minimum quantity that must be present in the repository for a direct brine release (Larson, 1996). The concentrations thus obtained were  $1.1 \times 10^{-3}$  m acetate,  $7.4 \times 10^{-3}$  m citrate,  $4.2 \times 10^{-6}$  m EDTA and  $4.7 \times 10^{-4}$  m oxalate (U.S. DOE, 1996b, Appendix SOTERM, Table SOTERM-4). The concentration of lactate was not estimated "because none was identified in the initial inventory, and [because] estimating its concentration ... from ... production and consumption by microbes is not possible" (U.S. DOE, Appendix SOTERM, p. SOTERM-37). (In fact, estimating the effects of microbial activity on the concentrations of acetate, citrate, EDTA, and oxalate is also impossible.) However, despite these efforts, the effects of organic ligands on the solubilities of actinides were not included in the FMT calculations for the CCA PA because the model for organic complexation of actinides was not deemed adequate at the time.

Because the effects of organics were not included in the FMT calculations, SNL used hand calculations and the HYDRAQL code, along with thermodynamic data for low-ionic-strength NaCl solutions, to assess the effects of organic ligands on actinide solubilities (U.S. DOE, 1996b, Appendix SOTERM, SOTERM.5). Both of these approaches suggested that transition metals present in the iron and steel to be emplaced in the WIPP will compete effectively with the actinides for the binding sites on the organic ligands, thus preventing significant complexation of actinides by organics. In particular, transition metals such as Fe and Ni will complex 97-99.8% of the EDTA expected in the WIPP. This conclusion was reasonable, despite the lack of an adequate thermodynamic model of organo-actinide complexation in brines, because: (1) corrosion of steel and

other Fe-base metals in waste containers (drums and boxes) and the waste will release significant quantities of other metals in addition to Fe and Ni, such as Cr, V, and Mn, given the large quantity of metallic Fe to be emplaced in the WIPP ( $>1.9 \times 10^9$  mol); (2) the waste contains a significant quantity of metallic Pb, which will also dissolve in brines and compete with the actinides for the binding sites on the organics; (3) EDTA forms stronger complexes with the actinides than the other organics considered in the CCA (acetate, citrate, and oxalate). Based on this approach, it was concluded that none of the four ligands of potential concern (acetate, citrate, EDTA, and oxalate) would significantly affect actinide solubilities.

Novak et al. (1996) used FMT and the thermodynamic database FMT\_HMW\_345\_960501FANG.CHEMDAT to calculate the solubilities of An(III), An(IV), and An(V) in SPC and ERDA-6 for the CCA PA. They asserted that instantaneous, reversible equilibria among dissolved actinide species and the actinide-bearing solids observed in the ASTP lab studies ( $\text{Am}(\text{OH})_3$ ,  $\text{ThO}_2(\text{am})$ , and  $\text{KNpO}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ) will control the solubilities under the conditions established by the equilibria among these brines and the minerals listed above.

Novak and Moore (1996) have been cited as the source of the solubilities used for the CCA PA (U.S. EPA, 1998d, Subsection 4.3, Tables 4.2 and 4.4), but Novak and Moore (1996) used FMT\_HMW\_345\_960325.CHEMDAT, an earlier version of the database that yielded An(III) solubilities that differed somewhat from those obtained by Novak et al. (1996).

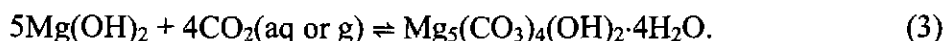
The ASTP did not establish a solubility model for U(VI); instead, it used literature data to estimate the solubilities of U(VI) in the WIPP (Hobart and Moore, 1996; U.S. DOE, 1996b, Appendix SOTERM, SOTERM-27 - SOTERM-28). These estimates have not been used for other actinides in the WIPP because Np and Pu will not persist in significant quantities in the +VI oxidation state.

## 5.2 PAVT Solubilities

The EPA concluded, based on a thorough review of the lab and modeling studies of actinide chemistry carried out for the CCA, that most features of the approach used to establish the dissolved-actinide source term for the CCA PA were adequate (U.S. EPA, 1998a, 1998b, 1998c, and 1998d). Those features found to be adequate include: (1) the use of Brine A and ERDA-6 to simulate Salado and Castile brines, respectively; (2) the use of EQ3/6 and FMT to define chemical conditions in the repository after filling and sealing, (3) the assertion that conditions in the repository will be strongly reducing, and that Th, U, Np, Pu, and Am will speciate essentially entirely as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III); (4) the use of the oxidation-state analogy to develop and apply solubility models for An(III), An(IV), and An(V); (5) the use of scoping calculations to rule out significant effects of organic ligands on actinide solubilities; (6) the use of FMT to predict the speciation and solubilities of actinides; (7) the conclusion that instantaneous, reversible, equilibria among dissolved actinide

species and the actinide-bearing solids observed in the ASTP lab studies will control solubilities; and (8) the use of estimates based on literature data for the solubilities of U(VI).

However, the EPA did not accept the assertion that the brucite-magnesite carbonation reaction (see Reaction 1) will buffer  $f_{\text{CO}_2}$  in WIPP disposal rooms. Instead, the EPA mandated that the brucite-hydromagnesite carbonation reaction be used to calculate  $f_{\text{CO}_2}$ . Furthermore, the EPA mandated that hydromagnesite with the composition  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  be used, not hydromagnesite with the composition  $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ . (Thermodynamic data for both of these forms of hydromagnesite are in the EQ3/6 and FMT databases.) Because the EPA specified hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) as the carbonation product, the reaction that will  $f_{\text{CO}_2}$  buffer is:



Magnesite is the thermodynamically stable, Mg-carbonate mineral under conditions expected in the WIPP. Moreover, magnesite is present in the Salado at the stratigraphic horizon of the repository. However, based on kinetic considerations, the EPA concluded that carbonation of brucite will produce metastable hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ), and that magnesite will replace hydromagnesite too slowly to control  $f_{\text{CO}_2}$  during the 10,000-year period of performance of the repository. Therefore, Novak (1997) used FMT to calculate that the brucite-hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) carbonation reaction will buffer  $f_{\text{CO}_2}$  at  $10^{-5.50}$  atm in both SPC and ERDA-6. The use of this brucite-hydromagnesite reaction to buffer  $f_{\text{CO}_2}$  did not change the pH calculated for these brines because the brucite dissolution reaction (Reaction 2) will buffer pH. Therefore, the pH depends on the solubility product for brucite and the activity of  $\text{H}_2\text{O}$  in WIPP brines, not the identity of the Mg-carbonate mineral present.

The EPA also found errors in FMT\_HMW\_345\_960501\_FANG.CHEMDAT, the thermodynamic database used for the CCA PA calculations. The erroneous data pertained to  $\text{Th}(\text{CO}_3)_5^{6-}$ ,  $\text{NpO}_2(\text{CO}_3)_3^{5-}$ , and  $\text{Am}(\text{CO}_3)_3^{3-}$ . Correction of the data for these complexes resulted in the stabilization of different Am- and Np-bearing solid phases in subsequent FMT calculations. Novak (1997) corrected these mistakes and designated the PAVT database as FMT\_970407.CHEMDAT.

Novak (1997) used FMT and FMT\_970407.CHEMDAT to calculate An(III), An(IV), and An(V) solubilities under conditions defined by equilibria among SPC and: (1) halite, anhydrite, brucite,  $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , and hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ), and; (2) halite, anhydrite, brucite,  $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , and hydromagnesite ( $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ); and (3) halite, anhydrite, brucite,  $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ , and nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ); and among ERDA-6 and:

(4) halite, anhydrite, glauberite, brucite, and hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ );  
(5) halite, anhydrite, glauberite, brucite, and hydromagnesite ( $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ );  
and (6) halite, anhydrite, glauberite, brucite, and nesquehonite.

The EPA recalculated these solubilities under the same conditions to verify Novak's (1997) results and obtained similar results (Trovato (1997, Attachment 2), U.S. EPA (1998a, Table 5), U.S. EPA (1998b, Subsection 4.10.4, Tables 4.10-1, 4.10-3 and 4.10-4; and Subsection 12.4, Table 12.4-1), and U.S. EPA (1998c, Subsections 5.26-5.32 and Section 6.0, Table 6.4). For the PAVT, the EPA used the solubilities calculated assuming equilibria among SPC, halite, anhydrite, brucite,  $Mg_2Cl(OH)_3 \cdot 4H_2O$ , and hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ); and among ERDA-6 halite, anhydrite, glauberite, brucite, and hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ).

Table 3 gives the solubilities (and other characteristics and parameters) calculated or estimated for the CCA PA, the solubilities calculated by Novak (1997) assuming that the brucite-hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) carbonation reaction will buffer  $f_{CO_2}$ , and the solubilities calculated using the same assumptions by the EPA for the PAVT.

### 5.3 CRA Solubilities

Our calculation of revised actinide solubilities for the CRA PA will mainly comprise features included in previous calculations for the CCA PA and/or the PAVT: (1) the use of Brine A and ERDA-6 to simulate Salado and Castile brines, respectively; (2) the use of FMT to define chemical conditions in the repository under conditions established by equilibria among brines, major Salado minerals, and MgO hydration and carbonation products; (3) the conclusion that Th, U, Np, Pu, and Am will speciate essentially entirely as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III); (4) the use of the oxidation-state analogy to develop solubility An(III), An(IV), and An(V) solubility models; (5) the use of FMT to predict actinide solubilities; (6) the assumption that instantaneous, reversible, equilibria will control actinide solubilities; and (7) the use of previously estimated U(VI) solubilities.

However, our calculations will also include four new features: (1) the use of GWB, along with Brine A, to simulate Salado brines; (2) redefinition of chemical conditions for those PA vectors without microbial activity and evaluation of the effects of these conditions on solubilities; (3) use of a revised and updated version of the FMT thermodynamic database; (4) inclusion in the FMT calculations of the effects of organic ligands on actinide solubilities.

Table 3. Comparison of Actinide Solubilities Calculated or Estimated for the CCA PA, Solubilities Calculated by Novak (1997), and Those Calculated for the PAVT.

Characteristic, Parameter, or Actinide Oxidation State	CCA PA <sup>1</sup> (solubilities in M)	Novak (1997) (solubilities in M)	PAVT <sup>2</sup> (solubilities in M)
Solids <sup>3</sup> in equilibrium with Brine A <sup>3</sup> or SPC <sup>4</sup>	Halite, anhydrite, brucite, Mg <sub>2</sub> Cl(OH) <sub>3</sub> ·4H <sub>2</sub> O, magnesite, Am(OH) <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O	Halite, anhydrite, brucite, Mg <sub>2</sub> Cl(OH) <sub>3</sub> ·4H <sub>2</sub> O, hydromagnesite (Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> - 4H <sub>2</sub> O), AmOHCO <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub>	Halite, anhydrite, brucite, Mg <sub>2</sub> Cl(OH) <sub>3</sub> ·4H <sub>2</sub> O, hydromagnesite (Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> - 4H <sub>2</sub> O), AmOHCO <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub>
Solids <sup>3</sup> in equilibrium with ERDA-6 <sup>5</sup>	Halite, anhydrite, glauberite, magnesite, Am(OH) <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O	Halite, anhydrite, glauberite, brucite, hydromagnesite (Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> - 4H <sub>2</sub> O), AmOHCO <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub>	Halite, anhydrite, glauberite, brucite, hydromagnesite (Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> - 4H <sub>2</sub> O), AmOHCO <sub>3</sub> , ThO <sub>2</sub> (am), and KNpO <sub>2</sub> CO <sub>3</sub>
Log f <sub>CO<sub>2</sub></sub> , Brine A	-6.9	-5.50	-5.50
pH, Brine A (standard units)	8.69	8.69	8.69
pH, ERDA-6 (standard units)	9.24	9.24	9.24
+III, Brine A	5.82 × 10 <sup>-7</sup>	9.40 × 10 <sup>-8</sup>	1.2 × 10 <sup>-7</sup>
+III, ERDA-6	6.52 × 10 <sup>-8</sup>	1.30 × 10 <sup>-8</sup>	1.3 × 10 <sup>-8</sup>
+IV, Brine A	4.4 × 10 <sup>-6</sup>	1.20 × 10 <sup>-8</sup>	1.3 × 10 <sup>-8</sup>
+IV, ERDA-6	6.0 × 10 <sup>-9</sup>	4.10 × 10 <sup>-8</sup>	4.1 × 10 <sup>-8</sup>

Table 3. Comparison of Actinide Solubilities Calculated or Estimated for the CCA PA, Solubilities Calculated by Novak (1997), and Those Calculated for the PAVT (cont.).

Characteristic, Parameter, or Actinide Oxidation State	CCA PA <sup>1</sup> (solubilities in M)	Novak (1997) (solubilities in M)	PAVT <sup>2</sup> (solubilities in M)
+V, Brine A	$2.3 \times 10^{-6}$	$1.20 \times 10^{-7}$	$2.4 \times 10^{-7}$
+V, ERDA-6	$2.2 \times 10^{-6}$	$4.60 \times 10^{-7}$	$4.8 \times 10^{-7}$
+VI, Brine A <sup>6</sup>	$8.7 \times 10^{-6}$	-	$8.7 \times 10^{-5}$
+VI, ERDA-6 <sup>6</sup>	$8.8 \times 10^{-6}$	-	$8.8 \times 10^{-6}$

1. From Novak, Moore, and Bynum (1996, Table 1, columns entitled “@Mg”); U.S. DOE (1996, Appendix SOTERM, Table SOTERM-2), except that Novak, Moore, and Bynum (1996) used molal instead of molar units.
2. From Trovato (1997, Attachment 2), U.S. EPA (1998a, Table 5), U.S. EPA (1998b, Subsection 4.10.4, Tables 4.10-1, 4.10-3 and 4.10-4; and Subsection 12.4, Table 12.4-1), and U.S. EPA (1998c, Subsections 5.26–5.32 and Section 6.0, Table 6.4).
3. Brine A = synthetic Salado brine (Molecke, 1983).
4. SPC  $\approx$  Brine A.
5. ERDA 6 = synthetic Castile brine (Popielak et al., 1983).
6. Estimated by Hobart and Moore (1996).

### 5.3.1 Use of GWB

We will use both Brine A and GWB to simulate intergranular Salado brines. We are adding GWB because this brine resembles the average composition of intergranular Salado brines at or near the stratigraphic horizon of the WIPP more closely than Brine A. GWB was established as a representative, intergranular Salado brine for laboratory studies of the efficacy of MgO at SNL in Albuquerque during the mid-to-late 1990s. GWB was established because investigators believed that the chemical behavior of MgO is sensitive to the Mg<sup>2+</sup> concentration of the experimental solutions, and because the Mg<sup>2+</sup> concentration of Brine A (1.44 M) is significantly higher than the average Mg<sup>2+</sup> concentration of intergranular Salado brines, about 1.0 M (Brush, 1989; Brush, 1990). Investigators at SNL in Carlsbad have also used GWB to simulate Salado brines in their



studies of MgO. The composition of GWB is very similar to that of Standard Brine 1 (SB-1), the brine established by Brush (1989) and referred to by Brush (1990) as most typical of intergranular Salado brines at or near the stratigraphic horizon of the repository. Brush (1989) referred to SB-1 as Performance Assessment Brine 1 (PAB-1); Brush (1990) renamed it SB-1.

We will continue to use both Brine A and GWB to facilitate comparison of our results with the solubilities used in the CCA PA and the PAVT. Table 4 compares the compositions of Brine A, GWB, and SB-1. Currently, there does not exist a reference for GWB comparable to those for Brine A and ERDA-6 (Molecke, 1983; Popielak et al., 1983). Therefore, Subsection 7.1, Documentation of GWB, describes the task of documenting the establishment GWB as a representative Salado brine for use in this and other WIPP modeling and laboratory studies.

### 5.3.2 Redefinition of Conditions for PA Vectors without Microbial Activity

We will redefine near-field chemical conditions for those PA vectors without microbial activity and evaluate the effects of these conditions on actinide solubilities. For the CCA PA, SNL developed a conceptual model with a probability of 0.5 for significant microbial degradation of CPR in the WIPP. Thus, there was significant microbial degradation of CPR, and concomitant microbial gas generation (mostly CH<sub>4</sub> and CO<sub>2</sub>), in about half of the PA vectors; and no microbial activity or gas generation in the other half of the vectors. Because CO<sub>2</sub> could increase the solubilities of actinides by acidifying brine or producing CO<sub>3</sub><sup>2-</sup>, which forms soluble complexes with several dissolved actinide species, the DOE included MgO as an engineered barrier in the repository design proposed in the CCA to consume essentially all of the CO<sub>2</sub>, and buffer f<sub>CO<sub>2</sub></sub> and pH within ranges favorable from the standpoint of actinide solubilities (U.S. DOE, 1996b, Appendix BACK). For the CCA PA and the PAVT, Novak et al. (1996), Novak (1997), and the EPA (Trovato, 1997; U.S. EPA, 1998a; U.S. EPA, 1998b; U.S. EPA, 1998c) asserted that the brucite-magnesite or the brucite-hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) carbonation reactions will buffer f<sub>CO<sub>2</sub></sub>. The brucite-hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) carbonation reactions is still the appropriate f<sub>CO<sub>2</sub></sub> buffer for the PA vectors with microbial activity, but not for the vectors without microbial activity.

Calcite (CaCO<sub>3</sub>) is more stable under expected WIPP conditions than magnesite, hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O or Mg<sub>4</sub>(CO<sub>3</sub>)<sub>3</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) or nesquehonite. Furthermore, calcite will precipitate readily under the low-temperature conditions expected in the WIPP. (Formation of calcite has been observed in GWB by about 16 days, and in ERDA-6 by 50 days in the SNL laboratory study of the carbonation of Premier MgO, the MgO currently being emplaced in the repository. These results will be described in the July 2003 SNL milestone report to the DOE.) Therefore, Novak et al. (1996) suppressed calcite (prevented it from forming) by “disabling” it in their input files,

Table 4. Compositions of Brine A, SB-1, and GWB Prior to Reaction

Element or Property	Brine A <sup>1</sup>	SB-1 <sup>2</sup>	GWB <sup>3</sup>
B(OH) <sub>x</sub> <sup>3-x</sup>	20 mM	152 mM	158 mM
Na <sup>+</sup>	1.83 M	3.9 M	3.53 M
Mg <sup>2+</sup>	1.44 M	1.0 M	1.02 M
K <sup>+</sup>	770 mM	500 mM	467 mM
Ca <sup>2+</sup>	20 mM	10 mM	14 mM
SO <sub>4</sub> <sup>2-</sup>	40 mM	160 mM	177 mM
Cl <sup>-</sup>	5.35 M	6.04 M	5.86 M
Br <sup>-</sup>	10 mM	13 mM	26.6 mM
Total inorganic C (as HCO <sub>3</sub> <sup>-</sup> )	10 mM	370 μM	-
pH	6.5	6.0	-
Sp gr	1.2	1.22	1.2
TDS	306,000 mg/L	385,000	-

1. From Molecke (1983).
2. From Brush (1989, 1990). Brush (1989) referred to SB-1 as PAB-1.
3. To be documented as described in Task 2 (see Subsection 7.2, Task 2: Documentation of GWB).

thereby allowing the formation of magnesite (the second-most-stable CO<sub>2</sub>-bearing solid); and Novak et al. (1997) suppressed calcite and magnesite, thus allowing the formation of hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O), the third-most-stable CO<sub>2</sub>-bearing solid. This was appropriate for the vectors with microbial activity because the large quantities of CO<sub>2</sub> produced in these vectors would overwhelm the capacity of dissolved Ca<sup>2+</sup> to precipitate CO<sub>2</sub> as calcite, thus leaving most of the microbial CO<sub>2</sub> to react with periclase, brucite, or Mg<sub>2</sub>Cl(OH)<sub>3</sub>·4H<sub>2</sub>O; thus producing magnesite, hydromagnesite, or nesquehonite. However, in the absence of microbial CO<sub>2</sub> production, the quantity of Ca<sup>2+</sup>

present would be sufficient to precipitate any CO<sub>2</sub> present as calcite without formation of metastable Mg-carbonates. Therefore, for the vectors without microbial activity, we will allow calcite to precipitate. The reaction that will buffer f<sub>CO<sub>2</sub></sub> is:



For the PA vectors with microbial activity, we will continue to assume that the brucite-hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) carbonation reaction will buffer f<sub>CO<sub>2</sub></sub>. Recent results from the lab study of MgO at SNL, in which the CO<sub>2</sub> concentrations of the controlled atmospheres are low relative to previous experiments, imply that hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) is the dominant carbonation product in both GWB and ERDA-6 under 5% CO<sub>2</sub> by about 91 days (Snider and Xiong, 2002). These results do not necessarily imply that magnesite will not nucleate and grow to a significant extent during the 10,000-year WIPP regulatory period. However, they are at least consistent with the EPA's conclusion that the brucite-hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) carbonation reaction will buffer f<sub>CO<sub>2</sub></sub>.

### 5.3.3 Use of Revised and Updated FMT Database

We will use FMT\_021120.CHEMDAT, the current version of the FMT thermodynamic database, for the CRA PA solubility calculations. This database is currently maintained in the SNL/WIPP (software) Configuration Management System (CMS).

Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2002f, 2003) established FMT\_021120.CHEMDAT by revising and updating FMT\_970407.CHEMDAT, the version of the FMT database used by Novak (1997) at the time of the PAVT. The new database features: (1) improved implementation of previously obtained laboratory data; (2) results of lab studies carried out at FSU and PNNL from the time of the PAVT through 1999; (3) results of recent lab studies carried out for applications other than the WIPP, especially the German radioactive waste management program.

The following subsections list the specific changes in the parameters for the inorganic species in the database.

#### 5.3.3.1 An(III)

The new version of the FMT database contains: (1) revised values of the normalized chemical potentials ( $\mu^0/RT$ ) based on revised solubility products for Am(OH)<sub>3</sub>(s) and AmOHCO<sub>3</sub>(s); (2) revised  $\mu^0/RT$ s for AmOH<sup>2+</sup>, Am(OH)<sub>2</sub><sup>+</sup>, and Am(OH)<sub>3</sub>(aq), based on revised stability constants for CmOH<sup>2+</sup>, Cm(OH)<sub>2</sub><sup>+</sup>, and Am(OH)<sub>3</sub>(aq), respectively; and revised Pitzer ion-interaction parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, and  $C^{(\phi)}$ 's; or  $\lambda$ 's) for AmOH<sup>2+</sup>, Am(OH)<sub>2</sub><sup>+</sup>, and Am(OH)<sub>3</sub>(aq), based on revised Pitzer

parameters for  $\text{CmOH}^{2+}$ ,  $\text{Cm}(\text{OH})_2^+$ , and  $\text{Am}(\text{OH})_3(\text{aq})$ ; (3) revised  $\mu^0/\text{RT}$ s and revised or new Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, and  $C^{(\phi)}$ 's; or  $\theta_{ij}$ 's and  $\psi_{ijk}$ 's) for  $\text{AmCO}_3^+$ ,  $\text{Am}(\text{CO}_3)_2^-$ , and  $\text{Am}(\text{CO}_3)_3^{3-}$ , based on revised or new data for  $\text{CmCO}_3^+$ ,  $\text{Cm}(\text{CO}_3)_2^-$ , and  $\text{Cm}(\text{CO}_3)_3^{3-}$ ; and addition of  $\mu^0/\text{RT}$  and Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, and  $C^{(\phi)}$ 's) for  $\text{Am}(\text{CO}_3)_4^{5-}$ , based on new data for  $\text{Cm}(\text{CO}_3)_4^{5-}$ ; (4) addition of  $\mu^0/\text{RT}$ s and Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, and  $C^{(\phi)}$ 's) for  $\text{AmSO}_4^+$  and  $\text{Am}(\text{SO}_4)_2^-$ , based on new data for  $\text{CmSO}_4^+$  and  $\text{Cm}(\text{SO}_4)_2^-$ ; (5) new Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, and  $C^{(\phi)}$ 's) for interactions between  $\text{K}^+$  and  $\text{Am}(\text{CO}_3)_2^-$ ,  $\text{Am}(\text{CO}_3)_3^{3-}$ ,  $\text{Am}(\text{CO}_3)_4^{5-}$ , and  $\text{Am}(\text{SO}_4)_2^-$ , based on existing parameters for  $\text{Na}^+$  and these complexes; (6) addition of  $\mu^0/\text{RT}$ s and Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's,  $C^{(\phi)}$ 's, and  $\theta_{ij}$ 's) for  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$ , based on new data for  $\text{CmCl}^{2+}$  and  $\text{CmCl}_2^+$ ; and (7) new Pitzer parameters ( $\theta_{ij}$ 's) for interactions between  $\text{Ca}^{2+}$  and  $\text{Am}^{3+}$ ,  $\text{AmCl}^{2+}$ , and  $\text{AmCl}_2^+$ , based on existing parameters for  $\text{Mg}^{2+}$  and these species. Furthermore, several Pu(III) species in the PAVT database ( $\text{Pu}^{3+}$ ,  $\text{PuOH}^{2+}$ ,  $\text{Pu}(\text{OH})_2^+$ ,  $\text{Pu}(\text{OH})_3(\text{aq})$ ,  $\text{PuCO}_3^+$ ,  $\text{Pu}(\text{CO}_3)_2^-$ , and  $\text{Pu}(\text{CO}_3)_3^{3-}$ ), for which parameters had been assigned by analogy with corresponding Am(III) species, were deactivated or removed from the database. Giambalvo (2002a) provided a detailed description of the parameters for An(III) in FMT\_970407.CHEMDAT, the database used to calculate solubilities for the PAVT; Giambalvo (2002a, 2003) described the An(III) parameters in FMT\_021120.CHEMDAT, the revised and updated database to be used for the CRA PA.

### 5.3.3.2 An(IV)

The new version of the FMT database contains: (1) new Pitzer parameters ( $\theta_{ij}$ 's and  $\psi_{ijk}$ 's) for interactions between  $\text{Ca}^{2+}$  and  $\text{Th}^{4+}$ , or among  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{Th}^{4+}$ , based on existing parameters for  $\text{Mg}^{2+}$  and these species; (2) a revised  $\mu^0/\text{RT}$  for  $\text{Th}(\text{OH})_4(\text{aq})$ ; and (3) new Pitzer ion-interaction parameters ( $\theta_{ij}$ 's and  $\psi_{ijk}$ 's) describing the interactions of  $\text{Th}(\text{CO}_3)_5^{6-}$  with  $\text{Cl}^-$  and of  $\text{Th}(\text{CO}_3)_5^{6-}$  with  $\text{Na}^+$  and  $\text{Cl}^-$ ; (3) new Pitzer parameters ( $\beta^{(0)}$ 's and  $\beta^{(1)}$ 's) for interactions between  $\text{K}^+$  and  $\text{Th}(\text{CO}_3)_5^{6-}$ , based on existing parameters for  $\text{Na}^+$  and this complex. Moreover, several U(IV) species in the PAVT database ( $\text{U}^{4+}$ ,  $\text{UOH}^{3+}$ ,  $\text{U}(\text{OH})_4(\text{aq})$ ,  $\text{U}(\text{OH})_2(\text{CO}_3)_2^{2-}$ ,  $\text{U}(\text{OH})_4(\text{CO}_3)_2^{6-}$ ,  $\text{U}(\text{CO}_3)_5^{6-}$ ,  $\text{U}(\text{SO}_4)_2(\text{aq})$ , and  $\text{U}(\text{SO}_4)_3^{2-}$ ), for which parameters had been assigned by analogy with corresponding Th(IV) species, were deactivated or removed from the database. Giambalvo (2002c) described the parameters for An(IV) in FMT\_970407.CHEMDAT, the PAVT database; Giambalvo (2002c, 2003) described the An(IV) parameters in FMT\_021120.CHEMDAT, the database for the CRA PA.

### 5.3.3.3 An(V)

The new version of the FMT database includes revised  $\mu^0/\text{RT}$ s for all of the Np-bearing solids and dissolved Np species. (These changes resulted from improvements in the precision of the parameter-conversion calculations, not from the use of different data sources, and are thus very minor.) The new database also includes new Pitzer parameters ( $\beta^{(0)}$ 's,  $\beta^{(1)}$ 's, a  $\beta^{(2)}$ , and a  $C^{(\phi)}$ ) for interactions between  $\text{Ca}^{2+}$  and  $\text{NpO}_2\text{CO}_3^-$ ,  $\text{NpO}_2(\text{CO}_3)_2^{3-}$ , and  $\text{NpO}_2(\text{CO}_3)_3^{5-}$ , based on existing parameters for  $\text{Mg}^{2+}$  and these

complexes. Giambalvo (2002d) described the An(V) data in FMT\_970407.CHEMDAT; Giambalvo (2002d, 2003) described the An(V) data in FMT\_021120.CHEMDAT.

### 5.3.4 Inclusion of Organic Ligands

Finally, we will include the effects of acetate, citrate, EDTA, and oxalate in the FMT solubility calculations for the CRA PA. FMT\_021120.CHEMDAT, the current version of the FMT database, includes all of the results of lab studies carried out at FSU (Choppin et al., 2001). In particular, it includes all of the data required to predict the complexation of dissolved An(III), An(IV), and An(V) species by acetate, citrate, EDTA, and oxalate. FMT\_021120.CHEMDAT also contains the data needed to predict the complexation of  $Mg^{2+}$  by these ligands and, thus, the extent to which competition between  $Mg^{2+}$  and the actinides for the binding sites on these ligands will reduce the extent of organoactinide complexation. Giambalvo (2002b, 2002e) described the data for organo-actinide complexation in FMT\_970407.CHEMDAT and FMT\_021120.CHEMDAT

## 6 SOFTWARE DESCRIPTION

We will use the speciation and solubility code FMT, Version 2.4, supported by FMT\_021120.CHEMDAT, the current thermodynamic database to calculate revised An(III), An(IV), and An(V) solubilities for the CRA PA. Subsection 5.3.3, Use of Revised and Updated FMT Database; and Subsection 5.3.4, Inclusion of Organic Ligands (see above) describe the current version of the FMT database. Wang (1998) validated FMT, Version 2.4, for An(III), An(IV), and An(V) speciation and solubility calculations in WIPP brines. The user's manual for Version 2.3 (Babb and Novak, 1997, and addenda) is still the current FMT user's manual. The addenda to Babb and Novak (1997) describe minor changes made during the upgrade from Version 2.3 to Version 2.4.

We will use FMT to calculate: (1) the mineral assemblages in equilibrium with the WIPP brines Brine A, GWB, and ERDA-6 after reactions among these brines,  $CO_2$  Salado minerals such as halite and anhydrite, and periclase; (2) the speciation and total concentration of nonradioactive constituents of WIPP brines, such as  $B(OH)_x^{3-x}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $Br^-$ , inorganic C, and  $f_{CO_2}$  and pH, in equilibrium with these brines and mineral assemblages; (3) the speciation and solubilities of Am(III), Th(IV), and Np(V) in equilibrium with solubility-controlling solids under these conditions. Section 7, Tasks, provides a detailed description of the FMT runs.

SNL/WIPP PA personnel will execute all of these FMT runs under the WIPP PA run control system. We will provide PA personnel with the input files for these runs; they will run them using FMT, Version 2.4, and FMT\_021120.CHEMDAT; and provide us the output files. Therefore, the FMT executable file, the database, and all of the I/O files used to calculate actinide solubilities for the CRA PA will be archived in the Sandia/WIPP CMS for future inspection by the EPA during its review of the CRA. The

implementation of this analysis under the WIPP PA run control system and the archiving of all relevant files in the CMS will also ensure that SNL can provide DOE with any and all files requested by reviewers such as the EEG.

SNL/WIPP PA personnel will run this FMT on a Compaq Computer Corp. (now a part of the Hewlett-Packard Co.) ES40 computer (also referred to as "BTO") with the Open VMS 7.3-1 operating system, or on the Compaq ES45 computer with Open VMS 7.3-1. They could also run FMT on other machines in the Open VMS cluster if other machines are qualified for such use.

## 7 TASKS

The three tasks required to calculate revised An(III), An(IV), and An(V) solubilities for the CRA PA are: (1) documentation of the establishment of a representative Salado brine for use in this and other modeling and laboratory studies; (2) recalculation of the concentrations of acetate, citrate, EDTA, and oxalate in WIPP brines, if necessary; (3) FMT solubility calculations. The first and second tasks must be completed before starting the third task to satisfy SNL/WIPP QA requirements; the second task must be completed before the third to ensure that up-to-date concentrations of these organic ligands are used in the solubility calculations.

The following subsections describe these tasks in detail.

### 7.1 Documentation of GWB

J. L. Krumhansl of Geochemistry Department 6118 established GWB as a representative, intergranular Salado brine for laboratory studies of the efficacy of MgO at SNL in Albuquerque during the mid-to-late 1990s. Krumhansl calculated the average concentrations of  $\text{Li}^+$ ,  $\text{B}(\text{OH})_x^{3-x}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and TDS in GWB from the results of an earlier study of the composition of brines seeping into the WIPP underground workings (Krumhansl et al., 1991). He then developed a recipe for this brine. Although he drafted a memorandum describing the establishment of GWB, he never completed the documentation of this brine by finalizing the memo and submitting it to the SNL/WIPP Records Center.

We will complete the documentation of GWB by carrying out an independent verification of the calculations used to define this brine and those used to develop the recipe. This verification will follow the procedure for routine calculations in NP 9-1, Appendix C (see Section 9, Applicable Procedures). We will describe the calculations that we will use to verify Krumhansl's original calculations, and will include Krumhansl's original, draft memo describing GWB as an appendix to our verification. We will submit the entire package for independent technical, quality-assurance, and management reviews according to NP 6-1 (Section 9). After resolution of the comments,

we will submit the package, along with the completed Document Review and Comment forms, to the SNL/WIPP Records Center as specified by NP 17-1 (Section 9).

## 7.2 Recalculation of the Concentrations of Organic Ligands

LANL is currently updating the WIPP TRU waste inventory for the CRA PA calculations (Downes and Guerin, 2003). This update could change the estimated quantities of acetate, citrate, EDTA, and oxalate in the inventory, and could result in the addition of lactate to the inventory. If the quantities of these organics change, we will recalculate the concentrations of these organics in WIPP brines in the same way used to calculate their concentrations at the time of the CCA PA (see Subsection 5.1, CCA Solubilities). If the updated inventory does not contain revised quantities of these organics, we will use the concentrations estimated at the time of the CCA.

## 7.3 FMT Calculations

We will calculate revised An(III), An(IV), and An(V) solubilities for the CRA PA in three WIPP brines: Brine A, GWB, and ERDA-6. Table 5 gives the compositions of these brines. Although we believe that GWB is more representative of intergranular Salado brines than Brine A (see Subsection 5.3.1, Use of GWB), we will use both GWB and Brine A to compare actinide solubilities calculated with these brines, and to compare our results for Brine A to those calculated for Brine A at the time of the PAVT (e.g., Novak, 1997). We will not include  $\text{Li}^+$  in our calculations with GWB because there are no data for  $\text{Li}^+$  in the FMT thermodynamic database.

For each brine, we will assume that each of the following carbonation reactions will buffer  $f_{\text{CO}_2}$ : (1) brucite-calcite, (2) brucite-magnesite, (3) brucite-hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ), (4) brucite-hydromagnesite ( $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ), or (5) brucite-nesquehonite. (The brucite dissolution reaction will buffer pH in all cases.) Because these carbonate minerals are listed in order of decreasing stability under expected WIPP conditions, we will not suppress any of these solids in those runs in which we want the brucite-calcite carbonation reaction to buffer  $f_{\text{CO}_2}$ ; we will suppress calcite in those runs in which we want the magnesite-brucite reaction to buffer  $f_{\text{CO}_2}$ ; we will suppress calcite and magnesite in those runs in which we want brucite-hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) reaction to buffer  $f_{\text{CO}_2}$ ; etc. We will assume that each of the five carbonation reactions will buffer  $f_{\text{CO}_2}$  to compare actinide solubilities calculated at different values of  $f_{\text{CO}_2}$ , and to compare our results for each buffer to those calculated at the same value of  $f_{\text{CO}_2}$  for the PAVT.

For each brine and carbonation reaction, we will conduct one set of calculations with the organic ligands acetate, citrate, EDTA, and oxalate present; and another without

Table 5. Compositions of Brine A, GWB, and ERDA-6 Prior to Reaction.

Element or Property	Brine A <sup>1</sup>	GWB <sup>2</sup>	ERDA-6 <sup>3</sup>
B(OH) <sub>x</sub> <sup>3-x</sup>	20 mM <sup>4</sup>	158 mM	63 mM
Na <sup>+</sup>	1.83 M	3.53 M	4.87 M
Mg <sup>2+</sup>	1.44 M	1.02 M	19 mM
K <sup>+</sup>	770 mM	467 mM	97 mM
Ca <sup>2+</sup>	20 mM	14 mM	12 mM
SO <sub>4</sub> <sup>2-</sup>	40 mM	177 mM	170 mM
Cl <sup>-</sup>	5.35 M	5.86 M	4.8 M
Br <sup>-</sup>	10 mM	26.6 mM	11 mM
Total inorganic C (as HCO <sub>3</sub> <sup>-</sup> )	10 mM	-	16 mM
pH	6.5	-	6.17
Sp gr	1.2	1.2	1.216
TDS	306,000 mg/L	-	330,000 mg/L

1. From Molecke (1983).
2. To be documented as described in Task 2 (see Subsection 7.2, Task 2: Documentation of GWB).
3. From Popielak (1983).
4. Reported by Molecke (1983) as BO<sub>3</sub><sup>3-</sup>.

organic ligands. For the calculations with organics, the concentrations estimated at the time of the CCA will be updated, if necessary (see Subsection 7.2, Recalculation of the Concentrations of Organic Ligands). We will calculate solubilities with and without organics to quantify the effects of organics, and to compare our results without organics to those calculated for the PAVT.



For the CRA PA, we will recommend one set of An(III), An(IV), and An(V) solubilities for the vectors with microbial activity and another set of solubilities for the vectors without microbial activity. For both microbial and nonmicrobial vectors, we will submit solubilities calculated with GWB (the more representative Salado brine) and with ERDA-6 (the Castile brine). Therefore, we will submit four sets of solubilities calculated under each of the following four sets of conditions: (1) GWB, with acetate, citrate, EDTA, and oxalate, in equilibrium with halite, anhydrite,  $Mg_2Cl(OH)_3 \cdot 4H_2O$ , brucite, and hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) (these conditions pertain to the microbial vectors); (2) ERDA-6, with organics, in equilibrium with halite, anhydrite, brucite, and hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) (these conditions also pertain to microbial vectors); (3) GWB, with organics, in equilibrium with halite, anhydrite,  $Mg_2Cl(OH)_3 \cdot 4H_2O$ , brucite, and calcite (these conditions pertain to nonmicrobial vectors); and (4) ERDA-6, with organics, in equilibrium with halite, anhydrite, glauberite, brucite, and calcite (these conditions also pertain to nonmicrobial vectors).

Alternatively, we could choose a solubility for each actinide oxidation state (An(III), An(IV), and An(V)) in the Salado brines by selecting the highest solubility from the four solubilities calculated for each oxidation state with organic ligands present (Brine A and the brucite-hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) carbonation reaction, Brine A and the brucite-calcite reaction, GWB and the brucite-hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) reaction, or GWB and the brucite-calcite reaction). This would avoid the need to modify PA codes to use different solubilities for vectors with and without microbial activity. It would also avoid the need to repeat the PA calculations or carry out an impact analysis if the EPA refuses to accept the use of GWB as the Salado brine, or if the EPA refuses to accept the brucite-calcite reaction as the  $f_{CO_2}$  buffer for nonmicrobial vectors. Rejection of GWB or the brucite-calcite reaction by the EPA would then imply that any PA calculations carried out with solubilities calculated for GWB or brucite and calcite overestimated the direct brine releases relative to those that would have been predicted for Brine A and brucite and hydromagnesite. We could also choose a solubility for each actinide oxidation state in ERDA-6 (the Castile brine) by selecting the higher solubility from the two solubilities calculated for each oxidation state with organic ligands present (ERDA-6 and the brucite-hydromagnesite ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) carbonation reaction, or ERDA-6 and the brucite-calcite reaction).

## 8 SPECIAL CONSIDERATIONS

LANL must finalize its estimates of the quantities of the acetate, citrate, EDTA, and oxalate to be emplaced in the repository – part of its update of WIPP TRU waste inventory for the CRA PA calculations – before we can start the second and third tasks of this analysis (see Section 7, Tasks). If this update results in changes in the quantities of these ligands, we will proceed as described in Subsection 5.1, CCA Solubilities; and Subsection 7.2, Recalculation of the Concentrations of Organic Ligands. If not, we will use the concentrations estimated for the CCA (Subsection 5.1, CCA Solubilities).

## 9 APPLICABLE PROCEDURES

The following NPs and Activity/Project Specific Procedure (SP) are applicable to the work described in this AP. This list does not identify the current version of these NPs and SPs; the current versions of these and other procedures are provided on the SNL NWMP web site ([www.nwmp.sandia.gov/onlinedocuments](http://www.nwmp.sandia.gov/onlinedocuments)).

- NP 2-1, "Qualification and Training,"
- NP 6-1, "Document Review Process,"
- NP 9-1, "Analyses,"
- NP 9-2, "Parameters,"
- NP 17-1, "Records,"
- NP 19-1, "Software Requirements,"

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