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**SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT**

AP-143

**Analysis Plan for the Calculation of Actinide Solubilities for
the WIPP CRA-2009 PABC**

Task 1.2.5

Effective Date: 05/06/09

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1 Introduction and Objectives

This AP describes how we will establish the solubilities of actinide elements for the U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) Performance Assessment Baseline Calculation (PABC), a WIPP compliance-related calculation. Actinide solubilities (the sums of the concentrations of the dissolved actinide species in chemical equilibrium with actinide-bearing solid phases under the conditions expected in WIPP disposal rooms) and the concentrations of colloidal (suspended) actinides, which are calculated from the solubilities, together constitute the actinide source term used in WIPP performance assessment (PA) calculations.

The PA calculations carried out for the CRA-2009 used the actinide solubilities established by Brush and Xiong (2005a, 2005b) and Brush (2005) for the PABC for the first WIPP Compliance Recertification Application (CRA-2004 PABC). These solubilities incorporated several changes specified by the EPA based on its review of the solubilities used for the original PA calculations for the CRA-2004 (CRA-2004 PA) (Brush and Xiong, 2003a; 2003b; 2003c; 2003d; 2003e). Brush and Xiong (2005a) described these changes in detail.

Because these changes required considerable time to implement, it is necessary to initiate analogous changes in the actinide solubilities established for the CRA-2004-PABC and used again for the CRA-2009 PA so that this work does not hold up the CRA-2009 PABC.

The EPA has never required significant changes in the procedures used to calculate the colloidal source term. Therefore, we assume that: (1) no changes will be specified for the colloidal source term for the CRA-2009 PABC, (2) there is no need to describe possible changes in this AP, and (3) we will use the same procedures to calculate the colloidal source term that were used for the CRA-2004 PABC for the CRA-2009 PABC. If the EPA specifies changes in the colloidal source term, we will implement these changes according to the procedures specified in the current version of NP 9-1, Analyses, Subsection 2.3, Other Analysis or Information Requests.

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

2 Approach

This section describes the approach that we will use to establish the solubilities of actinide elements under conditions expected in WIPP disposal rooms for the CRA-2009 PABC.

Subsection 2.1 describes how we will predict the long-term conditions in the WIPP. Subsection 2.2 discusses the calculations that we will use to define the solubilities of actinides in three of the four oxidation states that we expect under these conditions, and provides the estimated solubility that we will use for the fourth oxidation state.

Table 1. Abbreviations, Acronyms, Elements and Compounds, Initialisms, and Minerals.

Abbreviation, etc.	Definition
Am	americium
anhydrite	CaSO ₄
An	actinide element(s)
An(III)	actinide(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	(the WIPP) Actinide Source Term Program
B	aqueous or solid boron or boron-bearing species
Br	aqueous or solid bromine or bromine-bearing species
Brine A	a synthetic brine representative of intergranular Salado brines
brucite	Mg(OH) ₂
C	aqueous, gaseous, or solid carbon or carbon-bearing species
Ca	aqueous or solid calcium or calcium-bearing species
calcite	CaCO ₃
CBFO	(U.S. DOE) Carlsbad Field Office
CCA	(WIPP) Compliance Certification Application, submitted to the EPA in October 1996
Cl	aqueous or solid chloride or chloride-bearing species
Cm	curium
CMS	(SNL/WIPP software) Configuration Management System
CO ₂	carbon dioxide
CO ₃ ²⁻	carbonate ion
CPG	(SNL) Carlsbad Programs Group
CPR	cellulosic, plastic, and rubber (materials)
CRA-2004	first WIPP Compliance Recertification Application, submitted to the EPA in March 2004
CRA-2009	second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
DOE	(U.S.) Department of Energy
DRZ	disturbed rock zone
EDTA	ethylenediaminetetraacetate
EPA	(U.S.) Environmental Protection Agency
Eq.	Equation or equilibration
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)

Table 1. Abbreviations, Acronyms, Elements and Compounds, Initialisms, and Minerals (cont.).

Abbreviation, etc.	Definition
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
f_{CO_2}	fugacity (similar to the partial pressure) of CO_2
Fe	aqueous or solid iron or iron-bearing species
Florida State University	FSU
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
g	gaseous
glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
H_2O	water (aq, g, or contained in solid phases)
halite	NaCl
hydromagnesite ₄₃₂₃	$\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
hydromagnesite ₅₄₂₄	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
K	aqueous or solid potassium or potassium-bearing species
LANL - CO	Los Alamos National Laboratory - Carlsbad Operations
LLNL	Lawrence Livermore National Laboratory
M	molar
m	molal
magnesite	MgCO_3
Mg	aqueous or solid magnesium or magnesium-bearing species
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various impurities
mM	millimolar
Na	aqueous or solid sodium or sodium-bearing species
Nd	aqueous or solid neodymium or neodymium-bearing species
nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$
NP	(SNL Nuclear Energy and Global Security Technology Center 6700) Nuclear Waste Management Procedure
Np	aqueous or solid neptunium or neptunium-bearing species
OH-	hydroxide ion (aq or contained in solid phases)
oxalate	$\text{C}_2\text{O}_4^{2-}$ (aq or contained in solid phases)

Table 1. Abbreviations, Acronyms, Elements and Compounds, Initialisms, and Minerals (cont.).

Abbreviation, etc.	Definition
PA	performance assessment
PABC	Performance Assessment Baseline Calculations
PAVT	1997 WIPP Performance Assessment Verification Test
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
pH	the negative, common logarithm of the activity of H ⁺
Phase 3	Mg ₂ Cl(OH) ₃ ·4H ₂ O
Phase 5	Mg ₃ (OH) ₅ Cl·4H ₂ O
Pu	aqueous or solid plutonium or plutonium-bearing species
QA	quality assurance
Rev.	revision
RH	relative humidity
SG	specific gravity
SNL	Sandia National Laboratories
S	aqueous or solid sulfate (S(VI)) or sulfide (S(-II)) species
SPC	Salado Primary Constituents, a synthetic brine similar to Brine A
Th	aqueous or solid thorium or thorium-bearing species
TIC	total inorganic C
TRU	transuranic waste
U	aqueous or solid uranium or uranium-bearing species
whewellite	Ca oxalate hydrate, or CaC ₂ O ₄ ·H ₂ O
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
μ ⁰ /RT	dimensionless standard chemical potential

All of the assumptions, parameters, and procedures described in this section are consistent with the four conceptual models for WIPP near-field chemistry: Gas Generation, Chemical Conditions, Dissolved Actinide Source Term, and Colloidal Actinide Source Term. These conceptual models were described in detail by Wilson (1996a, 1996b, 1997a, 1997b). They were also discussed by the U.S. EPA (1998a, 1998b, 1998c, 1998f) as part of its review of the PA calculations for the DOE's original WIPP Compliance Certification Application (CCA PA) (U.S. DOE, 1996a). However, the EPA recently provided clear, concise, stand-alone descriptions of three of these conceptual models (Gas Generation, Chemical Conditions, and Dissolved Actinide Source Term), including minor changes made since the CCA (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A).

2.1 Chemical Conditions

Definition of the long-term chemical conditions expected in WIPP disposal rooms consists of: (1) use of standard brines to simulate fluids that could enter the repository from the Salado Formation (Fm.) and the Castile Fm.; (2) the assumption that instantaneous, reversible equilibria among these brines, major Salado minerals, and MgO hydration and carbonation products will control chemical conditions; and (3) use of a thermodynamic model or models to calculate these chemical conditions.

2.1.1 Use of Standard Brines

WIPP PA predicts that: (1) intergranular brine could seep into the disposal rooms from the disturbed rock zone (DRZ) in the surrounding Salado Fm. after the panels are filled and closed, (2) brine could flow down into the repository from overlying formations if future exploratory drilling inadvertently penetrates the repository, and (3) brine could flow up into the repository from reservoirs in the underlying Castile Fm. if drilling penetrates both the repository and a Castile brine reservoir. PA assumes that, in the second case listed above, brine from formations above the repository would react with Salado minerals to an extent sufficient to produce a composition identical to that of intergranular Salado brines. Furthermore, PA assumes that mixtures of Salado and Castile brines will have compositions and other properties intermediate between these brines, so that actinide solubilities for these end-member compositions can be used in PA. This eliminates the need for brine-mixing calculations and predictions of solubilities for the resulting mixtures. These assumptions and predictions are described in detail in U.S. DOE (1996a, 2004).

The WIPP Actinide Source Term Program (ASTP), a DOE program to establish actinide solubilities and colloidal actinide concentrations for the CCA PA (U.S. DOE, 1996a, Appendix SOTERM), used three synthetic solutions to simulate brines that could be present in the WIPP after filling and sealing: (1) Brine A, representative of intergranular brines from the Salado Fm. at or near the stratigraphic horizon of the repository (Molecke, 1983); (2) Salado Primary Constituents (SPC) brine, a simplified formulation of Brine A (Novak and Moore, 1996; Novak et al., 1996; and Novak, 1997); and (3) ERDA-6, typical of fluids in brine reservoirs in the Castile Fm. (Popielak et al., 1983). Novak et al. (1996) used SPC and ERDA-6 for the actinide solubility calculations for the CCA PA source term (U.S. DOE, 1996a, Appendix SOTERM); Novak (1997) used the same brines for the actinide solubility calculations for the Performance Assessment Verification Test (PAVT), which the EPA required as part of its review of the CCA.

After the CCA PA and the PAVT, Krumhansl et al. (1991) defined GWB as a representative, synthetic, intergranular Salado brine for use in laboratory studies of MgO at SNL in Albuquerque in the mid-to-late 1990s. Investigators used GWB for these studies instead of Brine A because GWB resembles the average composition of intergranular Salado brines at or near the stratigraphic horizon of the repository more closely than Brine A. This is especially true for Mg, which appears to have an important affect on parameters such as the pH of WIPP brines and the reaction of these brines with MgO, the WIPP engineered barrier. During the 2000s, investigators at SNL in Carlsbad have also used GWB to simulate Salado brines in

their laboratory and modeling studies of MgO. Snider (2003b) verified that GWB is the average composition of intergranular fluids collected from the Salado Fm. at the original stratigraphic horizon of the repository and analyzed by Krumhansl et al. (1991). Snider (2003b) also established a formulation for this brine.

Brush and Xiong (2003a, 2003b) carried out actinide solubility calculations with both Brine A and GWB to compare the results obtained for these Salado brines; they used ERDA-6 to simulate Castile brines. The solubilities obtained with GWB and ERDA-6 (Brush and Xiong, 2003d) were used for the CRA-2004 PA. Brush and Xiong (2005a) also conducted solubility calculations with Brine A, GWB, and ERDA-6; those obtained with GWB and ERDA-6 (Brush, 2005) were used for the CRA-2004 PABC. Table 2 provides the compositions and other parameters of Brine A, GWB and ERDA-6 before and after equilibration with most of the important solids in WIPP disposal rooms (see Subsection 2.1.2). Table 2 also provides the solubilities of actinide elements in the +III, +IV, and +V oxidation states (An(III), An(IV), and An(V)) in these brines after equilibration with these solids. The results obtained with all three of these brines were very similar, especially those obtained with Brine A and GWB.

Because GWB is more representative of intergranular Salado brines than Brine A and the results obtained with these brines were so similar, the EPA (2006, p. 8) stated that “use of the GWB formulation in place of Brine A for the CRA PA and future actinide solubility calculations is appropriate.”

Therefore, we will use GWB and ERDA-6, but not Brine A, for the CRA-2009 PABC. Omission of Brine A will constitute a minor change from the CRA-2004 PABC.

2.1.2 Use of Brine-Solid Equilibria to Control Chemical Conditions

It has been assumed for the actinide solubility calculations for all of the previous compliance-related WIPP PA calculations that instantaneous, reversible equilibria among WIPP brines, major minerals in the Salado Fm., and MgO hydration and carbonation products will control chemical conditions throughout a homogeneous repository. This assumption is reasonable given that the reactions among these brines, minerals, and MgO hydration and carbonation products will reach equilibrium rapidly with respect to the 10,000-year regulatory period. This assumption is also consistent with the conceptual model for near-field chemical conditions.

Two other important reactions - microbial consumption of cellulosic, plastic, and rubber (CPR) materials and concomitant production of CO₂ and other gases; and anoxic corrosion of steels and other iron- (Fe-)base (alloys and production of hydrogen (H₂) - will not necessarily occur rapidly with respect to the 10,000-year regulatory period. Therefore, PA incorporates these reactions at rates sampled from experimentally-based ranges and probability distributions. The PA implementation of these reactions is consistent with the conceptual model for gas generation. The effects of these microbial and corrosion reactions on chemical conditions are also included in the actinide solubility calculations as described below.

Table 2. Compositions of Brine A, GWB, and ERDA-6 (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids (see Subsection 2.1.2), and An(III), An(IV), and An(V) Solubilities (M) after Equilibration with Solids.

Element or Property	Brine A before Eq. ^A	Brine A after Eq. ^B	GWB before Eq. ^C	GWB after Eq. ^D	ERDA-6 before Eq. ^E	ERDA-6 after Eq. ^F
B(III)(aq)	0.020	0.0235	0.158	0.166	0.063	0.0624
Na(I)(aq)	1.83	4.12	3.53	4.35	4.87	5.24
Mg(II)(aq)	1.44	0.467	1.02	0.578	0.019	0.157
K(I)(aq)	0.770	0.906	0.467	0.490	0.097	0.0961
Ca(II)(aq)	0.020	0.0169	0.014	0.00895	0.012	0.0107
S(VI)(aq)	0.040	0.0934	0.177	0.228	0.170	0.179
Cl(-I)(aq)	5.35	5.75	5.86	5.38	4.8	5.24
Br(-I)(aq)	0.010	0.0118	0.0266	0.0278	0.011	0.0109
Ionic strength (m)	-	7.49	-	7.66	-	6.80
f _{CO₂} (atm)	-	3.13 × 10 ⁻⁶	-	3.16 × 10 ⁻⁶	-	3.16 × 10 ⁻⁶
TIC (mM)	10	0.353	-	0.350	16	0.428
pH (Pitzer scale ^G)	6.5	8.69	-	8.69	6.17	8.94
RH	-	0.729	-	0.732	-	0.748
SG	1.2	1.23	1.2	1.23	1.216	1.22

Table 2 continued on next page

Information Only

Table 2. Compositions of Brine A, GWB, and ERDA-6 (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids (see Subsection 2.1.2), and An(III), An(IV), and An(V) Solubilities (M) after Equilibration with Solids (continued from previous page).

Element or Property	Brine A before Eq. ^A	Brine A after Eq. ^B	GWB before Eq. ^C	GWB after Eq. ^D	ERDA-6 before Eq. ^E	ERDA-6 after Eq. ^F
An(III)	-	5.46×10^{-7}	-	3.87×10^{-7}	-	2.88×10^{-7}
An(IV)	-	5.58×10^{-8}	-	5.64×10^{-8}	-	6.79×10^{-8}
An(V)	-	1.82×10^{-7}	-	3.55×10^{-7}	-	8.24×10^{-7}

- A. Molecke (1983).
B. Values calculated by Brush and Xiong (2005a, 2005b) and Brush (2005, Run 3) with FMT (Babb and Novak, 1997 and addenda; Wang, 1998) for the WIPP CRA-2004 PABC.
C. Krumhansl et al. (1991) and Snider (2003b).
D. Values calculated by Brush and Xiong (2005a, 2005b) and Brush (2005, Run 7) with FMT (Babb and Novak, 1997 and addenda; Wang, 1998) for the WIPP CRA-2004 PABC.
E. Popielak et al. (1983).
F. Values calculated by Brush and Xiong (2005a, 2005b) and Brush (2005, Run 11) with FMT (Babb and Novak, 1997 and addenda; Wang, 1998) for the WIPP CRA-2004 PABC.
G. The “Pitzer scale” is an unofficial pH scale consistent with pH values calculated using single-ion activity coefficients based on the Pitzer activity-coefficient model for brines and evaporite minerals of Harvie et al. (1984), extended to include Nd(III), Am(III), and Cm(III); Th(IV); and Np(V) (see Subsection 2.2.1). The term “Pitzer” scale was proposed unofficially by T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA.

The geochemical speciation and solubility code Fracture Matrix Transport (FMT) (Babb and Novak, 1997 and addenda; Wang, 1998) has been used to predict near-field conditions after Salado and Castile brines equilibrate with major Salado minerals and MgO hydration and carbonation products. Brush and Xiong (2005a, 2005b) and Brush (2005) assumed that Brine A, GWB, or ERDA-6 (see Table 2) will equilibrate with: (1) halite (NaCl) and anhydrite (CaSO₄), two of the most abundant Salado minerals; (2) the MgO hydration and carbonation products brucite (Mg(OH)₂) and hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), respectively; and (3) hydrous, amorphous ThO₂; KNpO₂CO₃ and Am(OH)₃. In addition to these solids, FMT predicted that: (1) the solids Mg₂Cl(OH)₃·4H₂O and whewellite (Ca oxalate hydrate, or CaC₂O₄·H₂O) would precipitate from Brine A and GWB; and (2) glauberite (Na₂Ca(SO₄)₂) and whewellite would precipitate from ERDA-6 if these brines equilibrate with halite, anhydrite, brucite, and hydromagnesite. In this AP, hydromagnesite with the composition Mg₅(CO₃)₄(OH)₂·4H₂O is referred to as “hydromagnesite₅₄₂₄” because the Mg²⁺:CO₃²⁻:OH:H₂O molar ratio is 5:4:2:4.

Also, $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ is referred to as “phase 3” because the $\text{OH}^-:\text{Cl}^-$ molar ratio is 3. Because the conditions predicted for GWB and ERDA-6 (Table 2) were used for the An(III), An(IV), and An(V) solubility calculations for the CRA-2004 PABC, they are part of the current WIPP PA baseline. The An(III), An(IV), and An(V) solubilities used for the CRA-2004 PABC (Table 2) were also used for the CRA-2009 PA.

FMT predicted that equilibration of these brines with one or more the solids listed above will: (1) establish a total inorganic C (TIC) concentration of 0.350 mM in GWB, and decrease the TIC from 16 to 0.428 mM in ERDA-6; (2) buffer f_{CO_2} at 3.16×10^{-6} atm ($10^{-5.50}$ atm) in both brines; and (3) establish a pH of 8.69 in GWB, and increase the pH of ERDA-6 from 6.17 to 8.94 (see Table 2).

Brush and Xiong (2003a) reviewed the history of assumptions as to which brines, evaporite minerals, and MgO hydration and carbonation products will control chemical conditions in the WIPP. However, we should point out here that, for the CRA-2004 PABC, Brush and Xiong (2005a, 2005b) and Brush (2005) assumed that equilibria among GWB or ERDA-6 and the MgO hydration and carbonation products brucite, phase 3 (in the case of GWB), and hydromagnesite₅₄₂₄ will control f_{CO_2} and pH.

In particular, it is assumed that the brucite carbonation reaction

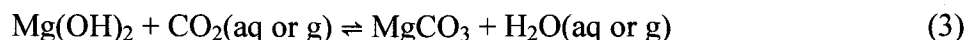


will buffer f_{CO_2} at 3.16×10^{-6} atm. In ERDA-6, FMT predicts that phase 3 will also be in equilibrium with hydromagnesite₅₄₂₄. However, carbonation of phase 3 has not been observed in the laboratory, either in studies carried out for the WIPP Project or (to the best of our knowledge) in those conducted for other applications. The brucite dissolution-precipitation reaction



will establish a pH of 8.69 in GWB and 8.94 in ERDA-6 (Table 2). The use of these reactions to predict f_{CO_2} and pH is part of the conceptual model for near-field chemical conditions.

However, hydromagnesite₅₄₂₄ is thermodynamically metastable with respect to magnesite (MgCO_3), the thermodynamically stable, Mg-carbonate mineral under the conditions expected in the WIPP. Furthermore, magnesite is present in the Salado at the stratigraphic horizon of the repository. Therefore, the reaction



would be expected to buffer f_{CO_2} at 1.20×10^{-7} atm ($10^{-6.92}$ atm) in GWB or 1.23×10^{-7} atm ($10^{-6.91}$ atm) in ERDA-6 *if* the kinetics of magnesite formation were fast enough for this phase to replace hydromagnesite₅₄₂₄ during the 10,000-year period of performance of the repository. Novak et al. (1996) used the brucite-magnesite carbonation reaction to calculate f_{CO_2} for

the actinide solubility calculations for the CCA PA. The EPA, however, concluded that the hydromagnesite₅₄₂₄-to-magnesite reaction might be too slow. Therefore, it specified that the brucite-hydromagnesite₅₄₂₄ carbonation reaction be used (Trovato, 1997). This is because this buffer conservatively increases f_{CO_2} by one order of magnitude, which in turn increases the solubilities of An(IV) by one-to-two orders of magnitude (Brush, 2005, Table 5). Use of the brucite-hydromagnesite₅₄₂₄ buffer does not preclude the possibility that magnesite will replace hydromagnesite₅₄₂₄ to a significant extent – or entirely - in 10,000 years. Based on its review of the CCA PA (U.S. DOE, 1996a, Chapter 6), the EPA concluded that hydromagnesite₅₄₂₄ will dehydrate to magnesite in hundreds to thousands of years (U.S. EPA, 1998f):

The available rate data indicate that some portion, perhaps all, of the hydromagnesite_[5424] will be converted to magnesite over the 10,000-year period for repository performance. The exact time required for complete conversion has not been established for all chemical conditions. However, the available laboratory and field data clearly indicate that magnesite formation takes from a few hundred to, perhaps, a few thousand years. Thus, the early repository conditions can be best represented by the equilibrium between brucite and hydromagnesite_[5424]. These conditions will eventually evolve to equilibrium between brucite and magnesite.

We will continue to use the brucite-hydromagnesite₅₄₂₄ carbonation reaction to calculate f_{CO_2} for the actinide solubility calculations for the PABC.

For the CRA-2004 PA, Brush and Xiong (2003a) defined separate, slightly different, chemical conditions characteristic of the absence of microbial activity for the actinide solubility calculations. They concluded that - in the absence of microbial activity – the reaction



would buffer f_{CO_2} , and specified that this f_{CO_2} buffer be used for nonmicrobial vectors. For the CCA PA, the PAVT, and the CRA-2004 PA, however, the conceptual model for microbial activity in WIPP disposal rooms included a probability of 0.5 for microbial activity. In the event of microbial activity, microbes could consume up to 100% of the cellulosic materials in the repository. Furthermore, there was a conditional probability of 0.5 that microbes could consume all of the plastic and rubber materials after consuming all cellulosic materials. Therefore, there was no microbial activity in about 50% of the PA vectors; possible microbial consumption of all cellulosic materials, but no plastic or rubber materials, in about 25% of the vectors; and possible consumption of all of the CPR materials in the remaining 25% of the vectors. Brush and Xiong (2003a) provided a detailed, geochemical explanation of why use of the brucite-calcite ($CaCO_3$) carbonation reaction to buffer f_{CO_2} , was appropriate in the absence of microbial activity. Therefore, values of f_{CO_2} obtained from Reaction 4 were used to calculate actinide solubilities for the nonmicrobial CRA-2004 PA vectors.

However, the EPA specified that the microbial conceptual model be changed for the CRA-2004 PABC such that there is a probability of 1 for microbial activity in the WIPP (Cotsworth, 2005, Enclosure 1). Furthermore, the EPA specified a probability of 1 that microbes could consume up to 100% of the cellulosic materials in the repository and a probability of 0.25 that microbes could consume all plastic and rubber materials after consuming all cellulosic materials. Therefore, there was possible microbial consumption of all of the cellulosic materials, but no plastic or rubber materials, in 100% of the vectors; and possible consumption of all CPR materials in 25% of the vectors. Thus, nonmicrobial vectors were eliminated from PA, and the brucite-calcite carbonation reaction was only used to buffer f_{CO_2} for the actinide solubility calculations for the CRA-2004 PA. We will continue to define chemical conditions only for the assumption that microbial activity and CO_2 production will occur, consistent with the CRA-2004 PABC.

The only change that we will consider for a CRA-2009 PABC (in addition to any possible changes requested by the EPA) would be to include the possibility of formation of $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$ instead of phase 3 in the FMT and EQ3/6 calculations with GWB. $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$ is referred to herein as "phase 5" because the $\text{OH}^-:\text{Cl}^-$ molar ratio in this solid is 5. Phase 5 or an amorphous $\text{Mg}\text{-OH}\text{-Cl}\text{-H}_2\text{O}$ phase, but not phase 3, has been observed in the laboratory hydration experiments with GWB (e.g., Snider, 2003a). Because the FMT thermodynamic database does not include a dimensionless standard chemical potential (μ^0/RT) for phase 5, FMT has predicted that equilibration of GWB with major Salado minerals and MgO hydration and carbonation products will produce phase 3.

Solubility experiments have been carried out at Sandia/Carlsbad to determine μ^0/RT for phase 5 and a write-up of this work is in preparation. We will add μ^0/RT for phase 5 to both the FMT and the EQ3/6 databases after this write-up has been reviewed and approved (see Subsections 2.2.4 and 4.1), and will determine the sensitivity of chemical conditions predicted with these codes to the presence of this phase. If, as expected, the presence of phase 5 does not affect these conditions - especially the pH - to a significant extent, we will include it in the solid-phase assemblage in equilibrium with GWB to reflect the experimental results, which indicate that it will be present instead of phase 3.

2.1.3 Use of FMT and EQ3/6 to Predict Chemical Conditions

The speciation and solubility code FMT (Babb and Novak, 1995; 1997 and addenda; Wang, 1998) has been used to predict chemical conditions in WIPP disposal rooms, consistent with the WIPP conceptual models for near-field chemistry (see Subsection 2.1.2). The reaction-path code EQ6 (Wolery and Daveler, 1992), part of the EQ3/6 geochemical software package (Daveler and Wolery, 1992; Wolery, 1992a; 1992b), has also been used to predict near-field chemical conditions. For example, Wang (1996a, 1996b) used EQ6 to show that the use of MgO as an engineered barrier would control chemical conditions in the repository, thereby establishing homogenous conditions throughout the repository by eliminating "microenvironments," in which conditions could differ from those in other microenvironments. However, FMT has always been used to predict the compositions of Salado and Castile brines, especially f_{CO_2} and pH, actually used for compliance-related actinide solubility calculations (i.e., Nowak et al. (1996) for the CCA PA; Nowak (1997) for the PAVT; Brush and Xiong,

(2003a, 2003b, 2003c, 2003d, 2003e) for the CRA-2004 PA; and Brush and Xiong (2005a, 2005b) and Brush (2005) for the CRA-2004 PABC).

Because FMT does not include a practicable reaction-path functionality equivalent to that of EQ6, FMT calculates both chemical conditions and actinide solubilities in the same runs. Initially, FMT users had to “build brines” by adding or subtracting chemical components until the resulting solutions were close to equilibrium with the expected solid-phase assemblage (i.e., halite, anhydrite, brucite, hydromagnesite₅₄₂₄, etc.). This assemblage was “expected” based on previous EQ6 calculations (e.g., Wang, 1996a; 1996b). When runs were carried out with brines with starting compositions close to equilibrium with the solids specified in the input files, FMT could adjust the composition without crashing (e.g., by precipitating small amounts of solid phases). Therefore, it could be said that FMT does have some reaction-path functionality, but it is not robust. The final brine compositions and other conditions predicted by FMT have been used as the “baseline” chemical conditions expected in the repository (see Table 2).

One of the goals of SNL’s WIPP chemistry program has been to replace FMT with EQ3/6 for both predictions of chemical conditions and actinide-solubility calculations. Replacement of FMT with EQ3/6 is desirable because: (1) EQ3/6 includes EQ6, a fully capable reaction-path component (FMT is essentially a speciation and solubility code, similar to the EQ3NR component of EQ3/6); (2) EQ3/6 is widely recognized and accepted by the geochemical community; and (3) EQ3/6 is much easier to use.

Prior to the 1996 CCA PA, EQ3/6 was qualified according to the SNL/WIPP software quality assurance (QA) requirements for calculations involving the nonradioactive elements in brines and evaporite minerals, but not for actinide-solubility calculations. Therefore, qualification of EQ3/6 for the latter application is underway (Wolery, 2008). We expect that this work will be completed in time to use EQ3/6 for both predictions of chemical conditions and actinide solubilities for the CRA-2009 PABC. In recent discussions with the DOE’s Carlsbad Field Office (CBFO), however, the EPA indicated that it would not review the qualification of EQ3/6 for actinide-solubility calculations prior to its second recertification of the WIPP.

Therefore, we will use both FMT and EQ6 to predict near-field chemical conditions, but we will use the results from FMT for the actinide-solubility calculations for the CRA-2009 PABC. We will use FMT in a manner identical to that used for the CRA-2004 PABC (Brush and Xiong, 2005a; Brush, 2005) and compare the results to those obtained using EQ6 (see below). We expect that the results will be essentially identical.

The use of EQ6 to predict chemical conditions will involve the following sequential reaction-path calculations with EQ6: (1) reaction of the WIPP brines GWB and ERDA-6 (see Table 2) with brucite from the hydration of all of the MgO emplaced in the repository, and with halite and anhydrite in the DRZ surrounding the repository (referred to as “Step 1”); and (2) carbonation of brucite to form hydromagnesite₅₄₂₄ (see Reaction 1) with the CO₂ produced by microbial consumption of all of the CPR materials in the repository by microbial denitrification and sulfate (SO₄²⁻) reduction (“Step 2”). We will not attempt to include anoxic corrosion of

steels and other Fe-base alloys in Step 2 because production of H_2 does not affect chemical conditions (H_2 will be inert under the conditions expected in the repository), and because production of H_2S , which could affect chemical conditions, can be neglected because it is assumed that this gas will react rapidly with steels and other Fe-base alloys.

The use of sequential EQ6 calculations (Steps 1 and 2 above) is reasonable because the reactions in Step 1 are fast with respect to the 10,000-year regulatory period, but those in Step 2 are not. The use of sequential calculations would also be consistent with the conceptual models for near-field chemistry, and their implementation in PA.

We will use quantities of materials (brine, halite, anhydrite, brucite, and CO_2) in these two-step simulations that correspond to the quantities that will be present and available in the WIPP after it is filled and sealed. These will include: (1) an EPA-approved estimate of the minimum brine volume required for a direct brine release (release of brine from the repository to the surface) (Clayton, 2008), (2) the quantities of halite and anhydrite present in the DRZ surrounding the repository (Brush et al., 2006, Subsection 3.2.3), (3) a molar quantity of brucite equal to that of the MgO to be emplaced in the repository, and (4) a molar quantity of CO_2 equal to that of the organic carbon (C) in the CPR materials to be emplaced. To calculate the quantities of halite and anhydrite, we will use the conservatively large DRZ currently implemented in PA and the results of Stein's (1985) mineralogical analysis of the Salado Fm. at or near the stratigraphic horizon of the repository; see Brush et al. (2006, Subsection 3.2.3) for a detailed explanation of this calculation. To calculate the quantity of CO_2 , we will use the latest estimate of the density of CPR materials in WIPP transuranic waste from Los Alamos National Laboratory – Carlsbad Operations (LANL - CO), probably the "PA roll-up" (a summary of inventory estimates required to carry out PA calculations) from the 2007 TRU waste inventory/2008 TRU waste inventory report), and assume that the yield of CO_2 from complete microbial consumption of CPR materials is 1 mol CO_2 per mol of organic C. This assumption is consistent with complete microbial consumption of all CPR materials by denitrification and SO_4^{2-} reduction and without any methanogenesis.

We will use spreadsheet calculations to scale the quantities of brine, halite, anhydrite, brucite, and CO_2 in the repository to 1 kg of H_2O for entry into the EQ3/6 input files for these simulations. EQ6 allows the user to specify the composition of the aqueous phase present at the start of a simulation. However, the code calculates the initial volume of this fluid by assuming that exactly 1 kg of H_2O is present and using the specific gravity specified by the user. Therefore, we will scale down the most recent minimum brine volume (Clayton, 2008) by scaling down the mass of H_2O in this brine to 1 kg of H_2O for use in the input files. We will then use the same scaling factor to reduce the masses of the solids.

The use of EQ6 described in this subsection bears some resemblance to that of Brush et al. (2006). However, there are two significant differences. First, we will equilibrate GWB or ERDA-6 with halite and anhydrite, but not with other Salado minerals such as gypsum, polyhalite, and magnesite during Step 1. Equilibration with just halite and anhydrite is consistent with the WIPP conceptual model for near-field chemical conditions and with previous predictions of chemical conditions for WIPP compliance-related solubility calculations (i.e., Novak et al. (1996) for the CCA PA; Novak (1997) for the PAVT; Brush and Xiong,

(2003a, 2003b, 2003c, 2003d, 2003e) for the CRA-2004 PA; and Brush and Xiong (2005a, 2005b) and Brush (2005) for the CRA-2004 PABC). Second, we will add a quantity of CO₂ equivalent to that produced by microbial consumption of all of the CPR materials in the repository without methanogenesis during Step 2, instead of by simulating microbial SO₄²⁻ reduction directly, which Brush et al. (2006) did in a novel way by titrating in “negative” hydrogen ion (H⁺) to simulate the consumption of this species and by assuming that the H₂S produced by SO₄²⁻ reduction is immediately consumed by metallic iron (Fe) or ferrous (Fe(II)-bearing) corrosion products.

2.2 Actinide Solubilities

Establishment of solubilities for the actinide source term usually would involve: (1) use of speciation and solubility models for Th(IV), Np(V), and Am(III) (Subsection 2.2.1); (2) inclusion of the effects of the organic ligands in TRU waste on Th(IV), Np(V), and Am(III) solubilities (Subsection 2.2.2); (3) use of the codes FMT and EQ3NR to calculate the solubilities of Th(IV), Np(V), and Am(III) (Subsection 2.2.3); (4) use of the FMT and EQ3/6 thermodynamic databases that are current at the time of these calculations (Subsection 2.2.4); (5) development of new uncertainty ranges and probability distributions for the Th(IV), Np(V), and Am(III) solubility predictions (Subsection 2.2.5); (6) predictions of the redox speciation of Th, U, Np, Pu, and Am under the chemical conditions expected in the WIPP (Subsection 2.2.6); (7) use of the oxidation-state analogy to apply the solubilities calculated for Th(IV), Np(V), and Am(III) to other actinides in the WIPP (Subsection 2.2.7); and (8) use of a solubility estimate for U(VI) (Subsection 2.2.8).

In recent discussions with the DOE’s Carlsbad Field Office (CBFO), however, the EPA indicated that the uncertainty ranges and probability distributions for the solubilities of Th(IV), Np(V), and Am(III) established for the CRA-2004 PABC should be used again for the CRA-2009 PABC. Therefore, new ranges and distributions will be developed for possible use in WIPP PA at some time in the future, but not for the CRA-2009 PABC.

2.2.1 Use of Thermodynamic Models for Th(IV), Np(V), and Am(III) Solubilities

It has been assumed for all of the previous compliance-related PA calculations that instantaneous, reversible equilibria among WIPP brines, actinide-bearing solids such as hydrous, amorphous ThO₂; and KNpO₂CO₃ and Am(OH)₃, and dissolved Th(IV), Np(V), and Am(III) species will control the solubilities of Th(IV), Np(V), and Am(III) throughout a homogeneous repository. These brines are assumed to be in equilibrium with halite, anhydrite, brucite, hydromagnesite₅₄₂₄, and other solids that are predicted to precipitate (see Subsection 2.1.2). This assumption, which is consistent with the conceptual model for actinide solubilities, is reasonable given that reactions among these brines, species, and solids will reach equilibrium rapidly with respect to the 10,000-year regulatory period. The sums of all of the dissolved species of Th(IV), Np(V), and Am(III) constitute the solubilities of these elements that will be used for the PABC source term. Sorption has never been included among the processes that will control the solubilities of Th(IV), Np(V), and Am(III) in WIPP disposal rooms. Omission of sorption may add conservatism to the actinide source term. We will continue to use these assumptions for the CRA-2009 PABC.

The ASTP established thermodynamic speciation and solubility models for Nd(III), Am(III), and Cm(III); Th(IV); and Np(V) by extending the Pitzer activity-coefficient model of Harvie et al. (1984) for brines and evaporite minerals to include Pitzer parameters for these actinide elements. The ASTP carried out laboratory experiments to obtain the Pitzer parameters required to extend the model of Harvie et al. (1984) to include Nd(III), Am(III), and Cm(III); and Th(IV). The ASTP used results from the literature for Np(V). U.S. DOE (1996a, Appendix SOTERM; 2004, Appendix PA, Attachment SOTERM) described this work in detail. The WIPP Project has not developed a model for actinides in the +VI oxidation state (An(VI)). Instead, the solubility of U(VI), the only actinide element expected to speciate in the +VI oxidation state under expected WIPP conditions, was estimated (Subsection 2.2.8).

The order of importance from the standpoint of PA of the radioelements in the TRU waste to be emplaced in the WIPP is $\text{Pu} \approx \text{Am} \gg \text{U} \approx \text{Th} \gg \text{Np} \approx \text{Cm} \approx$ fission products (Helton et al., 1998). However, Np and Cm were also included in the WIPP ASTP in case the sensitivity of the long-term performance of the WIPP to these radioelements changes. Therefore, the ASTP used predictions of the redox speciation of Th, U, Np, Pu, and Am in the WIPP (Subsection 2.2.6) and the oxidation-state analogy (Subsection 2.2.7) to extend the Th(IV) and the Am(III) speciation and solubility models to other actinides that will speciate in the +IV and +III oxidation states, respectively. Thus, the models developed by the ASTP are often referred to as the “An(III),” “An(IV),” and “An(V)” models. Based on experimental work carried out for the ASTP and for other applications, or predictions of redox speciation and the oxidation-state analogy, the An(III) model is applied to Pu(III), Am(III), and Cm(III); the An(IV) model is applied to Th(IV), U(IV), Np(IV), and Pu(IV); and the An(V) model is used only for Np(V).

The Th(IV), Np(V), and Am(III) solubility models were incorporated in the speciation and solubility component of FMT (Babb and Novak, 1995) for the CCA PA. Originally, FMT was developed as a reactive-transport code by C. F. Novak at the University of Texas at Austin (hence its name, “Fracture-Matrix Transport”). SNL’s WIPP chemistry team has revised FMT (e.g., Babb and Novak, 1997 and addenda; Wang, 1998), but has never qualified FMT for calculations other than speciation and solubility predictions according to the SNL/WIPP software QA requirements.

The ASTP also established a colloidal actinide source term for the CCA PA (U.S. DOE, 1996a, Appendix SOTERM). No additional studies of actinide colloids have been carried out since the CCA PA, and only minor changes were made in the colloidal source term for the CRA-2004 PA and the CRA-2004 PABC (Brush and Xiong, 2003a; U.S. DOE, 2004, Appendix PA, Attachment SOTERM). Therefore, this AP does not describe the colloidal source term (see Section 1).

Novak et al. (1996) used the Am(III), Th(IV), and Np(V) models implemented in FMT to calculate the solubilities of An(III), An(IV) and An(V) for the CCA PA. Table 3 provides these solubilities, along with the values of f_{CO_2} and pH predicted by FMT.

The EPA reviewed the ASTP's laboratory and modeling studies of actinide chemistry as part of its review of the CCA PA, and concluded that most features of the approach used to establish the dissolved-actinide source term for the CCA PA were adequate (U.S. EPA, 1998a, 1998d, 1998e, 1998f). However, the EPA did not accept the DOE's prediction that the brucite-magnesite carbonation reaction will buffer f_{CO_2} in WIPP disposal rooms. Instead, the EPA mandated that the brucite-hydromagnesite₅₄₂₄ carbonation reaction be used to calculate f_{CO_2} (see Subsection 2.1.2). Furthermore, the large difference in the solubilities of An(IV) predicted for Brine A and ERDA-6 (the former exceeded the latter by a factor of about 730) resulted in a review of and changes to the thermodynamic data for all three of the actinide oxidation states (see Subsection 2.2.4).

Therefore, Novak (1997) used FMT and the corrected database to recalculate the solubilities of An(III), An(IV), and An(V) under conditions defined by the brucite-hydromagnesite₅₄₂₄ carbonation reaction. (He also determined the sensitivity of f_{CO_2} and the solubilities of all three actinide oxidation states to other Mg-carbonates formed from brucite.) 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 (1998d, 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 (1998e, 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, $\text{Mg}_2\text{Cl}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, and hydromagnesite₅₄₂₄; and among ERDA-6 halite, anhydrite, glauberite, brucite, and hydromagnesite ($\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), referred to as "hydromagnesite₄₃₂₃." Table 3 provides the values of f_{CO_2} , pH, and the solubilities used for the PAVT.

Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2003) revised and updated the Th(IV), Np(V), and Am(III) solubility models for the CRA-2004 PA. Her changes included: (1) improved implementation of previously obtained laboratory data; (2) results of WIPP-funded laboratory studies carried out at Florida State University (FSU) and the Pacific Northwest National Laboratory from the time of the PAVT through 1999; (3) results of recent laboratory studies carried out for applications other than the WIPP, especially the German radioactive waste-management program. Giambalvo (2002a, 2002b, 2002c, 2002d) also provided good, concise descriptions of how the Th(IV), Np(V), and Am(III) solubility models were established and revised through the time of the CRA-2004 PA.

In addition to Giambalvo's changes, Brush and Xiong (2003a, 2003b, 2003d) defined separate, slightly different, chemical conditions characteristic of the absence of microbial activity for the solubility calculations for the CRA-2004 PA (Table 3). However, the EPA specified that the microbial conceptual model be changed for the CRA-2004 PABC such that there is a probability of 1 for microbial activity in the WIPP, and specified that the nonmicrobial vectors and the solubilities calculated for them be removed (see Subsection 2.1.2).

Brush and Xiong (2005a, 2005b) and Brush (2005) recalculated the solubilities of An(III), An(IV), and An(V) for the CRA-2004 PABC (Table 3).

Since the CRA-2004 PABC, laboratory studies of the solubility of Nd(III) in WIPP brines at LANL – CO have suggested that complexation of An(III) species by dissolved B(III) species might be important at $pC_{H^+} > \sim 7.5$ in GWB and $pC_{H^+} > \sim 7.5$ in ERDA-6 (Lucchini et al., 2007, Figure 5). Therefore, additional experiments are under way at LANL - CO to identify the Nd(III)-B(III) complex or complexes responsible for the increase in Nd(III) solubilities under these conditions and to obtain the Pitzer parameters required to include these complexes in the Am(III) speciation and solubility model. This addition will be implemented once sufficient qualified data have been obtained for the Nd(III)-B(III) complex(es).

2.2.2 Inclusion of Organic Ligands in Speciation and Solubility Models

We will continue to include the effects of acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate on the speciation and solubilities of Th(IV), Np(V), and Am(III) for the CRA-2009 PABC.

The effects of acetate, citrate, EDTA, and oxalate on actinide solubilities were not included in the CCA or the PAVT (Novak et al., 1996; U.S. DOE, 1996a, Appendix SOTERM; Novak, 1997) because laboratory studies by G.R. Choppin and his group at FSU to determine thermodynamic modeling parameters for organoactinide complexes were still under way.

Choppin et al. (2001) documented the completion of the experimental work required to include acetate, citrate, EDTA, lactate, and oxalate (the water-soluble organic ligands in TRU waste) in the Th(IV), U(VI), Np(V), and Am(III) solubility models. However, a U(VI) model has not been developed, and lactate has never been inferred to be present in TRU waste (e.g., U.S. DOE, 1996b; Crawford, 2003; Crawford and Leigh, 2003; Leigh, 2003, 2005a, 2005b). The FSU group also included experiments to obtain data on the complexation of dissolved Mg^{2+} by these organic ligands and, hence, the extent to which Mg^{2+} and dissolved Th(IV), U(VI), Np(V), and Am(III) will compete for the binding sites on these organic ligands, thereby reducing the complexation of these actinides.

Therefore, Brush and Xiong (2003a, 2003b, 2003c, 2003d) included the effects of acetate, citrate, EDTA, and oxalate on the solubilities of Th(IV), Np(V), and Am(III) for the CRA-2004 PA. Brush and Xiong (2003c) calculated the dissolved concentrations of acetate, citrate, EDTA, and oxalate by assuming that all of these organic ligands present in the waste (Crawford, 2003) will dissolve in 29,841 m³ of brine, “the smallest quantity of brine required to be in the repository [for] transport away from the repository” (Larson, 1996; U.S. DOE, 1996a). After the actinide solubility calculations for the CRA-2004 PA, Crawford and Leigh (2003) and Leigh (2003) corrected Crawford’s (2003) estimates of the total masses of organic ligands in the WIPP inventory. Because these corrections slightly decreased the masses of organic ligands, the solubilities used for the CRA-2004 PA were slightly higher than they would have been if they had been recalculated using the corrected organic-ligand concentrations.

Table 3. Comparisons of f_{CO_2} (atm), pH (Pitzer scale^A), and An(III), An(V), and An(V) Solubilities (M) Calculated Using the Nd(III), Am(III), and Cm(III); Th(IV); and Np(V) Models Implemented in FMT.

Property or Actinide Oxidation State	CCA PA, All Vectors, SPC ^B	CCA PA, All Vectors, ERDA-6 ^B	PAVT, All Vectors, SPC ^C	PAVT, All Vectors, ERDA-6 ^C	CRA-2004 PA, Microbial Vectors, GWB ^D	CRA-2004 PA, Microbial Vectors, ERDA6 ^D	CRA-2004 PABC, All Vectors, GWB ^E	CRA-2004 PABC, All Vectors, ERDA -6 ^E
f_{CO_2}	1.20×10^{-7}	1.23×10^{-7}	3.16×10^{-6}	3.16×10^{-6}	3.16×10^{-6}	3.16×10^{-6}	3.16×10^{-6}	3.16×10^{-6}
pH	8.69	9.24	8.69	9.24	8.69	9.02	8.69	8.94
An(III)	5.82×10^{-7}	6.52×10^{-8}	1.2×10^{-7}	1.3×10^{-8}	3.07×10^{-7}	1.69×10^{-7}	3.87×10^{-7}	2.88×10^{-7}
An(IV)	4.4×10^{-6}	6.0×10^{-9}	1.3×10^{-8}	4.1×10^{-8}	1.19×10^{-8}	2.47×10^{-8}	5.64×10^{-8}	6.79×10^{-8}
An(V)	2.3×10^{-6}	2.2×10^{-6}	2.4×10^{-7}	4.8×10^{-7}	1.02×10^{-6}	5.08×10^{-6}	3.55×10^{-7}	8.24×10^{-7}

A. The “Pitzer scale” is an unofficial pH scale consistent with pH values calculated using single-ion activity coefficients based on the Pitzer activity-coefficient model for brines and evaporite minerals of Harvie et al. (1984), extended to include Nd(III), Am(III), and Cm(III); Th(IV); and Np(V) (see Subsection 2.2.1). The term “Pitzer” scale was proposed unofficially by T. J. Wolery of LLNL.

B. Novak et al. (1996).

C. Trovato (1997, Attachment 2), U.S. EPA (1998a, Table 5), U.S. EPA (1998d, 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 (1998e, Subsections 5.26-5.32 and Section 6.0, Table 6.4).

D. Brush and Xiong (2003d).

E. Brush (2005, Table 5).

For the CRA-2004 PABC, Brush and Xiong (2005a, 2005b) and Brush (2005) also included the effects of acetate, citrate, EDTA, and oxalate on the speciation and solubilities of Th(IV), Np(V), and Am(III). Leigh (2005a, 2005b) reviewed the available information on the WIPP inventory and concluded that the masses of acetate, citrate, EDTA, and oxalate from Crawford and Leigh (2003) and Leigh (2003) should be used to calculate the concentrations of these organic ligands for the PABC. Brush and Xiong (2005b) used these masses and a new brine volume of 10,011 m³ of brine, “a reasonable minimum volume of brine in the repository required for a brine release” (Stein, 2005), to calculate these concentrations. Inclusion of these organic ligands: (1) did not increase the solubilities of Th(IV) in either GWB or ERDA; (2) increased the solubilities of Np(V) by factors of 1.50 (GWB) and 1.52 (ERDA-6), and (3) increased the solubilities of Am(III) by factors of 1.71 (GWB) and 3.32 (ERDA-6) (see Table 2 above for the PABC solubilities calculated with organic ligands).

Oxalate had a much greater effect on the solubilities of Am(III), and especially Np(V), in the actinide-solubility calculations for the CRA-2004 PA (Brush and Xiong, 2003d). This is because Brush and Xiong (2003c) assumed that all of the oxalate in the waste would dissolve in 29,841 m³ of brine, the minimum brine volume estimated by Larson (1996). However, when Xiong (2004a, 2004b) included thermodynamic data for Ca oxalate monohydrate (whewellite) in the FMT database, precipitation of this solid significantly decreased the dissolved oxalate concentration and the effects of this organic ligand on actinide solubilities.

We will continue to use the same assumptions as Brush and Xiong (2005b) to calculate the concentrations of acetate, citrate, EDTA, and oxalate, except that we would use: (1) the latest estimates of their masses in the WIPP inventory from LANL – CO, probably the PA roll-up from the 2007 TRU waste inventory/2008 TRU waste inventory report; and (2) an EPA-approved estimate of the minimum brine volume required for a brine release. Since Stein’s (2005) estimate of the minimum brine volume, Clayton (2006, 2008) has revised this volume twice. It is not clear which, if either, of these revisions the EPA would approve. Therefore, we might have to use all three estimates (i.e., Stein’s (2005) estimate for the CRA-2004 PABC, Clayton’s (2006) revised estimate, and Clayton’s 2008 revision) to calculate organic-ligand concentrations and perhaps even actinide solubilities. In any case, we will continue to allow whewellite to precipitate from GWB and ERDA-6 if - as expected - the oxalate concentration calculated by assuming that all of the oxalate in the waste dissolves in the minimum brine volumes results in supersaturation with respect to this solid.

2.2.3 Use of FMT and EQ3NR for Speciation and Solubility Calculations

The speciation and solubility code FMT (Babb and Novak, 1995; 1997 and addenda; Wang, 1998) has been used to predict actinide solubilities in WIPP disposal rooms. The chemical conditions expected in the repository (see Subsection 2.1.2 above) have also been predicted with EQ6. Because FMT does not include a reaction-path functionality equivalent to that of the EQ6 component of EQ3/6, FMT calculates both chemical conditions and actinide solubilities in the same runs (Subsection 2.1.3).

We will continue to use FMT in a manner identical to that used previously to calculate actinide speciation and solubilities for the CRA-2009 PABC. However, we will also use EQ3/6 and compare the results to those obtained with FMT.

When EQ3/6 was qualified according to the SNL/WIPP software QA requirements for calculations involving the nonradioactive elements in brines and evaporite minerals (Subsection 2.1.3), it was not qualified for actinide speciation and solubility calculations. Therefore, qualification of EQ3/6 for this application is underway (Wolery, 2008). It is expected that this work will be completed in time to use EQ3/6 for both predictions of chemical conditions and actinide solubilities for the CRA-2009 PABC.

Because it is assumed that instantaneous, reversible equilibria among WIPP brines, actinide-bearing solids such as hydrous, amorphous ThO_2 ; and KNpO_2CO_3 and $\text{Am}(\text{OH})_3$, and dissolved Th(IV), Np(V), and Am(III) species will control the solubilities of Th(IV), Np(V), and Am(III) (see Subsection 2.2.1), we would include these actinides in both Step 1 and Step 2 of the sequential EQ6 calculations described in Subsection 2.1.3. Therefore, we would calculate actinide solubilities under the initial chemical conditions in WIPP disposal rooms (prior to equilibration of GWB or ERDA-6 with solids such as halite, anhydrite, brucite and hydromagnesite₅₄₂₄) as well as under the long-term conditions predicted for the repository (Subsection 2.1.2). However, we would compare only those solubilities calculated for the long-term (postequilibration) conditions to those predicted by FMT for the CRA-2009 PABC. We would also determine the sensitivity of f_{CO_2} , pH, and actinide solubilities to factors such as whether organic ligands are present in GWB or ERDA-6, whether phase 3 or phase 5 is present in GWB (Subsection 2.1.2), and which Mg carbonate mineral is present. The effects of some of these factors have been determined previously, but we would use values of parameters from what will become the new WIPP PA baseline (e.g., the minimum brine volume required for a release, new concentrations of organic ligands, etc.) and the current thermodynamic database to update them.

2.2.4 FMT and EQ3/6 Thermodynamic Databases

We will use the most up-to-date version of the FMT and EQ3/6 thermodynamic databases to predict actinide speciation and solubilities for the CRA-2009 PABC.

Novak et al. (1996) used the FMT_HMW_345_960501FANG.CHEMDAT database to calculate the solubilities of An(III), An(IV), and An(V) for the CCA PA.

During its review of the ASTP's laboratory and modeling studies of actinide chemistry (see Subsection 2.2.1) the EPA also found errors in FMT_HMW_345_960501_FANG.CHEMDAT. 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.

Brush and Xiong (2003a, 2003b, 2003d) used the FMT_021120.CHEMDAT database for the actinide solubility calculations for the CRA-2004 PA source term. Giambalvo (2002a, 2002b, 2002c, 2002d, 2002e, 2003) established FMT_021120.CHEMDAT by revising and updating FMT_970407.CHEMDAT.

For the CRA-2004 PABC, five changes were made in the CRA-2004 PA database and four new versions were released. Xiong (2004a) corrected the molecular weight of oxalate ($\text{C}_2\text{O}_4^{2-}$) from 28.84000 to 88.0196 g, and added a value of -326.0981 for μ^0/RT for the stable solid Ca oxalate whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) to the database; and Xiong (2004b) released FMT_040628.CHEMDAT. Later, Xiong (2004c) changed the value of μ^0/RT for the dissolved Np(V)-acetate complex $\text{NpO}_2\text{Ac}(\text{aq})$ from -519.615 to -526.061, and Xiong (2004d) released FMT_041116.CHEMDAT. Next, Xiong (2004e) changed μ^0/RT for $\text{NpO}_2\text{Ac}(\text{aq})$ from -526.061 back to -519.615, and Xiong (2004f) released FMT_041210.CHEMDAT. Finally, Xiong et al. (2004) compared measured and predicted Th(IV), Np(V), and Am(III) solubilities to establish new uncertainty ranges and probability distributions for use in the CRA-2004 PABC (see Subsection 2.2.5) and found that the Th(IV) model significantly underpredicted the measured Th(IV) solubilities. Nowak (2005) identified the value of μ^0/RT for $\text{Th}(\text{OH})_4(\text{aq})$, -622.4700, as the cause of this problem. Although Brush and Xiong (2005a, Subsection 7.2) tentatively concluded that μ^0/RT for $\text{Th}(\text{OH})_4(\text{aq})$ should be changed from -622.4700 to -626.8467, Nowak (2005) recommended revising this parameter to -626.5853. This avoided having to make changes in the parameters for other Th(IV) species in the FMT database. (The value tentatively recommended by Brush and Xiong (2005a) was based on the formation constant for $\text{Th}(\text{OH})_4(\text{aq})$ in another database, in which the values of the parameters for several other Th(IV) species are slightly different from those in the FMT database.) Xiong (2005) released the corrected version of the database, FMT_050405.CHEMDAT. Xiong et al. (2005) used this database to revise the new uncertainty ranges and probability distributions for use in the CRA-2004 PABC, and Brush (2005) used it for the solubility calculations for the CRA-2004 PABC.

Xiong (2004a, 2004c, 2004e, 2005) and Nowak (2005) provided detailed explanations of the reasons for all of the changes to FMT database between the CRA-2004 PA and the CRA-2004 PABC. Brush and Xiong (2005a, Subsection 5.2.5.1) described the effects of the addition of whewellite to the database on the solubilities of oxalate and Np(V), and explained why this change did not affect the overall performance of the WIPP.

Qualification of EQ3/6 according to the SNL/WIPP software QA requirements for actinide speciation and solubility calculations is under way (see Subsection 2.2.3). This activity could result in changes to the EQ3/6 and FMT databases. If so, we will use the most up-to-date versions of these databases for the CRA-2009 PABC.

We will add μ^0/RT for phase 5 to both the FMT and the EQ3/6 databases, if the write-up describing the experimental work carried out to determine this parameter has been reviewed and approved in time (see Subsection 2.1.2).

Information Only

2.2.5 New Uncertainty Ranges and Probability Distributions

PA personnel use Latin hypercube sampling of uncertainty ranges and probability distributions established for calculated actinide solubilities to incorporate this source of uncertainty in their probabilistic calculations.

Bynum (1996a, 1996b, 1996c) carried out an analysis to estimate the uncertainties in the Th(IV), Np(V), and Am(III) solubility models implemented in FMT at the time of the CCA PA. These uncertainties were estimated mainly by comparing solubilities measured to develop these models and curves fitted to the data by the code NONLIN (Babb, 1996) to parameterize the Pitzer database. A few comparisons were also made between solubilities reported in the literature and FMT calculations for the conditions used in the experiments. The differences between logarithms (base 10) of measured Np(V) and Am(III) solubilities and logarithms of the values predicted by FMT for the same conditions were found to follow an approximately Gaussian distribution with a range from -2.0 to +1.4 log units. Those differences quantified the ratios of measured to calculated values. The distribution was used to represent the expected uncertainty distribution for the solubilities calculated by FMT for the CCA PA, the 1997 PAVT, and the CRA-2004 PA.

During its review of the ASTP's laboratory and modeling studies of actinide chemistry, the EPA made the following request (Cotsworth, 2004, Enclosure 1, Comment C-23-16):

DOE used the differences between modeled and measured actinide solubilities to estimate the uncertainties associated with actinide solubilities for the PA. Based on the figure presented in the CRA[-2004] [U.S. DOE, 2004, Appendix PA, Attachment SOTERM,] (Figure SOTERM-1), it appears DOE used the solubilities calculated for the CCA rather than for the CRA. However, DOE indicates that solubilities calculated for the CRA[-2004] were different than the CCA [U.S. DOE, 1996a, Appendix SOTERM,] (Table SOTERM-2).

DOE must re-evaluate the uncertainties associated with actinide solubilities using solubilities calculated for the CRA, and use this information in the CRA[-2004] PA.

Therefore, Xiong et al. (2004) compared measured and calculated Th(IV), Np(V), and Am(III) solubilities to establish new uncertainty ranges and probability distributions for use in the CRA-2004 PABC. They compared both previous (pre-CCA) measurements of actinide solubilities, including data used by Bynum (1996a, 1996b, 1996c) in the analysis for the CCA PA, and new (post-CCA) measurements of actinide solubilities. Xiong et al. (2004) used the FMT_040628.CHEMDAT thermodynamic database for their analysis (see Subsection 2.2.4). They produced probability distributions for the solubility calculations in the form of a distribution of differences between the logarithms (base 10) of measured and calculated solubilities.

The analysis of Xiong et al. (2004) differed from that of Bynum (1996a, 1996b, 1996c) in that: (1) Xiong et al. (2004) did not include any comparisons of solubilities measured to develop

the Th(IV), Np(V), or Am(III) models and curves fitted to the data by the code NONLIN (Babb, 1996) to parameterize the Pitzer database; (2) Xiong et al. (2004) established separate ranges and probability distributions for Th(IV), Np(V), and Am(III), as well as a combined distribution for all three oxidation states; and (3) Xiong et al. (2004) carried out the first comparisons for Th(IV) (Bynum did not include any comparisons for this oxidation state). Xiong et al. (2005) conducted 159 Th(IV) comparisons, 136 Np(V) comparisons, and 243 Am(III) comparisons, for a total of 538 comparisons for all three oxidation states.

Xiong et al. (2004) concluded that: (1) the Th(IV) solubility model implemented in FMT significantly underpredicted the measured Th(IV) solubilities, (2) the Np(V) model overpredicted the measured Np(V) solubilities slightly, (3) the Am(III) model overpredicted the measured Am(III) solubilities slightly, and (4) overall, the Th(IV), Np(V), and Am(III) models underpredicted the measured Th(IV), Np(V), and Am(III) solubilities.

Because the Th(IV) model significantly underpredicted the measured An(IV) solubilities, Nowak (2005) recommended that μ^0/RT for $\text{Th}(\text{OH})_4(\text{aq})$ be changed from -622.4700 to -626.5853 and Xiong (2005) released FMT_050405.CHEMDAT (Subsection 2.2.4). Xiong et al. (2005) also excluded the Th(IV) solubilities measured in solutions with ionic strengths < 3 M. This, along with the exclusion of data from Felmy et al. (1991) for $\text{pH} \leq 3.6$, decreased the number of An(IV) comparisons from 159 to 45. Nowak (2005), Xiong (2005), and Xiong et al. (2005) provided detailed explanations for all of these changes.

Xiong et al. (2005) then used FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005) to revise the new uncertainty ranges and probability distribution for Th(IV) for use in the CRA-2004, as well as the combined distribution for all three oxidation states. They did not revise the ranges and distributions for Np(V) and Am(III). Xiong et al. (2005) found that: (1) the Th(IV) model in FMT slightly underpredicted the measured Th(IV) solubilities, and (2) overall, the Th(IV), Np(V), and Am(III) models slightly overpredicted the measured Th(IV), Np(V), and Am(III) solubilities. Xiong et al. (2005) reiterated that: (1) the Np(V) model slightly overpredicted the measured Np(V) solubilities, and (2) the Am(III) model slightly overpredicted the measured Am(III) solubilities.

Brush et al. (2005) described how sampling of these ranges is implemented in PA.

We will use methods similar to those of Xiong et al. (2004, 2005) to re-establish uncertainty ranges and probability distributions for Th(IV), Np(V), and Am(III) solubilities for possible use in WIPP PA at some time in the future, but not for the CRA-2009 PABC (see Subsection 2.2). In addition, we will improve the process used by Xiong et al. (2004, 2005) to reflect criticisms by the EPA during its review of the new uncertainty ranges and probability distributions for use in the CRA-2004 PABC. These improvements would include: (1) better definition of the criteria for the selection of measured solubilities for inclusion in our comparisons, (2) better documentation of the application of these criteria to the solubility studies found in the open literature or unpublished reports, and (3) comparisons of solubilities measured in WIPP brines with predicted solubilities. With regard to the third point, LANL – CO has been measuring the solubility of Nd(III) in GWB and ERDA-6

(Lucchini et al., 2007, Figure 5). We will include these results in the An(III) comparisons when LANL – CO completes the qualification of these data according to the requirements of its QA program and sufficient qualified Pitzer parameters have been obtained for the Nd(III)-B(III) complex(es) described in Subsection 2.2.1 (see above).

2.2.6 Redox Speciation of Th, U, Np, Pu, and Am in the WIPP

We will continue to use the following oxidation-state distribution for dissolved actinides in the source term for the CRA-2009 PABC. Under the strongly reducing conditions expected in WIPP disposal rooms: (1) Th will have a probability of 1 of speciating entirely as Th(IV); (2) U will have a probability of 0.5 of speciating entirely as U(IV), and a probability of 0.5 of speciating entirely as U(VI); (3) Np will have a probability of 0.5 of speciating entirely as Np(IV) and a probability of 0.5 of speciating entirely as Np(V); (4) Pu will have a probability of 0.5 of speciating entirely as Pu(III) and a probability of 0.5 of speciating entirely as Pu(IV); (5) Am will have a probability of 1 of speciating entirely as Am(III). Furthermore, the sampled values of the oxidation states of these elements are correlated. Thus, there is a probability of 0.5 that Th, U, Np, Pu, and Am will speciate as Th(IV), U(IV), Np(IV), Pu(III), and Am(III), and an equal probability that they will speciate as Th(IV), U(VI), Np(V), Pu(IV), and Am(III). This is the same redox speciation that has been used for all of the previous WIPP compliance-related PA calculations, including the CRA-2004 PABC (Brush and Xiong, 2005a; Brush, 2005).

This redox speciation is based on the results of experimental studies summarized in the CCA (U.S. DOE, 1996a, Appendix SOTERM) and the CRA-2004 PA (U.S. DOE, 2004, Appendix PA, Attachment SOTERM). Strongly reducing conditions will be established by reactions among WIPP brines, metallic iron (Fe) and other metals in steel waste containers and/or the waste, and Fe(II)-bearing solids and/or dissolved species produced by anoxic corrosion of these metals. Microbial activity, to which the EPA has recently assigned a probability of 1, will also help create reducing conditions. It is recognized that Pu(V) and Pu(VI) could occur in isolated microenvironments in the repository. 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. Note that equilibria between or among the possible oxidation states of these actinides is not included in the conceptual models for actinide solubilities or colloidal actinides.

Based on the redox speciation of dissolved actinides given above and the order of importance of the radioelements presented in Subsection 2.2.1 (see above), the relative importance from the standpoint of PA of the actinide oxidation states in the WIPP is An(III) > An(IV) >> An(VI) >> An(V).

2.2.7 Use of the Oxidation-State Analogy for Actinides in the WIPP

We will continue to use the oxidation-state analogy to apply the solubilities calculated for Th(IV) to U(IV), Np(IV), and Pu(IV); and to apply the solubilities calculated for Am(III) to Pu(III). We will use the solubilities calculated for Np(V) only for Np(V). Finally, we will use

the revised estimate of the solubility of U(VI) (see Subsection 2.2.8) only for U(VI). All four of these applications of the oxidation-state analogy are consistent with the expected redox speciation of Th, U, Np, Pu, and Am described in Subsection 2.2.6 (above). This use of the oxidation-state analogy is identical to that of all of the previous WIPP compliance-related PA calculations, including the CRA-2004 PABC (Brush and Xiong, 2005a; Brush (2005).

Justification for the use of the oxidation-state analogy to use the solubilities (or other chemical properties) of actinides such as Th(IV) and Am(III) to predict the behavior of actinides that speciate in the same oxidation state was provided by U.S. DOE (1996a, Appendix SOTERM), Choppin (1999), and U.S. DOE (2004, Appendix PA, Attachment SOTERM).

2.2.8 Use of a Solubility Estimate for U(VI)

The ASTP did not develop a thermodynamic speciation and solubility model for the solubility of actinides in the +VI oxidation state (U(VI)). This is because: (1) the speciation of U(VI) is very complex, with many species that have overlapping stability fields (see, for example, Baes and Mesmer, 1976), which would make parameterization of a Pitzer model for U(VI) very difficult and time-consuming; and (2) U, the only actinide in the WIPP expected to speciate in the +VI oxidation state, is much less important than Pu and Am from the standpoint of PA (see Subsection 2.2.1).

Therefore, Hobart (1996) and Hobart and Moore (1996) estimated the solubility of U(VI) to be 1×10^{-5} m in both Salado and Castile brines for the CCA PA. This estimate, which was also described by U.S. DOE (1996a, Appendix SOTERM), was also used for the PAVT and CRA-2004 PA (U.S. DOE, 2004, Appendix PA, Attachment SOTERM).

During its review of the CRA-2004 PA, the EPA made the following comments on the DOE's documentation of the estimates of Hobart (1996) and Hobart and Moore (1996) (U.S. EPA, 2006, p.. 54):

The uranium(VI) solubility used in the CCA PA, the PAVT, and the CRA PA was 8.8×10^{-6} M (U.S. DOE 1996a, Appendix SOTERM Table SOTERM-2; U.S. DOE 2004b, Appendix PA Table PA-8 and Appendix PA, Attachment SOTERM, Table SOTERM-2). However, the text in both the CCA and the CRA erroneously states that Hobart and Moore (1996) estimated the solubility of uranium(VI) at pH 10 in the absence of carbonate to be 8.8×10^{-5} M. In addition to this typographical error, DOE appears to have created some confusion related to the concentration units used for the uranium(VI) concentrations. Both molal (moles/kg) and molar (moles/liter) units are used. For dilute solutions, these units are roughly equivalent because at 25 °C, 1 liter of aqueous solution should have a weight of approximately 1 kilogram. However, the density of the WIPP brines is approximately 1.2 kg/liter (U.S. DOE 2004b, Table 2-6). Thus, if the uranium(VI) concentration is 1×10^{-5} m (Hobart and Moore 1996), multiplication by the specific gravity would yield a concentration of 1.2×10^{-5} M.

Instead, DOE appears to have divided by the specific gravity, resulting in the use of a smaller uranium(VI) concentration.

The EPA was correct in concluding that “the text in both the CCA and the CRA erroneously states that Hobart and Moore (1996) estimated the solubility of uranium(VI) at pH 10 in the absence of carbonate to be $8.8 \times 10^{-5} \text{ M}$ ” (U.S. EPA, 2006, p. 54). Indeed, Hobart and Moore (1996) estimated the solubility of U(VI) at pH 10 in the absence of carbonate to be $1 \times 10^{-5} \text{ m}$.

However, a U(VI) concentration of $1 \times 10^{-5} \text{ m}$ (Hobart and Moore, 1996) is equivalent to approximately $(8.7\text{-}8.9) \times 10^{-6} \text{ M}$, depending on the brine, its density, and its composition used for conversion from molal to molar units, not $1.2 \times 10^{-5} \text{ M}$ as stated by the EPA (U.S. EPA, 2006, p. 54). To illustrate this, we started with the equation for conversion from molal to molar units for a simple binary solution (such as $\text{H}_2\text{O-NaCl}$) from Lide (2009, table entitled “Conversion Formulas for Concentration of Solutions”):

$$M = \frac{1000\rho m}{1000 + mE} \quad (5)$$

In Equation 5, M is the molar concentration of the solute in mol/L of solution, ρ is the density of the solution in g/cm^3 , m is the molal concentration of the solute in mol/kg H_2O , and E is the molecular weight of the solute in g/mol. For a multicomponent solution, Equation 5 can be generalized to:

$$M_i = \frac{1000\rho m_i}{1000 + \sum_j m_j E_j} \quad (6)$$

In Equation 6, M_i is the molar concentration of species i , ρ is the density of the solution, m_i is the molal concentration of species i , and E_i is the molecular weight of species i . All of these variables have the same units as those given for Equation 5.

For GWB:

$$M_{\text{U(VI)}} = (1000 \times \rho_{\text{GWB}} \times m_{\text{U(VI)}}) / (1000 + m_{\text{U(VI)}} \times E_{\text{U(VI)}} + m_{\text{Li}^+} \times E_{\text{Li}^+} + m_{\text{B}_4\text{O}_7^{2-}} \times E_{\text{B}_4\text{O}_7^{2-}} + m_{\text{Na}^+} \times E_{\text{Na}^+} + m_{\text{Mg}^{2+}} \times E_{\text{Mg}^{2+}} + m_{\text{K}^+} \times E_{\text{K}^+} + m_{\text{Ca}^{2+}} \times E_{\text{Ca}^{2+}} + m_{\text{SO}_4^{2-}} \times E_{\text{SO}_4^{2-}} + m_{\text{Cl}^-} \times E_{\text{Cl}^-} + m_{\text{Br}^-} \times E_{\text{Br}^-}). \quad (7)$$

Evaluating Equation 7 with the density and molal elemental concentrations in GWB obtained from Xiong (2008) yields:

$$M_{U(VI)} = (1000 \times 1.2368 \times m_{U(VI)}) / (1000 + 1 \times 10^{-5} m_{U(VI)} \times 238.029 \text{ g/mol U} + 0.00505 m_{Li^+} \times 6.941 \text{ g/mol Li} + 0.0445 m_{B_4O_7^{2-}} \times 155.2358 \text{ g/mol B}_4\text{O}_7 + 3.98 m_{Na^+} \times 22.98977 \text{ g/mol Na} + 1.15 m_{Mg^{2+}} \times 24.305 \text{ g/mol Mg} + 0.526 m_{K^+} \times 39.0983 \text{ g/mol K} + 0.156 m_{Ca^{2+}} \times 40.08 \text{ g/mol Ca} + 0.200 m_{SO_4^{2-}} \times 96.0576 \text{ g/mol SO}_4 + 6.32 m_{Cl^-} \times 35.453 \text{ g/mol Cl} + 0.0300 m_{Br^-} \times 79.904 \text{ g/mol Br}) = 8.841 \times 10^{-6}. \quad (8)$$

This value is close to that of 8.7×10^{-6} M, the value given by U.S. DOE (1996a, Appendix SOTERM, Table 2). We cannot reproduce the latter value exactly because we do not know which brine (Brine A or SPC), brine density, or brine composition (before or after equilibration with major Salado minerals and MgO hydration and carbonation products) was used for U.S. DOE (1996a, Appendix SOTERM, Table 2).

For ERDA-6:

$$M_{U(VI)} = (1000 \times \rho_{ERDA-6} \times m_{U(VI)}) / (1000 + m_{U(VI)} \times E_{U(VI)} + m_{B_4O_7^{2-}} \times E_{B_4O_7^{2-}} + m_{Na^+} \times E_{Na^+} + m_{Mg^{2+}} \times E_{Mg^{2+}} + m_{K^+} \times E_{K^+} + m_{Ca^{2+}} \times E_{Ca^{2+}} + m_{SO_4^{2-}} \times E_{SO_4^{2-}} + m_{Cl^-} \times E_{Cl^-} + m_{Br^-} \times E_{Br^-}). \quad (9)$$

Evaluating Equation 9 with the density and molal elemental concentrations in ERDA-6 obtained from Xiong (2008) yields:

$$M_{U(VI)} = (1000 \times 1.1918 \times m_{U(VI)}) / (1000 + 1 \times 10^{-5} m_{U(VI)} \times 238.029 \text{ g/mol U} + 0.0176 m_{B_4O_7^{2-}} \times 155.2358 \text{ g/mol B}_4\text{O}_7 + 5.44 m_{Na^+} \times 22.98977 \text{ g/mol Na} + 0.0213 m_{Mg^{2+}} \times 24.305 \text{ g/mol Mg} + 0.109 m_{K^+} \times 39.0983 \text{ g/mol K} + 0.0134 m_{Ca^{2+}} \times 40.08 \text{ g/mol Ca} + 0.187 m_{SO_4^{2-}} \times 96.0576 \text{ g/mol SO}_4 + 5.20 m_{Cl^-} \times 35.453 \text{ g/mol Cl} + 0.0123 m_{Br^-} \times 79.904 \text{ g/mol Br}) = 8.918 \times 10^{-6}. \quad (10)$$

This value is close to that of 8.8×10^{-6} M in U.S. DOE (1996a, Appendix SOTERM, Table 2).

It is also worth comparing the molar and molal elemental and species concentrations predicted by FMT, which was qualified according to the SNL/WIPP software QA requirements (Babb and Novak, 1995; Babb and Novak, 1997 and addenda; Wang, 1998). The molar concentrations predicted by FMT are always lower than the molal concentrations predicted for the same element or species. In particular, the numerical value of the molar solubility of Np(V) predicted for GWB for the CRA-2004 PABC is 87.1% of its molal value (Brush, 2005, FMT Run 7). (Np has a molecular weight very close to that of U, so it is the best element for this comparison.) Similarly, the numerical value of the molar solubility of Np(V) predicted for ERDA-6 is 87.9% of its molal value (Brush, 2005, FMT Run 11).

During its review of the CRA-2004 PA, the EPA specified that a U(VI) solubility of 1×10^{-3} M be used for the PABC. The EPA specified this value during a DOE-EPA teleconference on March 2, 2005. In the CCA PA, PAVT, and CRA-2004 PA, Bynum's (1996a, 1996b, 1996c) uncertainty range of -2.0 to $+1.4$ log units for the difference between the logarithm of the measured solubilities and the logarithm of the calculated solubilities (Subsection 2.2.5) was applied to the estimate of Hobart (1996) and Hobart and Moore (1996). There is no reference for this teleconference. Later, the EPA provided its justification for its revised estimate (U.S. EPA, 2006, pp. 55-58).

The EPA estimate of 1×10^{-3} M is higher by a factor of about 100 than that of Hobart (1996) and Hobart and Moore (1996). However, this increase did not have a significant effect on the direct brine releases calculated for the CRA-2004 PABC (Garner and Leigh, 2005; Leigh et al. 2005). This is because: (1) U is much less important than Pu and Am from the standpoint of PA (see Subsection 2.2.1), and (2) the fixed value assigned to this estimate by the EPA eliminated the possibility of sampling low-probability, high U(VI) solubilities (those from the upper end of the uncertainty range) that would have existed if an uncertainty range had been specified for U(VI).

PA personnel will continue to use a fixed value of 1×10^{-3} M for the solubility of U(VI) for the CRA-2009 PABC, unless the EPA specifies a new value or approves a new value and/or range and probability distribution based on results from LANL - CO's ongoing laboratory study of U(VI) solubilities.

3 Software List

We will use the speciation and solubility code FMT, Version 2.4, supported by the version of the FMT thermodynamic database produced under Task 1 (see Subsection 4.1) for the actinide-solubility calculations for the CRA-2009 PABC (see Subsections 2.1.3 and 2.2.3). Wang (1998) validated FMT, Version 2.4, for calculations involving the nonradioactive elements in brines and evaporite minerals, and for actinide speciation and solubility calculations in WIPP brines.

SNL/WIPP PA personnel will execute all of the 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 the qualified version of FMT, Version 2.4, and the current version of the FMT database (Subsection 4.1); 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-2009 PABC would be archived in the Sandia/WIPP CMS for future inspection by the EPA during its review of the PABC. 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 the EPA.

SNL/WIPP PA personnel will run FMT on a Compaq Computer Corp. ES40, ES45, or ES47 computer running the Open VMS 8.2 operating system.

We will also use the version of EQ3/6 that is qualified for actinide-solubility calculations according to SNL/WIPP software QA requirements (Wolery, 2008) to predict long-term chemical conditions in the WIPP (see Subsection 2.1.3) and calculate actinide solubilities for these conditions (Subsection 2.2.3). We will compare the results obtained with EQ3/6 to those obtained with FMT.

We or other members of the SNL/WIPP Chemistry Team designated by us will run the version of EQ3/6 qualified for actinide-solubility calculations on personal computers qualified for this version according to SNL/WIPP software QA requirements.

4 Tasks

The tasks that will be required to calculate the speciation and solubilities of An(III), An(IV), and An(V) for the CRA-2009 PABC are: (1) establishment of new FMT and EQ3/6 thermodynamic databases (see Subsection 4.1); (2) calculation of new organic-ligand concentrations (Subsection 4.3); and (3) use of FMT and EQ3/6 to predict long-term chemical conditions in WIPP disposal rooms and Th(IV), Np(V), and Am(III) solubilities under these conditions (Subsection 4.4).

We will also re-establish uncertainty ranges and probability distributions for the calculated solubilities of Th(IV), Np(V), and Am(III) for possible use in WIPP PA at some time in the future, but not for the CRA-2009 PABC (see Subsection 2.2).

The rest of this section describes these tasks in detail.

4.1 Establishment of New Thermodynamic Databases

Task 1 will comprise adding μ^0/RT for phase 5 to the current versions of the FMT and the EQ3/6 databases, if the write-up describing the experimental work carried out to determine this parameter has been reviewed and approved in time (see Subsection 2.1.2). We will make this change by preparing a memorandum that describes this addition, the source of this parameter, and our reason(s) for making this change. After all of the reviews required by SNL/WIPP NP 19-1, we will distribute this memorandum to the appropriate recipients and submit it to the SNL/WIPP Records Center. Next, we would make this change in the FMT and EQ3/6 databases. Finally, we will prepare an e-mail message authorizing the appropriate PA personnel to release the new version of the database and, after all of the required reviews, distribute it to the appropriate recipients and submit it to the Records Center.

Yongliang Xiong, Repository Performance Dept. 6712, will carry out Task 1. Completion of this task will require about one month, and must be accomplished by July 31, 2009.

4.2 Establishment of New Uncertainty Ranges and Probability Distributions

Task 2 will consist of re-establishing uncertainty ranges and probability distributions for our calculated Th(IV), Np(V), and Am(III) solubilities. Because the EPA indicated that the uncertainty ranges and probability distributions for the solubilities of Th(IV), Np(V), and Am(III) established for the CRA-2004 PABC should be used again for the CRA-2009 PABC, the objective of this task is to develop new ranges and distributions for possible use in WIPP PA at some time in the future, not for the CRA-2009 PABC.

We will use methods similar to those of Xiong et al. (2004, 2005) to re-establish these ranges and distributions (see Subsection 2.2.5). This task will include: (1) carrying out a literature search for published and unpublished reports on laboratory measurements of actinide solubilities that might be used in the comparison with our calculated solubilities; (2) specifying criteria for inclusion of measured solubilities in our comparison; (3) selecting measured solubilities according to these criteria; (4) using EQ3NR to calculate solubilities under the conditions reported for the measured solubilities; (5) establishing separate ranges and distributions for Th(IV), Np(V), and Am(III), as well as a combined distribution for all three oxidation states; (6) correcting one or more of the thermodynamic models, if necessary, and rerunning the comparison for that oxidation state or those oxidation states; and (7) completing an analysis report documenting each of the items in this task according to the requirements of NP 9-1.

The comparisons of measured and predicted solubilities could involve several hundred code calculations (Subsection 2.2.5). Therefore, it will not be feasible to conduct them with both FMT and EQ3/6. When EQ3/6 was qualified according to the SNL/WIPP software QA requirements for calculations involving the nonradioactive elements in brines and evaporite minerals (Subsection 2.1.3), it was not qualified for actinide solubility calculations. When the qualification of EQ3/6 for actinide-solubility calculations (Wolery, 2008) is completed we will use it for these comparisons. We will not use FMT.

Calculations of actinide solubilities under the conditions reported for the measured solubilities can begin after a new thermodynamic database has been established for EQ3/6 (see Subsection 4.1).

Laurence H. (Larry) Brush, Dept. 6712; Ahmed Ismail, Performance Assessment and Decision Analysis Dept. 6711; Je-Hun Jang, Dept. 6712; and Edwin James Nowak, S. M. Stoller Corp. will carry out Task 2. We will not start this task until the qualification of EQ3/6 for actinide speciation and solubility calculations (Wolery, 2008) has been completed. Completion of Task 2 will require about four months. Because this task does not have to be completed before PA personnel run PANEL and NUTS for the CRA-2009 PABC,

there is no firm deadline for its completion. However, we anticipate completing it by September 30, 2009.

4.3 Calculation of New Organic-Ligand Concentrations

Task 3 will involve: (1) obtaining the latest estimates of the masses of acetate, citrate, EDTA, and oxalate in the WIPP TRU waste inventory from LANL – CO, probably the PA roll-up from the 2007 TRU waste inventory/2008 TRU waste inventory report; (2) dividing them by the minimum brine volume required for a brine release; and (3) completing an analysis report documenting task according to the requirements of NP 9-1.

It is possible that the start of a CRA-2009 PABC could be delayed long enough that the PA roll-up from the 2008 TRU waste inventory/2009 TRU waste inventory report is available. If so, we will use these estimates, not those from the previous PA roll-up. It is also possible that either of these inventories could contain lactate to the inventory. If so, we will calculate its dissolved concentration and include it in the actinide-solubility calculations.

It is also unclear whether the EPA will approve either of Clayton's (2006, 2008) revision of Stein's (2005) estimate of the minimum brine volume, which was used for the actinide-solubility calculations for the CRA-2004 PABC. Therefore, we might have to use Stein's (2005) estimate to calculate new organic-ligand concentrations for the CRA-2009 PABC.

Larry Brush and Yongliang Xiong, both 6712, will conduct Task 3. Completion of this task will take about one month, and must be accomplished by July 31, 2009.

4.4 Predictions of Chemical Conditions and New Th(IV), Np(V), and Am(III) Solubilities

Task 4 will consist of predicting the long-term chemical conditions in the WIPP and calculating the speciation and solubilities of Th(IV), Np(V), and Am(III) in GWB and ERDA-6 (see Subsections 2.1.3 and 2.2.4) under these conditions. These solubilities will also be used for other An(III) and An(IV) radioelements in WIPP TRU waste (U(IV), Np(IV), Pu(III), and Pu(IV)) (Subsection 2.2.1).

We will continue to use FMT in a manner identical to that used previously to calculate chemical conditions, and actinide speciation and solubilities for the CRA-2009 PABC. However, we will also use EQ3/6 and compare the results to those obtained with FMT, if the qualification of EQ3/6 for actinide-solubility calculations according to the SNL/WIPP software QA requirements were completed in time (Wolery, 2008). If not, we will use only FMT (Subsections 2.1.3 and 2.2.3).

The chemical conditions expected in the repository are those characteristic of equilibrium among GWB or ERDA-6 and halite, anhydrite, brucite, phase 3 (in the case of GWB), hydromagnesite₅₄₂₄, and glauberite (in the case of ERDA-6) (Subsection 2.1.2).

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The brucite carbonation reaction will buffer f_{CO_2} and the brucite dissolution reaction will control the pH in these calculations. We will investigate the sensitivity of chemical conditions and Th(IV), Np(V), and Am(II) solubilities to: (1) whether phase 3 or phase 5 is present in GWB (Subsections 2.1.2 and 4.1); (2) whether carbonation of brucite produces calcite, magnesite, hydromagnesite₅₄₂₄, hydromagnesite₄₃₂₃, or nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$); and (3) whether the organic ligands acetate, citrate, EDTA, and oxalate are present (Subsections 2.2.2 and 4.3). We will suppress calcite (prevent its formation by disabling it in the input file) to force the brucite-magnesite carbonation reaction to buffer f_{CO_2} , and would suppress both calcite and magnesite to force the brucite-hydromagnesite₅₄₂₄ carbonation reaction to buffer f_{CO_2} , etc., to investigate the sensitivity of chemical conditions and actinide solubilities to which carbonate mineral forms. We will also include the organic ligand lactate in the actinide-solubility calculations if it is identified in the TRU waste inventory.

However, the actinide solubilities used for the CRA-2009 PABC will be those calculated under conditions buffered by the brucite-hydromagnesite₅₄₂₄ carbonation reaction with organic ligands present. We would include phase 5 in the solid-phase assemblage for GWB for the CRA-2009 PABC solubility calculations if, as expected, it does not affect the pH, because recent experimental results indicate that it will be present instead of phase 3.

Finally, we will complete an analysis report documenting all of the work in this task according to the requirements of NP 9-1.

Task 4 can begin either after a new thermodynamic database has been established for FMT or EQ3/6, or without a new database (see Subsection 4.1). Task 4 cannot begin until Task 3 is completed (see Subsection 4.3).

Larry Brush and Yongliang Xiong, both 6712, will perform Task 4. Completion of this task will require about one month, and must be accomplished by August 31, 2009. Task 4 must be completed before PA personnel can run PANEL and NUTS for the CRA-2009 PABC.

5 Special Considerations

LANL - CO must provide the latest estimates of the masses of acetate, citrate, EDTA, and oxalate in the WIPP TRU waste inventory, probably the PA roll-up from the 2007 TRU waste inventory/2008 TRU waste inventory report. We need these estimates of the quantities of organic ligands for Task 3 (see Subsection 4.3), which we must complete prior to starting Task 4 (Subsection 4.4). However, it is possible that the start of a CRA-2009 PABC could be delayed long enough that the PA roll-up from the 2008 TRU waste inventory/2009 TRU waste inventory report would be available. If so, we will use these estimates, not those from the previous PA roll-up.

In the unlikely event that LANL - CO does not provide any new estimates of the masses of acetate, citrate, EDTA, and oxalate, we would use those provided by for the CRA-2004 PABC (Crawford and Leigh, 2003; Leigh, 2003) to calculate the concentrations of organic ligands for the CRA-2009 PABC (Subsections 2.2.2 and 4.3).

We will include the results of LANL - CO's measurements of the solubility of Nd(III) in GWB and ERDA-6 (Lucchini et al. (2007) in the comparisons of measured and predicted An(III) solubilities when LANL - CO completes the qualification of these data according to the requirements of its QA program and sufficient qualified Pitzer parameters have been obtained for the Nd(III)-B(III) complex(es) described in Subsection 2.2.1. Because the EPA indicated that the uncertainty ranges and probability distributions for the solubilities of Th(IV), Np(V), and Am(III) established for the CRA-2004 PABC should be used again for the CRA-2009 PABC (Subsection 2.2), the schedule for obtaining the qualified data from LANL - CO will not impact the CRA-2009 PABC.

Finally, in order to complete Task 3 and Task 4 (Subsections 4.3 and 4.4, respectively), we need the EPA to specify whether we should use Clayton's (2006) or his (2008) revisions of Stein's (2005) estimate of the minimum brine volume, which was used for the actinide-solubility calculations for the CRA-2004 PABC. If the EPA does not approve either of Clayton's (2006, 2008) revisions, or if the EPA does not approve either of these revisions by June 30, 2009, we would have to reuse Stein's (2005) estimate to calculate new organic-ligand concentrations for the CRA-2009 PABC in order to meet the schedules specified above for Tasks 3 and 4.

6 Applicable Procedures

The following NPs 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/WIPP Online Documents web site (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;" and NP 19-1, "Software Requirements."

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Brush, Laurence H

Laurence H. Brush

From: Ismail, Ahmed
Sent: Tuesday, May 05, 2009 9:53 AM
To: Brush, Laurence H
Cc: Nemer, Martin B
Subject: RE: AP-143

Hi, Larry:

I am in ABQ today, but I should be in tomorrow. If you need a signature today (5/5/2009), I hereby extend signature authority to Martin Nemer for documents associated with AP-143.

Thanks,

--AEI

=====
Ahmed E. Ismail
Sandia National Labs
NHPA/502 || MS 1395 || 505 845-2117
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From: Brush, Laurence H
Sent: Tuesday, May 05, 2009 9:52 AM
To: Ismail, Ahmed
Subject: AP-143

Ahmed,

AP-143 is ready for your signature. Are you coming in the office today?

Larry

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