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Sandia National Laboratories
Waste Isolation Pilot Plant

Results of Calculations of Actinide Solubilities for the WIPP Performance-Assessment Baseline Calculations

Work Carried Out under Task 4 of the Analysis Plan for the Calculation of Actinide Solubilities for the WIPP PABC, AP 120, Rev. 0
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TABLE OF CONTENTS

1 ABBREVIATIONS, ACRONYMS, AND INITIALISMS

Table 1 defines the abbreviations, acronyms, and initialisms used in this report.

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
acetate	$CH_3CO_2^-$
a_{H_2O}	(thermodynamic) activity of water
Am	americium
am	amorphous
An	actinide
An(III)	actinide element(s) in the +III oxidation state
An(IV)	actinide element(s) in the +IV oxidation state
An(V)	actinide element(s) in the +V oxidation state
An(VI)	actinide element(s) in the +VI oxidation state
anhydrite	$CaSO_4$
AP	analysis plan
aq	aqueous
B, $B(OH)_3^x$	boron, boric acid
Br, Br^-	bromine, bromide (ion)
Brine A	a synthetic brine representative of intergranular Salado brines
brucite	$Mg(OH)_2$
C	carbon
Ca, Ca^{2+}	calcium, calcium ion
CCA	(WIPP) Compliance Certification Application
calcite	$CaCO_3$
citrate	$((CO_2H)(CH_2))_2C(CO_2)OH^-$
Cl, Cl^-	chlorine, chloride ion
CMS	(Compaq Computer Corp., now a part of the Hewlett-Packard Co.) DECset Code Management System
CO_2	carbon dioxide
CO_3^{2-}	carbonate ion
CRA	(WIPP) Compliance Recertification Application
DOE	(U.S.) Department of Energy
EDTA	ethylenediaminetetraacetate $(CH_2CO_2H)_2N(CH_2)_2N(CH_2CO_2H)(CH_2CO_2)^-$

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

Abbreviation, Acronym, or Initialism	Definition
EPA	(U.S.) Environmental Protection Agency
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
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code (the component that calculates transport is not used)
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
H or H^+	hydrogen or hydrogen ion
halite	NaCl
HCO_3^-	bicarbonate
hydromagnesite	$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ or $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
I	ionic strength
K, K^+	potassium, potassium ion
kg	kilogram(s)
L	liter(s)
M	molar
m	meter(s) or molal
magnesite	$MgCO_3$
Mg, Mg^{2+}	magnesium, magnesium ion
mg	milligram(s)
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various concentrations of impurities
mM	millimolar
N	nitrogen
Na or Na^+	sodium, sodium ion
Np	neptunium
O	oxygen
OH^-	hydroxide ion
oxalate	$(CO_2H)(CO_2)^-$
ρ	density
PA	performance assessment
PABC	(WIPP) Performance Assessment Baseline Calculations
PAVT	(WIPP) Performance Assessment Verification Test

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

Abbreviation, Acronym, or Initialism	Definition
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
pH	the negative, common logarithm of the activity of H^+
Pu	plutonium
Rev.	Revision
RH	relative humidity
SO_4^{2-}	sulfate ion
Sp. gr.	specific gravity
SPC	Salado Primary Constituents (brine), a synthetic solution similar to Brine A - but without the minor constituents
TDS	total dissolved solids
Th	thorium
U	uranium
WIPP	(U.S. DOE) Waste Isolation Pilot Plant

2 INTRODUCTION

This analysis report describes how we calculated the speciation and solubilities of actinide (An) elements in the +III, +IV, and +V oxidation states (An(III), An(IV), and An(V)) for use in the An source term in the performance assessment (PA) calculations for the U.S. Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) Performance Assessment Baseline Calculations (PABC). This report also includes the new estimate of the solubility of U(VI), and discusses a change in the colloidal actinide source term required for the PABC.

These solubilities will replace those calculated in 2003 (Brush and Xiong, 2003a; 2003b; 2003c) for the PA calculations for the first WIPP Compliance Recertification Application (CRA-2004 PA) (U.S. DOE, 2004, Attachment PA, Appendix SOTERM), submitted to the U.S. Environmental Protection Agency (EPA) in March 2004, the solubilities currently in the WIPP Project's technical baseline.

We carried out the analysis described in this report under the fourth task of the analysis plan (AP) for the actinide-solubility calculations for the PABC (Brush and Xiong, 2005a, Subsection 7.4). This AP also included the new U(VI) solubility estimate and the change in the colloidal actinide source term required for the PABC (Brush and Xiong, 2005a, Subsection 7.5).

The other tasks covered by the AP for the PABC actinide-solubility calculations were: (1) recalculation of organic-ligand concentrations, (2) revision of the thermodynamic database used for the An(IV) speciation and solubility calculations, and (3) re-establishment of the uncertainty range and probability distribution for An(IV) solubility predictions (Brush and Xiong, 2005a, Subsections 7.1, 7.2, and 7.3, respectively. These activities have already been completed and documented elsewhere, but are summarized briefly below.

Leigh (2005a, 2005b) reviewed the most recent information on the inventory of the TRU waste to be emplaced in the WIPP and concluded that we should continue to use the masses of organic ligands estimated by Crawford and Leigh (2003) and Leigh (2003) to calculate the concentrations of acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate in WIPP brines for the PABC. Stein (2005) then re-evaluated the assumption that all of the acetate, citrate, EDTA, and oxalate in the waste 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, 1996). Stein (2005) concluded that continued use of 29,841 m^3 of brine would be inappropriate, and recommended a new value of 10,011 m^3, "a reasonable minimum volume of brine in the repository required for a brine release." Brush and Xiong (2005b, Table 4) then recalculated the organic-ligand concentrations for the PABC.

Xiong et al. (2004) re-established the uncertainty range and probability distribution for An(III), An(IV), and An(V) solubility predictions in response to an EPA request

(Cotsworth, 2004, Enclosure 1, Comment C-23-16) to update the ranges and distributions established by Bynum (1996a, 1996b, 1996c) for the PA calculations for the WIPP Compliance Certification Application (CCA). Xiong et al. (2004) concluded that (1) the An(III) thermodynamic speciation and solubility model implemented in the speciation and solubility code Fracture-Matrix Transport (FMT) (Babb and Novak, 1997 and addenda; Wang, 1998) slightly overpredicted the measured An(III) solubilities; (2) the An(IV) model in FMT significantly underpredicted the measured An(IV) solubilities; (3) the An(V) model in FMT slightly overpredicted the measured An(V) solubilities; and (4) overall, the An(III), An(IV), and An(V) models in FMT together significantly underpredicted the measured An(III), An(IV), and An(V) solubilities. Xiong et al. (2004) used the thermodynamic database FMT_040628.CHEMDAT for their analysis. Because the An(IV) model in FMT significantly underpredicted the measured An(IV) solubilities, Nowak (2005) identified the value of the dimensionless standard chemical potential (μ^0/RT) for $Th(OH)_4(aq)$ in FMT_040628.CHEMDAT, -622.4700, as the cause of this problem; and recommended that μ^0/RT for $Th(OH)_4(aq)$ be changed from -622.4700 to -626.5853. Xiong (2005) made this change and released the corrected version of the database, FMT_050405.CHEMDAT.

Xiong et al. (2005) used FMT_050405.CHEMDAT to establish a revised uncertainty range and probability distribution for An(IV) solubility predictions and a revised composite range and distribution for An(III), An(IV), and An(V) solubility predictions. Xiong et al. (2005) did not revise the ranges and distributions for An(III) and An(V) solubility predictions established by Xiong et al. (2004).

3 METHODS USED FOR CALCULATIONS

This section describes how we calculated An(III), An(IV), and An(V) solubilities for the PABC source term.

3.1 Chemical Conditions

Definition of the chemical conditions for the An(III), An(IV), and An(V) solubility calculations for the PABC source term featured: (1) use of Generic Weep Brine (GWB) (Snider, 2003) and Energy Research and Development Administration (WIPP Well) 6 (ERDA-6) (Popielak et al., 1983) to simulate Salado and Castile brines, respectively; (2) the assumption that instantaneous, reversible equilibria among GWB or ERDA-6, major Salado minerals such as halite (NaCl) and anhydrite ($CaSO_4$), and the MgO hydration and carbonation products brucite ($Mg(OH)_2$) and hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) will control chemical conditions, such as f_{CO_2}, pH, and brine composition; (3) elimination of separate, slightly different chemical conditions characteristic of the absence of microbial activity from the calculations; and (4) use of FMT to calculate these chemical conditions. Brush and Xiong (2005a, Subsection 5.1) described each of these features in detail. Brush and Xiong (2003a) provided a detailed review of the An solubility calculations for the CCA PA, the 1997 WIPP Performance Assessment Verification Test (PAVT), and the CRA-2004 PA calculations.

We used GWB to calculate An solubilities for the PABC because: (1) GWB is more representative of intergranular Salado brine than Brine A (Molecke, 1983), and (2) the solubilities obtained with these brines are very similar (Brush and Xiong, 2003c; Downes, 2003a, 2003b). However, we also calculated solubilities with Brine A to allow the EPA to compare the results obtained with these Salado brines. Table 2 provides the compositions of Brine A, GWB, and ERDA-6.

We used the brucite-hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) carbonation reaction (Brush and Xiong, 2005a, Subsection 5.1.2, Reaction 1) to buffer f_{CO_2} in the An solubility calculations for the PABC. We did so because the EPA specified that this reaction be used for the PAVT and all subsequent An-solubility calculations, based on its review of the An source term used for the CCA PA (U.S. EPA, 1998a; 1998b; 1998c; 1998d; 1998e). However, magnesite ($MgCO_3$) is the thermodynamically stable, Mg-carbonate mineral under the conditions expected in the WIPP, and is present in the Salado at the stratigraphic horizon of the repository. Therefore, the brucite-magnesite carbonation reaction (Brush and Xiong, 2005a, Subsection 5.1.2, Reaction 3) would be expected to buffer f_{CO_2} in the WIPP *if* the kinetics of magnesite formation were fast enough for this phase to replace hydromagnesite or other metastable, hydrous Mg carbonates during the 10,000-year period of performance of the repository. Therefore, we also calculated solubilities with magnesite present instead of hydromagnesite to compare the results obtained with these buffers. The brucite dissolution reaction buffered the pH (Brush and Xiong, 2005a, Subsection 5.1.2, Reaction 2).

Table 2. Compositions of Brine A, GWB, andERDA-6 Prior to Reaction. See text for sources.

Element or Property	Brine A	GWB	ERDA-6
$B(OH)_x^{3-x}$	20 mM	158 mM	63 mM
Na^+	1.83 M	3.53 M	4.87 M
Mg^{2+}	1.44 M	1.02 M	19 mM
K^+	770 mM	467 mM	97 mM
Ca^{2+}	20 mM	14 mM	12 mM
SO_4^{2-}	40 mM	177 mM	170 mM
Cl^-	5.35 M	5.86 M	4.8 M
Br^-	10 mM	26.6 mM	11 mM
Total inorganic C (as HCO_3^-)	10 mM	-	16 mM
pH	6.5	-	6.17
Sp. gr.	1.2	1.2	1.216
TDS	306,000 mg/L	-	330,000 mg/L

3.2 An Solubilities

The An(III), An(IV), and An(V) speciation and solubility calculations for the PABC source term featured: (1) use of thermodynamic speciation and solubility models based on the Pitzer activity-coefficient model to calculate Th(IV), Np(V), and Am(III) solubilities; (2) use of instantaneous, reversible equilibria among GWB or ERDA-6 and An-bearing solids such as amorphous ThO_2 (ThO_2(am)), $KNpO_2CO_3$, and $Am(OH)_3$ to control An solubilities; (3) recalculation of organic-ligand concentrations for inclusion in the solubility calculations; (4) use of FMT to calculate Th(IV), Np(V), and Am(III) solubilities; (5) use of the FMT thermodynamic database FMT_050405.CHEMDAT; (6) speciation of Th, U, Np, Pu, and Am entirely as Th(IV), U(IV) or U(VI), Np(IV) or Np(V), Pu(III) or Pu(IV), and Am(III); (7) use of 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) (the model developed for Np(V) was used only for Np(V)); and (8) use of the new uncertainty ranges and probability

distributions established by Xiong et al. (2004) for the solubilities calculated for An(III) and An(V) solubilities, and use of the range and distributions of Xiong et al. (2005) for the An(IV) solubilities. Brush and Xiong (2005a, Subsection 5.2) discussed these features in detail.

Table 3 provides the concentrations of acetate, citrate, EDTA, and oxalate calculated by Brush and Xiong (2005b) based on guidance from Leigh (2005a, 2005b) and input from Stein (2005). (This work was summarized in Section 2 above.) Although we included these organic ligands in the An solubility calculations for the PABC, we also calculated solubilities without organic ligands present to determine the effects of these complexants. Table 3 also compares the concentrations calculated for the PABC with previously calculated concentrations. The CCA concentrations are from U.S. DOE (1996, Appendix SOTERM, Table SOTERM-4, column labeled "Organic Concentration (scaled);" the CRA-2004 PA concentrations are from Brush and Xiong (2003b, Table 4, column labeled "CRA Concentration (M)"); the corrected CRA-2004 PA concentrations are from Brush and Xiong (2003d, Table 4, column labeled "Corrected Concentration for a 10-Panel, Homogeneous Repository (M), This Report"); and the PABC concentrations are from Brush and Xiong (2005b, Table 4, column labeled "PABC (M)").

Table 3. Concentrations of Organic Ligands for a Homogeneous 10-Panel Repository. See text for sources.

Organic Ligand	CCA (m)	CRA-2004 PA (M)	CRA-2004 PA, Corrected[C] (M)	PABC[D] (M)
Acetate	1.1×10^{-3}	5.05×10^{-3}	3.56×10^{-3}	1.06×10^{-2}
Citrate	7.4×10^{-3}	3.83×10^{-4}	2.71×10^{-4}	8.06×10^{-4}
EDTA	4.2×10^{-6}	3.87×10^{-6}	2.73×10^{-6}	8.14×10^{-6}
Oxalate	4.7×10^{-4}	2.16×10^{-2}	1.53×10^{-2}	4.55×10^{-2}

Table 4 lists the FMT runs carried out for the PABC. Runs 7 and 11 provided the solubilities actually used in these PA calculations; the other 10 runs were carried out to: (1) compare the effects of Brine A and GWB, (2) compare the effects of the brucite-hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) and brucite-magnesite f_{CO_2} buffers, and (3) determine the effects of organics.

Table 4. FMT Runs Carried Out for the PABC. Runs 7 and 11 provided the solubilities used for the PABC calculations. All runs archived in the CMS Analysis Directory PAA:[ANALYSIS.CRA1BC.FMT], Library LIBCRA1BC_FMT, Class CRA1BC-0.

FMT Run Identifier, Official	Unofficial, Abbreviated Run Number	Brine	Buffer	Organics
FMT_CRA1BC_BRA_MAG_ORGS_001.IN, FMT_CRA1BC_ BRA_MAG_ORGS_001.INGUESS, FMT_CRA1BC_ BRA_MAG_NOOORGS_001.OUT, etc.	1	Brine A	Brucite-magnesite	Yes
FMT_CRA1BC_BrA_Mag_NoOrgs_002	2	Brine A	Brucite-magnesite	No
FMT_CRA1BC_BrA_Hmag_Orgs_003	3	Brine A	Brucite-hydromagnesite[A]	Yes
FMT_CRA1BC_BrA_Hmag_NoOrgs_004	4	Brine A	Brucite-hydromagnesite[A]	No
FMT_CRA1BC_GWB_Mag_Orgs_005	5	GWB	Brucite-magnesite	Yes
FMT_CRA1BC_GWB_Mag_NoOrgs_006	6	GWB	Brucite-magnesite	No
FMT_CRA1BC_GWB_Hmag_Orgs_007	7	GWB	Brucite-hydromagnesite[A]	Yes
FMT_CRA1BC_GWB_Hmag_NoOrgs_008	8	GWB	Brucite-hydromagnesite[A]	No
FMT_CRA1BC_E6_Mag_Orgs_009	9	ERDA-6	Brucite-magnesite	Yes
FMT_CRA1BC_E6_Mag_NoOrgs_010	10	ERDA-6	Brucite-magnesite	No
FMT_CRA1BC_E6_Hmag_Orgs_011	11	ERDA-6	Brucite-hydromagnesite[A]	Yes
FMT_CRA1BC_E6_Hmag_NoOrgs_012	12	ERDA-6	Brucite-hydromagnesite[A]	No

A. Used hydromagnesite with the composition $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$.

4 RESULTS OF CALCULATIONS

Table 5 provides the solubilities of An(III), An(IV), and An(V) from our FMT calculations for the PABC. Table 5 also provides the ionic strength (I), log f_{CO_2}, ρ, pH, and relative humidity (RH) calculated by FMT. These results are from the FMT output files archived in the CMS in Analysis Directory PAA:[ANALYSIS.CRA1BC.FMT], Library LIBCRA1BC_FMT, Class CRA1BC-0. The official names of these runs are given in Table 4. Runs 7 and 11 provided the solubilities that will actually be used in the PABC.

We obtained the An(III), An(IV), and An(V) solubilities in Table 5 from the table entitled "Elemental Abundances for Flash Problem" near the end of each FMT output file. The An(III) solubilities are from the row labeled "Am(III);" the An(IV) solubilities are from the row labeled "Th(IV);" the An(V) solubilities are from "Np(V)." Note that each of these solubilities is equal to the sum of all of the aqueous Am(III), Th(IV), or Np(V) species listed in the table entitled "Table of Concentrations for Batch Systems," which follows the table entitled "Elemental Abundances for Flash Problem." We obtained I, log f_{CO_2}, ρ, pH, and RH from the data listed below the table entitled "Table of Concentrations for Batch Systems." Note that the activity of H_2O (a_{H_2O}) in these brines (or in the gaseous phase in equilibrium with these brines) can be obtained from the equation a_{H_2O} = RH/100).

Table 5 does not provide other information in the FMT output files, such as concentration of aqueous An(III), An(IV), and An(V) species, concentrations of the aqueous species of stable elements such as Na, Cl, etc., or the solids in equilibrium with these brines, all of which are also listed in the table entitled "Table of Concentrations for Batch Systems." We may report these results in a subsequent, revised version of this analysis report, or use them for other analyses.

Table 5. An Solubilities (M) and Other Properties from the FMT Calculations for the PABC. All results rounded to three significant figures.

Prop. or An Ox. State	FMT Run 1 (Brine A, mag, w orgs	FMT Run 2 (Brine A, mag, w/o orgs)	FMT Run 3 (Brine A, hmag, w orgs)	FMT Run 4 (Brine A, hmag, w/o orgs)	FMT Run 5 (GWB, mag, w orgs)	FMT Run 6 (GWB, mag, w/o orgs)	FMT Run 7 (GWB, hmag, w orgs)	FMT Run 8 (GWB, hmag, w/o orgs)	FMT Run 9 (ERDA-6, mag, w orgs)	FMT Run 10 (ERDA-6, mag, w/o orgs)	FMT Run 11 (ERDA-6, hmag, w orgs)	FMT Run 12 (ERDA-6, hmag, w/o orgs)
An(III)	5.45×10^{-7}	3.34×10^{-7}	5.46×10^{-7}	3.35×10^{-7}	3.87×10^{-7}	2.26×10^{-7}	3.87×10^{-7}	2.26×10^{-7}	2.87×10^{-7}	8.60×10^{-8}	2.88×10^{-7}	8.67×10^{-8}
An(IV)	4.53×10^{-8}	4.55×10^{-8}	5.58×10^{-8}	5.60×10^{-8}	4.57×10^{-8}	4.59×10^{-8}	5.64×10^{-8}	5.66×10^{-8}	4.84×10^{-8}	4.87×10^{-8}	6.79×10^{-8}	7.20×10^{-8}
An(V)	3.22×10^{-6}	1.58×10^{-6}	1.82×10^{-7}	1.21×10^{-7}	6.59×10^{-6}	3.43×10^{-6}	3.55×10^{-7}	2.36×10^{-7}	1.08×10^{-5}	3.65×10^{-6}	8.24×10^{-7}	5.38×10^{-7}
I (m)	7.49	7.39	7.49	7.39	7.66	7.54	7.66	7.54	6.80	6.72	6.80	6.72
log f_{CO_2}	-6.92	-6.92	-5.50	-5.50	-6.92	-6.92	-5.50	-5.50	-6.91	-6.91	-5.50	-5.50
ρ (kg/m^3)	1230	1230	1230	1230	1230	1230	1230	1230	1220	1220	1220	1220
pH	8.69	8.69	8.69	8.69	8.69	8.69	8.69	8.69	8.94	9.02	8.94	9.02
RH (%)	72.9	73.0	72.9	73.0	73.2	73.3	73.2	73.3	74.8	74.8	74.8	74.8

5 OTHER CHANGES IN THE An SOURCE TERM

There are two other changes that will be made in the An source term for the PABC. Both of these changes were described by Brush and Xiong (2005a).

5.1 Use of New Solubility Estimate for U(VI)

The EPA specified that a revised estimate of 1×10^{-3} M be used for the solubility of U(VI) in WIPP brines for the PABC source term. The EPA specified this value during a DOE-EPA teleconference on March 2, 2005.

The EPA estimate of 1×10^{-3} M is higher by a factor of about 100 than that of Hobart and Moore (1996), who estimated a solubility of 1×10^{-5} m in both Salado and Castile brines. Their estimate, also described in U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM), was also used for the PAVT and the CRA-2004 PA.

During the same teleconference, the EPA also specified that a fixed value be used for their revised estimate. In the CCA PA, the PAVT, and the CRA-2004 PA, the uncertainty range of +1.4 and -2.0 orders of magnitude was applied to the U(VI) solubility estimate of Hobart and Moore (1996).

5.2 Revision to the Colloidal Source Term

We will eliminate separate, somewhat different colloidal An concentrations characteristic of the absence of microbial activity from the PABC An source term.

Brush and Xiong (2003a) concluded that inclusion of microbial colloids, one of the four types of colloids described in U.S. DOE (1996, Appendix SOTERM) and U.S. DOE (2004, Appendix PA, Attachment SOTERM), in nonmicrobial vectors was inconsistent with the probability of 0.5 for significant microbial activity featured in the conceptual model of microbial activity in the WIPP included in the CCA PA, the PAVT, and the CRA-2004 PA.

However, the EPA has specified that the microbial conceptual model be changed for the PABC such that there will be a probability of 1 for significant microbial activity in the WIPP (Cotsworth, 2005). Therefore, nonmicrobial vectors will be eliminated from the PABC and microbial colloids will be included in all of the PABC vectors.

6 CONCLUSIONS

Table 6 compares the solubilities of An(III), An(IV), and An(V) calculated for the PABC with the An solubilities calculated for the CCA PA, the PAVT, and the CRA-2004 PA. Table 5 also compares the values of I, log f_{CO_2}, ρ, pH, and RH calculated by FMT, where available. The CCA PA results are from Novak, Moore, and Bynum (1996) and U.S. DOE (1996, Appendix SOTERM), except that Novak, Moore, and Bynum (1996) used molal instead of molar units. U.S. EPA (1998e) and, perhaps, others 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, Moore, and Bynum (1996) and U.S. DOE (1996). The PAVT results are from Trovato (1997). Novak (1997) also calculated An solubilities for the PAVT, the EPA used the results of its own calculations. The CRA-2004 PA results are from Brush and Xiong (2003c) and Downes (2003a).

Comparison of these results is complicated because several assumptions or other factors changed from calculation to calculation. These include: (1) the assumption as to which carbonation reaction will buffer f_{CO_2} (e.g., brucite-magnesite, brucite-hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), or brucite-calcite); (2) whether organic ligands were included in the calculations; and (3) other changes in the FMT thermodynamic database. We may compare these results in more detail in a subsequent, revised version of this analysis report, or in other analysis reports.

Table 6. Comparison of An Solubilities (M) and Other Properties from these and previous FMT Calculations. All results rounded to three significant figures. See text for sources.

Prop. or An Ox. State	CCA (SPC, mag, w/o orgs, all vectors)	CCA (ERDA-6, mag, w/o orgs, all vectors)	PAVT (SPC, hmag, w/o orgs, all vectors)	PAVT (ERDA-6, hmag, w/o orgs, all vectors)	CRA PA (GWB, hmag, w orgs, microbial)	CRA PA (GWB, calcite, w orgs, nonmicrobial)	CRA PA (ERDA-6, hmag, w orgs, microbial)	CRA PA (ERDA-6, calcite, w orgs, nonmicrobial)	PABC (GWB, hmag, w orgs, all vectors)	PABC (ERDA-6, hmag, w orgs, all vectors)
An(III)	5.82×10^{-7}	6.52×10^{-8}	1.2×10^{-7}	1.3×10^{-8}	3.07×10^{-7}	3.07×10^{-7}	1.69×10^{-7}	1.77×10^{-7}	3.87×10^{-7}	2.88×10^{-7}
An(IV)	4.4×10^{-6}	6.0×10^{-9}	1.3×10^{-8}	4.1×10^{-8}	1.19×10^{-8}	1.24×10^{-8}	2.47×10^{-8}	5.84×10^{-9}	5.64×10^{-8}	6.79×10^{-8}
An(V)	2.3×10^{-6}	2.2×10^{-6}	2.4×10^{-7}	4.8×10^{-7}	1.02×10^{-6}	9.72×10^{-7}	5.08×10^{-6}	2.13×10^{-5}	3.55×10^{-7}	8.24×10^{-7}
I (m)	NA[A]	NA[A]	NA[A]	NA[A]	7.54	7.54	6.73	6.76	7.66	6.80
log f_{CO_2}	-6.89	-6.89	-5.50	-5.50	-5.50	-5.48	-5.50	-6.15	-5.50	-5.50
ρ (kg/m^3)	NA[A]	NA[A]	NA[A]	NA[A]	1230	1230	1220	1220	1230	1220
pH	8.69	9.24	8.69	9.24	8.69	8.69	9.02	8.99	8.69	8.94
RH (%)	NA[A]	NA[A]	NA[A]	NA[A]	73.3	73.3	74.8	74.8	73.2	74.8

A. NA = not available.

7 REFERENCES

Babb, S.C., and C.F. Novak. 1997 and addenda. "User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations." Albuquerque, NM: Sandia National Laboratories. ERMS 243037.

Brush, L.H., and Y.-L. Xiong. 2003a. "Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Analysis Plan AP-098, Rev. 1." April 14, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527714.

Brush, L.H., and Y.-L. Xiong. 2003b. "Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application." Analysis report, April 14, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527567.

Brush, L.H., and Y.-L. Xiong. 2003c. "Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application." Analysis report, May 8, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 529131.

Brush, L.H., and Y.-L. Xiong. 2003d. "Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application and for Evaluating Assumptions of Homogeneity in WIPP PA." Analysis report, September 11, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 531488.

Brush, L.H., and Y.-L Xiong, 2005a. "Calculation of Actinide Solubilities for the WIPP Performance-Assessment Baseline Calculations, Analysis Plan AP-120, Rev. 0. April 4, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539255.

Brush, L.H., and Y.-L. Xiong, 2005b. "Calculation of Organic-Ligand Concentrations for the WIPP Performance-Assessment Baseline Calculations." Analysis report, May 4, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539635.

Bynum, R.V. 1996a. "Estimation of Uncertainty for Predicted Actinide Uncertainties." Analysis plan, AP-024, Rev. 0, May 22, 2004. Albuquerque, NM: Sandia National Laboratories. ERMS 410354.

Bynum, R.V. 1996b. "Update of Uncertainty Range and Distribution for Actinide Solubilities to Be Used in CCA NUTS Calculation." Memorandum to M.S. Tierney and C.T. Stockman, May 22, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 238268.

Bynum, R.V. 1996c. "Analysis to Estimate the Uncertainty for Predicted Actinide Solubilities." Analysis report, Rev. 0, September 6, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 241374.

Cotsworth, E. 2004. Untitled letter with enclosure to R.P. Detwiler with third set of CRA comments and requests for additional information, September 2, 2004. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation. ERMS 536771.

Cotsworth, E. 2005. Untitled letter with enclosure to I. Triay with first set of changes and corrections to the CRA PA, March 4, 2005. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation. ERMS 538858.

Crawford, B.A., and C.D. Leigh. 2003. "Estimate of Complexing Agents in TRU Waste for the Compliance Recertification Application." Analysis report, August 28, 2003. Carlsbad, NM: Los Alamos National Laboratory. ERMS 531107.

Downes, P.S. 2003a. "Spreadsheet Calculations of Actinide Solubilities for the WIPP Compliance Recertification Application." Memorandum to L.H. Brush, April 21, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 528395.

Downes, P.S. 2003b. "Spreadsheet Calculations of Actinide Solubilities for the WIPP Compliance Recertification Application in Support of AP-098, 'Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Analysis Plan AP-098, Rev. 1.'" Analysis report, July 22, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 530441.

Hobart, D.E., and R.C. Moore. 1996. "Analysis of Uranium(VI) Solubility Data for WIPP Performance Assessment: Implementation of Analysis Plan AP-028." Analysis report, August 12, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 236488.

Larson, K.W. 1996. "Brine-Waste Contact Volumes for Scoping Analysis of Organic Ligand Concentration." Memorandum to R.V. Bynum, March 13, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 236044.

Leigh, C.D. 2003. "New Estimates of the Total Masses of Complexing Agents in the WIPP Inventory for Use in the 2003 WIPP Performance Assessment." Memorandum to L.H. Brush, September 3, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 531319.

Leigh, C.D. 2005a. "Organic Ligand Masses TRU Waste Streams from TWBID Revision 2.1 Version 3.13 Data Version D4.15." Memorandum to L.H. Brush, April 14, 2005, Carlsbad, NM: Sandia National Laboratories. ERMS 539354.

Leigh, C.D. 2005b. "Organic Ligand Masses TRU Waste Streams from TWBID Revision 2.1, Version 3.13, Data Version D4.15, Revisions 1." Memorandum to L.H. Brush, April 18, 2005, Carlsbad, NM: Sandia National Laboratories. ERMS 539550.

Molecke, M.A. 1983. *A Comparison of Brines Relevant to Nuclear Waste Experimentation.* SAND83-0516. Albuquerque, NM: Sandia National Laboratories.

Novak, C.F. 1997. "Calculation of Actinide Solubilities in WIPP SPC and ERDA-6 Brines under MgO Backfill Scenarios Containing either Nesquehonite or Hydromagnesite as the Mg-CO_3 Solubility-Limiting Phase." Memorandum to R.V. Bynum, April 21, 1997. Albuquerque, NM: Sandia National Laboratories. ERMS 246124.

Novak, C.F., and R.C. Moore. 1996. "Estimates of Dissolved Concentrations for +III, +IV, +V, and +VI Actinides in a Salado and a Castile Brine under Anticipated Repository Conditions." Memorandum to M.D. Siegel, March 28, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 236207.

Novak, C.F., R.C. Moore, and R.V. Bynum. 1996. "Prediction of Dissolved Actinide Concentrations in Concentrated Electrolyte Solutions: A Conceptual Model and Model Results for the Waste Isolation Pilot Plant (WIPP)." Unpublished presentation at the 1996 International Conference on Deep Geological Disposal of Radioactive Waste, September 16-19, 1996, Winnipeg, Manitoba, Canada. ERMS 418098, SAND96-2695C.

Nowak, E.J., 2005. "Recommended Change in the FMT Thermodynamic Data Base." Memorandum to L. H. Brush, April 1, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539227.

Popielak, R.S., R.L. Beauheim, S.R. Black, W.E. Coons, C.T. Ellingson and R.L. Olsen. 1983. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico*. TME 3153. Carlsbad, NM: U.S. Department of Energy WIPP Project Office.

Snider, A.C. 2003. "Verification of the Definition of Generic Weep Brine and the Development of a Recipe for This Brine." Analysis report, April 8, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527505.

Stein, J.S. 2005. "Estimate of Volume of Brine in Repository That Leads to a Brine Release." Memorandum to L.H. Brush, April 19, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539372.

Trovato, E.R. 1997. Untitled letter from E.R. Trovato to G. Dials with enclosures (parameters that are no longer of concern and parameters that DOE must use for the PAVT), April 25, 1997. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air. ERMS 247206.

U.S. DOE. 1996. *Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant, Vol. 1-21.* DOE/CAO-1994-2184. Carlsbad, NM: U.S. Department of Energy Carlsbad Area Office.

U.S. DOE. 2004. *Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, Vol. 1-8.* DOE/WIPP 2004-3231. Carlsbad, NM: U.S. Department of Energy Carlsbad Field Office.

U.S. EPA. 1998a. "40 CFR 194, Criteria for the Certification and Recertification of the Waste Isolation Pilot Plant's Compliance with the Disposal Regulations. Certification Decision: Final Rule," *Federal Register.* Vol. 63, 27354-27406. Washington, DC: U.S. EPA Office of Radiation and Indoor Air.

U.S. EPA. 1998b. "Compliance Application Review Documents for the Criteria for the Certification and Recertification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations: Final Certification Decision. CARD 23: Models and Computer Codes." EPA Air Docket A93-02-V-B-2. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air.

U.S. EPA. 1998c "Technical Support Document for Section 194.23 – Models and Computer Codes." EPA Air Docket A93-02-V-B-6. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air.

U.S. EPA. 1998d. "Technical Support Document for Section 194.23: Parameter Justification Report." EPA Air Docket A93-02-V-B-14. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air.

U.S. EPA. 1998e. "Technical Support Document for Section 194.24: EPA's Evaluation of DOE's Actinide Source Term." EPA Air Docket A-93-02-V-B-17. Washington, DC: U.S. Environmental Protection Agency Office of Radiation and Indoor Air.

Wang, Y. 1998. "WIPP PA Validation Document for FMT (Version 2.4), Document Version 2.4." Carlsbad, NM: Sandia National Laboratories. ERMS 251587.

Xiong, Y.-L. 2005. "Release of FMT_050405.CHEMDAT." E-mail to J.F. Kanney and J.J. Long, April 5, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539304.

Xiong, Y.-L., E.J. Nowak, and L.H. Brush. 2004. "Updated Uncertainty Analysis of Actinide Solubilities for the Response to EPA Comment C-23-16." Analysis report, December 17, 2004. Carlsbad, NM: Sandia National Laboratories. ERMS 538219.

Xiong, Y.-L., E.J. Nowak, and L.H. Brush. 2005. "Updated Uncertainty Analysis of Actinide Solubilities for the Response to EPA Comment C-23-16 (Supersedes ERMS 538219)." Analysis report, April 29, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 539595.

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