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Prediction of Baseline Actinide Solubilities for Surplus Plutonium Disposition

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1 INTRODUCTION

This analysis report provides the baseline solubilities of Th(IV), Np(V), and Am(III) in two standard Waste Isolation Pilot Plant (WIPP) brines in support of the Surplus Plutonium Disposition (SPD) Analysis (Zeitler, 2018). These actinide solubilities (the sums of the concentrations of all dissolved actinide species in chemical equilibrium with actinide-bearing solid phases under the conditions expected in WIPP disposal rooms) are often referred to as the "baseline solubilities" because they comprise unique values predicted using thermodynamic models for each actinide element and WIPP brine under expected near-field chemical conditions. However, PA codes actually use actinide solubilities that are the outputs of the baseline solubility process model together with sampled uncertainty factors that describe possible deviations of the predicted Th(IV) and Am(III) solubilities from experimentally measured solubilities.

The two standard WIPP brines used in this analysis are Generic Weep Brine (GWB) and Energy Research and Development Administration (WIPP Well) 6 brine (ERDA-6). 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, 2003). ERDA-6 (Popielak et al., 1983) is a synthetic brine representative of fluids in brine reservoirs in the Castile Fm., which underlies the Salado Fm.

In addition to the baseline solubilities of Th(IV), Np(V), and Am(III) this analysis report also provides the compositions of these brines and the values of parameters such as f_{CO_2}, pH, pcH, and TIC. The parameter f_{CO_2} is the fugacity of carbon dioxide (CO_2), which is similar to its partial pressure, in the brines. The pH is the negative, common logarithm of the activity of H^+. The pcH is the negative, common logarithm of the molar concentration of H^+. Finally, TIC is the total inorganic carbon concentration of the brines.

This analysis does not provide any solubilities for U(VI) because a thermodynamic speciation-and-solubility model has not been developed for U(VI). Instead, the EPA specified that an estimate of 1×10^{-3} M be used for the solubility of U(VI) in GWB and ERDA-6. This estimate has been used beginning with the CRA-2004 PABC. Furthermore, the EPA specified a fixed value for its estimate of the solubility of U(VI) in GWB and ERDA-6 (U.S. EPA, 2006).

The SPD baseline solubilities were calculated using the thermodynamic database DATA0.FM1 (Xiong, 2011a) and the code EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011b). The same versions were used for the CRA-2014 analysis.

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

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
Ac, acetate	CH_3COO^- or $CH_3CO_2^-$
Am, Am(III)	americium, americium in the +III oxidation state
am	amorphous
anhydrite	$CaSO_4$
AP	analysis plan
Aq	aqueous
aragonite	$CaCO_3$,a polymorph of $CaCO_3$ that is metastable with respect to calcite
Atm	atmosphere(s)
B, B(III)	boron, boron in the +III oxidation state
Br, Br(−I)	bromine, bromine in the −I oxidation state
Brucite	$Mg(OH)_2$
C	carbon
Ca, Ca(II), Ca^{2+}	calcium, calcium in the +II oxidation state, calcium ion
Calcite	$CaCO_3$, the thermodynamically stable polymorph of $CaCO_3$
Cerussite	$PbCO_3$
Cit, 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
CMS	(Sandia/WIPP software) Configuration Management System
CO_2	carbon dioxide
CO_3^{2-}	carbonate
cr	crystalline
DB	(thermodynamic) database
CRA-2004	the first WIPP Compliance Recertification Application, submitted to the EPA in March 2004
CRA-2009	the second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
CRA-2014	the third WIPP Compliance Recertification Application, submitted to the EPA in March 2014

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

Abbreviation, Acronym, or Initialism	Definition
DBR	direct brine release
dolomite	$CaMg(CO_3)_2$, a carbonate mineral that nucleates and grows slowly under low-temperature conditions and is often suppressed (prevented from forming) in geochemical modeling calculations
DRZ	disturbed rock zone
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
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
earlandite	$Ca_3[C_3H_5O(COO)_3]_2 \cdot 4H_2O$
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
Fm.	Formation
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
Gypsum	$CaSO_4 \cdot 2H_2O$
H or H_2, H^+	hydrogen or hydrogen ion
Halite	NaCl
H_2O	water (aq, g, or contained in solid phases)
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
I	ionic strength, defined by $I = \frac{1}{2} \times \Sigma_i(M_i \times z_i^2)$, in which M_i and z_i are the molarity and charge of species i
I/O	input/output
K, K(I)	potassium, potassium in the +I oxidation state
kg	kilogram(s)
Lead oxalate	PbC_2O_4(cr)
litharge	PbO
M	Molar, $mol \cdot dm^{-3}$

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

Abbreviation, Acronym, or Initialism	Definition
m	meters or molal, $mol \cdot kg^{-1}$
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
mM	millimolar
Na, Na(I), Na^+	sodium, sodium in the +I oxidation state, sodium ion
nesquehonite	$MgCO_3 \cdot 3H_2O$
Np, Np(V)	neptunium, neptunium in the +V oxidation state
O or O_2	oxygen
OH, OH^-	hydroxide or hydroxide ion
Ox, oxalate	$(COO)_2^{2-}$ or $C_2O_4^{2-}$
PA	performance assessment
PABC	Performance Assessment Baseline Calculations
Pb, Pb(II)	Lead, lead in the +II oxidation state
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^+
polyhalite	$K_2MgCa_2(SO_4)_4 \cdot 2H_2O$
QA	quality assurance
Rev.	revision
RH	relative humidity
S, S(VI), SO_4^{2-}	sulfur, sulfur in the +VI oxidation state, sulfate ion
SCA	S. Cohen and Associates
SNL	Sandia National Laboratories
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C
U, U(IV), U(VI)	uranium, uranium in the +IV oxidation state, uranium in the +VI oxidation state
whewellite	$CaC_2O_4 \cdot H_2O$
WIPP	Waste Isolation Pilot Plant
wt %	weight percent

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2 METHODS

The objective of this analysis is to provide the solubilities of the actinide elements Th(IV), Np(V), and Am(III) in the standard WIPP brines GWB and ERDA-6 (as equilibrated with important phases in and around the repository), as a function of the volume of these brines in the repository. This report also provides the important chemical properties and predicted compositions of the reacted GWB and ERDA-6 brines in the repository. Brush et al. (2012a) described the methods used to calculate the solubilities of Th(IV), Np(V), and Am(III) for use in WIPP PA, the reasoning behind using GWB and ERDA-6 brine compositions, and the how and why these solubilities are applied to other actinides included in WIPP PA. The methods used for this analysis were identical to those used by Brush et al. (2012b).

The concentrations of acetate (CH_3COO^-), citrate ($(CH_2COO)_2C(OH)(COO)^{3-}$), EDTA (ethylenediaminetetraacetate, or $CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$), and oxalate ($(COO)_2^{2-}$) dissolved in volumes of GWB and ERDA-6 brine that are 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 m^3 are from Domski (2018). Table 2 (see next page) provides the concentrations of these organic ligands used for this analysis. Acetate, citrate, EDTA, and oxalate are the organic ligands in TRU waste that could form complexes with actinide elements and thus increase their solubilities. A volume of 17,400 m^3 is the minimum brine volume required for a direct brine release (DBR) from the repository (Clayton, 2008). A DBR is defined as a release of brine that could occur 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). Factors of 1, 2, 3, 4, and 5 were used, at the request of WIPP PA personnel, who determined that all of the DBRs in the CRA-2014 PA had volumes that varied between 1 and 5 × the minimum volume of 17,400 m^3. Domski (2018) calculated the concentrations of acetate, citrate, EDTA, and oxalate in 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 $m^3$of brine by assuming that the total masses of these organic ligands in the waste would dissolve completely in these volumes of brine.

EQ3/6 was used 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"), the following compounds were added to GWB and ERDA-6:(1) acetate, citrate, EDTA, and oxalate; and (2) ThO_2(am), $KNpO_2CO_3$, 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 et al., 2012a). In step 2, these brines were reacted 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 et al., 2012a) and the solubilities of Th(IV), Np(V), and Am(III) and the compositions of GWB and ERDA-6 were predicted 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 ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) — control the new compositions of the brines and parameters such as f_{CO_2}, pH, pcH, TIC.

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Table 2. Dissolved Concentrations of Organic Ligands (M) in the Minimum Brine Volume Required for a DBR and for Volumes That Are 2 ×, 3 ×, 4 ×, and 5 × the Minimum Volume.

Organic Ligand	Minimum Required for a DBR	2 × Minimum	3 × Minimum	4 × Minimum	5 × Minimum
Acetate	2.52×10^{-2}	1.26×10^{-2}	8.39×10^{-3}	6.29×10^{-3}	5.03×10^{-3}
Citrate	2.70×10^{-3}	1.35×10^{-3}	9.01×10^{-4}	6.76×10^{-4}	5.41×10^{-4}
EDTA	3.23×10^{-4}	1.61×10^{-4}	1.08×10^{-4}	8.06×10^{-5}	6.45×10^{-5}
Oxalate	1.34×10^{-2}	6.70×10^{-3}	4.47×10^{-3}	3.35×10^{-3}	2.68×10^{-3}

For step 1, the speciation and solubility code EQ3NR was used to add the organic ligands and the actinide-bearing solids to GWB and ERDA-6. The initial concentrations of acetate, citrate, EDTA, and oxalate were set equal to those in volumes of GWB and ERDA-6 that are 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 m^3. The initial value of the total inorganic carbon (TIC) concentrations of both brines were set 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) it was assumed that the initial TIC content of GWB was equal to that of ERDA-6. (The initial value of the TIC did not affect the values of the TIC predicted during the rest of the calculations). The code charge balanced on H^+; speciated all of the dissolved elements; and calculated the values of parameters such as f_{CO_2}, pH, and TIC. The code also wrote 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).

Table 3 summarizes these EQ3/6 calculations for GWB and ERDA-6.

Table 3. Summary of EQ3/6 Calculations Carried Out with GWB and ERDA-6 for this Analysis.

Description of Step	GWB	ERDA-6
1	Used EQ3NR to add organic ligands and actinide-bearing solids	Used EQ3NR to add organic ligands and actinide-bearing solids

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2	Used EQ6 to titrate in halite, anhydrite, brucite, and hydromagnesite	Used EQ6 to titrate in halite, anhydrite, brucite, and hydromagnesite

For step 2, the quantities of halite, anhydrite, brucite, and hydromagnesite similar to those that will be present in the repository after it is filled and sealed were used but were 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. To calculate the quantities of halite and anhydrite, the mass contained in the conservatively large DRZ volume currently implemented in WIPP PA was used, along with 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, it was assumed 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, it was also assumed 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.

EQ6 was used in closed-system mode (model variable IOPT1 = 0) for step 2. 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. Certain mineral phases were suppressed (prevented from precipitating), including 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. These phases were suppressed to ensure that this analysis was consistent with the near-field chemical conceptual models (SCA, 2008; Brush et al., 2012a).

The solids halite, anhydrite, brucite, and hydromagnesite were titrated by EQ6 into solutions corresponding to the GWB and ERDA-6 compositions output from step 1. Halite and anhydrite were used to represent the most important minerals in the Salado Fm. at or near the stratigraphic horizon of the repository, and brucite and hydromagnesite were used to represent the expected hydration and carbonation products of MgO (the WIPP engineered barrier). As EQ6 titrated in these solids, halite and anhydrite dissolved until the brine became saturated with these solids (i.e., until the concentrations of Na^+, Cl^-, Ca^{2+}, and SO_4^{2-} reached their solubility limits). The reaction then continued until brucite and hydromagnesite reached equilibrium at which point the reaction path terminated. As EQ6 calculates a reaction path, it tracks all of the properties of the solution including the moles of solids that dissolved and/or precipitated, the

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speciation all of the dissolved elements; and the values of parameters such as f_{CO_2}, pcH, TIC, etc.. This information is recorded in the EQ6 output file, *.6o. The output was extracted from each EQ6 *.6o file by running the Excel macro "GetEQData.xls." This macro extracts all of the EQ6 output into an Excel spreadsheet.

Table 4. Locations of the Excel Spreadsheets, I/O Files, etc., Used in the EQ3/6 Calculations for this Analysis.

Description or Title of File(s)	Location of File(s)
Spreadsheet: *SPD_Conc_density_calcs_brines.xls*	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip
Spreadsheet: *Ligand-concentrations.xlsx*	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip
Spreadsheet: *SPD_2018-09-27.xlsx*	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip
EQ3/6 DB DATA0.FMT.R2 also called DATA0.FM1	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip
Excel macro *GetEQData_v101f.xls*	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip
EQ3/6 I/O files	/cvs/CVSLIB/WIPP_SPECIAL_ANALYSES/SPD /SPD_2018-09_files.zip

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3 RESULTS

Table 5 (see next page) provides the compositions; the solubilities of Th(IV), Np(V), and Am(III); and parameters such as f_{CO_2}, pcH, and TIC for volumes of GWB that are 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 m^3, the minimum brine volume required for a direct brine release (DBR) from the repository (Clayton, 2008). Table 6 provides comparable information for ERDA-6. Brush et al. (2012a, Subsection 2.1.2) described the solid phases that will control the compositions and other conditions in these brines, and the solubilities of the important actinides in TRU waste, after these brines and solids equilibrate. In particular, the brucite-hydromagnesite carbonation reaction will control f_{CO_2} and the total inorganic C content of the brines.

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Table 5. EQ3/6 Predictions of the Compositions and Solubilities of Th(IV), Np(V), and Am(III) in Five Different Volumes of GWB (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]	2 × Minimum	3 × Minimum	4 × Minimum	5 × Minimum
B(III)(aq)	1.86E-01	1.86E-01	1.86E-01	1.86E-01	1.86E-01
Na(I)(aq)	4.77	4.78	4.78	4.78	4.78
Mg(II)(aq)	0.333	0.321	0.317	0.315	0.314
K(I)(aq)	0.550	0.549	0.549	0.549	0.549
Ca(II)(aq)	0.0110	0.0112	0.0113	0.0113	0.0113
S(VI)(aq)	0.218	0.210	0.208	0.206	0.205
Cl(-I)(aq)	5.36	5.38	5.39	5.39	5.39
Br(-I)(aq)	0.0313	0.0313	0.0313	0.0313	0.0313
Th(IV)(aq)	6.05E-08	6.06E-08	6.07E-08	6.07E-08	6.07E-08
Np(V)(aq)	2.88E-07	2.24E-07	2.02E-07	1.91E-07	1.85E-07
Am(III)(aq)	1.08E-05	5.49E-06	3.72E-06	2.83E-06	2.30E-06
fCO2 (atm)	3.14E-06	3.14E-06	3.14E-06	3.14E-06	3.14E-06
I	6.44	6.42	6.42	6.42	6.41
pH[B]	8.82	8.82	8.82	8.82	8.82
pcH	9.54	9.54	9.54	9.54	9.54
RH (%)[C]	73.50%	73.54%	73.56%	73.56%	73.57%
TIC[D]	3.79E-04	3.79E-04	3.79E-04	3.79E-04	3.79E-04

Footnotes for Table 5 provided on next page.

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Footnotes for Table 5:

A. Based on a minimum brine volume of 17,400 m^3 (Clayton, 2008)
B. 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). T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA, proposed the term "Pitzer scale" unofficially.
C. RH = relative humidity. The value of the RH divided by 100 yields the value of the activity of H_2O in GWB.
D. TIC = total inorganic C.

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Table 6. EQ3/6 Predictions of the Compositions of and Solubilities of Th(IV), Np(V), and Am(III) in Five Different Volumes of ERDA-6 (M Unless Otherwise Noted).

Element or Property	1 × Minimum[A]	2 × Minimum	3 × Minimum	4 × Minimum	5 × Minimum
B(III)(aq)	0.0623	0.0623	0.0623	0.0623	0.0623
Na(I)(aq)	5.30	5.32	5.33	5.33	5.33
Mg(II)(aq)	0.136	0.120	0.115	0.113	0.111
K(I)(aq)	0.0960	0.0959	0.0959	0.0959	0.0959
Ca(II)(aq)	0.0118	0.0119	0.0119	0.0119	0.0120
S(VI)(aq)	0.181	0.175	0.172	0.171	0.171
Cl(-I)(aq)	5.23	5.25	5.26	5.26	5.26
Br(-I)(aq)	0.0109	0.0109	0.0109	0.0109	0.0109
Th(IV)(aq)	7.04E-08	7.13E-08	7.17E-08	7.18E-08	7.20E-08
Np(V)(aq)	9.41E-07	7.56E-07	6.97E-07	6.68E-07	6.51E-07
Am(III)(aq)	6.95E-06	3.45E-06	2.31E-06	1.75E-06	1.41E-06
f_{CO2} (atm)	3.14E-06	3.14E-06	3.14E-06	3.14E-06	3.14E-06
I	5.97	5.95	5.94	5.94	5.94
pH[B]	8.99	9.01	9.02	9.02	9.02
pcH	9.69	9.71	9.72	9.72	9.72
RH (%)[C]	0.747	0.747	0.748	0.748	0.748
TIC[D]	4.57E-04	4.67E-04	4.71E-04	4.73E-04	4.75E-04

Footnotes for Table 6 provided on next page.

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Footnotes for Table 6:

A. Based on a minimum brine volume of 17,400 m^3 (Clayton, 2008).
B. 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). T. J. Wolery of Lawrence Livermore National Laboratory (LLNL) in Livermore, CA, proposed the term "Pitzer scale" unofficially.
C. RH = relative humidity. The value of the RH divided by 100 yields the value of the activity of H_2O in ERDA-6.
D. TIC = total inorganic C.

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In Figures 1 through 6, comparisons of predicted actinide solubilities for the SPD analysis and the CRA-2014 PA for both GWB and ERDA-6 are shown. These figures show that the predicted actinide solubilities in +III oxidation state for the SPD analyses are higher than those for the CRA-2014. The predicted actinide solubilities in +IV and +V oxidation states are almost identical for these two analyses. The increased concentrations of EDTA in the SPD calculations, > 4X CRA-2014, has a greater influence on the Am(III) concentration than either the Th(IV) or Np(V) concentrations because the solubility product (Log Ksp) of the solubility controlling phase for americium is four orders of magnitude greater than the thorium phase, and approximately 18 orders of magnitude higher than the neptunium phase. Combined with relative strength of the AmEDTA- aqueous complex compared to those of Th and Np there is an exaggerated increase in Am solubility.

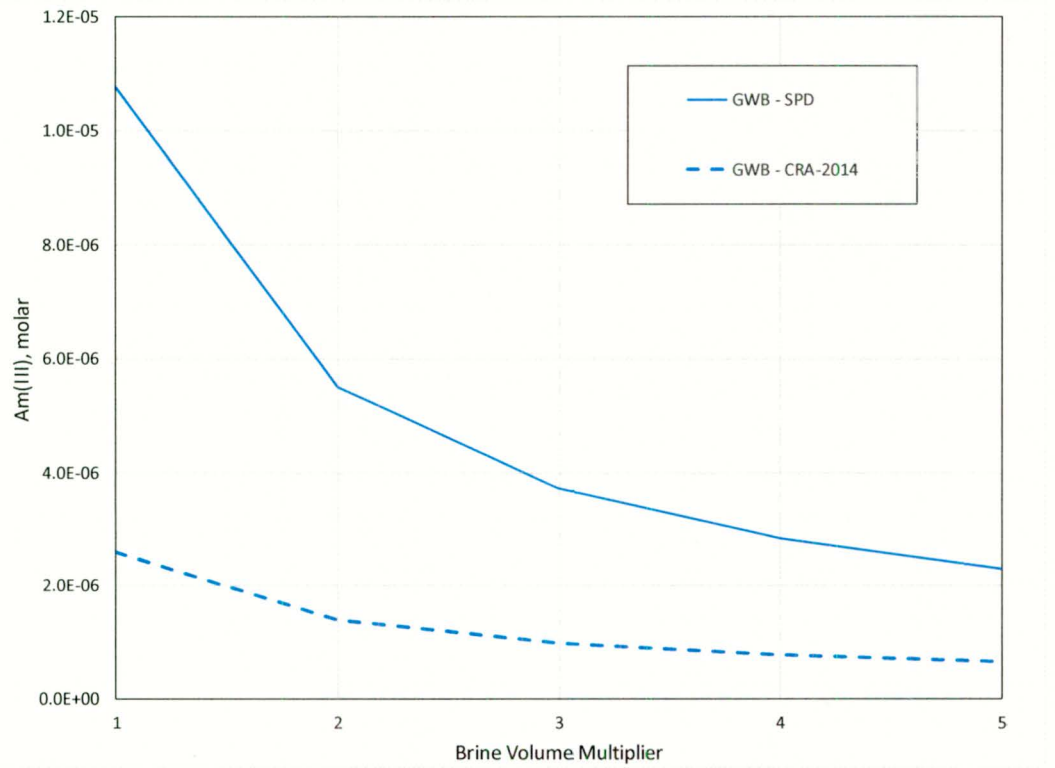


Figure 1. A comparison of predicted actinide solubilities in +III oxidation state in GWB for CRA-2014 with those for the SPD analyses.

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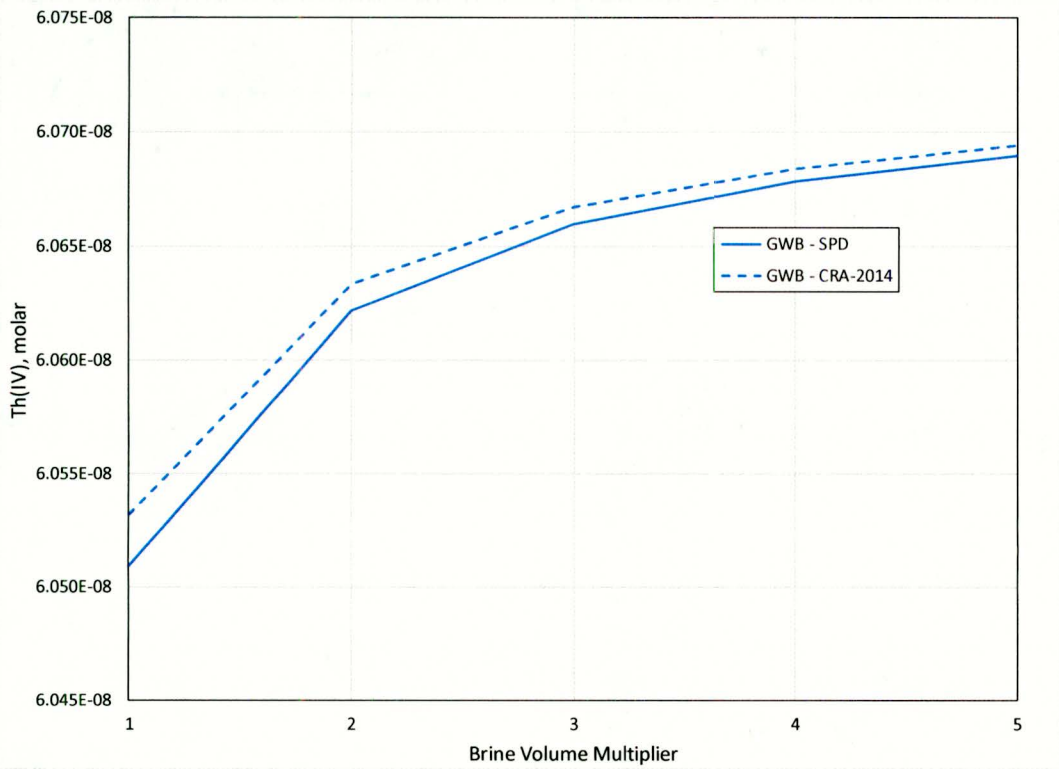


Figure 2. A comparison of predicted actinide solubilities in +IV oxidation state in GWB for CRA-2014 with those for the SPD analyses.

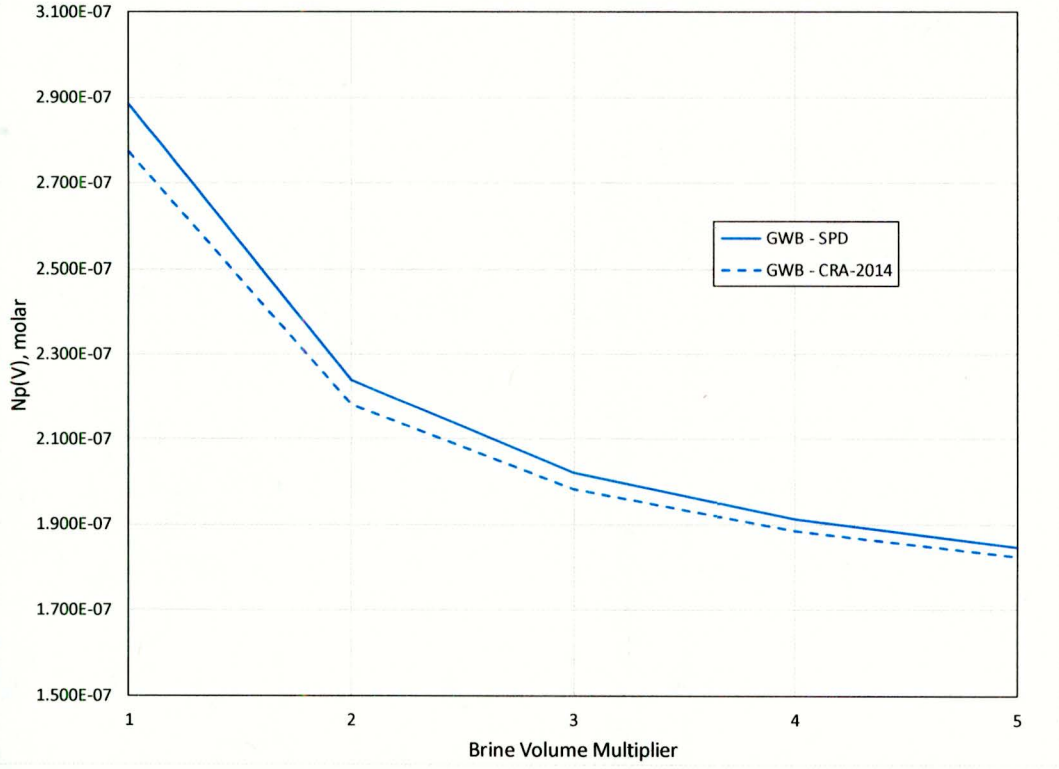


Figure 3. A comparison of predicted actinide solubilities in +V oxidation state in GWB for CRA-2014 with those for the SPD analyses.

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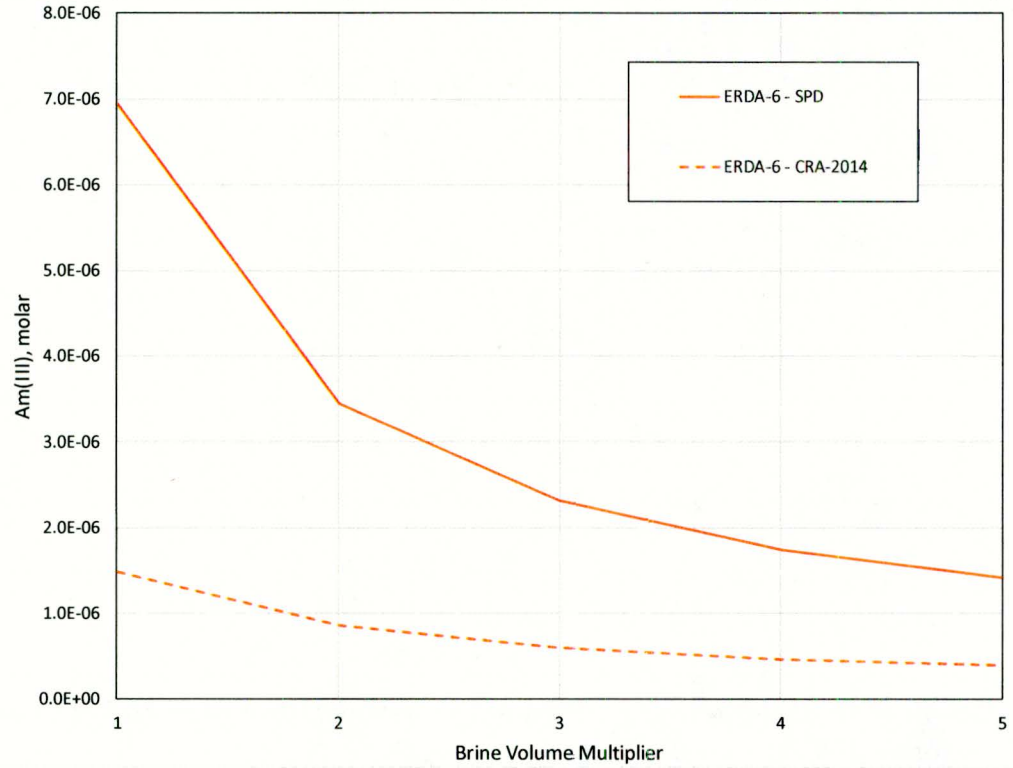
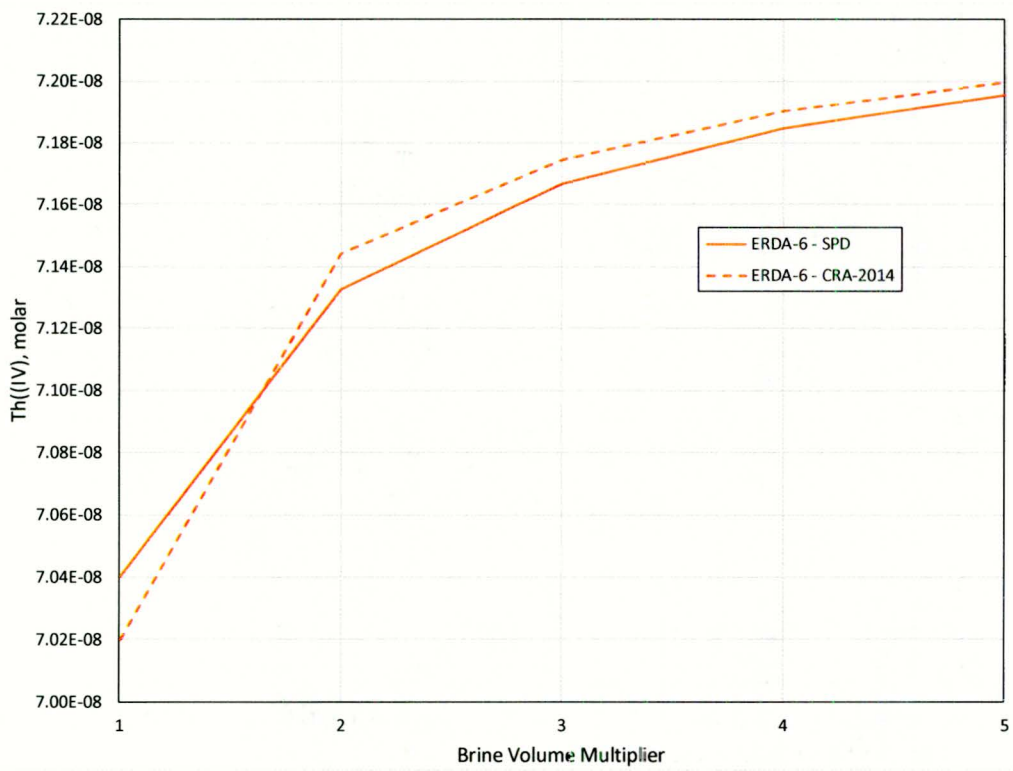


Figure 4. A comparison of predicted actinide solubilities in +III oxidation state in ERDA-6 for CRA-2014 with those for the SPD analyses.



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Figure 5. A comparison of predicted actinide solubilities in +IV oxidation state in ERDA-6 for CRA-2014 with those for the SPD analyses.

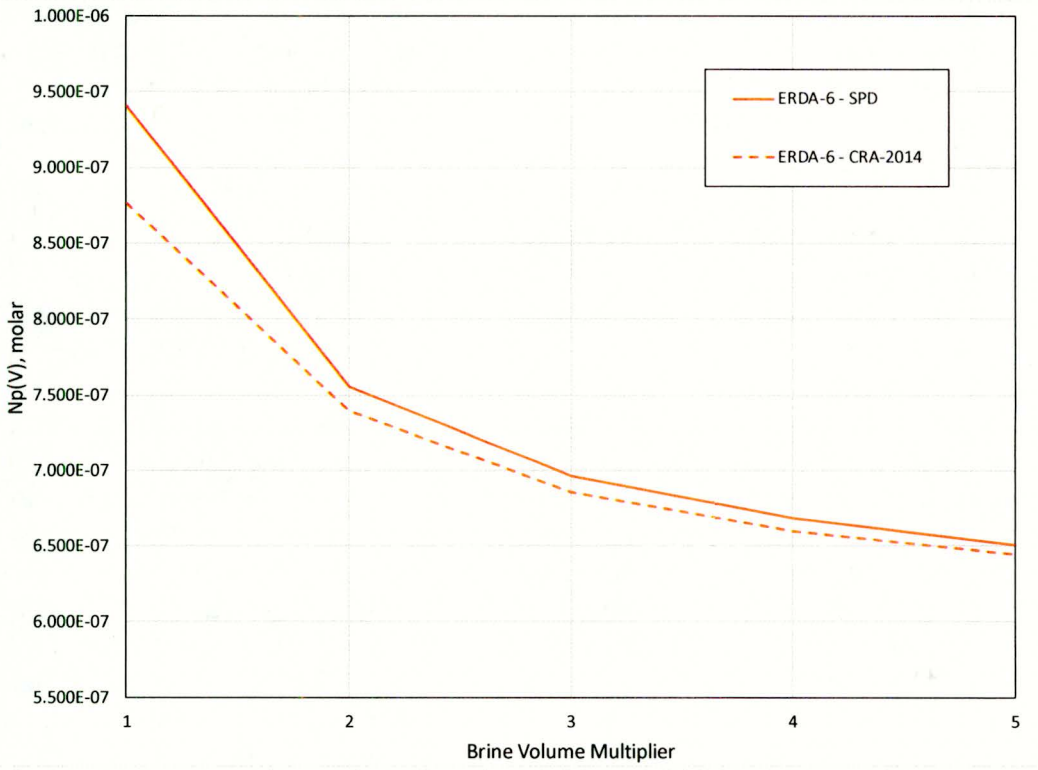


Figure 6. A comparison of predicted actinide solubilities in +V oxidation state in ERDA-6 for CRA-2014 with those for the SPD analyses.

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4 CONCLUSIONS

This analysis report provides baseline solubilities of Th(IV), Np(V), and Am(III) in two standard Waste Isolation Pilot Plant (WIPP) brines for the SPD analysis. The two standard brines used in this analysis are Generic Weep Brine (GWB) and ERDA-6. GWB represents intergranular Salado Formation (Fm.) brines at or near the stratigraphic horizon of the repository. ERDA-6 represents fluids in brine reservoirs in the Castile Fm. EQ3/6, Version 8.0a, and DATA0.FM1 were used for this analysis.

Table 5 (see Section 3 above) provides the compositions; the solubilities of Th(IV), Np(V), and Am(III); and parameters such as f_{CO_2}, pcH, and TIC for volumes of GWB that are 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 m^3, the minimum brine volume required for a direct brine release (DBR) from the repository (Clayton, 2008). Table 6 provides comparable information for ERDA-6.

The increased EDTA in the inventory for the SPD case is 4.4 times greater than that in the inventory used for the CRA-2014 baseline solubility calculations. The increased EDTA concentration of the brines had the effect of increasing the solubility of the Am(III) solubility controlling phase, $Am(OH)_3(s)$, which is the only solid Am(III) phase considered in the these calculations. The Am(III) concentrations increased from 2.6E-06 to 1.1E-05 molar in GWB, and 1.5E-06 to 7.0E-06 molar in ERDA-6, both for the 1 x minimum brine volume case. Also of note is that the increase in EDTA did not affect the concentrations of Th(IV) and Np(V) as it did the Am(III) concentration. The reason for this being the relatively high solubility of the americium solubility controlling phase ($Am(OH)_3(s)$) compared to those of thorium and neptunium, and the strength of the AmEDTA- aqueous complex compared to the complexes of Th(IV) and Np(V).

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