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Sandia National Laboratories
Waste Isolation Pilot Plant

Prediction of Baseline Actinide Solubilities for CRA 2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FM4

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1 INTRODUCTION

This analysis report provides the new baseline solubilities of Th(IV), Np(V), and Am(III) in two standard Waste Isolation Pilot Plant (WIPP) brines as a function of the volumes of these brines in the repository for CRA-2019. 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) and the concentrations of colloidal (suspended) actinides (calculated from the baseline solubilities) together constitute the actinide source term used in WIPP performance assessment (PA) calculations. These solubilities are often referred to as the "baseline solubilities" because they comprise unique values predicted using thermodynamic models for each actinide analog element and WIPP brine under expected near-field chemical conditions. The PA codes use the actinide solubilities, and a sampled uncertainty multiplier that describes possible deviations of the predicted baseline Th(IV) and Am(III) solubilities from experimentally measured solubilities. The reason for using these uncertainty factors is to account for uncertainties in the model and data that comprise the thermodynamic database. The uncertainty factor distributions are calculated and documented in a separate analysis.

The two standard WIPP brines used in these analyses are Generic Weep Brine (GWB) and Energy Research and Development Administration (WIPP Well) 6 (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.

Uranium solubility is not calculated in this baseline solubility model. The analysis does not provide any solubilities for U(VI) because a thermodynamic speciation-and-solubility model has not been developed for U(VI). Rather, the EPA (U.S. EPA, 2006) has specified that a value of 1×10^{-3} M be used in PA calculations for the solubility of U(VI) in GWB and ERDA-6. This value has been used since the CRA-2004 PABC.

This analysis report also provides the chemical compositions of the reacted brines, and the values of parameters such as ionic strength, activity of water, f_{CO_2}, pH, pcH, and Total Inorganic Carbon (TIC). These intensive properties provide important data regarding the state of the system. All of this data for CRA 2019 are tabulated below.

Compared to CRA-2014 PA the CRA-2019 PA baseline solubility model used an updated organic ligand inventory (Sisk-Scott, 2019), and will include two additional reactants that are contained in the waste being stored at the repository, these are lead represented as litharge (PbO) in the model, and iron represented as $Fe(OH)_2$ in the model. A new Pitzer thermodynamic database, DATA0.FM4, was used for the CRA-2019 PA baseline solubility model it includes the lead and iron systems and parameter additions and updates.

This baseline solubility analysis differs from that of Brush and Domski (2013) by the use of an updated thermodynamic database for EQ3/6, Version 8.0a, (EQ3/6) (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b). The new baseline solubilities are calculated using the updated database, DATA0.FM4 (Domski 2019).

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There are a number of updates featuring the advances in chemistry/geochemistry relevant to the WIPP conditions since CRA-2009, in the updated database, DATA0.FM4. They are summarized as follows.

First, additional solubility-limiting phases are being added, one for each of the organic ligands, EDTA [$Ca_2EDTA \cdot 7H_2O(s)$], citrate (earlandite), and oxalate (glushinskite) for the models for EDTA, citrate, and oxalate. New aqueous species, $NaEDTA^{3-}$ and $MgHEDTA^{-}$ are also being included in DATA0.FM4 while updated log K values for $EDTA^{4-}$, $HEDTA^{3-}$, H_2EDTA^{2-}, H_3EDTA^{-} , $H_3Citrate$, $H_2Citrate^{-}$, $MgHCitrate$, $Mg(H_2Citrate)^{+}$, $MgCitrate^{-}$, $CaCitrate^{-}$, $CaHCitrate$, $Ca(H_2Citrate)^{+}$, and $MgOxalate_2^{2-}$ are being included in DATA0.FM4. Log K values for solids and species containing Mg^{2+} and $Oxalate^{2-}$ and Pitzer interaction coefficients for Na^{+} and $Oxalate^{2-}$ are being changed for CRA-2019. Pitzer coefficients were added to the parameters to complete the fit to the data. The coefficients added are for the interaction between MgOxalate(aq) and Na^{+} and Mg^{2+}, and Na^{+} and $Mg(Oxalate)_2^{2-}$. Interactions between these two ions are not included in DATA0.FM1.

Secondly, new to CRA-2019 is the addition of aqueous Pb^{2+} and Fe^{2+} to the WIPP Chemical Conditions Process Model. The DOE is limiting the models for both Pb^{2+} and Fe^{2+} to the inorganic systems. Reactions for lead include four lead-bearing solids: PbO(litharge), $PbCO_3$(cerussite), $Pb(SO_4)(s)$, and $Pb_2CO_3Cl_2$. The aqueous species included are: Pb^{2+}, $PbCl^{+}$, $PbCl_2(aq)$, $PbCl_3^{-}$, $PbCO_3(aq)$, $Pb(CO_3)_2^{2-}$, $Pb(CO_3)Cl^{-}$, $PbOH^{+}$, $Pb(OH)_2(aq)$, $Pb(SO_4)(aq)$, and $Pb(CO_3)(OH)^{-}$. There is evidence (Xiong 2014a; Xiong 2014b) that Pb^{2+} may form species with EDTA, citrate, and oxalate and that formation of lead-bearing solids with EDTA, citrate, and oxalate may occur (Xiong 2014a; Xiong 2014b). However, development of parameters to support addition of those reactions is still underway and they will not be included in CRA-2019. Addition of interactions between Pb^{2+} and Fe^{2+} and the organic ligands, EDTA, citrate, and oxalate, will be considered for inclusion in CRA-2024. The iron reactions include four iron-bearing solids: $Fe(OH)_2(s)$ (Ferrous iron hydroxide), $Fe_2Cl(OH)_3(s)$ (hibbingite), $FeCO_3(s)$ (siderite), $Fe_2CO_3(OH)_2(s)$ (chukanovite). It is assumed that these solids are in their crystalline form. The aqueous species included are: $FeOH^{+}$, $Fe(OH)_2(aq)$, $Fe(OH)_3^{-}$, $Fe(OH)_4^{2-}$, $FeCO_3(aq)$, $Fe(CO_3)_2^{2-}$.

Third, the revised solubility constant for hydromagnesite(5424) was incorporated into the DATA0.FM4. Recently, an error in transcription was discovered when the data from Robie and Hemingway (1973) was compared to that in DATA0.FM1. The error is in the FMT thermodynamic database fmt_050405.chemdat (Xiong et al. 2005) where the μ^0/RT value attributed to Robie and Hemingway (1973) does not match what was reported by Robie and Hemingway (1973). Using the standard free energy of formation (-5,864.74 kJ/mol), value derived from Robie and Hemingway (1973), the log K value for the reaction is 31.49.

Per a September 2018 Technical Exchange meeting (2018), DOE agreed to use EPA's recommended corrected log K value of 31.49 from Robie and Hemingway (1973) in the CRA-2019.

The changes to the CRA-2019 baseline solubility model are substantial compared to CRA-2014 PA with the addition of the lead and iron reactants to the model, allowing calcite to form, and the

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various new and updated parameter values. Therefore, a forthcoming detailed technical memorandum will be written which explores all the possible cases such that an understanding of the how the chemistry, i.e., the actinide solubilities, are influenced by the changes to the model.

Note, this analysis was performed using the same process described as used through the submission of CRA-2014, and therefore is a deviation from AP-153, Revision 1.

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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, to be submitted to the EPA in March 2014

Table 1 continued on next page

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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
$Mg_3Cl(OH)_5 \cdot 4H_2O$	Magnesium chloride hydroxide tetrahydrate, phase 5
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 reacted with near-field natural and emplaced materials as a function of the brine volume in the repository for use in PA calculations. Likewise, this report also provides the predicted compositions of GWB and ERDA-6 after equilibration with the important solids in the repository that accompany the actinide solubility values. 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, why the brines GWB and ERDA-6 are used, how these solubilities are applied to other actinides included in WIPP PA, etc.

2.1 Inputs

The baseline solubility model has a number of inputs, these include the brine compositions, brine physical properties (density and total dissolved solids), the organics concentrations, the actinide solubility controlling phases, and the mass (moles) of reactants (halite, anhydrite, brucite, hydromagnesite5424, $Fe(OH)_2$, and litharge). The EQ3/6 code is comprised of two separate codes, EQ3NR and EQ6, each of which requires different inputs. EQ3NR uses the solution composition, the organics input, and the actinide solubility controlling phases and calculates the speciated solution composition and saturation index for all pertinent phases. The EQ6 code uses an output file of EQ3NR called a "pickup" file, which contains the solution information, and numerically titrates the reactants specified in the EQ6 input file, into this solution until the system reaches equilibrium, or until all of the reactants are expended. The resulting equilibrium final composition provides the actinide concentrations that are used in PA.

The unreacted ERDA-6 (Popielak et al., 1983), and GWB (Krumhansl et al., 1991; Snider, 2003) brine compositions, TDS, and densities that were used as input for the EQ3NR code are listed in Table 2.

Table 2. Input brine compositions, TDS, and densities used for the Baseline Solubility simulations.

	ERDA-6	GWB	
Na^+	4.87	3.53	Molarity
K^+	9.70×10^{-02}	4.67×10^{-01}	Molarity
Mg^{2+}	1.90×10^{-02}	1.02	Molarity
Ca^{2+}	1.20×10^{-02}	1.40×10^{-02}	Molarity
Cl^-	4.80	5.86	Molarity
HCO_3^-	1.60×10^{-02}	1.60×10^{-02}	Molarity
$SO4^{2-}$	1.70×10^{-01}	1.77×10^{-01}	Molarity
$B(OH)_4^-$	6.30×10^{-02}	1.58×10^{-01}	Molarity
Br^-	1.10×10^{-02}	2.66×10^{-02}	Molarity
H^+	6.00	6.00	pH
TDS	313167.7	368202.9	mg/L
Density	1.20138	1.2366	g/cm^3

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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 pH for both brines is set to 6.0, and when the code is executed EQ3NR charge balances the solution by adjusting the pH. When using molar input values they must be scaled by the solution density which was calculated in the spreadsheet *Conc_density_calcs_CRA-2019_PA.xlsx.*

In addition to the brine data (Table 2) the scaled organics concentrations are also used as input for EQ3NR. 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 that are 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 17,400 m^3 are from Sisk-Scott (2019). Table 3 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 increase their solubilities. The brine volume, 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.). Brush and Domski (2012) used factors of 1, 2, 3, 4, or 5 to scale the organics concentrations, at the request of WIPP PA personnel, who determined that all of the DBRs in the CRA 2009 PABC had volumes that varied between 1 and 5 × the minimum volume of 17,400 m^3. For CRA-2019 Sisk-Scott (2019) 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 (Table 3).

Table 3. 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	2.83×10^{-2}	1.42×10^{-2}	9.45×10^{-3}	7.09×10^{-3}	5.67×10^{-3}
Citrate	2.30×10^{-3}	1.15×10^{-3}	7.68×10^{-4}	5.76×10^{-4}	4.61×10^{-4}
EDTA	7.92×10^{-5}	3.96×10^{-5}	2.64×10^{-5}	1.98×10^{-5}	1.58×10^{-5}
Oxalate	1.13×10^{-2}	5.65×10^{-3}	3.77×10^{-3}	2.82×10^{-3}	2.26×10^{-3}

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The final EQ3NR inputs are the solubility controlling phases used to set the An(III), An(IV), and An(V) concentrations. For An(III) $Am(OH)_3(s)$ is used as the solubility controlling phase, which represents a crystalline form of americium hydroxide. The degree of crystallinity has a direct effect on the log K of this phase with the solubility decreasing as the crystallinity increases. It has been a topic of discussion as to the reasoning behind DOE's choice of using the crystalline form of the $Am(OH)_3$ solid phase, and whether crystalline or amorphous phases would be dominant over the 10,000 year regulatory period. There is no way of knowing with any certainty which form would be dominant, and it is probable that some mixed phase intermediate might be the most appropriate choice. However, we must take the practical approach and use single Log K, and one that is consistent with the americium model included in the database:

From Giambalvo (2002):

"The Am-hydrolysis model is self-consistent, consistent with the Am-chloride model, and consistent with the choice of $Am(OH)_3(s)$ Ksp."

For this reason, the crystalline form of $Am(OH)_3(s)$ is used in the baseline solubility model.

The An(IV) model uses the amorphous form of thorium oxide, $ThO_2(am)$, as the solubility controlling phase. This is phase has been used as the An(IV) solubility controlling phase since the CCA, and it is consistent with the thorium model included in the database. With regard to the apparent contradiction with the An(III) model which employs the crystalline form a recent study of Simonnet et al. (2016) showed that crystalline forms of ThO_2 could not be formed at low temperatures, and that temperatures exceeding 850 °C are required for the crystalline form.

The solubility controlling phase for An(V) since the CCA has been $KNpO_2CO_3$. Brush and Garner (2005) made the argument that dissolved An(V) releases do not affect the long-term performance of the WIPP, so this phase will continued to be used for the CRA-2019 PA.

Inputs for EQ6 include the pickup file (*.3p) generated by EQ3NR, and the total moles of each reactant phase to be included in the model. The reactant quantities are scaled to 1 kg of solvent water, the mass on which EQ3/6 operates. In a computation, documented in the spreadsheet, *AP-153_Scaling of Solids_2019.xlsx*, the quantities of carbon PAIR 2018 (Van Soest 2018), brine, halite, anhydrite, brucite, hydromagnesite, $Fe(OH)_2$, and litharge used as inputs were calculated. The quantities 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 the 17,400 m^3 of brine to 1 kg of water. These values can be seen in Table 4 for the current PAIR 2018 (Van Soest 2018).

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Table 4. Summary of carbon, lead, halite, anhydrite, brucite, hydromagnesite calculations for this analysis.

Component	*PAIR 2018*	
Moles Carbon	9.31E+08 mol	
Litharge	GWB:	4.35E+00 mol
	ERDA-6:	4.26E+00 mol
$Fe(OH)_2$-Hex	GWB:	4.61E+01 mol
	ERDA-6:	4.51E+01 mol
Brucite	GWB:	3.67E+01mol
	ERDA-6:	3.59E+01 mol
Hydromagnesite5424	GWB:	7.34E+00 mol
	ERDA-6:	7.19E+00 mol
Halite	GWB:	3.49E+03 mol
	ERDA-6:	3.41E+03 mol
Anhydrite	GWB:	1.66E+02 mol
	ERDA-6:	1.63E+02 mol

The "moles of carbon" number represents the total moles of carbon in the CPR in the PAIR (see Table 5-5 and Table 5-7 in the PAIR-2018 spreadsheet, it is the sum of the "waste", "packaging", and "total emplaced and operational" values in both the CH and RH columns). It should be calculated as:

(Mass_Cellulose + (REFCON:PLASFAC*Mass_Plastic) + Mass_Rubber) / REFCON:MW_CELL

REFCON_PLASFAC is the mass (kg) ratio of plastics to equivalent carbon and has a value of 1.7. MW_CELL is the molecular weight of cellulose ($C_6H_{10}O_5$) normalized to one mole of carbon (162.1406 g/mol / 6 mol C/mol cellulose / 1000 g/kg = 2.7023e-2 kg/mol_carbon). Each mole of carbon in the CPR can generate one mole of CO_2, which can react with brucite to form hydromagnesite. The stoichiometry is different for the two reactions, four moles of carbon are required to form one mole of hydromagnesite5424. The total moles of carbon are shown in Table 4 and documented in the spreadsheet titled *AP-153_Scaling of Solids_2019.xlsx*.

The moles of reactant halite, anhydrite, brucite, hydromagnesite5424, $Fe(OH)_2$, and litharge are scaled to the EQ3/6 working mass of solution based on the brines density, GWB and ERDA-6, and the volume of brine in the repository. Additionally, the moles of MgO, (brucite, hydromagnesite) are determined based on the moles of carbon as discussed above.

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The source of iron in the repository are the waste packaging materials and the waste, and it has been widely accepted that in the WIPP environment iron hydroxide ($Fe(OH)_2$–Hex in DATA0.FM4) will be the primary corrosion product, and solubility-limiting phase for iron in the repository (Telander and Westerman, 1997, Roselle 2013, U.S.DOE 2014, and U.S. DOE2014a).

Note that lead is input as litharge, PbO, because archaeological studies have indicated that litharge was formed when lead was corroded (Turgoose, 1985; Anguilano, 2012) under anoxic conditions. Indeed, there was a thick litharge layer in the lead gallo-roman sarcophagus buried in the bank of the Rhône river at Lyon, France, for about 1500 years (Rocca et al., 2004).

It should be noted that the amounts of most of the reactants used as model inputs are present in excess, in other words the chemical system comes to equilibrium before brucite, hydromagnesite, halite, and anhydrite are expended, however, both litharge and $Fe(OH)_2$ do react completely.

2.2 Model Setup

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 predicted 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 ($Mg(OH)_2$), hydromagnesite5424 ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), litharge (PbO), and $Fe(OH)_2$ and their reacted product phases — control the new compositions of the brines and parameters such as f_{CO_2}, pH, pcH, TIC.

The EQ3/6 baseline solubility runs are completed in two steps. For step 1, the speciation and solubility code EQ3NR was used to "solve the initial solutions", in other words the code reads the input files containing the data discussed above, and speciates the solution and calculates the mineral saturation index values for GWB and ERDA-6 in the presence of organics and the actinide phases. There are five input files for each brine each representing a different brine volume, the only input that changes are the organics concentrations. EQ3NR outputs two ascii files, a user friendly output file (*.3o) which is useful to the analyst as it provides solution speciation data, mineral saturation information, and other intensive solution properties, and a second file, the pickup file (*.3p) which contains the same information but in a format that is used by EQ6 to setup the reaction path run.

For step 2, the reaction-path code EQ6 was used to titrate the solids halite, anhydrite, brucite, hydromagnesite, $Fe(OH)_2$ and litharge into GWB and ERDA-6 resultant solutions from step 1. Halite and anhydrite were used 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),

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litharge to represent the corroded lead product when lead shielding in the waste packages is corroded under anoxic conditions, the corroded waste drum and waste iron materials are represented by $Fe(OH)_2$ ($Fe(OH)_2$-Hex in DATA0.FM4). The EQ6 input values for each reactant are tabulated in Table 4.

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. Mineral phases that were suppressed for the CRA-2019 PA (prevented from precipitating) included aragonite ($CaCO_3$), 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. In previous baseline solubility analyses, for example Brush and Domski (2014), calcite was also suppressed based on Brush et al., (2006) analysis which concluded that a mixed calcium-magnesium carbonate phase would be a more stable phase in the presence of high Mg^{2+} and SO_4^{2-} concentrations. However, during the modeling process it was noted that unrealistic chemical conditions prevailed for parts of the reaction paths and by allowing calcite to form these conditions were alleviated. A detailed analysis of the effect of allowing calcite to precipitate will be included in a forthcoming technical memorandum.

Notice that as Brush et al. (2012a, Subsection 4.3) anticipated using steps 2a and 2b for the current analysis, combination of these two steps into step 2 for this analysis was a deviation from AP-153, Rev. 1.

All files are archived at "/nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019". Table 5 provides the location of the specific files.

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Table 5. 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 *AP-153_Scaling of Solids_2019.xlsx*	In zip file CRA-2019_AP153Rev1Task3Data.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019
Spreadsheet *Conc_density_calcs_CRA-2019_PA.xlsx*	In zip file CRA-2019_AP153Rev1Task3Data.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019
EQ3/6 DB DATA0.FM4	In zip file CRA-2019_AP153Rev1Task3Data.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019
Excel macro GetEQData.xls	In zip file CRA-2019_AP153Rev1Task3Data.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019
EQ3/6 I/O files and Excel spreadsheets with extracted data	In zip file CRA-2019_AP153Rev1Task3Data.zip, /nfs/data/CVSLIB/WIPP_EXTERNAL/ap153_files/CRA-2019

The output was extracted from the EQ6 *.6o files by running the Excel macro "GetEQData.xls." This macro extracts all of the EQ6 output into an Excel spreadsheet.

All of our EQ3/6 input and output (I/O) files, the Excel macro GetEQData.xls, and the Excel spreadsheets that contain the output extracted with GetEQData.xls are in zip file CRA-2019_AP153Rev1Task3Data.zip.

3 RESULTS

Each of the EQ6 runs followed relatively complex reaction paths with product phases including whewellite, cerussite, hibbingite, calcite, glauberite and phase 5 with minor borax in the ERDA-6 runs. A detailed accounting of the reaction paths will be provided in a forthcoming memo.

The output from EQ6 consisted of output files (*.6o) for each brine and brine volume, which detail the chemistry of each reaction step, and includes the calculated moles of solids that dissolved and/or precipitated, speciated solution composition, the total dissolved elements; and the intensive solution properties as the reaction progressed. The Excel macro "GetEQData.xls." was used to

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extract the actinide elemental concentrations and species concentrations which are presented below.

Table 6 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 7 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.

Table 8 shows the dissolved species distributions predicted for Th(IV) in the minimum volume and 5 × the minimum volume of GWB. Table 9 shows the species distributions for Th(IV) in the minimum volume and 5 × the minimum volume of ERDA-6 . Tables 10, 11, 12, and 13 provide comparable information for Np(V) and Am(III).

Table 14 compares the solubilities of Th(IV), Np(V), and Am(III) predicted for the minimum brine volume of 17,400 m^3 for the CRA-2019 PA with those predicted for the CRA-2014 PA and the CRA-2019 PA. Table 14 also compares the values of f_{CO_2} and pH predicted for these compliance-related calculations.

To gain an understanding of how the changes to the database and the addition of lead and iron reactants to CRA-2019 PA baseline solubility model impacted the results a matrix of runs using both DATA0.FM1 and DATA0.FM4 databases will be presented in a forthcoming memorandum.

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Table 6. 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)	0.224	0.231	0.233	0.234	0.235
Na(I)(aq)	4.69	4.71	4.71	4.71	4.71
Mg(II)(aq)	0.348	0.336	0.332	0.330	0.329
K(I)(aq)	0.663	0.682	0.688	0.692	0.694
Ca(II)(aq)	0.0109	0.0107	0.0106	0.0106	0.0105
Fe(II)(aq)	2.61E-05	2.61E-05	2.60E-05	2.60E-05	2.60E-05
S(VI)(aq)	0.232	0.233	0.234	0.234	0.234
Cl(-I)(aq)	5.40	5.43	5.43	5.44	5.44
Br(-I)(aq)	0.0378	0.0388	0.0392	0.0394	0.0395
Pb(II)(aq)	1.90E-02	1.90E-02	1.90E-02	1.91E-02	1.91E-02
Th(IV)(aq)	5.45E-08	5.45E-08	5.45E-08	5.45E-08	5.45E-08
Np(V)(aq)	4.02E-07	2.83E-07	2.42E-07	2.21E-07	2.09E-07
Am(III)(aq)	1.63E-07	1.58E-07	1.56E-07	1.55E-07	1.54E-07
f_{CO_2} (atm)	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
I	6.53	6.55	6.55	6.55	6.55
pH[B]	8.82	8.82	8.82	8.82	8.82
pcH	9.54	9.55	9.55	9.55	9.55
RH (%)[C]	0.732	0.732	0.732	0.732	0.732
TIC[D]	2.50E-04	2.50E-04	2.50E-04	2.50E-04	2.50E-04

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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 GWB.
D. TIC = total inorganic C.

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Table 7. 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)	0.281	0.282	0.282	0.282	0.283
Na(I)(aq)	4.66	4.70	4.72	4.72	4.73
Mg(II)(aq)	0.435	0.391	0.374	0.365	0.360
K(I)(aq)	0.499	0.563	0.590	0.604	0.612
Ca(II)(aq)	0.0128	0.0119	0.0116	0.0114	0.0113
Fe(II)(aq)	2.67E-05	2.64E-05	2.64E-05	2.63E-05	2.63E-05
S(VI)(aq)	0.224	0.228	0.229	0.230	0.231
Cl(-I)(aq)	5.22	5.29	5.32	5.34	5.35
Br(-I)(aq)	0.0566	0.0639	0.0669	0.0684	0.0694
Pb(II)(aq)	1.88E-02	1.90E-02	1.90E-02	1.90E-02	1.91E-02
Th(IV)(aq)	5.44E-08	5.44E-08	5.44E-08	5.44E-08	5.44E-08
Np(V)(aq)	1.20E-06	7.27E-07	5.52E-07	4.61E-07	4.05E-07
Am(III)(aq)	1.78E-07	1.63E-07	1.58E-07	1.54E-07	1.52E-07
f_{CO_2} (atm)	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
I	6.48	6.52	6.53	6.54	6.55
pH[B]	8.82	8.82	8.82	8.82	8.82
pcH	9.52	9.53	9.53	9.54	9.54
RH (%)[C]	0.732	0.732	0.732	0.732	0.732
TIC[D]	2.50E-04	2.50E-04	2.50E-04	2.50E-04	2.50E-04

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Footnotes for Table 7 provided on next page.

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Footnotes for Table 7:

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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Table 8. Comparisons of Distributions of Dissolved Th(IV) Species in the Minimum Volume and 5 × the Minimum Volume of GWB. Percentages of solubilities < 0.01 were not reported. The solubility-controlling solid was hydrous, amorphous ThO2.

GWB, minimum volume			GWB, 5 × minimum volume		
Th(IV) Species	Concentration (M)	Percent of Solubility	Th(IV) Species	Concentration (M)	Percent of Solubility
$Th(OH)_4(aq)$	4.48E-08	82.33%	$Th(OH)_4(aq)$	4.48E-08	82.27%
$Th(OH)_3CO_3^-$	9.62E-09	17.67%	$Th(OH)_3CO_3^-$	9.66E-09	17.73%
$Th(CO_3)_5^{6-}$	4.30E-18	-	$Th(CO_3)_5^{6-}$	2.69E-18	-
$Th(SO_4)_3^{2-}$	2.07E-18	-	$Th(SO_4)_3^{2-}$	1.95E-18	-
ThEDTA(aq)	2.62E-19	-	ThEDTA(aq)	5.32E-20	-
$ThCit^+$	2.22E-19	-	$ThCit^+$	4.15E-20	-
$Th(SO_4)_2(aq)$	6.87E-20	-	$Th(SO_4)_2(aq)$	6.69E-20	-
$ThAc_2^{2+}$	6.32E-20	-	$ThAc_2^{2+}$	2.65E-21	-
$ThAc^{3+}$	1.93E-21	-	$ThAc^{3+}$	3.70E-22	-
$ThOx^{2+}$	2.67E-23	-	$ThOx^{2+}$	2.31E-23	-
Th^{4+}	3.34E-25	-	Th^{4+}	2.73E-25	-
Total	5.45E-08	100.00%	Total	5.45E-08	100.00%

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Table 9. Comparisons of Distributions of Dissolved Th(IV) Species in the Minimum Volume and 5 × the Minimum Volume of ERDA-6. Percentages of solubilities < 0.01 were not reported. The solubility-controlling solid was hydrous, amorphous ThO2.

ERDA-6, minimum volume			ERDA-6, 5 × minimum volume		
Th(IV) Species	Concentration (M)	Percent of Solubility	Th(IV) Species	Concentration (M)	Percent of Solubility
$Th(OH)_4(aq)$	4.48E-08	82.44%	$Th(OH)_4(aq)$	4.48E-08	82.26%
$Th(OH)_3CO_3^-$	9.55E-09	17.56%	$Th(OH)_3CO_3^-$	9.66E-09	17.74%
$Th(CO_3)_5^{6-}$	3.53E-17	-	$Th(CO_3)_5^{6-}$	6.54E-18	-
$Th(SO_4)_3^{2-}$	2.84E-18	-	$Th(SO_4)_3^{2-}$	2.28E-18	-
$ThCit^+$	1.20E-18	-	$ThCit^+$	2.00E-19	-
ThEDTA(aq)	1.06E-18	-	ThEDTA(aq)	2.36E-19	-
$ThAc_2^{2+}$	1.04E-18	-	$ThAc_2^{2+}$	5.36E-20	-
$Th(SO_4)_2(aq)$	7.79E-20	-	$Th(SO_4)_2(aq)$	7.08E-20	-
$ThAc^{3+}$	1.10E-20	-	$ThAc^{3+}$	1.98E-21	-
$ThOx^{2+}$	4.67E-23	-	$ThOx^{2+}$	2.87E-23	-
Th^{4+}	8.40E-25	-	Th^{4+}	4.13E-25	-
Total	5.44E-08	100.00%	Total	5.44E-08	100.00%

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Table 10. Comparisons of Distributions of Dissolved Np(V) Species in the Minimum Volume and 5 × the Minimum Volume of GWB. Percentages of solubilities < 0.01 were not reported. The solubility-controlling solid was KNpO2CO3.

GWB, minimum volume			GWB, 5 × minimum volume		
Np(V) Species	Concentration (M)	Percent of Solubility	Np(V) Species	Concentration (M)	Percent of Solubility
$NpO_2Ac(aq)$	2.35E-07	58.34%	$NpO_2Ac(aq)$	4.86E-08	23.30%
NpO_2^+	7.05E-08	17.52%	NpO_2^+	6.69E-08	32.07%
$NpO_2CO_3^-$	6.48E-08	16.12%	$NpO_2CO_3^-$	6.30E-08	30.18%
NpO_2Ox^-	2.68E-08	6.66%	NpO_2Ox^-	2.60E-08	12.44%
$NpO_2(OH)(aq)$	3.41E-09	0.85%	$NpO_2(OH)(aq)$	3.33E-09	1.60%
NpO_2Cit^{2-}	1.40E-09	0.35%	NpO_2Cit^{2-}	2.74E-10	0.13%
$NpO_2(CO_3)_2^{3-}$	6.26E-10	0.16%	$NpO_2(CO_3)_2^{3-}$	5.94E-10	0.28%
$NpO_2(OH)_2^-$	6.75E-12	-	$NpO_2(OH)_2^-$	6.65E-12	-
$NpO_2(CO_3)_3^{5-}$	3.61E-12	-	$NpO_2(CO_3)_3^{5-}$	3.08E-12	-
NpO_2EDTA^{3-}	8.04E-15	-	NpO_2EDTA^{3-}	1.46E-15	-
NpO_2HEDTA^{2-}	2.70E-17	-	NpO_2HEDTA^{2-}	5.13E-18	-
$NpO_2H_2EDTA^-$	3.62E-21	-	$NpO_2H_2EDTA^-$	6.76E-22	-
Total	4.02E-07	100.00%	Total	2.09E-07	100.00%

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Table 11. Comparisons of Distributions of Dissolved Np(V) Species in the Minimum Volume and 5 × the Minimum Volume of ERDA-6. Percentages of solubilities < 0.01 were not reported. Percentages do not add up to 100% because concentrations were rounded to three significant figures before calculating percentages. The solubility-controlling solid was KNpO2CO3.

ERDA-6, minimum volume			ERDA-6, 5 × minimum volume		
Np(V) Species	Concentration (M)	Percent of Solubility	Np(V) Species	Concentration (M)	Percent of Solubility
$NpO_2Ac(aq)$	9.81E-07	81.50%	$NpO_2Ac(aq)$	2.23E-07	55.11%
NpO_2^+	9.66E-08	8.02%	NpO_2^+	7.76E-08	19.17%
$NpO_2CO_3^-$	8.03E-08	6.67%	$NpO_2CO_3^-$	6.94E-08	17.15%
NpO_2Ox^-	3.36E-08	2.79%	NpO_2Ox^-	2.90E-08	7.16%
NpO_2Cit^{2-}	7.30E-09	0.61%	NpO_2Cit^{2-}	1.35E-09	0.33%
$NpO_2(OH)(aq)$	4.11E-09	0.34%	$NpO_2(OH)(aq)$	3.63E-09	0.90%
$NpO_2(CO_3)_2^{3-}$	8.51E-10	0.07%	$NpO_2(CO_3)_2^{3-}$	6.73E-10	0.17%
$NpO_2(OH)_2^-$	7.89E-12	-	$NpO_2(OH)_2^-$	7.19E-12	-
$NpO_2(CO_3)_3^{5-}$	7.54E-12	-	$NpO_2(CO_3)_3^{5-}$	3.99E-12	-
NpO_2EDTA^{3-}	5.73E-14	-	NpO_2EDTA^{3-}	8.13E-15	-
NpO_2HEDTA^{2-}	1.58E-16	-	NpO_2HEDTA^{2-}	2.64E-17	-
$NpO_2H_2EDTA^-$	2.18E-20	-	$NpO_2H_2EDTA^-$	3.48E-21	-
Total	1.20E-06	100.00%	Total	4.05E-07	100.00%

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Table 12. Comparisons of Distributions of Dissolved Am(III) Species in the Minimum Volume and 5 × the Minimum Volume of GWB. Percentages of solubilities < 0.01 were not reported. Percentages do not add up to 100% because concentrations were rounded to three significant figures before calculating percentages. The solubility-controlling solid was $Am(OH)_3(s)$.

GWB, minimum volume			GWB, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$Am(OH)_2^+$	1.43E-07	88.17%	$Am(OH)_2^+$	1.48E-07	96.08%
$AmEDTA^-$	1.07E-08	6.55%	$AmEDTA^-$	2.25E-09	1.46%
AmCit(aq)	3.35E-09	2.06%	AmCit(aq)	7.12E-10	0.46%
$AmAc^{2+}$	2.79E-09	1.71%	$AmAc^{2+}$	6.12E-10	0.40%
$Am(OH)^{2+}$	1.35E-09	0.83%	$Am(OH)^{2+}$	1.34E-09	0.87%
$Am(OH)_3(aq)$	7.75E-10	0.48%	$Am(OH)_3(aq)$	8.07E-10	0.52%
$AmCO_3^+$	1.66E-10	0.10%	$AmCO_3^+$	1.64E-10	0.11%
$Am(CO_3)_2^-$	8.56E-11	0.05%	$Am(CO_3)_2^-$	8.68E-11	0.06%
$AmSO_4^+$	4.13E-11	0.03%	$AmSO_4^+$	4.08E-11	0.03%
$Am(CO_3)_3^{3-}$	1.34E-11	0.01%	$Am(CO_3)_3^{3-}$	1.33E-11	0.01%
$Am(SO_4)_2^-$	7.10E-12	-	$Am(SO_4)_2^-$	7.19E-12	-
$AmOx^+$	7.09E-12	-	$AmOx^+$	6.81E-12	-
Am^{3+}	5.28E-12	-	Am^{3+}	4.97E-12	-
$AmCl^{2+}$	6.63E-13	-	$AmCl^{2+}$	6.31E-13	-
$Am(CO_3)_4^{5-}$	4.40E-13	-	$Am(CO_3)_4^{5-}$	3.83E-13	-

Table 12 continued on next page.

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Table 12. Comparisons of Distributions of Dissolved Am(III) Species in the Minimum Volume and 5 × the Minimum Volume of GWB (continued). Percentages of solubilities < 0.01 were not reported. Percentages do not add up to 100% because concentrations were rounded to three significant figures before calculating percentages. The solubility-controlling solid was $Am(OH)_3(s)$ (continued).

GWB, minimum volume			GWB, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$AmCl_2^+$	2.58E-14	-	$AmCl_2^+$	2.44E-14	-
Total	1.63E-07	100.00%	Total	1.54E-07	100.00%

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Table 13. Comparisons of Distributions of Dissolved Am(III) Species in the Minimum Volume and 5 × the Minimum Volume of ERDA-6. Percentages of solubilities < 0.01 were not reported. Percentages may not add up to 100% because concentrations were rounded to three significant figures before calculating percentages. The solubility-controlling solid was $Am(OH)_3(s)$.

ERDA-6, minimum volume			ERDA-6, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$Am(OH)_2^+$	1.19E-07	66.79%	$Am(OH)_2^+$	1.35E-07	88.70%
$AmEDTA^-$	3.73E-08	21.00%	$AmEDTA^-$	9.47E-09	6.22%
AmCit(aq)	1.08E-08	6.10%	AmCit(aq)	2.83E-09	1.86%
$AmAc^{2+}$	8.51E-09	4.79%	$AmAc^{2+}$	2.48E-09	1.63%
$Am(OH)^{2+}$	1.37E-09	0.77%	$Am(OH)^{2+}$	1.35E-09	0.89%
$Am(OH)_3(aq)$	6.50E-10	0.37%	$Am(OH)_3(aq)$	7.54E-10	0.49%
$AmCO_3^+$	1.72E-10	0.10%	$AmCO_3^+$	1.66E-10	0.11%
$Am(CO_3)_2^-$	8.15E-11	0.05%	$Am(CO_3)_2^-$	8.55E-11	0.06%
$AmSO_4^+$	4.27E-11	0.02%	$AmSO_4^+$	4.11E-11	0.03%
$Am(CO_3)_3^{3-}$	1.44E-11	0.01%	$Am(CO_3)_3^{3-}$	1.37E-11	0.01%
$AmOx^+$	7.85E-12	-	$AmOx^+$	6.91E-12	-
Am^{3+}	7.11E-12	-	Am^{3+}	5.79E-12	-
$Am(SO_4)_2^-$	6.76E-12	-	$Am(SO_4)_2^-$	7.08E-12	-
$AmCl^{2+}$	8.50E-13	-	$AmCl^{2+}$	7.15E-13	-
$Am(CO_3)_4^{5-}$	8.21E-13	-	$Am(CO_3)_4^{5-}$	4.88E-13	-

Table 13 continued on next page.

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Table 13. Comparisons of Distributions of Dissolved Am(III) Species in the Minimum Volume and 5 × the Minimum Volume of ERDA-6 (continued). Percentages of solubilities < 0.01 were not reported. Percentages may not add up to 100% because concentrations were rounded to three significant figures before calculating percentages. The solubility-controlling solid was Am(OH)3 (continued).

ERDA-6, minimum volume			ERDA-6, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$AmCl_2^+$	3.40E-14	-	$AmCl_2^+$	2.77E-14	-
Total	1.78E-07	100.00%	Total	1.52E-07	100.00%

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Table 14. Comparison of Actinide Solubilities (M), fCO2 (atm), and pH (Pitzer scale) from the CRA-2014 PA and the current PA, CRA-2019 PA.

Property or Actinide Oxidation State	CRA-2014 PA ($GWB_{min. vol.}$, Hydromagnesite, with Organics, All Vectors)[A]	CRA-2014 PA ($ERDA\text{-}6_{min. vol.}$, Hydromagnesite, with Organics, All Vectors)[A]	CRA-2019 ($GWB_{min. vol.,}$, Hydromagnesite, with Organics, Pb, Fe All Vectors)[B]	CRA-2019 ($ERDA\text{-}6_{min. vol.,}$, Hydromagnesite, Pb, Fe with Organics, All Vectors)[B]
Th(IV)	6.05×10^{-8}	7.02×10^{-8}	5.45×10^{-8}	5.44×10^{-8}
Np(V)	2.77×10^{-7}	8.76×10^{-7}	4.02×10^{-7}	1.20×10^{-6}
Am(III)	2.59×10^{-6}	1.48×10^{-6}	1.63×10^{-7}	1.78×10^{-7}
f_{CO_2}	3.14×10^{-6}	3.14×10^{-6}	2.02×10^{-6}	2.02×10^{-6}
pH	8.82	8.99	8.82	8.82

A. Brush and Domski (2014)
B. This Study

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3.1 Discussion

Examination of Table 14 shows that the decrease in the Am(III) concentration for CRA-2019 compared to CRA-2014 is substantial for both brines. To understand this decrease we must consider any changes to thermodynamic and/or Pitzer parameters between DATA0.FM1 and DATA0.FM4 that would impact the Am chemical system.

Tables 15 and 16 compare the EDTA aqueous species concentrations for GWB and ERDA-6 respectively.

Table 15. Comparison of EDTA Aqueous Species for 1x volume for GWB from CRA-2014 and CRA-2019.

Species	CRA-2014 GWB 1x vol (M)	CRA-2019 GWB 1x vol (M)
$MgEDTA^{2-}$ *	8.33E-05	1.11E-04
$AmEDTA^{-}$	2.44E-06	1.07E-08
$CaEDTA^{2-}$ *	1.43E-06	1.61E-06
$EDTA^{4-}$	3.16E-10	1.69E-14
$HEDTA^{3-}$ *	6.26E-11	1.23E-12
NpO_2EDTA^{3-}	1.57E-12	8.04E-15
H_2EDTA^{2-} *	1.24E-13	1.98E-15
NpO_2HEDTA^{2-}	5.43E-15	2.70E-17
ThEDTA(aq)	6.29E-17	2.62E-19
$NpO_2H_2EDTA^{-}$	8.18E-19	3.62E-21
H_3EDTA^{-} *	1.21E-20	2.19E-22
$H_4EDTA(aq)$ *	1.33E-27	1.32E-29
$CaHEDTA^{2-}$ *	0.00E+00	7.45E-11
$NaEDTA^{3-}$ *	0.00E+00	9.74E-12
$MgHEDTA^{2-}$ *	0.00E+00	8.03E-12

*Updated or added for DATA0.FM4

Table 15. Comparison of EDTA Aqueous Species for 1x volume for ERDA-6 from CRA-2014 and CRA-2019.

Species	CRA-2014 ERDA-6 1x vol (M)	CRA-2019 ERDA-6 1x vol (M)
$MgEDTA^{2-}$ *	5.98E-05	4.01E-04
$CaEDTA^{2-}$ *	2.80E-06	6.70E-06
$AmEDTA^{-}$	1.39E-06	3.73E-08
$EDTA^{4-}$	1.70E-10	1.22E-13
$HEDTA^{3-}$ *	4.32E-11	5.84E-12
NpO_2EDTA^{3-}	4.05E-12	5.73E-14
H_2EDTA^{2-} *	1.00E-13	7.92E-15

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Species	CRA-2014 ERDA-6 1x vol (M)	CRA-2019 ERDA-6 1x vol (M)
NpO_2HEDTA^{2-}	1.83E-14	1.58E-16
ThEDTA(aq)	2.66E-17	1.06E-18
$NpO_2H_2EDTA^-$	3.25E-18	2.18E-20
H_3EDTA^{-} *	8.22E-21	8.65E-22
H_4EDTA(aq) *	5.54E-28	5.11E-29
$MgHEDTA^{2-}$ *	0.00E+00	2.86E-10
$NaEDTA^{3-}$ *	0.00E+00	3.55E-11
$CaHEDTA^{2-}$ *	0.00E+00	3.08E-11

*Updated or added for DATA0.FM4

The important features of Tables 14 and 15 are the increased concentrations of $MgEDTA^{2-}$ and $CaEDTA^{2-}$ for CRA-2019 compared to CRA-2014. These increased concentrations account for the decreased $AmEDTA^-$ concentration, which accounts for the decreased total americium concentration. Table 16 provides the Log K values used in both DATA0.FM1, which was the database used for CRA-2014, and DATA0.FM4 used in the current analysis. Changing the Log K from -10.1 to -10.9 for $MgEDTA^{2-}$ does not seem like a big change, however, it increases the stability of the complex enough relative to the $AmEDTA^-$ complex that it has a significant impact on the americium solubility.

Table 16. Updated Log K values for Americium, Magnesium, and Calcium EDTA Aqueous Species used in DATA0.FM4.

Reaction	Log K	Database	Source
$AmEDTA^- \leftrightarrow Am^{3+} + EDTA^{4-}$	-18.97	DATA0.FM1 and DATA0.FM4	Choppin et al. (2001)
$MgEDTA^{2-} \leftrightarrow Mg^{2+} + EDTA^{4-}$	-10.1	DATA0.FM1	Giambalvo (2002)
$MgEDTA^{2-} \leftrightarrow Mg^{2+} + EDTA^{4-}$	-10.90	DATA0.FM4	Hummel et al. (2005)
$CaEDTA^{2-} \leftrightarrow Ca^{2+} + EDTA^{4-}$	-10.1	DATA0.FM1	Giambalvo (2002)
$CaEDTA^{2-} \leftrightarrow Ca^{2+} + EDTA^{4-}$	-12.69	DATA0.FM4	Hummel et al. (2005)

4 CONCLUSIONS

This analysis report provides the new baseline solubilities of Th(IV), Np(V), and Am(III) in two standard Waste Isolation Pilot Plant (WIPP) brines as a function of the volumes of these brines in the repository. 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 simulates fluids in brine reservoirs in the Castile Fm. EQ3/6, Version 8.0a, and DATA0.FM4 was used for this analysis.

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Tables 6 and 7 (see Section 3 above) provide the aqueous compositions; the actinide solubilities, and the intensive solution properties for GWB and ERDA-6 at the five volumes, respectively.

Tables 8 and 9 (Section 3) shows the dissolved species distributions predicted for Th(IV) in the minimum volume and 5 × the minimum volume of GWB and ERDA-6, respectively. Tables 10, 11, 12 and 13 provide comparable information for Np(V) and Am(III).

Table 14 (Section 3) compares the solubilities of Th(IV), Np(V), and Am(III) predicted for the minimum brine volume of 17,400 m^3 from this study compared with those predicted for the CRA-2014 PA. Table 14 also compares the values of f_{CO_2} and pH predicted for these compliance-related calculations.

Notice that the Am(III) solubilities predicted by this work decrease by factors of ~16 for both GWB and ERDA-6, respectively, in comparison with the Am(III) solubilities predicted for the CRA-2014 PA (Brush and Domski, 2013). This decrease in Am(III) solubility can be attributed directly to changes made to the thermodynamic data for the magnesium and calcium aqueous complexes in DATA0.FM4. It should be noted that data of Hummel et al., (2005) used to update the Log K values of these complexes were derived using the SIT aqueous model, which is not consistent with the other parameters in the database which were derived using the Pitzer model. This inconsistency may be partially responsible for this somewhat drastic change in Am(III) solubility. Neither Th(IV) or Np(V) solubility changed that much for CRA-2019 compared to CRA-2014 to warrant scrutiny.

A forthcoming technical memorandum will examine the impact of the updated Pitzer thermodynamic database, the addition of lead and iron reactants on the bulk solution chemistry and the actinide solubilities, and how allowing calcite to precipitate influenced the chemistry. In addition, the memo will also analyze and discuss the reaction paths of the reacted GWB and ERDA-6 brines and provide a history of the solid phase evolution of these chemical systems.

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