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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-153
Revision 1

Analysis Plan for WIPP Near-Field Geochemical Process Modeling

Task 1.4.1.1

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1   Introduction and Objectives

This analysis plan (AP) describes the near-field geochemical process modeling to be carried out for the U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) after completion of the Performance Assessment Baseline Calculation (PABC) for the second WIPP Compliance Recertification Application (CRA-2009) through submission of the third WIPP CRA (CRA-2014) to the U.S. Environmental Protection Agency (EPA).

The objectives of the geochemical modeling to be carried out between the CRA-2009 PABC through submission of the CRA-2014 PA include:

(1) Predictions with EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 — the version of the EQ3/6 database (DB) (Xiong, 2011a) — of the compositions of the WIPP brines Generic Weep Brine (GWB) and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) during and after reactions with the solids in WIPP disposal rooms. GWB is a synthetic brine representative of intergranular Salado Formation (Fm.) brines at or near the stratigraphic horizon of the repository (Krumhansl et al., 1991; Snider, 2003b). ERDA-6 is a synthetic brine representative of fluids in brine reservoirs in the Castile Fm. (Popielak et al., 1983). This task, completed in June 2011 by Brush et al. (2011a), predicted compositions of GWB and ERDA-6 intermediate between their in situ compositions and those expected after equilibration with the solids in the repository. Los Alamos National Laboratory — Carlsbad Operations (LANL — CO) is using these predictions to synthesize brines for experiments to determine the effects of parameters such as pH on the speciation and solubilities of actinide elements in the repository (e.g., Lucchini et al., 2007; Borkowski et al., 2009; Borkowski, 2010).

(2)   Predictions   with   EQ3/6   and   DATA0.FMT.R0.16,   FMT,   and FMT_050405.CHEMDAT — the same DB used for the CRA-2009 PABC — of actinide solubilities for volumes of brine larger than the minimum brine volume required for a release of radionuclides from the repository. This task, completed in September 2011 by Brush et al. (2011b), will enable Sandia National Laboratories' (SNL's) WIPP PA personnel to use actinide solubilities calculated for the actual volumes of brine predicted for each release of brine from the repository.

(3) Predictions of actinide solubilities with EQ3/6 and DATA0.FM1 for the same brine volumes used for Task 2 (to be completed by March 2012). Subsection 4.3 (see below) describes this task in detail.

(4) Updated uncertainty analyses of predictions with EQ3NR and DATA0.FM1 of Th(IV) and Am(III) solubilities and, if possible, Np(V) solubilities for the CRA-2014 PA and, perhaps, the CRA-2014 PABC (to be completed by September 2012). Subsection 4.4 describes this task in detail.

(5) Predictions of actinide solubilities with EQ3/6 and an updated DB (to be released in September 2012) for the same brine volumes used for Tasks 2 and 3 for the CRA-2014 PA and/or PABC (to be completed by December 2012). This new DB will contain values of μ^0/RT

and Pitzer parameters for Fe- and Pb-bearing solids and dissolved sulfide, Fe, and Pb species. Subsection 4.5 discusses this task.

(6) Updated uncertainty analyses of predictions with EQ3NR and an updated DB (to be released in September 2012) of Th(IV) and Am(III) solubilities and, if possible, Np(V) solubilities for the CRA-2014 PA and/or PABC (to be completed by March 2013). Subsection 4.6 describes this task.

This is a compliance-level analysis.

Table 1 defines the abbreviations, acronyms, elements and compounds, initialisms, and mineral names used in this AP.

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

Abbreviation, etc.	Definition
acetate	CH_3COO^- or $CH_3CO_2^-$
Am, Am(III)	americium, americium in the +III oxidation state
anhydrite	$CaSO_4$
An, An(III), An(IV), An(V), An(VI)	actinide element(s), actinide(s) in the +III, +IV, +V, or +VI oxidation state
AP	analysis plan
aq	aqueous
ASTP	(the WIPP) Actinide Source Term Program
atm	atmosphere(s)
B, B(II)	boron, boron in the +II oxidation state
Br, Br(−I)	bromine, bromine in the −I oxidation state
Brine A	a synthetic brine representative of intergranular Salado brines
brucite	$Mg(OH)_2$
C	carbon
Ca, Ca(II)	calcium, calcium in the +II oxidation state
calcite	$CaCO_3$
CCA	(WIPP) Compliance Certification Application, submitted to the EPA in October 1996
citrate	$(CH_2COO)_2C(OH)(COO)^{3-}$ or $(CH_2CO_2)_2C(OH)(CO_2)^{3-}$
Cl, Cl(−I), Cl$^-$	chlorine, chlorine in the −I oxidation state, chloride ion
Cm	curium
CMS	(SNL/WIPP software) Configuration Management System
CO_2	carbon dioxide
CO_3	carbonate
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
CRA-2014	third WIPP Compliance Recertification Application, submitted to the EPA in March 2014
DB	database
DBR	direct brine release
DOE	(U.S.) Department of Energy
DRZ	disturbed rock zone

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

Abbreviation, etc.	Definition
EDTA	ethylenediaminetetraacetate, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$ or $(CH_2CO_2)_2N(CH_2)_2N(CH_2CO_2)^{4-}$
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)
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	iron
Florida State University	FSU
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
g	gaseous
glauberite	$Na_2Ca(SO_4)_2$
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
H or H_2	hydrogen
halite	NaCl
H_2O	water (aq, g, or contained in solid phases)
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ or perhaps $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$
I	ionic strength
K, K(I)	potassium, potassium in the +I oxidation state
kg	kilogram(s)
LANL — CO	Los Alamos National Laboratory - Carlsbad Operations
LLNL	Lawrence Livermore National Laboratory
M	molar
m	meter(s) or molal
magnesite	$MgCO_3$
Mg, Mg(II)	magnesium, magnesium in the +II oxidation state
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various impurities

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

Abbreviation, etc.	Definition
mM	millimolar
Na, Na(I)	sodium, sodium in the +I oxidation state
Nd	neodymium
Nesquehonite	$MgCO_3 \cdot 3H_2O$
NP	Nuclear Waste Management Procedure
Np, Np(V)	neptunium, neptunium in the +V oxidation state
OH, OH-	hydroxide or hydroxide ion
Oxalate	$(COO)^{2-}$ or $C_2O_4^{2-}$
P	density
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^+
pcH	the negative, common logarithm of the molar concentration of H^+
phase 3	$Mg_2Cl(OH)_3 \cdot 4H_2O$
phase 5	$Mg_3Cl(OH)_5 \cdot 4H_2O$
pmH	the negative, common logarithm of the molal concentration of H^+
Pu, Pu(III), Pu(IV)	plutonium, plutonium in the +III or +IV oxidation state
QA	quality assurance
Rev.	Revision
RH	relative humidity
SCA	S. Cohen and Associates
SNL	Sandia National Laboratories
S, S(VI), SO_4^{2--}	sulfur, sulfur in the +VI oxidation state, sulfate ion
SPC	Salado Primary Constituents, a synthetic brine similar to Brine A
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C
TRU	transuranic waste
U, U(IV), U(VI)	uranium, uranium in the +IV or +VI oxidation state
Whewellite	Ca oxalate hydrate, or $CaC_2O_4 \cdot H_2O$
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
μ^0/RT	dimensionless standard chemical potential

2   Approach

This section describes the approach to be used for near-field geochemical modeling to be carried out for the WIPP after completion of the CRA-2009 PABC and prior to submission of the CRA-2014.   In particular, it explains how the approach to be used is consistent with the four conceptual models for WIPP near-field chemistry: Chemical Conditions, Gas Generation, Colloidal Actinide Source Term, and Dissolved Actinide Source Term. Wilson et al. (1996a, 1996b, 1997a, 1997b) described these models in detail in their reports on their peer review of all 24 conceptual models used in the PA for the DOE's WIPP Compliance Certification Application (CCA PA) (U.S. DOE, 1996a). The EPA also described the near-field conceptual models as part of its certification of the WIPP (U.S. EPA, 1998a, 1998b, 1998c, 1998f).   Recently, the EPA provided clear, concise, stand-alone descriptions of three of these four conceptual models (Chemical Conditions, Gas Generation, and Dissolved Actinide Source Term), including several minor changes it made since the CCA (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A).   Furthermore, all of the assumptions and parameters used in the approach described below have been approved by the EPA during its certification and recertifications of the WIPP, except for calculations used to determine the sensitivity of chemical conditions or actinide solubilities to deviations from EPA specifications.

Subsection 2.1 describes the approach used for predictions involving long-term chemical conditions in the WIPP. Subsection 2.2 discusses the approach used to predict the solubilities of actinides in three of the four oxidation states that we expect under these conditions, and provides the estimated solubility used for the fourth oxidation state.

2.1   Chemical Conditions

Prediction 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 Fm. or the Castile Fm. (Subsection 2.1.1); (2) the assumption that instantaneous, reversible equilibria among these brines, major Salado minerals, MgO hydration and carbonation products, and the organic ligands dissolved from transuranic (TRU) waste will control chemical conditions in the repository (Subsection 2.1.2); and (3) use of the codes FMT and EQ3/6 model or models to predict these conditions (Subsection 2.1.3).

2.1.1 Use of Standard Brines

We will continue to use the standard brines GWB and ERDA-6 (see below) for the predictions of chemical conditions to be carried out under this AP.

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 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.

At the time of the CCA PA and the PAVT, SNL investigators began to use GWB, defined by Krumhansl et al. (1991), for their laboratory studies of MgO. They used GWB 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 dissolved 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, SNL investigators continued to use 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 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.

During its first recertification of the WIPP (U.S. EPA, 2006a), the EPA approved substitution of GWB for Brine A (U.S. EPA, 2006b) because: (1) GWB is more representative of intergranular Salado brines than Brine A, and (2) the actinide solubilities predicted for Brine A and GWB are very similar. The EPA (2006b, p. 8) stated that "use of the GWB formulation in place of Brine A for the [CRA-2004 PA and PABC] and future actinide-solubility calculations is appropriate."

Therefore, Brush and Xiong, (2009a) and Brush et al. (2009) used GWB and ERDA-6, but not Brine A, for the actinide-solubility calculations for the CRA-2009 PABC. (The same solubilities used for the CRA-2004 PABC were used again for the CRA-2009 PA.) Omission of Brine A was a minor change from the CRA-2004 PABC.

Subsection 2.1.2 (see below) provides the compositions of GWB and ERDA-6 before and after equilibration with the solids in WIPP disposal rooms.

2.1.2 Use of Equilibria among Brine, Solids, and Organic Ligands to Control Chemical Conditions

We will continue to assume that equilibria among WIPP brines, solids, and the organic ligands dissolved from TRU waste (see Subsection 2.2.2 below) will control chemical conditions in the calculations to be conducted for this AP.

It has been assumed for the geochemical modeling for the CCA PA, the PAVT, the CRA-2004 PABC, and the CRA-2009 PABC that instantaneous, reversible equilibria among brines, major Salado minerals, various MgO hydration and carbonation products, and organic ligands dissolved from the waste will control chemical conditions throughout a homogeneous repository. This assumption is reasonable because these reactions will equilibrate rapidly with respect to the 10,000-year regulatory period. This assumption is also consistent with the Chemical Conditions conceptual model (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A).

Brush and Xiong (2005a, 2005b), Brush (2005), Brush and Xiong (2009a, 2009b) and Brush et al. (2009) assumed that GWB or ERDA-6 will equilibrate with: (1) halite (NaCl) and anhydrite (CaSO$_4$), two of the most abundant Salado minerals; (2) the MgO hydration and carbonation products brucite (Mg(OH)$_2$), phase 3 (Mg$_2$Cl(OH)$_3$·4H$_2$O) or phase 5 Mg$_3$Cl(OH)$_5$·4H$_2$O (in Brine A and GWB but not in ERDA-6) and hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O), respectively; (3) organic ligands dissolved from the waste (see Subsection 2.2.2 below); and (4) hydrous, amorphous ThO$_2$; KNpO$_2$CO$_3$ and Am(OH)$_3$. They used the speciation and solubility code FMT (Babb and Novak, 1997 and addenda; Wang, 1998) to predict near-field conditions after Salado and Castile brines equilibrate with major Salado minerals, MgO hydration and carbonation products, and organic ligands. We refer to Phase 3 and phase 5 as such because the OH:Cl molar ratio is 3 or 5, respectively. We assume that hydromagnesite has the composition Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O, because — although another polymorph with the composition Mg$_4$(CO$_3$)$_3$(OH)$_2$·3H$_2$O might exist — it has never been observed or predicted in any of our WIPP-related laboratory or modeling studies. In addition to these solids, FMT has predicted that: (1) whewellite (Ca oxalate hydrate, or CaC$_2$O$_4$·H$_2$O) will precipitate from Brine A and GWB, if these brines equilibrate with halite, anhydrite, brucite, phase 3 or phase 5, and hydromagnesite; and (2) glauberite (Na$_2$Ca(SO$_4$)$_2$) and whewellite will precipitate from ERDA-6, if these brines equilibrate with halite, anhydrite, brucite, and hydromagnesite.

Tables 2 and 3 provide the compositions of GWB and ERDA-6, respectively, before and after equilibration with the solids in WIPP disposal rooms. The results obtained for both of these brines were similar to those obtained for the CRA-2004 PABC; the differences are probably the result of the different concentrations of organic ligands in WIPP brines calculated for the CRA-2004 PABC (Brush and Xiong, 2005b) and the CRA-2009 PABC (Brush and Xiong, 2009b).

Table 2. Composition of GWB (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids.

Element or Property	GWB before Eq.,[A]	GWB w Organics after Eq., w Phase 3, CRA-2004 PABC Run 7[B]	GWB w Organics after Eq., w Phase 3, CRA-2009 PABC Run 5[C]	GWB w Organics after Eq., w Phase 5, CRA-2009 PABC Run 19[D]
B(III)(aq)	0.158	0.166	0.176	0.180
Na(I)(aq)	3.53	4.35	4.31	4.52
Mg(II)(aq)	1.02	0.578	0.584	0.463
K(I)(aq)	0.467	0.490	0.521	0.532
Ca(II)(aq)	0.014	0.00895	0.0098	0.010
S(VI)(aq)	0.177	0.228	0.210	0.214
Cl(-I)(aq)	5.86	5.38	5.40	5.37
Br(-I)(aq)	0.0266	0.0278	0.0297	0.0283
I (m)	-	7.66	7.64	7.52
f_{CO_2} (atm)	-	3.16×10^{-6}	3.14×10^{-6}	3.14×10^{-6}
TIC (mM)	-	0.350	0.350	0.358

Table 2 continued on next page

Table 2.   Composition of GWB (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids (continued).

Element or Property	GWB before Eq.[A]	GWB w Organics after Eq., w Phase 3, CRA-2004 PABC Run 7[B]	GWB w Organics after Eq., w Phase 3, CRA-2009 PABC Run 5[C]	GWB w Organics after Eq., w Phase 5, CRA-2009 PABC Run 19[D]
pH (Pitzer scale[E])	-	8.69	8.69	8.74
pcH[F]	-	9.39	9.40	9.45
pmH[G]	-	9.33	9.34	9.39
RH (%)	-	73.2	73.2	73.4
ρ (kg/m^3)	-	1230	1233	1234

A. Krumhansl et al. (1991) and Snider (2003b).
B. Values calculated by Brush and Xiong (2005a, 2005b) and Brush (2005, FMT Run 7) for the CRA-2004 PABC.   Run 7 carried out with the DB FMT_050405.CHEMDAT, which includes only phase 3.
C. Values calculated by Brush and Xiong (2009a, 2009b) and Brush et al. (2009, FMT Run 5) for the CRA-2009 PABC.   Run 5 carried out with the DB FMT_050405.CHEMDAT, which includes only phase 3.
D. Values calculated by Brush and Xiong (2009a, 2009b) and Brush et al. (2009, FMT Run 19) for the CRA-2009 PABC.   Run 19 carried out with the DB FMT_090720.CHEMDAT, which includes both phase 3 and phase 5.
E. 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).   The term "Pitzer scale" was proposed unofficially by T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA.
F. The negative, common logarithm of the molar concentration of H^+.
G. The negative, common logarithm of the molal concentration of H^+.

Table 3. Composition of ERDA-6 (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids (see text).

Element or Property	ERDA-6 before Eq.[A]	ERDA-6 w Organics after Eq., w/o Phase 3, CRA-2004 PABC Run 11[B]	ERDA--6 w Organics after Eq., w/o Phase 3, CRA-2009 PABC Run 13[C]	ERDA-6 w Organics after Eq., w/o Phase 3, 5, CRA-2009 PABC Run 23[D]
B(III)(aq)	0.063	0.0624	0.0624	0.0624
Na(I)(aq)	4.87	5.24	5.28	5.28
Mg(II)(aq)	0.019	0.157	0.136	0.136
K(I)(aq)	0.097	0.0961	0.0961	0.0961
Ca(II)(aq)	0.012	0.0107	0.0112	0.0112
S(VI)(aq)	0.170	0.179	0.176	0.176
Cl(-I)(aq)	4.8	5.24	5.23	5.23
Br(-I)(aq)	0.011	0.0109	0.0109	0.0109
I (m)	-	6.80	6.77	6.77
f_{CO_2} (atm)	-	3.16×10^{-6}	3.14×10^{-6}	3.14×10^{-6}
TIC (mM)	16	0.428	0.448	0.448
pH (Pitzer scale[E])	6.17	8.94	8.98	8.98
pcH[F]	-	9.64	9.68	9.68
pmH[G]	-	9.59	9.63	9.63
RH (%)	-	74.8	74.8	74.8

Table 3 continued on next page

Table 3.   Composition of ERDA-6 (M Unless Otherwise Noted) and Other Parameters (Units as Noted) before and after Equilibration with Solids (continued).

Element or Property	ERDA-6 before Eq.[A]	ERDA-6 w Organics after Eq., w/o Phase 3, CRA-2004 PABC Run 11[B]	ERDA-6 w Organics after Eq., w/o Phase 3, CRA-2009 PABC Run 13[C]	ERDA-6 w Organics after Eq., w/o Phase 3, 5, CRA-2009 PABC Run 23[D]
ρ (kg/m^3)	-	1220	1220	1220

A. Popielak et al. (1983).
B. Values calculated by Brush and Xiong (2005a, 2005b) and Brush (2005, FMT Run 11) for the CRA-2004 PABC. Run 11 carried out with the DB FMT_050405.CHEMDAT, which includes only phase 3.
C. Values calculated by Brush and Xiong (2009a, 2009b) and Brush et al. (2009, FMT Run 13) for the CRA-2009 PABC. Run 13 carried out with the DB FMT_050405.CHEMDAT, which includes only phase 3.
D. Values calculated by Brush and Xiong (2009a, 2009b) and Brush et al. (2009, FMT Run 23) for the CRA-2009 PABC. Run 23 carried out with the DB FMT_090720.CHEMDAT, which includes both phase 3 and phase 5.
E. 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). The term "Pitzer scale" was proposed unofficially by T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA.
F. The negative, common logarithm of the molar concentration of H^+.
G. The negative, common logarithm of the molal concentration of H^+.

Two other important reactions – anoxic corrosion of steels and other Fe-base alloys in the waste containers and the waste, and concomitant production of H_2; and possible halophilic or halotolerant microbial consumption of cellulosic, plastic, and rubber (CPR) materials in the waste and waste-packaging materials, and concomitant production of CO_2 and other gases; 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 implementation of these reactions in WIPP PA is consistent with the conceptual model for gas generation (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A). The effects of these corrosion and possible microbial reactions on near-field chemical conditions are also included in the actinide-solubility calculations as described below.

Tables 2 and 3 (see above) show that, for the CRA-2009 PABC, FMT predicted that equilibration of these brines with the solids and organic ligands listed above and the CO_2 from possible microbial activity will: (1) establish a total inorganic C (TIC) concentration of 0.350 or 0.358 mM in GWB (depending on whether phase 3 or phase 5 is present), and decrease the TIC from 16 to 0.448 mM in ERDA-6; (2) buffer f_{CO_2} at 3.14×10^{-6} atm ($10^{-5.50}$ atm) in both brines; and (3) establish a pH of 8.69 or 8.74 in GWB, and increase the pH of ERDA-6 from 6.17 to 8.98. Because the conditions predicted for GWB (Table 2) and ERDA-6 (Table 3) were used for the Th(IV), Np(V), and Am(III) solubility calculations for the CRA-2009 PABC, they became part of the WIPP PA baseline when the EPA recertified the WIPP on November 18, 2010 (U.S. EPA, 2010a; 2010b).

Since the PAVT, it has been assumed that the brucite carbonation reaction

$$5Mg(OH)_2 + 4CO_2(aq\ or\ g) \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \tag{1}$$

will buffer f_{CO_2} at about 3×10^{-6} atm. For GWB, FMT has predicted that phase 3 or phase 5 will also be in equilibrium with hydromagnesite. However, carbonation of phase 3 or phase 5 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

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^- \tag{2}$$

will establish a pH of about 9 in both GWB and ERDA-6. The use of these reactions to predict f_{CO_2} and pH is part of the conceptual model for near-field chemical conditions (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A).

However, hydromagnesite is metastable thermodynamically 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

$$Mg(OH)_2 + CO_2(aq\ or\ g) \rightleftharpoons MgCO_3 + H_2O(aq\ or\ g) \tag{3}$$
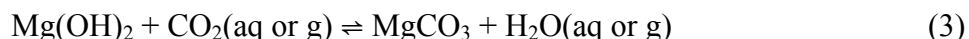
would buffer f_{CO_2} at 1.20×10^{-7} atm ($10^{-6.90}$ atm) in GWB or 1.23×10^{-7} atm ($10^{-6.91}$ atm) in ERDA-6 (Brush et al., 2009) *if* the kinetics of magnesite formation were fast enough for this phase to replace hydromagnesite during the 10,000-year period of performance of the repository. Note that these results were obtained with the thermodynamic DB FMT_050405.CHEMDAT, which includes only phase 3. We cite these results because this DB was used to predict the actinide solubilities used for the CRA-2009 PABC.

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 hydromagnesite-magnesite reaction might be too slow. Therefore, it specified that

the brucite-hydromagnesite carbonation reaction be used (Trovato, 1997). This is because this buffer conservatively increases f_{CO_2} by a factor of 26 (both brines) (Brush et al., 2009, Tables 10 and 11). Use of the brucite-hydromagnesite buffer does not preclude the possibility that magnesite will replace hydromagnesite 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 hydromagnesite 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 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. These conditions will eventually evolve to equilibrium between brucite and magnesite.

For the CRA-2004 PABC and the CRA-2009 PABC, the EPA also specified that the brucite-hydromagnesite carbonation reaction be used to buffer f_{CO_2} for our actinide-solubility calculations.

Whether or not hydromagnesite persists has less effect on the solubilities of Th(IV) and Am(III) than it does on f_{CO_2}: FMT and the DB FMT_050405.CHEMDAT, which includes only phase 3, predicted that, if hydromagnesite persists, the solubilities of Th(IV) and Am(III) would be 5.63×10^{-8} M and 1.66×10^{-6} M, respectively, in GWB, and 6.98×10^{-8} M and 1.51×10^{-6} M in ERDA-6 (Brush et al., 2009). If magnesite forms, the solubilities of Th(IV) and Am(III) would be 4.56×10^{-8} M and 1.66×10^{-6} M in GWB, and 4.85×10^{-8} M and 1.51×10^{-6} M in ERDA-6 (Brush et al., 2009). From the perspective of WIPP PA, these decreases in Th(IV) and Am(III) are clearly insignificant. The decreases predicted for Np(V) are greater than those predicted for Th(IV) and Am(III) (see Brush et al., 2009), but Np releases have essentially no effect on WIPP PA (Brush and Garner, 2005).

Because the EPA has always specified that the brucite-hydromagnesite carbonation reaction be used to buffer f_{CO_2} for our actinide-solubility calculations, we will continue to use hydromagnesite for all such calculations carried out under this AP. However, we may use other buffers for sensitivity studies.

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

$$Mg(OH)_2 + Ca^{2+} + CO_2(aq \text{ or } g) \rightleftharpoons CaCO_3 + Mg^{2+} + H_2O(aq \text{ or } g) \tag{4}$$

would buffer f_{CO_2}, and used this buffer be used for nonmicrobial vectors. For the CCA PA, the PAVT, and the CRA-2004 PA, the conceptual model for microbial activity in the WIPP 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 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 CPR materials in the remaining 25% of the vectors. Brush and Xiong (2003a) provided a detailed explanation of why the 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.

The EPA, however, 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 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 CCA PA, PAVT, CRA-2004 PABC, and CRA-2009 PABC (e.g., by using the brucite-hydromagnesite carbonation reaction to buffer f_{CO_2}). However, we may use the brucite-calcite buffer for sensitivity studies.

Finally, laboratory studies of the hydration and carbonation of MgO at SNL in Carlsbad have shown that phase 5 precipitates from GWB instead of phase 3, but that neither of these phases precipitates from ERDA-6 (Wang & Bryan, 2000; Wang et al., 2001; Snider and Xiong, 2002; Snider, 2003a; Snider et al., 2004; Deng et al., 2007). However, FMT_050405.CHEMDAT (Xiong, 2005) — the thermodynamic DB used for the CRA-2004 PABC — contains phase 3 but not phase 5. Therefore, Xiong et al. (2009b; 2010) carried out solubility experiments to determine μ^0/RT for phase 5, and Xiong (2009) added the value of μ^0/RT obtained by Xiong et al. (2009b) to the FMT DB and released FMT_090720.CHEMDAT.

Tables 2 and 3 show that the DB FMT_090720.CHEMDAT, which includes both phase 3 and phase 5, predicts that phase 5 will precipitate from GWB instead of phase 3, but that neither of these phases will precipitate from ERDA-6. Therefore, FMT and this DB yield predictions that agree with the laboratory studies cited above.

Table 2 shows that FMT predicted a somewhat different composition for GWB after precipitation of phase 5 than it predicted after precipitation of phase 3. On the other hand,

Table 3 shows that the use of different DBs did not result in any predicted differences for ERDA-6. This is because neither phase 3 nor phase 5 precipitated from ERDA-6.

2.1.3 Use of EQ3/6 to Predict Chemical Conditions

We will use EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011a; 2011b), to predict near-field chemical conditions (and the solubilities of actinide elements under these conditions) in the work to be performed under AP-153, Rev. 1. We will no longer use FMT to predict chemical conditions (or actinide solubilities).

When Brush and Xiong (2011) completed the original version of AP-153, Wolery (2008), Wolery et al. (2010), and Xiong (2011a, 2011b) had qualified EQ3/6, Version 8.0a, and the DATA0.FM1 thermodynamic DB for actinide-solubility calculations according to SNL/WIPP QA procedures. However, the EPA had not reviewed and approved SNL's qualification of EQ3/6 or DATA0.FM1. Therefore, Brush and Xiong (2011) planned to use both EQ3/6 and FMT for AP-153 to obtain additional verification that these codes predict essentially identical conditions (and solubilities).

However, the EPA recently approved the qualification of EQ3/6, Version 8.0a, and DATA0.FM1 for compliance-related, actinide-solubility calculations. Therefore, additional verification that EQ3/6 and FMT produce identical results is no longer necessary. Thus, we will use EQ3/6 — but not FMT — for all WIPP geochemical process modeling from now on.

Replacement of FMT with EQ3/6 was 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.

2.2   Actinide Solubilities

Predictions of solubilities for the WIPP actinide source term involve: (1) use of thermodynamic speciation and solubility models for Th(IV), Np(V), and Am(III) (see Subsection 2.2.1 below); (2) inclusion of the effects of the organic ligands dissolved from TRU waste on Th(IV), Np(V), and Am(III) speciation and solubilities (see Subsection 2.2.2); (3) use of the code EQ3NR to calculate the solubilities of Th(IV), Np(V), and Am(III) (Subsection 2.2.3); (4) use of DATA0.FM1, the EQ3/6 DB that has been reviewed and approved by the EPA (Subsection 2.2.4); (5) use of 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).

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

We will continue to use thermodynamic models for Th(IV), Np(V), and Am(III) described in this subsection and the oxidation state analogy (see Subsection 2.2.7 below)

to predict the speciation and solubilities of Th(IV), U(IV), Np(IV), and Pu(IV); Np(V); and Pu(III) and Am(III) . These models are based on the Pitzer activity-coefficient model for brines and evaporite minerals of Harvie et al. (1984), which the WIPP Project extended to include Th(IV); Np(V); and Nd(III), Am(III), and Cm(III).

It has been assumed for the CCA PA, the PAVT, the CRA-2004 PABC, and the CRA-2009 PABC that instantaneous, reversible equilibria among: (1) Salado- or Castile-Fm. brines; (2) organic ligands dissolved from TRU waste; (3) dissolved Th(IV), Np(V), and Am(III) species; and (4) actinide-bearing solids such as hydrous, amorphous ThO_2; and $KNpO_2CO_3$ and $Am(OH)_3$ will control the solubilities of Th(IV), Np(V), and Am(III) throughout a homogeneous repository. This assumption is reasonable because these reactions will equilibrate rapidly with respect to the 10,000-year regulatory period. This assumption is also consistent with the Dissolved Actinide Source Term conceptual model (SCA, 2008, Subsections 2.2, 2.3, and 2.4, and Appendix A). Salado or Castile brines are also assumed to be in equilibrium with halite, anhydrite, brucite, hydromagnesite, and other solids that will precipitate (see Subsection 2.1.2).

Sorption has never been included among the processes that will control the dissolved or colloidal concentrations of Th(IV), Np(V), and Am(III) in WIPP disposal rooms, or during the transport of these radioelements by brine up an intrusion borehole to the Culebra Member of the Rustler Fm. or to the surface (direct brine releases, or DBRs). Omission of sorption from the actinide source term and borehole transport may add conservatism to WIPP PA. Sorption has been included in all compliance-related Culebra transport modeling.

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 the naturally occurring elements in brines and evaporite minerals to include new or existing 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 WIPP PA of the radioelements in the TRU waste to be emplaced in the WIPP is Pu $\approx$ Am $>>$ U $\approx$ Th $>>$ Np $\approx$ 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, and predictions of redox speciation and the oxidation-state analogy, the An(III) model is applied to

Pu(III), Am(III), and Cm(III); and the An(IV) model is applied to Th(IV), U(IV), Np(IV), and Pu(IV). The An(V) model is used only for Np(V) because Np is the only actinide in TRU waste that is expected to speciate in the +V oxidation state.

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 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 colloidal actinides have been carried out since the CCA PA, and only minor changes were made in the colloidal source term for the CRA-2004 PABC and the CRA-2009 PABC. Therefore, this AP does not discuss the colloidal source term.

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) in Salado Primary Constituents (SPC), a synthetic brine similar to Brine A, for the CCA PA. Table 4 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 (U.S. DOE, 1996a), 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}. Instead, the EPA specified that the brucite-hydromagnesite carbonation reaction be used to calculate f_{CO_2} (see Subsection 2.1.2). Furthermore, the large difference in the An(IV) solubilities predicted for SPC and ERDA-6 (the former exceeded the latter by a factor of about 730; see Table 4 below) resulted in a review of and changes to the thermodynamic data for all three of the actinide oxidation states (Subsection 2.2.4).

Table 4. Comparison of Actinide Solubilities (M), f_{CO_2} (atm), and pH (Pitzer Scale[A]) from These and Previous Compliance-Related FMT Calculations. Results rounded to three significant figures if more than three were provided.

Property or Actinide Oxidation State	CCA (SPC, Magnesite, w/o Organics, All Vectors)[B]	CCA (ERDA-6, Magnesite, w/o Organics, All Vectors)[B]	PAVT (SPC, Hydro-magnesite, w/o Organics, All Vectors)[C]	PAVT (ERDA-6, Hydro-magnesite, w/o Organics, All Vectors)[C]	CRA-2004 PA (GWB, Hydro-magnesite, w Organics, Microbial Vectors)[D]	CRA-2004 PA (ERDA-6, Hydro-magnesite, w Organics, Microbial Vectors)[D]	CRA-2004 PABC (GWB, Hydro-magnesite, w Organics, All Vectors)[E]	CRA-2004 PABC (ERDA-6, Hydro-magnesite, w Organics, All Vectors)[E]	CRA-2009 PABC (GWB, Hydro-magnesite, w Organics, All Vectors)[F]	CRA-2009 PABC (ERDA-6, Hydro-magnesite, w Organics, All Vectors)[G]
Th(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}	5.63×10^{-8}	6.98×10^{-8}
Np(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}	3.90×10^{-7}	8.75×10^{-7}
Am(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}	1.66×10^{-6}	1.51×10^{-6}
f_{CO_2}	1.29×10^{-7}	1.29×10^{-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}	3.14×10^{-6}	3.14×10^{-6}
pH	8.69	9.24	8.69	9.24	8.69	9.02	8.69	8.94	8.69	8.98

[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). The term "Pitzer scale" was proposed unofficially by T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA.
[B]From Novak et al. (1996) and U.S. DOE (1996a, Appendix SOTERM), except that Novak et al. (1996) used molal instead of molar units. U.S. EPA (1998f) cited Novak and Moore (1996) as the source of the CCA PA solubilities, but the Am(III) solubilities from Novak and Moore (1996) differ from those in Novak et al. (1996) and U.S. DOE (1996a).
[C]From Trovato (1997). Novak (1997) also calculated actinide solubilities for the PAVT, but the EPA used the results of its own calculations.
[D]From Brush and Xiong (2003a, 2003b, 2003c, 2003d) and U.S. DOE (2004, Appendix SOTERM).
[E]Brush and Xiong (2005a, 2005b) and Brush (2005). These solubilities were also used for the CRA-2009 PA calculations.
[F]This report, FMT Run 5.
[G]This report, FMT Run 13.

Therefore, Novak (1997) used FMT and the corrected DB to recalculate the solubilities of Th(IV), Np(V), and Am(III) under the conditions defined by the brucite-hydromagnesite 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 then 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, $Mg_2Cl(OH)_3 \cdot 4H_2O$, and hydromagnesite; and among ERDA-6 halite, anhydrite, glauberite, brucite, and hydromagnesite. Table 4 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) incorporation of the 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) incorporation of the results of recent laboratory studies carried out for applications other than the WIPP, especially the German studies relevant to disposal of radioactive waste in salt domes. 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 about mid-2002. The EPA reviewed and approved these changes, which were relatively minor, during its review of the CRA-2004. These changes were incorporated in the PA baseline established by the CRA-2004 PABC.

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. 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 (Subsection 2.1.2).

Brush and Xiong (2005a, 2005b) and Brush (2005) recalculated the solubilities of Th(IV), Np(V), and Am(III) for the CRA-2004 PABC (Table 4).

Since the CRA-2004 PABC, a laboratory study of the solubility of Nd(III) in 5 M NaCl, ERDA-6, and GWB at LANL – CO have suggested that complexation of An(III) species by dissolved B(III) species might be important at pcH > 7.4 in GWB and pcH > 8.1 in ERDA-6 (Lucchini et al., 2007; Borkowski et al., 2009; Borkowski, 2010)). Therefore, additional experiments are under way 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 stability constant(s) and Pitzer ion-interaction parameters required to include them in the Am(III) speciation and solubility model. This complex (or complexes) will be added to the model as soon as enough QA'ed data have been obtained.

2.2.2 Inclusion of Organic Ligands in Speciation and Solubility Models

We will continue to include the effects of the acetate (CH_3COO^- or $CH_3CO_2^-$), citrate (($CH_2COO)_2C(OH)(COO)^{3-}$ or $(CH_2CO_2)_2C(OH)(CO_2)^{3-}$), ethylenediaminetetraacetate (EDTA, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$ or $(CH_2CO_2)_2N(CH_2)_2N(CH_2CO_2)^{4-}$), and oxalate ($(COO)^{2-}$ or $C_2O_4^{2-}$) dissolved from TRU waste in the Th(IV), Np(V), and Am(III) solubility calculations to be carried out under this AP. These are the only four organic ligands in TRU waste that dissolve in aqueous solutions such as WIPP brines and could thus increase the solubilities of these actinides.

The effects of acetate, citrate, EDTA, and oxalate on actinide solubilities were not included in the CCA (Novak et al., 1996; U.S. DOE, 1996a, Appendix SOTERM) or the PAVT (Novak, 1997) because laboratory studies by G.R. Choppin and his group at Florida State University (FSU) to determine stability constants and Pitzer ion-interaction 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 in the Th(IV), Np(V), and Am(III) solubility models. However, 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; Crawford et al., 2009). 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), Np(V), and Am(III) will compete for the binding sites on these organic ligands, thereby reducing the complexation of these actinides.

Brush and Xiong (2003a, 2003b, 2003c, 2003d) included the effects of acetate, citrate, EDTA, and oxalate on the speciation and solubilities of Th(IV), Np(V), and Am(III) for the CRA-2004 PA. These were the first actinide-solubility calculations for a compliance-related WIPP PA that included the effects of organic ligands. Brush and Xiong (2003c) calculated the dissolved concentrations of these organic ligands by assuming that: (1) all ligands present in the waste (Crawford, 2003) will dissolve in 29,841 m^3 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); and (2) these concentrations persist throughout the 10,000-year WIPP regulatory period. The second assumption obviates the need to predict the rates at which and the extent to which microbial consumption of CPR materials produces and consumes organic ligands. Both of these assumptions are consistent with the conceptual models for WIPP near-field chemistry and their implementation in WIPP PA.

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 (Brush and Xiong, 2003e), 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 5.   Comparisons of Organic-Ligand Concentrations Calculated for the CCA, the CRA-2004 PA, the CRA-2004 PABC, and the CRA-2009 PABC.

Organic Ligand	CCA[A] (m)	CRA-2004 PA[B] (M)	CRA-2004 PABC[C] and CRA-2009 PA (M)	CRA-2009 PABC[D] (M)
Acetate	1.1×10^{-3}	5.05×10^{-3}	1.06×10^{-2}	1.94×10^{-2}
Citrate	7.4×10^{-3}	3.83×10^{-4}	8.06×10^{-4}	2.38×10^{-3}
EDTA	4.2×10^{-6}	3.87×10^{-6}	8.14×10^{-6}	6.47×10^{-5}
Oxalate	4.7×10^{-4}	2.16×10^{-2}	4.55×10^{-2}	1.73×10^{-2}

A. U.S. DOE (1996b, Appendix SOTERM, Table SOTERM-4. Organic ligands were not included in the actinide-solubiliity calculations for the CCA PA.
B. Brush and Xiong (2003, Table 4).
C. Brush and Xiong (2005b, Table 4.
D. Brush and Xiong (2009b, Table 5).

Brush and Xiong (2005a, 2005b) and Brush (2005) also included the effects of acetate, citrate, EDTA, and oxalate on the solubilities of Th(IV), Np(V), and Am(III) for the CRA-2004 PABC. 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 their concentrations for the CRA-2004 PABC. Brush and Xiong (2005b) used these masses and a new brine volume of 10,011 m^3 of brine, "a reasonable minimum volume of brine in the repository required for a brine release" (Stein, 2005), to calculate their concentrations.

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 than did acetate, citrate, or EDTA (Brush and Xiong, 2003d). However, when Xiong (2004a, 2004b) included thermodynamic data for Ca oxalate monohydrate (whewellite) in the FMT DB, precipitation of this solid significantly decreased the dissolved oxalate concentration and the effects of this organic ligand on the solubilities of Np(V) and Am(III) for the CRA-2004 PABC.

Brush and Xiong (2009a, 2009b) and Brush et al. (2009) continued to include acetate, citrate, EDTA, and oxalate in the actinide-solubility calculations for the CRA-2009 PABC. They used: (1) the latest TRU waste inventory from LANL — CO (Crawford et al., 2009), and (2) a new brine volume of 17,400 m^3 of brine, "a reasonable minimum volume of brine in

the repository required for a [DBR]" (Clayton, 2008).   After Stein's (2005) estimate of the minimum brine volume, Clayton (2006, 2008) revised this estimate twice; and the EPA approved Clayton's (2008) estimate during its review of the CRA-2009.   Brush and Xiong (2009a, 2009b) and Brush et al. (2009) continued to allow whewellite to precipitate from GWB and ERDA-6.

Table 5 summarizes the concentrations of acetate, citrate, EDTA, and oxalate calculated for the CCA, the CRA-2004 PA, the CRA-2004 PABC, and the CRA-2009 PABC.   The most significant change from the standpoint of its effects on actinide solubilities has been the increase in the concentration of EDTA, which is mainly the result of the increase in the mass of EDTA in the TRU waste inventory.

Inclusion of these organic ligands in the actinide-solubility calculations for the CRA-2009 PABC: (1) had essentially no effect on the solubility of Th(IV) in either GWB or ERDA, relative to organic-ligand-free calculations; (2) increased the solubility of Np(V) by factors of 1.76 (GWB) and 1.63 (ERDA-6), and (3) increased the solubility of Am(III) by factors of 7.38 (GWB) and 17.4 (ERDA-6) (Brush et al., 2009, Tables 10 and 11).   The large effect of organic ligands on the solubility of Am(III) relative to those of Th(IV) and Np(V) is mainly due to EDTA.

We will continue to use the concentrations of acetate, citrate, EDTA, and oxalate calculated by Brush and Xiong (2009b) for the actinide-solubility calculations to be carried out under this AP, except in Tasks 3 and 5: for these tasks, we will use concentrations of organic ligands less than these, commensurate with volumes of brine larger than the minimum brine volume required for a DBR (see Subsections 4.3 and 4.5 below). If LANL – CO's estimates of the masses of organic ligands in the TRU waste to be emplaced in the WIPP change or if the EPA allows us to take credit for microbial consumption of organic ligands, we will revise the concentrations of organic ligands calculated by Brush and Xiong (2009b).

2.2.3 Use of EQ3NR for Actinide Speciation and Solubility Calculations

We will continue to assume for EQ3/6 calculations that (1) instantaneous, reversible equilibria among Salado- or Castile-Fm. brines; (2) organic ligands dissolved from TRU waste; (3) dissolved Th(IV), Np(V), and Am(III) species; and (4) actinide-bearing solids such as hydrous, amorphous ThO_2; and $KNpO_2CO_3$ and $Am(OH)_3$ will control the solubilities of Th(IV), Np(V), and Am(III) throughout a homogeneous repository.

2.2.4 EQ3/6 Thermodynamic DBs

We used or will use the following thermodynamic DBs for the tasks that were or will be completed under this AP: (1) DATA0.FM1 (see Subsection 2.1.2 above) for Task 1 (completed in June 2011), (2) DATA0.FMT.R0.16 and FMT_050405.CHEMDAT for Task 2 (completed in September 2011), (3) DATA0.FM1 for Task 3 (to be completed by March 2012), (4) DATA0.FM1 for Task 4 (to be completed by September 2012), (5) an updated DB to be released in September 2012 for Task 5 (to be completed by December 2012), and

(6) an updated DB (to be released in September 2012) for Task 6 (to be completed by March 2013).

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

During its review of the ASTP's laboratory and modeling studies of actinide chemistry, part of its review of the CCA (see Subsection 2.2.1 above) the EPA found errors in FMT_HMW_345_960501_FANG.CHEMDAT. The erroneous data pertained to $Th(CO_3)_5^{6-}$, $NpO_2(CO_3)_3^{5-}$, and $Am(CO_3)_3^{3-}$. Correction of the data for these complexes resulted in the stabilization of different Am(III)- and Np(V)-bearing solid phases in subsequent FMT calculations. Novak (1997) corrected these mistakes and designated the PAVT DB as FMT_970407.CHEMDAT.

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

For the CRA-2004 PABC, five changes were made in the CRA-2004 PA DB and four new versions were released. Xiong (2004a) corrected the molecular weight of oxalate from 28.84000 to 88.0196 g, and added a value of -326.0981 for μ^0/RT for the stable Ca-oxalate solid whewellite to the DB; and Xiong (2004b) released FMT_040628.CHEMDAT. Later, Xiong (2004c) changed the value of μ^0/RT for the dissolved Np(V)-acetate complex $NpO_2Ac(aq)$ from -519.615 to -526.061, and Xiong (2004d) released FMT_041116.CHEMDAT. Next, Xiong (2004e) changed μ^0/RT for $NpO_2Ac(aq)$ 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 $Th(OH)_4(aq)$, -622.4700, as the cause of this problem. Although Brush and Xiong (2005a, Subsection 7.2) tentatively concluded that μ^0/RT for $Th(OH)_4(aq)$ 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 DB. (The value tentatively recommended by Brush and Xiong (2005a) was based on the formation constant for $Th(OH)_4(aq)$ in another DB, in which the values of the parameters for several other Th(IV) species are slightly different from those in the FMT DB.) Xiong (2005) released the corrected version of the DB, FMT_050405.CHEMDAT. Xiong et al. (2005) used this DB to revise the new uncertainty ranges and probability distributions for use in the CRA-2004 PABC, and Brush (2005) used it for the actinide- 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 DB 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 DB on the solubilities of oxalate and Np(V), and explained why this change did not affect the overall performance of the WIPP.

Brush and Xiong (2009a) and Brush et al. (2009) also used FMT_050405.CHEMDAT, which contains only phase 3, to predict the Th(IV), Np(V), and Am(III) solubilities used for the CRA-2009 PABC (see Subsection 2.1.2 above). However, laboratory studies of MgO at SNL in Carlsbad showed that phase 5 precipitates from GWB instead of phase 3, Therefore, Xiong et al. (2009b) determined μ^0/RT for phase 5, and Xiong (2009) added this value of μ^0/RT to the FMT DB and released FMT_090720.CHEMDAT (Subsection 2.1.2).

Wolery (2008), Wolery et al. (2010), and Xiong (2011a, 2011b) qualified EQ3/6, Version 8.0a, and DATA0.FM1 for actinide-solubility calculations according to SNL/WIPP QA procedures. DATA0.FM1 differs from FMT_050405.CHEMDAT and the equivalent EQ3/6 DB DATA0.FMT.R0.16 (Wolery et al., 2010) in that: (1) DATA0.FM1 contains an updated value of 0.392 for the Debye-Hückel slope of the osmotic coefficient A_ϕ (FMT still contains the old value of 0.39 because it is hard-wired into the code and cannot be changed without significant effort), and (2) DATA0.FM1 contains values of the dimensionless standard chemical potential (μ^0/RT) for both phase 3 and phase 5. (FMT_050405.CHEMDAT contains only phase 3.).

When Brush and Xiong completed the original version of AP-153, Wolery (2008), Wolery et al. (2010), and Xiong (2011a, 2011b) had qualified EQ3/6, Version 8.0a, and DATA0.FM1 for actinide-solubility calculations according to SNL/WIPP QA procedures. However, the EPA had not reviewed and approved SNL's qualification of EQ3/6 or DATA0.FM1. Therefore, Brush and Xiong (2011) planned to use both EQ3/6 and DATA0.FMT.R0.16 and DATA0.FM1, and FMT and FMT_050405.CHEMDAT for AP-153 to obtain additional verification that these codes and DBs predict essentially identical conditions and actinide solubilities.

However, the EPA recently approved the qualification of EQ3/6, Version 8.0a, and DATA0.FM1 for compliance-related, actinide-solubility calculations according to SNL/WIPP QA procedures. Therefore, additional verification that EQ3/6 and FMT produce identical results is unnecessary, so we will use EQ3/6 and DATA0.FM1— but not DATA0.FMT.R0.16 or FMT and FMT_050405.CHEMDAT — for all geochemical modeling from now on.

2.2.5 Uncertainty Ranges and Probability Distributions for Actinide Solubilities

PA personnel use Latin hypercube sampling of uncertainty ranges and probability distributions established for predictions of actinide solubilities to incorporate this source of uncertainty in their probabilistic calculations. Brush et al. (2005) described how sampling of these ranges is implemented in PA.

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 DB. 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.

The EPA reviewed the WIPP Project's laboratory and modeling studies of actinide chemistry as part of its review of the CRA-2004 (U.S. DOE, 2004). 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 DB for their analysis (see Subsection 2.2.4 above). 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 DB; (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 Th(OH)$_4$(aq) be changed from -622.4700 to -626.5853 and Xiong (2005) released FMT_050405.CHEMDAT (see 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 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) concluded 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.

Xiong et al. (2009a) used 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 the CRA-2009 PABC, including FMT_050405.CHEMDAT. However, they improved the process used by Xiong et al. (2004, 2005) to address criticisms by the EPA during its review of the revised uncertainty ranges and probability distributions used in the CRA-2004 PABC. These improvements included: (1) better definition of the criteria for the selection of measured solubilities for inclusion in the comparisons, (2) better documentation of the application of these criteria to the solubility studies found in the open literature or unpublished reports, and (3) more comparisons of solubilities measured in WIPP brines with predicted solubilities (Lucchini et al., 2007; Borkowski et al., 2009; Borkowski, 2010).

Xiong et al. (2009a) performed 140 Th(IV) comparisons, an increase of 95 from Xiong et al. (2005); and 346 Nd(III) and Am(III) comparisons, an increase of 103 from Xiong et al. (2005); for a total of 486 comparisons for both oxidation states. They did not include Np(V) in their analysis because time was limited and Np(V) was assigned a lower priority than Th(IV) and Am(III). (WIPP PA does not sample the uncertainties associated with Np(V) solubilities.)

Xiong et al. (2009a) found that: (1) the Th(IV) model in FMT overpredicted the measured (Th(IV) solubilities; and (2) the Am(III) model also overpredicted the measured Am(III) solubilities.

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

We will continue to use the following oxidation-state distributions for dissolved actinides for 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).   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 was used for the CCA PA (Novak et al., 1996; U.S. DOE, 1996a, Appendix SOTERM); the PAVT (Novak, 1997); the CRA-2004 PABC (Brush and Xiong, 2005a; 2005b; Brush, 2005); and the CRA-2009 PABC (Brush and Xiong, 2009a; 2009b; and Brush et al., 2009).

This redox speciation is based on the results of experimental studies summarized in the CCA (U.S. DOE, 1996a, Appendix SOTERM), the CRA-2004 (U.S. DOE, 2004, Appendix PA, Attachment SOTERM), and the CRA-2009 (U.S. DOE, 2009, Appendix 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 assigned a probability of 1 during its review of the CRA-2004, 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 dissolved 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 current 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 used for the CCA PA (Novak et al., 1996;

U.S. DOE, 1996a, Appendix SOTERM); the PAVT (Novak, 1997); the CRA-2004 PABC
(Brush and Xiong, 2005a; 2005b; Brush, 2005); and the CRA-2009 PABC (Brush and Xiong,
2009a; 2009b; and Brush et al., 2009).

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)

We will continue to use an estimated U(VI) solubility of 1×10^{-3} M (see below) for
the for the actinide-solubility calculations to be carried out under this AP.

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, 2006b, 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 U(VI) at pH 10 in the absence of carbonate to be 8.8×10^{-5} M" (U.S. EPA, 2006b, p. 54). Indeed, Hobart and Moore (1996) estimated the solubility of U(VI) at pH 10 in the absence of carbonate to be 1×10^{-5} m.

However, a U(VI) concentration of 1×10^{-5} m (Hobart and Moore, 1996) is equivalent to approximately $(8.7-8.9) \times 10^{-6}$ M, depending on the brine, its density, and its composition used for conversion from molal to molar units. Brush and Xiong (2009a, Subsection 2.2.8, pp. 28-29) provided a step-by-step calculation converting molal to molar units to document this correction.

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, 2006b, pp. 55-58).

The EPA's 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 DBRs 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).

The EPA's estimate of 1×10^{-3} M was also used for the CRA-2009 PABC (Brush and Xiong, 2009a; Brush et al., 2009); therefore, we will continue to use it for the actinide-solubility calculations covered by this AP.

3   Software List

We will use EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a). Subsection 2.2.4 (see above) explains how DATA0.FM1 differs from DATA0.FMT.R0.16 (Wolery et al., 2010) and the equivalent FMT DB FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005).

We will not use FMT for any of the tasks carried out under AP-153, Rev. 1, because the EPA has approved the use of EQ3/6 and DATA0.FM1 for WIPP compliance-related, actinide-solubility calculations and there is thus no need to continue using FMT.

SNL/WIPP PA personnel will execute all EQ3/6 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 EQ3/6, Version 8.0a, and DATA0.FM1; and provide us the output files. Therefore, the executable file, the DB, and all of the I/O files used for this AP will be archived in the Sandia/WIPP CMS for future inspection by the EPA during any review of this work. 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.

P. S. Domski, Repository Performance Dept. 6212, will run EQ3/6, Version 8.0a, and the EQ3/6 DB DATA0.FM1 runs under the WIPP PA run-control system. Jennifer J. Long, Performance Assessment and Decision Analysis Dept. 6211, will assist Domski if necessary. Therefore, the executable file, the DB(s), and all of the I/O files used for this AP will be archived in the Sandia/WIPP CMS for future inspection by the EPA during any review of this work. 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.

4   Tasks

The geochemical modeling tasks that were or will be carried out for this AP are: (1) predictions with EQ3/6 and DATA0.FM1 of the compositions of the standard brines GWB and ERDA-6 during and after reactions with the solids in WIPP disposal rooms (completed in June 2011); (2) predictions with EQ3/6 and DATA0.FMT.R0.16, FMT, and FMT_050405.CHEMDAT of actinide solubilities for volumes of brine larger than the minimum brine volume required for a release of radionuclides from the repository (completed in September 2011); (3) predictions of actinide solubilities with EQ3/6 and DATA0.FM1 for the same brine volumes used for Task 2 (to be completed by March 2012); (4) updated uncertainty analyses of predictions with EQ3/6 and DATA0.FM1 of Th(IV) and Am(III) solubilities and, if possible, Np(V) solubilities (to be completed by September 2012); and (5) predictions with EQ3/6 and a possible new DB of Th(IV), Np(V), and Am(III) solubilities for the CRA-2014 PA and/or PABC (to be completed by September 2012).

The rest of this section describes these tasks in detail.

4.1   Predictions of the Compositions of Brines during and After Reactions with Solids

Brush et al. (2011a) completed Task 1 (see above) in June 2011. Their analysis report describes the methods used for Task 1, their deviations from the original version of AP-153 (Brush and Xiong, 2011), and their results.

There is currently no need to carry out additional work related to Task 1 because Brush et al. (2011a) used EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a).

Subsection 2.2.4 (see above) explains how DATA0.FM1 differs from DATA0.FMT.R0.16 (Wolery et al., 2010) and the equivalent FMT DB FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005).

Subsection 2.2.4 also provides a detailed history of the DBs used for previous WIPP compliance-related actinide-solubility calculations.

4.2 Predictions of Actinide Solubilities for Volumes of Brine Larger Than the Minimum Volume Required for a Radionuclide Release

Brush et al. (2011b) completed Task 2 (see the introduction to Section 4 above) in September 2011. Their analysis report describes the methods used for Task 2 and their results. Their analysis did not deviate from the methods described in the original version of AP-153 (Brush and Xiong, 2011, Subsection 4.2).

Brush et al. (2011b) used EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and FMT, Version 2.4 (Babb and Novak, 1997 and addenda; Wang, 1998) for their analysis. However, they used FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005) and the equivalent EQ3/6 DB, DATA0.FMT.R0.16 (Wolery et al., 2010). Brush et al. (2011b) used the DB used for (or equivalent to that used for) the CRA-2009 PABC so that the only differences between their results and those obtained for the PABC would be due to the larger brine volumes and lower organic-ligand concentrations they included in their analysis.

Therefore, we will revise the analysis of Brush et al. (2011b) by using EQ3/6 and DATA0.FM1. Subsection 4.3 (see below) describes this revision.

4.3 Revised Predictions of Actinide Solubilities with EQ3/6 and DATA0.FM1 for Brine Volumes Larger Than the Minimum Volume Required for a Radionuclide Release

We will revise the analysis carried out under Task 2 of Brush and Xiong (2011) by using EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a). Subsection 2.2.4 (see above) explains how DATA0.FM1 differs from DATA0.FMT.R0.16 (Wolery et al., 2010) and the equivalent FMT DB FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005).

We will not use FMT for this or any of the other tasks conducted under AP-153, Rev. 1, because the EPA has approved the use of EQ3/6 and DATA0.FM1 for WIPP compliance-related, actinide-solubility calculations and there is thus no need to continue using FMT.

We will continue to use volumes of GWB and ERDA-6 that are $1 \times$, $2 \times$, $3 \times$, $4 \times$, and $5 \times 17{,}400$ m^3, the minimum volume of brine in the repository required for a direct brine release (DBR) from the repository (Clayton, 2008); these are the same volumes used by Brush et al.

(2011b). They used factors of 2, 3, 4, or 5 at the request of WIPP PA personnel, who determined that all of the DBRs in the CRA-2009 PABC had volumes that varied between the minimum brine volume and $5 \times$ the minimum volume. A DBR is defined as a release of brine that occurs directly from the repository to the surface above the repository (i.e., without lateral transport through an offsite transport pathway such as the Culebra Member of the Rustler Fm.).

We will also continue to use the concentrations of acetate, citrate, EDTA, and oxalate calculated by Brush et al. (2011b, Table 5). This table is reproduced herein as our Table 6.

Table 6. Concentrations of Organic Ligands (M) in Brine Volumes That Are $1 \times$, $2 \times$, $3 \times$, $4 \times$, and $5 \times$ the Minimum Volume Required for a Release from the Repository (Brush et al., 2011b, Table 5).

Organic Ligand	$1 \times$ Minimum[A, B]	$2 \times$ Minimum	$3 \times$ Minimum	$4 \times$ Minimum	$5 \times$ Minimum
Acetate	1.94×10^{-2}	9.70×10^{-3}	6.47×10^{-3}	4.85×10^{-3}	3.88×10^{-3}
Citrate	2.38×10^{-3}	1.19×10^{-3}	7.93×10^{-4}	5.95×10^{-4}	4.76×10^{-4}
EDTA	6.47×10^{-5}	3.24×10^{-5}	2.16×10^{-5}	1.62×10^{-5}	1.29×10^{-5}
Oxalate	1.73×10^{-2}	8.65×10^{-3}	5.77×10^{-3}	4.32×10^{-3}	3.46×10^{-3}

A. Based on a minimum brine volume of 17,400 m^3 (Clayton, 2008)
B. Organic ligand concentrations calculated by Brush and Xiong (2009) for the WIPP CRA-2009 PABC.

We will use EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b) to simulate the reaction of GWB and ERDA-6 with the important solids in the WIPP. In the first step of this reaction (referred to herein as "step 1"), we will add the following compounds to GWB and ERDA-6: (1) acetate, citrate, EDTA, and oxalate; and (2) ThO$_2$(am), KNpO$_2$CO$_3$, and Am(OH)$_3$(s)), the solids most likely to control the solubilities of Th(IV), Am(III), and Np(V) in the repository (Brush and Xiong, 2011). In step 2, we will react these brines with the important solids in the repository (see below) in a manner consistent with the conceptual models for WIPP near-field chemistry (SCA, 2008; Brush and Xiong, 2011) and predict the solubilities of Th(IV), Np(V), and Am(III) and the compositions of GWB and ERDA-6 after equilibration with the important solids. After equilibration, the compositions of these brines define so-called invariant points (one each for GWB and ERDA-6), because the solids specified in the conceptual models — especially brucite (Mg(OH)$_2$) and hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O) — control the new compositions of the brines and

parameters such as the fugacity (similar to the partial pressure) of CO_2 (f_{CO_2}), pH, and total inorganic carbon (TIC).

For step 1, we will use the speciation and solubility code EQ3NR to add the organic ligands and the actinide-bearing solids to GWB and ERDA-6. We set the initial concentrations of acetate, citrate, EDTA, and oxalate equal to those in volumes of GWB and ERDA-6 that are $1 \times$, $2 \times$, $3 \times$, $4 \times$, and $5 \times 17,400$ m^3. We will set the initial value of the total inorganic carbon (TIC) concentrations of both brines at 16 mM for this step because: (1) Popielak et al, (1983) reported that the average TIC content of ERDA-6 was 16 mM, (2) the initial TIC of GWB was not determined, so (3) we will assume that the initial TIC content of GWB was equal to that of ERDA-6. (Brush et al., 2011b, found that the initial value of the TIC did not affect the values of the TIC predicted during the rest of the calculations). The code will charge balance on H$^+$; speciate all of the dissolved elements; and calculate the values of parameters such as f_{CO_2}, pH, and TIC. The code will also write a "pickup" file (*.3p file) for step 2. The *.3p file is called a pickup file because it is copied and pasted into an EQ6 input file, and provides all of the information on the solution and solids required for the next EQ6 run (see below).

For step 2, we will use the reaction-path code EQ6 to titrate the solids halite (NaCl), anhydrite (CaSO$_4$), brucite, and hydromagnesite into GWB. (We will use a slightly different procedure, described below, for ERDA-6.) We will use halite and anhydrite to simulate the most important minerals in the Salado Fm. at or near the stratigraphic horizon of the repository; and brucite and hydromagnesite to simulate the expected hydration and carbonation products, respectively, of MgO (the WIPP engineered barrier). As EQ6 titrates in these solids, halite and anhydrite will dissolve until the brine becomes saturated with these solids (i.e., until the concentrations of Na$^+$, Cl$^-$, Ca^{2+}, and SO$_4^{2-}$ reach their solubility limits). The reaction will then continue until brucite and hydromagnesite equilibrate with GWB (i.e., until GWB reaches its invariant point). EQ6 will then calculate the moles of solids that dissolved and/or precipitated, speciate all of the dissolved elements; and recalculate the values of parameters such as f_{CO_2}, pcH, TIC, etc.

For ERDA-6, we will first use EQ6 to titrate just halite and anhydrite into the brine (step 2a). During this step, EQ6 will titrate halite and anhydrite into ERDA-6 until this brine becomes saturated with these solids (i.e., until Na$^+$, Cl$^-$, Ca^{2+}, and SO$_4^{2-}$ reach their solubility limits). At the end of step 2a, EQ6 will write a pickup file (*.6p file), which will provide all of the information on the solution and solids required for step 2b. During step 2b, EQ6 will titrate in brucite and hydromagnesite as ERDA-6 remains saturated with halite and anhydrite. The reaction will continue until brucite and hydromagnesite equilibrate with ERDA-6 (i.e., until this brine reaches its invariant point). EQ6 will then calculate the moles of solids that dissolved and/or precipitated, speciate all of the dissolved elements; and recalculate the values of parameters such as f_{CO_2}, pcH, TIC, etc.

Table 7 summarizes the EQ3/6 calculations that we will carry out for GWB and ERDA-6.

Table 7.   Summary of EQ3/6 Calculations to Be Carried Out with GWB and ERDA-6 for Task 3.

Description of Step	GWB	ERDA-6
1	Will use EQ3NR to add organic ligands and actinide-bearing solids	Will use EQ3NR to add organic ligands and actinide-bearing solids
2	Will use EQ6 to titrate in halite, anhydrite, brucite, and hydromagnesite	-
2a	-	Will use EQ6 to titrate in halite and anhydrite
2b	-	Will used EQ6 to titrate in brucite and hydromagnesite

For step 2 (GWB) or steps 2a and 2b (ERDA-6), we will use quantities of brine, halite, anhydrite, brucite, and hydromagnesite similar to those that will be present in the repository after it is filled and sealed, but scaled down by the same factor used to scale down the quantity of water contained in 17,400 m^3 of brine to 1 kg of water. EQ3/6 allows the user to specify the composition and specific gravity of the aqueous phase present at the start of a run. However, the code assumes that exactly 1 kg of H_2O is present in the solution and uses the specific gravity entered by the user to calculate the volume of solution. We will use spreadsheet calculations to scale down (1) the quantities of halite and anhydrite present in the disturbed rock zone (DRZ) surrounding the repository, and (2) the quantity of MgO that will be emplaced in the repository. To calculate the quantities of halite and anhydrite, we will use the conservatively large DRZ currently implemented in WIPP PA and the assumption that the DRZ comprises 90 wt % halite and 10 wt % anhydrite.   This mineralogical composition is similar to Brush's (1990) interpretation of the results of Stein's (1985) mineralogical analysis of the Salado Fm. at or near the stratigraphic horizon of the repository: Brush (1990) concluded that, for use in geochemical modeling, the Salado consists of 93.2 wt % halite and 1.7 wt % each of anhydrite, gypsum ($CaSO_4 \cdot 2H_2O$), magnesite ($MgCO_3$), and polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$).   However, we will assume for this analysis that the Salado contains 90 wt % halite and 10 wt % anhydrite because the conceptual models for WIPP near-field chemistry include only halite and anhydrite (SCA, 2008).   For run 1, we will also assume that the MgO that will be emplaced in the repository will be present half as brucite and half as hydromagnesite; this assumption ensured that ample CO_2 was present without having to use a microbial reaction to titrate in CO_2.

We will use EQ6 in closed-system mode (model variable IOPT1 = 0) for step 2 (GWB) or steps 2a and 2b ERDA-6. Closed-system mode consists of the simulated titration (addition) of the reactants described above to GWB or ERDA-6. "Closed-system" means that no reactants or products can leave the system after the reactants are titrated in, which simulates the WIPP under undisturbed conditions. We will suppress (prevent from precipitating) the solids aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), hydromagnesite with the composition $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$, and nesquehonite ($MgCO_3 \cdot 3H_2O$) throughout step 2 or steps 2 and 2b. We will suppress these phases to ensure that this analysis is consistent with the near-field chemical conceptual models (SCA, 2008; Brush and Xiong, 2011).

We will use the EQ3/6 DB DATA0.FM1 (Xiong, 2011a) for this task. Subsection 2.2.4 (see above) describes the differences between DATA0.FM1 and DATA0.FMT.R0.16 (Wolery et al., 2010), which is identical to FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005), the DB used by Brush et al. (2009) to predict the solubilities of Th(IV), Np(V), and Am(III) for the CRA-2009 PABC. Brush and Xiong (2011) provided a detailed history of the DBs used for WIPP compliance-related actinide-solubility calculations.

We will extract the output from these EQ6 *.6o files by running the Excel macro "GetEQData.xls." This macro extracts all of the EQ6 output into an Excel spreadsheet.

We will document any deviations from the procedures described above in the analysis report for Task 3.

We will provide the locations of all of the spreadsheet and EQ3/6 I/O files used for our calculations. We will also provide run-control information for the EQ3/6 calculations carried out for this task.

Finally, we will complete a report that contains the results of this analysis.

L. H. Brush, Radiological Consequences Management and Response Dept. 6222; P. S. Domski, and Y.-L. Xiong, Repository Performance Dept. 6212; will carry out Task 3. The estimated completion date of this task is March 31, 2012.

4.4   Updated Uncertainty Analyses of Solubility Predictions for Th(IV), Am(III), and, If Possible, Np(V), with EQ3/6 and DATA0.FM1

We will update the uncertainty analysis carried out by Xiong et al. (2010) for the CRA-2009 PABC. They compared experimentally measured solubilities of Th(IV), Nd(III), and Am(III) with the solubilities predicted using the Th(IV) and Am(III) thermodynamic models implemented in FMT (Babb and Novak, 1997 and addenda; Wang, 1998). If time permits, we will also update the uncertainty analysis of Np(V) solubilities conducted by Xiong et al. (2005).

We will use the methods of Xiong et al. (2010) as closely as possible (see below), except that we will use EQ3NR, part of EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a).

We will perform literature searches for published papers and unpublished reports on laboratory studies of Th(IV), Np(V), Nd(III), Am(III) and Cm(III) solubilities. These literature searches will probably identify thousands of published papers and unpublished reports on actinide chemistry. Therefore, we will carry out preliminary evaluations of these studies by applying the criteria described below to the information provided in the abstracts of these papers and reports. Because of the large number of papers and reports that will probably be identified by the literature searches, it will not be practicable to document which criteria were used to include or exclude these studies from the final evaluations (see below). During the preliminary evaluations, we will exclude all papers and reports that, in our judgment, obviously fail to meet these criteria. In those cases in which it is not obvious that a paper or report should be excluded, we will retain them for the final evaluations. Furthermore, we will use at least two of the authors of this AP to conduct the final evaluations and, if these two authors cannot agree on whether to include or exclude a paper or report, another author will assist in the final evaluation.

The methods used for this analysis are similar to those used by Xiong et al. (2004, 2005). We compared experimentally measured solubilities of Th(IV), Nd(III), and Am(III) with the Th(IV) and Am(III) solubilities predicted using the thermodynamic models implemented in FMT (Babb and Novak, 1997 and addenda; Wang, 1998). We then constructed histograms and cumulative distribution functions (CDFs) of the differences between the logarithms (base 10) of the measured and predicted solubilities. We constructed separate histograms and CDFs for the Th(IV) and Am(III) models. These CDFs will be used for the CRA-2014 PA.

We will apply the general criteria established by Xiong et al. (2009, 2011) for inclusion or exclusion of the results of experimentally measured solubilities in our comparisons. We will also apply the specific criterion established by Xiong et al. (2005) for the experimentally measured solubilities of Th(IV).

We will use the commercially available software application Data Thief to obtain numerical values of experimental variables such as pcH or pmH and the resulting solubilities from scatter plots of the experimentally measured solubilities, if tabulations of these values were not provided by the investigators. Most of the published papers and unpublished reports included in our previous uncertainty analyses did not include data tables.

We will set up EQ3N/R input files to predict the solubilities of Th(IV); Np(V); and Nd(III), Am(III), and Cm(III) for the conditions reported for each of the measured solubilities in the laboratory studies selected by the final evaluations. However, if two or more identical results were reported (i.e., identical values of pcH or pH and solubility for two or more experiments), we will conduct only one EQ3NR run for these experiments.

We will use the EQ3/6 DB DATA0.FM1 (Xiong, 2011a) for this task. Subsection 2.2.4 (see above) describes the differences between DATA0.FM1 and DATA0.FMT.R0.16

(Wolery et al., 2010), which is identical to FMT_050405.CHEMDAT (Nowak, 2005; Xiong, 2005), the DB used by Xiong et al. (2009, 2011) for the uncertainty analyses to for the CRA-2009 PABC. We will recalculate all of the solubilities predicted by Xiong et al. (2009, 2011), because we will use a different DB (DATA0.FM1) than they did (FMT_050405.CHEMDAT).

Paul S. Domski will carry out the EQ3NR calculations under the PA run-control system used for WIPP compliance-related calculations.

Finally, we will construct frequency distributions of differences (D) between the logs of the measured and predicted actinide solubilities (S_m and S_p, respectively) and display them in tabular and histogram forms in Microsoft Excel spreadsheets using Excel's "histogram" data analysis tool in this commercial spreadsheet software. Negative values of D indicate that the Th(IV), Np(V), or Am(III) model implemented in EQ3NR predicted a solubility greater than the corresponding measured value (overprediction of solubility by the model); positive values of D indicate that the model predicted a solubility less than the measured value (underprediction).

The bin numbers (N) in the histograms are defined as follows:

Bin N contains values of D greater than $N - 0.15$ and less than or equal to N, where $D = \log_{10}(S_m) - \log_{10}(S_p)$.

Examples of the definitions of bins follow:

Bin -0.3 contains values of D greater than -0.45 and less than or equal to -0.3;
Bin -0.15 contains values of D greater than -0.30 and less than or equal to -0.15;
Bin 0 contains values of D greater than -0.15 and less than or equal to 0; and
Bin 0.15 contains values of D greater than 0 and less than or equal to 0.15.

We will document any deviations from the procedures described above in the analysis report for Task 3.

We will provide the locations of all of the spreadsheet and EQ3/6 I/O files used for our calculations. We will also provide run-control information for the EQ3/6 calculations carried out for this task.

Finally, we will complete a report on this analysis.

L. H. Brush, Radiological Consequences Management and Response Dept. 6222; P. S. Domski, and Y.-L. Xiong, Repository Performance Dept. 6212; will carry out Task 4. The estimated completion date of this task is September 30, 2012.

4.5 Revised Predictions of Actinide Solubilities with EQ3/6 and an Updated DB for Brine Volumes Larger Than the Minimum Volume Required for a DBR for the CRA-2014 PA and/or PABC

We will update the analysis carried out under Task 3 (see Subsection 4.3 above) of this revised AP by using EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and an updated DB to be released in September 2012. This updated DB will contain values of μ^0/RT and Pitzer parameters for Fe- and Pb-bearing solids and dissolved sulfide, Fe, and Pb species is available in time.

We will use the methods described for Task 3 (Subsection 4.3) for this analysis.

L. H. Brush, Radiological Consequences Management and Response Dept. 6222; P. S. Domski, and Y.-L. Xiong, Repository Performance Dept. 6212; will carry out Task 5. The estimated completion date of this task is December 31, 2012.

4.6 Revised Uncertainty Analyses of Solubility Predictions for Th(IV), Am(III), and, If Possible, Np(V), with EQ3/6 and an Updated DB

We will revise the uncertainty analysis carried out under Task 4 (see Subsection 4.4) of this revised AP by using EQ3NR, part of EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and an updated DB to be released in September 2012.

We will use the methods described for Task 4 (Subsection 4.4) for this analysis.

L. H. Brush, Radiological Consequences Management and Response Dept. 6222; P. S. Domski, and Y.-L. Xiong, Repository Performance Dept. 6212; will carry out Task 6. The estimated completion date of this task is March 31, 2012.

5 Special Considerations

There are no special considerations for the work to be carried out under this AP.

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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