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Sandia National Laboratories
Waste Isolation Pilot Plant

Prediction of Baseline Actinide Solubilities for the Replacement Panels Planned Change Request (RPPCR) Performance Assessment

Work Carried Out under Task 3 of the Analysis Plan for WIPP Near-Field Geochemical Process Modeling, AP 153, Rev. 1.
To be included in the AP-153 records package

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WIPP: 4.4.1.1.1: TD: QA-L: RECERT: 555726

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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 the Replacement Panels Planned Change Request (RPPCR), and, as necessary, the 2024 Compliance Recertification Application (CRA-2024). The RPPCR investigates the effect on performance of increasing the number of waste storage panels from ten to nineteen, this change in area of the repository had the effect of increasing the direct brine release (DBR) volume from 17,400 m^3 (Clayton, 2008) to 33, 804 m^3 (King, 2021). 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. This data for the RPPCR are tabulated in the following sections.

The RPPCR baseline solubility model differs from the 2019 Compliance Recertification Application Deferred Performance Assessment (CRA-2019 DPA) baseline solubility model (Domski and Sisk-Scott, 2019) in four ways: 1) The updated WIPP thermodynamic database DATA0.FM6 (Domski, 2023a) was used rather than DATA0.FM4; 2) the RPPCR is based on a new 19-panel repository geometry, which increased the direct brine release volume (King, 2021) which affects the scaling of the reactants used in the solubility model; and 3) a new inventory for was issued for the RPPCR (Van Soest, 2022) which provides updated inventories for the reactants

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used in the solubility model; and 4) updated model assumptions with regard to calcite precipitation, Phase 5 precipitation, and scaling of the reactants.

In this analysis report the U.S. Department of Energy (DOE) have addressed issues related to model assumptions. Issues 6, 7, 28, and 41 of the U.S. Environmental Protection Agency (EPA) (Peake, 2022) have been addressed in this report. These issues are further discussed in the following sections.

Some of the primary assumptions employed in the CRA-2019 DPA were changed for the RPPCR baseline solubility model. These include the lead and iron reactants, where PbO and $Fe(OH)_2$ were used in the CRA-2019 DPA calculations they were replaced with hydrocerussite ($2PbCO_3.Pb(OH)_2(s)$) and hibbingite ($Fe_2Cl(OH)_3$), respectively. For the RPPCR calcite ($CaCO_3$) was suppressed and aragonite was allowed to precipitate should it become saturated during the course of the simulations (EPA Issue 6). Furthermore, for the RPPCR the magnesium oxy-chloride phase, Phase 5 ($Mg_3Cl(OH)_5{\cdot}4H_2O$), was suppressed based on the analysis of Domski and Nemer (2023) (EPA Issues 7 and 41). The amounts of the reactants were scaled to brine volume (EPA Issue 28).

Note, this analysis was performed using the same process described as used through the submission of CRA-2019 DPA, and therefore is a deviation from AP-153, Revision 1. This analysis report, as per NP 9-1, is considered a compliance decision 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
CPR	Cellulose, plastic and rubber
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
CRA-2019 DPA	The fourth WIPP Compliance Recertification Application, Deferred Performance Assessment submitted to the EPA in March 2019
RPPA-2022	Replacement Panels Performance Assessment
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)
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 was 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 a function of the volume of these brines in the repository. This report also provides the predicted compositions of GWB and ERDA-6 after equilibration with the important solids in the repository. Brush et al. (2012) 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. The methods that we used for this analysis were identical to those used by Domski and Sisk-Scott (2019), however, some of the assumptions have to be changed (the lead and iron reactants, and suppression of calcite and phase 5).

We used EQ3/6, Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010) to simulate the reaction of GWB and ERDA-6 with the important solids in the WIPP. In the first step of this reaction (referred to herein as "step 1"), we added the following compounds to GWB and ERDA-6: (1) acetate, citrate, EDTA, and oxalate; and (2) ThO_2(s), $KNpO_2CO_3$, and $Am(OH)_3$(am)), the solids most likely to control the solubilities of Th(IV), Am(III), and Np(V) in the repository (Brush et al., 2012). In Step 2, we reacted these brines with the important solids in the repository (see below) in a manner consistent with the conceptual models for WIPP near-field chemistry (SCA, 2008; Brush et al., 2012) 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 — in particular 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 fCO_2, pH, pcH, TIC.

2.1 Model Setup

Calculation of the actinide baseline solubilities follows a two-step process:

Step 1: Calculation of Initial Solution Compositions with EQ3NR

- EQ3NR is used to equilibrate and speciate the brine compositions (ERDA-6 & GWB) with the inventory scaled masses of the organic ligands (acetate, oxalate, citrate, and EDTA).
- The actinide concentrations of the initial solutions are set via equilibrium with solubility controlling phases ($Am(OH)_3$(am), ThO_2(s), and $KNpO_2CO_3$).
- The conditions of relatively low pH and high carbonate concentration (Table 3 below) of the initial solution ensures that an excess mass of actinides dissolve in this step.
- The initial solution composition(s), which includes the dissolved actinide concentrations are then passed to Step 2 and are reacted with the solids and subject to the evolving chemical environment where the stable actinide solubility controlling phases may form.

Step 2: Calculation of Equilibrium Solution Compositions with EQ6

- Using EQ6, the initial solution compositions from Step 1 are reacted with:
  - Inventory-scaled masses of the MgO barrier (50% brucite and 50% hydromagnesite)
  - Iron and lead reactants representing the waste containers and radiation shielding

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  - Salado Formation minerals halite and anhydrite
- The model includes the effects of organic ligand complexation and mineral phase dissolution and precipitation.
- The model provides the actinide solubilities and the near-field chemistry including:
  - Equilibrium pH
  - Carbon dioxide fugacity
  - Activity of water
  - Total inorganic carbon
  - Ionic strength
  - Concentration of all dissolved constituents
  - Solid phase budget

EQ3/6 was used to simulate the reaction of GWB and ERDA-6 with the important components in the WIPP. In Step 1, EQ3NR is used and the following compounds were added to GWB and ERDA-6: (1) The organic ligands (acetate, citrate, EDTA, and oxalate); and (2) $ThO_2(s)$, $KNpO_2CO_3$, and $Am(OH)_3(am)$), the solids most likely to control the solubilities of Th(IV), Np(V), and Am(III) in the repository (Brush et al., 2012). The low pH and high carbonate values of GWB and ERDA-6 (Table 3) ensure that an excess of the actinide solubility controlling phases dissolve in Step 1.

In Step 2, EQ6 reacts the initial brine compositions from Step 1 with the important solid geologic, engineered barrier, and waste components in the repository in a manner consistent with the conceptual models for WIPP near-field chemistry (SCA, 2008; Brush et al., 2012). 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 — particularly brucite ($Mg(OH)_2$) and hydromagnesite5424 ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) — control the new compositions of the brines and parameters such as f_{CO_2}, pH, pcH, TIC.

As outlined above 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, dissolves the solubility-controlling actinide phases in the presence of organics, and calculates the mineral saturation index values for GWB and ERDA-6. The low pH and high carbonate concentrations of the initial brine compositions ensures that an excess amount of the solubility-controlling actinide phases dissolve in the brines in Step 1. There are five input files for each brine each representing a different brine volume, the only input that changes are the organic ligand 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, hibbingite and hydrocerussite into GWB and ERDA-6 resultant solutions from

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Step 1. Halite and anhydrite were used to simulate the most important minerals [1]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), hydrocerussite 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 hibbingite ($Fe_2Cl(OH)_3$). The EQ6 input values for each reactant are tabulated in Table 5. The input reactant moles (Table 5) was scaled to reflect the increasing brine volume, this scaling addresses the EPA Issue 28 (Peake, 2022).

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 RPPCR (prevented from precipitating) included Calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$), hydromagnesite with the composition $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$, phase 5 ($Mg_3Cl(OH)_5.4H_2O$), and $Am(OH)_3(s)$. Also suppressed was the aqueous species $FeEDTA^{2-}$ throughout Step 2.

Note, the EQ3/6 simulations are performed in two steps which implies there may a temporal dependance on the order which the solid materials are contacted by GWB or the ERDA-6 brines. This is not the case. All of the important solid materials are contacted with the brines simultaneously; this supports the conceptual model assumption of chemical homogeneity and solubility equilibrium, and allows for the assumption of instantaneous reactions (Wilson, 1996).

For the CRA-2019 DPA Domski and Sisk-Scott (2019) allowed calcite to precipitate because its saturation index, for some cases, was in excess of 1.5 log units above saturation. However, calcite precipitation in complex brines may be inhibited by the presence of ions such as Mg^{2+} and Fe^{2+} (Brush et al., 2006; Katz et al., 1993; and Zhu et al., 2018). It has been observed that in conditions where calcite inhibitors may be present that a disordered, more soluble form of $CaCO_3$ may precipitate such as non-biogenic aragonite. Jaohari et al. (2000) observed aragonite to precipitate from synthetic seawater on an iron substrate in the presence of Mg^{2+} ions – two conditions that could be expected at WIPP. For the RPPCR baseline solubility calculations calcite was suppressed such that it may reach over saturation to the point where aragonite becomes saturated and precipitates. The EPA had identified calcite formation as Issue 6 in the letter by Peake (2022), and the RPPCR provides a more reasoned argument of $CaCO_3$ precipitation than Domski and Sisk-Scott (2019).

The current WIPP thermodynamic database, DATA0.FM6, includes an aqueous species for Iron – EDTA, $FeEDTA^{2-}$. The inclusion and implementation of this species for calculating actinide solubilities was a topic of discussion at the October 25, 2022 technical exchange between the DOE and the EPA. At a later meeting, on December 12, 2022, between the DOE and the EPA it was agreed that this species would not be used when calculating actinide solubilities for the RPPCR and CRA-2024, because it was proposed that the inclusion of this single aqueous species was not a complete parameterization of the metal – organic ligand system, and the model should be further

[1] During the CRA-2019 DPA completeness evaluation the EPA requested that a sensitivity study be performed which included polyhalite as a reactant, the results shows it had little effect on actinide solubility (Knerr, 2021).

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developed before it is included it in the calculation of actinide solubility values. Omission of the FeEDTA complex will yield more conservation, i.e., higher dissolved actinide concentrations, then if the complex were allowed to form in the calculations. Rather than including the effects of this complex on the actinide solubility values used for performance assessment, additional runs of the solubility model were executed to demonstrate the impact of $FeEDTA^{2-}$ on actinide solubilities. The results and discussion of these model runs are presented in Appendix A.

In addition to the Iron – EDTA aqueous complex, and new for compliance calculations, DATA0.FM6 also includes two Iron – Citrate aqueous complexes (Domski, 2023a). These two complexes, $FeCitrate^{-}$ and $FeOHCitrate^{2-}$, were allowed in the RPPCR baseline solubility calculations. To demonstrate the effect these two complexes had on actinide solubility additional model runs were executed with these two complexes suppressed and the results are presented in Appendix B.

Notice that as Brush et al. (2012, 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. See Brush et al. (2012, Subsection 4.3) for a description of steps 2a and 2b.

All files are archived at "/data/cvs/CVSLIB/WIPP_EXTERNAL/ap200_files/RPPCR". Table 2 provides the location of the specific files.

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Table 2. 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_RPPCR.xlsx*	In zip file RPPCR_AP153R1.zip, /data/cvs/CVSLIB/WIPP_EXTERNAL/ap153_files/RPPCR
Spreadsheet: *Conc_density_calcs_RPPCR.xlsx*	In zip file RPPCR_AP153R1.zip, /data/cvs/CVSLIB/WIPP_EXTERNAL/ap153_files/RPPCR
EQ3/6 DB DATA0.FM6	In zip file RPPCR_AP153R1.zip, /data/cvs/CVSLIB/WIPP_EXTERNAL/ap153_files/RPPCR
Excel macro *GetEQData_v101f.xls*	In zip file RPPCR_AP153R1.zip, /data/cvs/CVSLIB/WIPP_EXTERNAL/ap153_files/RPPCR
EQ3/6 I/O files and Excel spreadsheets with extracted data	In zip file RPPCR_AP153R1.zip, /data/cvs/CVSLIB/WIPP_EXTERNAL/ap153_files/RPPCR

The output was extracted from the EQ6 *.6o files by running the Excel macro "GetEQData_v101f.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_v101f.xls, and the Excel spreadsheets that contain the output extracted with GetEQData_v101f.xls are in zip file RPPCR_AP-153R1.zip.

2.2 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 the important solid phases in the repository (halite, anhydrite, brucite, hydromagnesite5424, iron, and lead reactants). The EQ3/6 code is comprised of two separate codes, EQ3NR used for Step 1, and EQ6 used for Step 2, each of which requires different inputs. Step 1, EQ3NR, uses the brine compositions (Table 3), the organics input (Table 4), and the actinide solubility controlling phases and calculates the speciated solution composition and saturation index for all pertinent phases. For Step 2, the EQ6 code uses an output file of EQ3NR called a "pickup" file, which contains the initial solution information, EQ6 uses this composition and numerically titrates the reactants (Table 5) 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 chemical properties of the solution and the actinide concentrations that are used in PA.

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The unreacted ERDA-6 (Popielak et al., 1983), and GWB (Krumhansl et al., 1991; Snider, 2003) brine compositions that were used as input for the EQ3NR code are listed in Table 3.

Table 3. Input brine compositions, TDS, and densities used for the Baseline Solubility simulations.

	ERDA-6	GWB	
Na^+	4.87	3.53	Molarity
K^+	9.70E-02	4.67E-01	Molarity
Mg^{2+}	1.90E-02	1.02	Molarity
Ca^{2+}	1.20E-02	1.40E-02	Molarity
Cl^-	4.80	5.86	Molarity
HCO_3^-	1.60E-02	1.60E-02	Molarity
$SO4^{2-}$	1.70E-01	1.77E-01	Molarity
$B(OH)_4^-$	6.30E-02	1.58E-01	Molarity
Br^-	1.10E-02	2.66E-02	Molarity
H^+	7.00	7.00	pmH
TDS[A]	313167.7	368202.9	mg/L
Density[A]	1.20138	1.2366	g/cm^3

A – The TDS and density values in Table 3 are not used in the EQ3NR input files because they do not account for the organic ligands. The EQ3NR input values may be found in the *Conc_density_calcs_RPPCR.xlsx* spreadsheet.

The initial value of the total inorganic carbon (TIC), represented as HCO_3^-, 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 pmH for both brines is set to 7.0. When using molar input values they must be scaled by the solution density which is calculated in the spreadsheet, *Conc_density_calcs_RPPCR.xlsx* and includes the concentrations of organic ligands.

In addition to the brine composition data (Table 3) the scaled organics concentrations are also used as input for EQ3NR (Domski, 2023b). 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 × DBR volume, 33,804 m^3 (King, 2021), are from Domski (2023b). Table 4 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, 33,804 m^3, is the minimum brine volume required for a direct brine release (DBR) from the repository (King, 2021). Domski (2023b) 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. For RPPCR Domski (2023b) calculated the concentrations of acetate, citrate, EDTA, and oxalate in 1 ×, 2 ×, 3 ×, 4 ×, and 5 × 33,804 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 4).

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Table 4. 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	1.72E-02	8.59E-03	5.73E-03	4.29E-03	3.44E-03
Citrate	1.79E-03	8.93E-04	5.95E-04	4.46E-04	3.57E-04
EDTA	4.22E-05	2.11E-05	1.41E-05	1.06E-05	8.45E-06
Oxalate	5.76E-03	2.88E-03	1.92E-03	1.44E-03	1.15E-03

The final EQ3NR inputs are the solubility controlling phases used to set the An(III), An(IV), and An(V) concentrations. For An(III) the amorphous americium hydroxide phase, $Am(OH)_3(am)$, is set as solubility controlling phase. This amorphous phase, contained in DATA0.FM6 (Domski, 2023a), is new in the WIPP database, and is ~2.4 log units more soluble than the previously used americium hydroxide phase, $Am(OH)_3(s)$. The amorphous form of $Am(OH)_3$ was chosen as the solubility controlling phase over more crystalline forms, even though over the long-term the crystalline form may be more prevalent, for two reasons: 1) The amorphous is more soluble and provides the upper concentration limit (Wilson, 1996); and 2) from a physical/chemical point of view, and with regard to An(III)-hydroxide phases Neck et al. (2009) pointed out:

> *"The use of the notation "crystalline" and "amorphous" to describe a solid phase and thereby its solubility is an oversimplification. The X-ray diffraction (XRD) data give only information of the bulk structure, while the solubility is determined by the surface characteristics or by fractions of smaller ("amorphous") particles included in a bulk crystalline solid."*

For these reasons the amorphous form of americium hydroxide was chosen as the solubility controlling An(III) phase for Step 1 of the simulations.

The An(IV) model uses the amorphous form of thorium oxide, $ThO_2(s)$, as the solubility controlling phase. This 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.

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 RPPCR.

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Inputs for EQ6 include the pickup file (*.3p) generated in Step 1 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 initial mass of water on which EQ3/6 operates; subsequent dissolution/precipitation reactions can add or remove water from the system. In a computation, documented in the spreadsheet, *AP-153_Scaling of Solids_RPPCR.xlsx*, the quantities of carbon PAIR 2022 (Van Soest 2022), brine, halite, anhydrite, brucite, hydromagnesite, hibbingite, and hydrocerussite 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 33,804 m^3 of brine to 1 kg of water. These values can be found in PAIR 2022 (Van Soest 2022).

Table 5. Reactants (moles) in the Minimum Brine Volume Required for a DBR and for Volumes That Are 2 ×, 3 ×, 4 ×, and 5 × the Minimum Volume.

Total Carbon from CPR: 1.12E+09 moles

Total MgO: Total Carbon from CPR (1.12E+09 moles) x MgO excess factor (1.2) = 1.35E+09 moles

Reactant (mols)	Brine/Volume Factor	1x	2x	3x	4x	5x
Halite	GWB	3.52E+03	1.76E+03	1.17E+03	8.80E+02	7.04E+02
	ERDA-6	3.44E+03	1.72E+03	1.15E+03	8.60E+02	6.88E+02
Anhydrite	GWB	1.68E+02	8.39E+01	5.59E+01	4.20E+01	3.36E+01
	ERDA-6	1.64E+02	8.20E+01	5.47E+01	4.10E+01	3.28E+01
Brucite	GWB	2.30E+01	1.15E+01	7.65E+00	5.74E+00	4.59E+00
	ERDA-6	2.25E+01	1.12E+01	7.48E+00	5.61E+00	4.49E+00
Hydromagnesite	GWB	4.59E+00	2.30E+00	1.52E+00	1.15E+00	9.19E-01
	ERDA-6	4.49E+00	2.25E+00	1.50E+00	1.12E+00	8.98E-01
Hibbingite	GWB	1.28E+01	6.41E+00	4.27E+00	3.21E+00	2.56E+00
	ERDA-6	1.25E+01	6.27E+00	4.18E+00	3.13E+00	2.51E+00
Hydrocerussite	GWB	4.58E-01	2.29E-01	1.53E-01	1.15E-01	9.17E-02
	ERDA-6	4.48E-01	2.24E-01	1.49E-01	1.12E-01	8.96E-02

In Table 5 the "Total carbon from CPR" represents the total moles of carbon in the CPR from the PAIR (see Table 5-5 and Table 5-7 in the "*PAIR-2022 Tables.xlsx*"spreadsheet (VanSoest, 2022), it is the sum of the "waste", "packaging", and "total emplaced and operational" values in both the contact handled (CH) and remote handled (RH) columns). It should be calculated as:

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

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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). The total moles of MgO are calculated by multiplying the total moles of carbon from the CPR by the MgO excess factor, 1.2, i.e. $MgO_{moles} = 1.2 \times \Sigma C_{moles}$. The MgO excess factor is a safety factor to account for possible variations in the mass of CPR. Each mole of carbon in the CPR can generate one mole of CO_2, which can react with the MgO hydration product brucite to form hydromagnesite. The stoichiometry is different for the two reactions, five moles of carbon are required to form one mole of hydromagnesite5424. The total moles of carbon are shown in Table 5 and documented in the spreadsheet titled *AP-153_Scaling of Solids_RPPCR.xlsx*.

Note, the density and total dissolved solids (TDS) values from the unreacted brines in Table 3 were used to calculate the solids scaling factor[2] for each brine volume. The conceptual model assumption is that GWB, or ERDA-6, contacts and reacts with the geologic (halite and anhydrite), engineered barrier (MgO), and waste form (actinide phases, organics, CPR, steel, and lead) simultaneously. This supports the conceptual model assumption of chemical homogeneity and solubility equilibrium, and allows for the assumption of instantaneous reactions (Wilson, 1996). The brines which contact these components are the unreacted end-member GWB and ERDA-6 compositions (Table 3), as such their density and TDS are independent of brine volume.

The sources of iron in the repository are the waste packaging materials and the waste, and it has been widely stated that in the WIPP environment ferrous iron hydroxide should be the primary corrosion product, and solubility-limiting phase for iron in the repository (Telander and Westerman, 1997, Roselle 2013, U.S.DOE 2014). However, EQ3/6 simulations show that ferrous hydroxide converts directly to hibbingite ($Fe_2Cl(OH)_3$), the stable iron phase in the chemical conditions predicted for the WIPP near-field environment. In addition, Rémazeilles et al. (2009) identified hibbingite as the primary anoxic corrosion product on an Roman iron ingot that was submerged in seawater for ~2000 years. Rémazeilles et al. (2009) state:

> *"The main phase is an iron(II) hydroxychloride ($Fe_2(OH)_3Cl$) and is in contact with the metal."*
>
> *"The presence of iron hydroxychlorides (β and γ-$Fe_2(OH)_3Cl$) and akaganeite in the rust layer is typical of corrosion processes of iron in concentrated chloride solutions."*
>
> *"The formation of the iron hydroxychloride on the iron Roman ingots would have then required specific conditions at the steel surface that are absence of oxygen, slight acidification of the electrolyte since the pH value of seawater is rather close to 8.2, and/or increase of the chloride concentration."*

Based on the natural analog observations of Rémazeilles et al. (2009), and its thermodynamic stability of hibbingite over other ferrous iron phases, it will be specified as the iron reactant in the baseline solubility simulations.

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[2] Solid Scaling Factor = $1/([\rho_{brine} - TDS] \times Vol_{DBR})$, ρ_{brine} = brine density (kg/m^3), TDS = brine total dissolved solids (kg/m^3), Vol_{DBR} = DBR volume (m^3)

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Lead in the repository originates as radiation shielding used in the waste canisters. Archaeological studies have indicated that there was a mixed layer of PbO and Pb-carbonates 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). From Rocca et al. (2004):

"...a thick duplex layer consisting of $PbO/PbCO_3/Pb_3(CO_3)_2(OH)_2$ with significant intergranular corrosion was observed. Even though in a medium rich in carbonate species such as HCO_3^- and in contact with a significant partial pressure of oxygen due to the microbial activity in the soil, the lead monoxide PbO is not stable. Indeed, the thermodynamic data of lead compounds show that the lead carbonates (cerussite, hydrocerussite and plombonacrite) should be the most stable corrosion products."

For the RPPCR baseline solubility calculations it was assumed that all of the metallic lead has transformed to hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), and thus it was used as the EQ6 reactant phase.

The baseline solubility model includes three man-made components, the MgO engineered barrier, steel, represented as iron, waste containers, and lead radiation shielding. These three components are represented in the model as four solid reacting phases: 1) The MgO engineered barrier system is represented as 50-50 by moles of Mg combination of brucite ($Mg(OH)_2$(s)) and hydromagnesite ($Mg_5(CO_3)4(OH)_2.4H_2O$); 2) the iron comprising the waste containers is represented as hibbingite ($Fe_2Cl(OH)_3$); and 3) and the lead shielding is represented as hydrocerussite ($Pb_3(CO_3)_2(OH)_2$). Each of these four solid phases requires water (brine) to form. However, inflows and outflows of brine are not calculated in EQ3/6. Rather they are calculated in PA, within the BRAGFLO code. A one-way loose coupling between the two models is achieved by producing a table of solubilities in EQ3/6 from a minimum brine volume required for a release, or 1 DBR, increasing to a maximum of 5 DBR volumes with solubilities calculated at 1x, 2x, 3x, 4x, and 5x the minimum volume. That table is then used as a lookup table in PA to determine the solubilities based on the amount of brine in the repository at the time of a release.

The sources of this water for hydration of the model components in the repository may originate from water vapor in the closed repository, brine draining from the disturbed rock zone (DRZ), brine flow from the Salado Formation, and brine entering the repository from a Castile Formation and/or the Culebra member of the Rustler Formation via a borehole penetrating these formations. This is discussed further in Section PA-4.2 of Appendix PA (DOE, 2019).

3 RESULTS

The output from Step 2 consisted of EQ6 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_v101f.xls." was used to 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 × 33,804 m^3, the

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minimum brine volume required for a direct brine release (DBR) from the repository (King, 2021). Table 7 provides comparable information for ERDA-6. Brush et al. (2012, 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 carbon 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).

Tables 14 and 15 show the solid phase budgets for the minimum brine volume case (1x) for GWB and ERDA-6, respectively. The tables provide the initial and final masses (moles) on an EQ3/6 scale, for both the reactant and product phases, as well as their change in mass (moles) for each phase. Negative values of "Delta Mass" indicates dissolution, and positive values indicate precipitation.

Compared to the results of the CRA-2019 DPA (Domski and Sisk-Scott, 2019) the RPPCR had fewer product phase minerals for each brine type. For GWB the products included Phase 3, whewellite, and the An(V) solubility controlling phase $KNpO_2CO_3$ (Table 14), and for ERDA-6 which included whewellite, and the An(V) solubility controlling phase $KNpO_2CO_3$ (Table 15).

Note from Tables 14 and 15 that the stable An(III) phase is $AmOHCO_3(s)$ for both brine types, this was predicted by Domski (2022) when the amorphous americium hydroxide phase is used to set the An(III) concentration in Step 1 of the simulation, and the less soluble form [$Am(OH)_3(s)$] is suppressed. This point was discussed at the DOE technical exchange with the EPA at the October 25, 2022 meeting.

Table 16 and 17 compares the solubilities of Th(IV), Np(V), and Am(III) in GWB and ERDA-6, respectively, predicted for the minimum brine volume of 33,804 m^3 for the RPPA with those predicted for the CRA-2014 PA and the CRA-2019 PA. Table 14 and 15 also compares the values of f_{CO_2} and pH predicted for these compliance-related calculations.

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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)	0.185	0.185	0.185	0.185	0.185
Na(I)(aq)	4.40	4.41	4.41	4.41	4.41
Mg(II)(aq)	0.794	0.777	0.772	0.769	0.767
K(I)(aq)	0.548	0.547	0.547	0.547	0.547
Ca(II)(aq)	0.013	0.013	0.013	0.013	0.013
Fe(II)(aq)	5.37E-05	4.17E-05	3.77E-05	3.58E-05	3.46E-05
S(VI)(aq)	0.210	0.206	0.205	0.204	0.204
Cl(-I)(aq)	4.97	5.00	5.01	5.01	5.02
Br(-I)(aq)	0.0312	0.0312	0.0311	0.0311	0.0311
Pb(II)(aq)	1.14E-02	1.14E-02	1.14E-02	1.14E-02	1.14E-02
Th(IV)(aq)	5.34E-08	5.34E-08	5.34E-08	5.34E-08	5.34E-08
Np(V)(aq)	4.95E-07	4.21E-07	3.96E-07	3.84E-07	3.76E-07
Am(III)(aq)	3.40E-06	1.86E-06	1.33E-06	1.07E-06	9.09E-07
fCO_2 (atm)	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
Ionic Strength (m)	7.92	7.91	7.90	7.90	7.89
pH[B]	8.74	8.74	8.74	8.74	8.74
pcH	9.36	9.36	9.36	9.36	9.36
RH (%)[C]	73.14%	73.16%	73.17%	73.17%	73.17%
TIC[D]	2.32E-04	2.32E-04	2.32E-04	2.32E-04	2.32E-04

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Mass of Water (kg)	0.743	0.744	0.745	0.745	0.745

Footnotes for Table 6:

A. Based on a minimum brine volume of 33,804 (King, 2021)
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)	0.062	0.062	0.062	0.062	0.062
Na(I)(aq)	5.10	5.12	5.12	5.13	5.13
Mg(II)(aq)	0.387	0.367	0.361	0.358	0.356
K(I)(aq)	0.096	0.096	0.096	0.096	0.096
Ca(II)(aq)	0.013	0.013	0.013	0.013	0.013
Fe(II)(aq)	5.69E-05	4.02E-05	3.45E-05	3.16E-05	2.99E-05
S(VI)(aq)	0.174	0.171	0.170	0.170	0.169
Cl(-I)(aq)	5.03	5.05	5.05	5.06	5.06
Br(-I)(aq)	0.0109	0.0109	0.0109	0.0109	0.0109
Pb(II)(aq)	5.37E-03	5.21E-03	5.16E-03	5.13E-03	5.12E-03
Th(IV)(aq)	5.73E-08	5.74E-08	5.75E-08	5.75E-08	5.75E-08
Np(V)(aq)	1.80E-06	1.50E-06	1.41E-06	1.36E-06	1.33E-06
Am(III)(aq)	3.51E-06	1.93E-06	1.39E-06	1.13E-06	9.59E-07
f_{CO_2} (atm)	2.02E-06	2.02E-06	2.02E-06	2.02E-06	2.02E-06
Ionic Strength (m)	7.06	7.04	7.04	7.03	7.03
pH[B]	8.82	8.83	8.83	8.83	8.83
pcH	9.46	9.47	9.47	9.48	9.48
RH (%)[C]	74.46%	74.49%	74.50%	74.50%	74.51%
TIC[D]	2.47E-04	2.48E-04	2.48E-04	2.49E-04	2.49E-04

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Mass of Water (kg)	0.893	0.893	0.893	0.893	0.893

Footnotes for Table 7:

A. Based on a minimum brine volume of 33,804 m^3 (King, 2021)
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 ThO_2.

GWB, minimum volume			GWB, 5 × minimum volume		
Th(IV) Species	Concentration (M)	Percent of Solubility	Th(IV) Species	Concentration (M)	Percent of Solubility
$Th(OH)_4(aq)$	4.52E-08	84.72%	$Th(OH)_4(aq)$	4.52E-08	84.80%
$Th(OH)_3(CO_3)^-$	8.15E-09	15.28%	$Th(OH)_3(CO_3)^-$	8.11E-09	15.20%
ThEDTA(aq)	3.78E-17		$Th(CO_3)_5^{6-}$	1.52E-17	
$Th(CO_3)_5^{6-}$	1.87E-17		$Th(SO4)_3^{2-}$	1.15E-17	
$Th(SO4)_3^{2-}$	1.28E-17		ThEDTA(aq)	7.65E-18	
$Th(SO_4)_2(aq)$	3.23E-19		$Th(SO_4)_2(aq)$	2.95E-19	
$ThCitrate^+$	1.43E-19		$ThCitrate^+$	2.79E-20	
$Th(Acetate)_2^{2+}$	4.24E-20		$Th(Acetate)_2^{2+}$	1.61E-21	
$ThAcetate^{3+}$	8.04E-21		$ThAcetate^{3+}$	1.41E-21	
$ThOxalate^{2+}$	2.66E-22		$ThOxalate^{2+}$	2.39E-22	
Th^{4+}	7.63E-24		Th^{4+}	6.43E-24	
	5.34E-08	100.00%		5.34E-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 ThO_2.

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
$Th(OH)_4(aq)$	4.73E-08	82.61%	$Th(OH)_4(aq)$	4.74E-08	82.38%
$Th(OH)_3CO_3^-$	9.96E-09	17.39%	$Th(OH)_3CO_3^-$	1.01E-08	17.62%
ThEDTA(aq)	3.07E-17		ThEDTA(aq)	6.07E-18	
$Th(SO_4)_3^{2-}$	3.96E-18		$Th(SO_4)_3^{2-}$	3.24E-18	
$Th(CO_3)_5^{6-}$	1.82E-18		$Th(CO_3)_5^{6-}$	1.41E-18	
$ThCit^+$	1.82E-19		$Th(SO_4)_2(aq)$	6.07E-20	
$Th(SO_4)_2(aq)$	7.21E-20		$ThCit^+$	3.45E-20	
$ThAc_2^{2+}$	2.04E-20		$ThAc_2^{2+}$	7.60E-22	
$ThAc^{3+}$	2.52E-21		$ThAc^{3+}$	4.30E-22	
$ThOx^{2+}$	1.46E-22		$ThOx^{2+}$	1.23E-22	
Th^{4+}	2.29E-24		Th^{4+}	1.82E-24	
Total:	5.73E-08	100.00%	Total:	5.75E-08	100.00%

Tables 8 and 9 show that the most important aqueous species for Th(IV) is $Th(OH)_4(aq)$ at ~76%, and $Th(OH)_3CO_3^-$ ~24% by mass. The aqueous species formed with organic ligands are inconsequential with regard to the Th(IV) solubility.

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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 $KNpO_2CO_3$.

GWB, minimum volume			GWB, 5 × minimum volume		
Np(V) Species	Concentration (M)	Percent of Solubility	Np(V) Species	Concentration (M)	Percent of Solubility
NpO_2^+	1.95E-07	39.51%	NpO_2^+	1.95E-07	51.79%
$NpO_2Ac(aq)$	1.48E-07	29.93%	$NpO_2CO_3^-$	8.19E-08	21.77%
$NpO_2CO_3^-$	8.03E-08	16.23%	$NpO_2Oxalate^-$	6.34E-08	16.86%
$NpO_2Oxalate^-$	6.49E-08	13.12%	$NpO_2Ac(aq)$	3.04E-08	8.09%
$NpO_2OH(aq)$	5.02E-09	1.01%	$NpO_2OH(aq)$	5.15E-09	1.37%
$NpO_2Citrate^{2-}$	5.49E-10	0.11%	$NpO_2(CO_3)_2^{3-}$	3.64E-10	0.10%
$NpO_2(CO_3)_2^{3-}$	3.51E-10	0.07%	$NpO_2Citrate^{2-}$	1.09E-10	0.03%
$NpO_2(OH)_2^-$	7.92E-12		$NpO_2(OH)_2^-$	8.11E-12	
NpO_2EDTA^{3-}	2.86E-12		NpO_2EDTA^{3-}	5.62E-13	
$NpO_2(CO_3)_3^{5-}$	8.46E-14		$NpO_2(CO_3)_3^{5-}$	9.89E-14	
NpO_2HEDTA^{2-}	6.02E-15		NpO_2HEDTA^{2-}	1.22E-15	
$NpO_2H_2EDTA^-$	8.78E-19		$NpO_2H_2EDTA^-$	1.80E-19	
Total:	4.95E-07	100.00%	Total:	3.76E-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 $KNpO_2CO_3$.

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_2^+	6.20E-07	34.42%	NpO_2^+	5.88E-07	44.36%
$NpO_2Ac(aq)$	5.39E-07	29.89%	$NpO_2CO_3^-$	4.16E-07	31.35%
$NpO_2CO_3^-$	4.13E-07	22.94%	$NpO_2Oxalate^-$	1.89E-07	14.28%
$NpO_2Oxalate^-$	2.02E-07	11.22%	$NpO_2Ac(aq)$	1.08E-07	8.12%
$NpO_2(OH)(aq)$	2.18E-08	1.21%	$NpO_2(OH)(aq)$	2.16E-08	1.63%
NpO_2Cit^{2-}	2.87E-09	0.16%	$NpO_2(CO_3)_2^{3-}$	2.79E-09	0.21%
$NpO_2(CO_3)_2^{3-}$	2.67E-09	0.15%	NpO_2Cit^{2-}	5.66E-10	0.04%
$NpO_2(OH)_2^-$	4.09E-11		$NpO_2(OH)_2^-$	4.15E-11	
NpO_2EDTA^{3-}	6.20E-12		$NpO_2(CO_3)_3^{5-}$	2.01E-12	
$NpO_2(CO_3)_3^{5-}$	1.77E-12		NpO_2EDTA^{3-}	1.17E-12	
NpO_2HEDTA^{2-}	2.71E-14		NpO_2HEDTA^{2-}	5.35E-15	
$NpO_2H_2EDTA^-$	6.29E-18		$NpO_2H_2EDTA^-$	1.25E-18	
	1.80E-06	100.00%		1.33E-06	100.00%

The Np(V) speciation for GWB and ERDA-6 (Tables 10 and 11) is distributed over seven species with ~75% of the Np(V) distributed, more or less equally, between three species, NpO_2^+, $NpO_2CO_3^-$, and $NpO_2Ac(aq)$. A fourth species, $NpO_2Oxalate^-$, complexes with ~10% of the Np(V) and the remaining three species, $NpO_2(OH)(aq)$, $NpO_2(CO_3)_2^{3-}$, and NpO_2Cit^{2-}, account for ~1.5% or less of the totalNp(V).

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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 $Am(OH)_3$(am).

GWB, minimum volume			GWB, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$AmEDTA^-$	3.15E-06	92.47%	$AmEDTA^-$	6.43E-07	70.72%
$Am(OH)_2^+$	2.36E-07	6.95%	$Am(OH)_2^+$	2.53E-07	27.79%
$AmOH^{2+}$	8.51E-09	0.25%	$AmOH^{2+}$	8.50E-09	0.94%
$AmAc^{2+}$	5.96E-09	0.18%	$Am(OH)_3$(aq)	1.76E-09	0.19%
AmCit(aq)	2.02E-09	0.06%	$AmAc^{2+}$	1.21E-09	0.13%
$Am(OH)_3$(aq)	1.71E-09	0.05%	$AmCO_3^+$	8.20E-10	0.09%
$AmCO_3^+$	8.22E-10	0.02%	AmCit(aq)	4.21E-10	0.05%
$AmSO_4^+$	3.57E-10	0.01%	$AmSO_4^+$	3.48E-10	0.04%
$Am(CO_3)_2^-$	2.17E-10		$Am(CO_3)_2^-$	2.17E-10	0.02%
Am^{3+}	1.07E-10		Am^{3+}	1.05E-10	0.01%
$AmOx^+$	6.25E-11		$AmOx^+$	6.16E-11	
$Am(SO_4)_2^-$	6.13E-11		$Am(SO_4)_2^-$	5.76E-11	
$Am(CO_3)_3^{3-}$	3.46E-11		$Am(CO_3)_3^{3-}$	3.39E-11	
$AmCl^{2+}$	1.26E-11		$AmCl^{2+}$	1.17E-11	
$Am(CO_3)_4^{5-}$	1.11E-12		$Am(CO_3)_4^{5-}$	1.10E-12	

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 $Am(OH)_3$(am) (continued).

GWB, minimum volume			GWB, 5 × minimum volume		
Am(III) Species	Concentration (M)	Percent of Solubility	Am(III) Species	Concentration (M)	Percent of Solubility
$AmCl_2^+$	6.69E-13		$AmCl_2^+$	6.23E-13	
Total:	3.40E-06	100.00%	Total:	9.09E-07	100.00%

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 $Am(OH)_3$(am).

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
$AmEDTA^-$	3.22E-06	91.64%	$AmEDTA^-$	6.59E-07	68.70%
$Am(OH)_2^+$	2.81E-07	8.01%	$Am(OH)_2^+$	2.91E-07	30.37%
$AmOH^{2+}$	5.15E-09	0.15%	$AmOH^{2+}$	4.92E-09	0.51%
$AmAc^{2+}$	2.25E-09	0.06%	$Am(OH)_3$(aq)	2.00E-09	0.21%
$Am(OH)_3$(aq)	1.94E-09	0.06%	$AmCO_3^+$	6.48E-10	0.07%
AmCit(aq)	1.73E-09	0.05%	$AmAc^{2+}$	4.35E-10	0.05%

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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
$AmCO_3^+$	6.65E-10	0.02%	AmCit(aq)	3.48E-10	0.04%
$Am(CO_3)_2^-$	2.85E-10		$Am(CO_3)_2^-$	2.92E-10	0.03%
$AmSO_4^+$	1.49E-10		$AmSO_4^+$	1.36E-10	0.01%
Am^{3+}	5.19E-11		Am^{3+}	4.80E-11	
$AmOx^+$	3.84E-11		$AmOx^+$	3.53E-11	
$Am(CO_3)_3^{3-}$	3.19E-11		$Am(CO_3)_3^{3-}$	3.25E-11	
$Am(SO_4)_2^-$	1.89E-11		$Am(SO_4)_2^-$	1.67E-11	
$AmCl^{2+}$	3.85E-12		$AmCl^{2+}$	3.39E-12	
$Am(CO_3)_4^{5-}$	1.78E-13		$Am(CO_3)_4^{5-}$	1.67E-13	
$AmCl_2^+$	1.64E-13		$AmCl_2^+$	1.42E-13	
Total:	3.51E-06	100.00%	Total	9.59E-07	100.00%

The Am(III) speciation for GWB and ERDA-6 are shown in Tables 12 and 13. The most important Am(III) species is $AmEDTA^-$ followed by second hydrolysis species $Am(OH)_2^+$. The 5 x minimum value case shows that as the EDTA budget decreases the Am(III) concentration decreases by a factor of ~10. This value may reflect the limiting Am(III) concentration for WIPP conditions for situations where the EDTA concentration is limited by dilution, or complexed with other metals, such as iron (see Appendix A).

Table 14. Solid budgets for the reactant and product phases at the initiation of Step 2 and for the final equilibrium for GWB brine with the repository solids. Note: Positive values of delta mass indicate precipitation, and negative indicate dissolution.

Phase	Initial Mass (moles)	Final Mass (moles)	Delta Mass (moles)
Halite	3520.50[a]	3519.80	-0.70

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Phase	Initial Mass (moles)	Final Mass (moles)	Delta Mass (moles)
Anhydrite	168.00	168.00	0.00
Brucite	23.00	20.12	-2.88
Hydromagnesite5424	4.59	4.50	-0.09
Hibbingite	12.80	12.80	0.00
Hydrocerussite	4.58E-01	4.55E-01	-3.23E-03
$AmOHCO_3(c)$	1.60E-02	3.81E-01	3.65E-01
$ThO_2(s)$	2.82E-08	3.52E-08	7.01E-09
KNpO2CO3	0.00	1.09E-05	1.09E-05
Phase 3	0.00	1.84	1.84
Whewellite	0.00	4.69E-03	4.69E-03

a – The initial mass of halite is greater than that specified in Table 5 because halite was supersaturated in Step 1 and was precipitated at the start of Step 2.

Table 15. Solid budgets for the reactant and product phases at the initiation of Step 2 and for the final equilibrium for ERDA-6 brine with the repository solids. Note: Positive values of delta mass indicate precipitation, and negative indicate dissolution.

Phase	Initial Mass (moles)	Final Mass (moles)	Delta Mass (moles)
Halite	3440.00	3439.70	-0.30
Anhydrite	164.00	163.99	-0.01
Brucite	22.50	22.42	-0.08
Hydromagnesite5424	4.49	4.43	-0.06
Hibbingite	12.50	12.50	0.00
Hydrocerussite	0.45	0.45	0.00
$AmOHCO_3(c)$	1.60E-02	2.54E-01	2.38E-01

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Phase	Initial Mass (moles)	Final Mass (moles)	Delta Mass (moles)
$ThO_2(s)$	5.97E-09	6.20E-08	5.60E-08
$KNpO_2CO_3$	0.00	2.03E-05	2.03E-05
Whewellite	0.00	5.16E-03	5.16E-03

The solids inventories for GWB and ERDA-6 show that the stable An(III) phase was $AmOHCO_3(c)$, and not $Am(OH)_3(am)$ which was used in Step 1 to set the An(III) concentration. Domski (2022) showed that at the expected WIPP conditions, water activity and $fCO_2(g)$, the americium hydroxy carbonate phase, $AmOHCO_3(c)$, would be stable and not the amorphous hydroxide phase. Additionally, Phase 3 was stable in the GWB equilibrium mineral assemblage and absent from the ERDA-6 assemblage. The higher initial magnesium concentration (Table 3) leads to the formation of Phase 3 in GWB.

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Table 16. Comparison of GWB Actinide Solubilities (M), f_{CO_2} (atm), and pH (Pitzer scale) from the CRA-2014 PA, CRA-2019 DPA, and RPPCR.

Property or Actinide Oxidation State	CRA-2014 PA ($GWB_{min. vol.}$, Hydromagnesite, with Organics, All Vectors)[A]	CRA-2019 ($GWB_{min. vol.,}$, Hydromagnesite, with Organics, Pb, Fe All Vectors)[B]	RPPCR ($GWB_{min. vol.,}$, Hydromagnesite, with Organics, Pb, Fe All Vectors)[C]
Th(IV)	6.05E-08	5.45E-08	5.34E-08
Np(V)	2.77E-07	4.02E-07	4.95E-07
Am(III)	2.59E-06	1.63 E-07	3.40E-06
f_{CO_2}	3.14E-06	2.02E-06	2.02E-06
pH	8.82	8.82	8.74

A. Brush and Domski (2013)
B. Domski and Sisk-Scott (2019)
C. This Study

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Table 17. Comparison of ERDA-6 Actinide Solubilities (M), f_{CO_2} (atm), and pH (Pitzer scale) from the CRA-2014 PA, CRA-2019 DPA, and RPPCR.

Property or Actinide Oxidation State	CRA-2014 PA (ERDA-$6_{min. vol.}$, Hydromagnesite, with Organics, All Vectors)[A]	CRA-2019 (ERDA-$6_{min. vol.,}$, Hydromagnesite, Pb, Fe with Organics, All Vectors)[B]	RPPCR (ERDA-$6_{min. vol.,}$, Hydromagnesite, with Organics, Pb, Fe All Vectors)[C]
Th(IV)	7.02E-08	5.44E-08	5.73E-08
Np(V)	8.76E-07	1.20E-06	1.80E-06
Am(III)	1.48E-06	1.78E-07	3.51E-06
f_{CO_2}	3.14E-06	2.02E-06	2.02E-06
pH	8.99	8.82	8.82

A. Brush and Domski (2013)
B. Domski and Sisk-Scott (2019)
C. This Study

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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 Replacement Panels 19-Panel 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.

The RPPCR baseline solubility model differs from the CRA-2019 DPA baseline solubility model in four ways: 1) The thermodynamic database DATA0.FM6 (Domski, 2023a) was used rather than DATA0.FM4. DATA0.FM6 includes updates to the iron model, a new Pitzer based lead model, inclusion of an amorphous Am – hydroxide phase, updates to the Mag – Oxalate system, and inclusion Earlandite (Domski, 2023a); 2) The RPPCR is based on a new 19-panel repository geometry, which increased the direct brine release volume which affects the scaling of the reactants used in the solubility model (King, 2021); 3) A new inventory was issued for the RPPCR (Van Soest, 2022) which provides updated inventories for the reactants used in the solubility model; and 4) updated model assumptions with regard to calcite precipitation, Phase 5 precipitation, and scaling of the reactants.

Tables 6 and 7 (see Section 3 above) provide the equilibrium 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).

Tables 16 and 17 (Section 3) compare the solubilities of Th(IV), Np(V), and Am(III) predicted for the minimum brine volume of 33,804 m^3 from this study compared with those predicted for the CRA-2014 PA and CRA-2019 DPA. Tables 14 and 15 also compare the values of f_{CO_2} and pH predicted for these compliance-related calculations.

The dissolved An(IV) and An(V) concentrations for the RPPCR are nearly identical to the those for the CRA-2019 DPA and the CRA-2014 PA (Tables 16 and 17). The reason for is the An(IV) and An(V) thermodynamic models contained in the databases used for these analyses have not changed compared to those included in DATA0.FM6. The An(III) concentrations calculated for the RPPCR increased significantly compared to the CRA-2019 DPA while they were nearly identical to those calculated for the CRA-2014 PA. Here again, the An(III) model used in the CRA-2019 DPA was a significant deviation, in terms of the parameterization of aqueous species that most affect actinide solubilities, from that used in the RPPCR and the CRA-2014 PA.

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APPENDIX A. The Effect of Iron EDTA Aqueous Species on Actinide Solubility

EQ3/6 simulations for the minimum volume cases for GWB and ERDA-6 were completed in which the aqueous species $FeEDTA^{2-}$ was allowed to form. These results are compared to the RPPCR results, presented in this report, where $FeEDTA^{2-}$ was suppressed.

Table A-1. Comparison of the GWB baseline solubility minimum brine volume case results with the equivalent case which includes the formation of the $FeEDTA^{2-}$ aqueous complex.

Property	$FeEDTA^{2-}$ Suppressed[1]	$FeEDTA^{2-}$ Allowed
Pitzer pH	8.74	8.74
pcH	9.36	9.36
a(w)	0.73	0.73
Ionic Strength (m)	7.92	7.92
Mass of Water (kg)	0.743	0.743
Am(III)(aq) (M)	3.40E-06	2.60E-07
Np(V)(aq) (M)	4.95E-07	4.95E-07
Th(IV)(aq) (M)	5.34E-08	5.34E-08
Fe(II)(aq) (M)	5.37E-05	1.03E-04

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Table A-2. Comparison of the GWB baseline solubility minimum brine volume results with Fe - EDTA aqueous species suppressed to the equivalent case which allows the formation of the $FeEDTA^{2-}$ aqueous complex.

$FeEDTA^{2-}$ Suppressed[1]			$FeEDTA^{2-}$ Allowed		
Species	Molarity	Percentage	Species	Molarity	Percentage
$MgEDTA^{2-}$	4.60E-05	92.85%	$FeEDTA^{2-}$	4.94E-05	99.87%
$AmEDTA^{-}$	3.15E-06	6.35%	$MgEDTA^{2-}$	6.09E-08	0.12%
$CaEDTA^{2-}$	3.95E-07	0.80%	$AmEDTA^{-}$	4.17E-09	0.01%
$EDTA^{4-}$	2.28E-10		$CaEDTA^{2-}$	5.23E-10	
$HEDTA^{3-}$	3.75E-11		$EDTA^{4-}$	3.02E-13	
NpO_2EDTA^{3-}	2.86E-12		$HEDTA^{3-}$	4.96E-14	
H_2EDTA^{2-}	5.47E-14		NpO_2EDTA^{3-}	3.78E-15	
NpO_2HEDTA^{2-}	6.02E-15		H_2EDTA^{2-}	7.24E-17	
ThEDTA(aq)	3.78E-17		NpO_2HEDTA^{2-}	7.97E-18	
$NpO_2H_2EDTA^{2-}$	8.78E-19		ThEDTA(aq)	5.01E-20	
H_3EDTA^{-}	5.42E-21		$NpO_2H_2EDTA^{2-}$	1.16E-21	
H_4EDTA(aq)	7.06E-28		H_3EDTA^{-}	7.18E-24	
$FeEDTA^{2-}$	NA		H_4EDTA(aq)	9.35E-31	
	Total:	100.00%		Total:	100.00%

1 – Baseline Solubility

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Table A-3. Comparison of the ERDA-6 baseline solubility minimum brine volume case results with the equivalent case which includes the formation of the $FeEDTA^{2-}$ aqueous complex.

Property	$FeEDTA^{2-}$ Suppressed[1]	$FeEDTA^{2-}$ Allowed
Pitzer pH	8.82	8.82
pcH	9.46	9.46
a(w)	0.74	0.74
Ionic Strength (m)	7.06	7.06
Mass of Water (kg)	0.893	0.893
Am(III)(aq) (M)	3.51E-06	2.96E-07
Np(V)(aq) (M)	1.80E-06	1.80E-06
Th(IV)(aq) (M)	5.73E-08	5.73E-08
Fe(II)(aq) (M)	5.69E-05	9.85E-05

1 – Baseline Solubility

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Table A-4. . Comparison of the ERDA-6 baseline solubility minimum brine volume results with Fe - EDTA aqueous species suppressed to the equivalent case which allows the formation of the $FeEDTA^{2-}$ aqueous complex.

$FeEDTA^{2-}$ Suppressed[1]			$FeEDTA^{2-}$ Allowed		
Species	Molarity	Percentage	Species	Molarity	Percentage
$MgEDTA^{2-}$	3.77E-05	90.60%	$FeEDTA^{2-}$	4.16E-05	99.92%
$AmEDTA^{-}$	3.22E-06	7.73%	$MgEDTA^{2-}$	3.12E-08	0.07%
$CaEDTA^{2-}$	6.97E-07	1.67%	$AmEDTA^{-}$	2.66E-09	0.01%
$EDTA^{4-}$	7.36E-11		$CaEDTA^{2-}$	5.76E-10	
$HEDTA^{3-}$	2.18E-11		$EDTA^{4-}$	6.08E-14	
NpO_2EDTA^{3-}	6.20E-12		$HEDTA^{3-}$	1.80E-14	
H_2EDTA^{2-}	5.56E-14		NpO_2EDTA^{3-}	5.12E-15	
NpO_2HEDTA^{2-}	2.71E-14		H_2EDTA^{2-}	4.59E-17	
ThEDTA(aq)	3.07E-17		NpO_2HEDTA^{2-}	2.24E-17	
$NpO_2H_2EDTA^{2-}$	6.29E-18		ThEDTA(aq)	2.54E-20	
H_3EDTA^{-}	6.04E-21		$NpO_2H_2EDTA^{2-}$	5.20E-21	
H_4EDTA(aq)	5.97E-28		H_3EDTA^{-}	5.00E-24	
$FeEDTA^{2-}$	NA		H_4EDTA(aq)	4.94E-31	
	Total:	100.00%		Total:	100.00%

1 – Baseline Solubility

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Results

The simulation results (Tables A-1 and A-3) reveal that for both GWB and ERDA-6 allowing the Iron – EDTA aqueous complex, $FeEDTA^{2-}$ to form results in decrease of the An(III) solubility by greater than a factor of ten. The EDTA speciation data presented in Tables A-2 and A-4 clearly show that when allowed to form $FeEDTA^{2-}$ sequesters ~99.9% of the EDTA which would otherwise be available to form complexes with other cationic species, and thus causing the An(III) solubility to decrease. By allowing $FeEDTA^{2-}$ to form the solubility of Fe^{2+} increase by about a factor of two.

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APPENDIX B. The Effect of Iron Citrate Aqueous Species on Actinide Solubility

The baseline solubility calculations presented in this report include the Fe – Citrate species $FeCitrate^-$ and $FeOHCitrate^{2-}$, both of which are new for the RPPCR. To examine their impact on actinide solubilities EQ3/6 simulations, for the minimum volume cases for GWB and ERDA-6, were completed in which these aqueous species were suppressed, and the results are presented in this appendix.

Table B-1. Comparison of the GWB baseline solubility minimum brine volume case results with the equivalent case with the Fe - Citrate aqueous complexes suppressed.

Property	Fe – Citrate Species Allowed[1]	Fe – Citrate Species Suppressed
Pitzer pH	8.74	8.74
pcH	9.36	9.36
a(w)	0.731	0.731
Ionic Strength (m)	7.923	7.923
Mass of Water (kg)	0.743	0.743
Am(III)(aq) (M)	3.40E-06	3.40E-06
Np(V)(aq) (M)	4.95E-07	4.95E-07
Th(IV)(aq) (M)	5.34E-08	5.34E-08
Fe(II)(aq) (M)	5.37E-05	3.00E-05

1 – Baseline Solubility

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Table B-2. Comparison of the GWB baseline solubility minimum brine volume case which includes Fe - Citrate aqueous species results with the equivalent case with the Fe - Citrate aqueous complexes suppressed.

	Fe – Citrate Species Allowed[1]			Fe – Citrate Species Suppressed	
Species	Molarity	Percentage	Species	Molarity	Percentage
$MgCitrate^-$	2.02E-03	96.12%	$MgCitrate^-$	2.04E-03	97.21%
$Citrate^{3-}$	4.05E-05	1.93%	$Citrate^{3-}$	4.09E-05	1.95%
$FeOHCitrate^{2-}$	2.37E-05	1.13%	$CaCitrate^-$	1.76E-05	0.84%
$CaCitrate^-$	1.74E-05	0.83%	AmCitrate(aq)	2.04E-09	
$FeCitrate^-$	5.46E-08		$HCitrate^{2-}$	1.52E-09	
AmCitrate(aq)	2.02E-09		$NpO2Citrate^{2-}$	5.55E-10	
$HCitrate^{2-}$	1.50E-09		$H_2Citrate^-$	1.00E-14	
$NpO2Citrate^{2-}$	5.49E-10		$ThCitrate^+$	1.44E-19	
$H_2Citrate^-$	9.93E-15		$H_3Citrate$(aq)	4.00E-21	
$ThCitrate^+$	1.43E-19		$FeCitrate^-$	NA	
$H_3Citrate$(aq)	3.96E-21		$FeOHCitrate^{2-}$	NA	
	Total:	100.00%		Total:	100.00%

1 – Baseline Solubility

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Table B-3. Comparison of the ERDA-6 baseline solubility minimum brine volume case results with the equivalent case with the Fe - Citrate aqueous complexes suppressed.

Property	Fe – Citrate Species Allowed[1]	Fe – Citrate Species Suppressed
Pitzer pH	8.82	8.82
pcH	9.46	9.46
a(w)	0.74	0.74
Ionic Strength (m)	7.06	7.06
Mass of Water (kg)	8.93E-01	8.93E-01
Am(III)(aq) (M)	3.51E-06	3.51E-06
Np(V)(aq) (M)	1.80E-06	1.80E-06
Th(IV)(aq) (M)	5.73E-08	5.73E-08
Fe(II)(aq) (M)	5.69E-05	2.36E-05

1 – Baseline Solubility

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Table B-4. Comparison of the ERDA-6 baseline solubility minimum brine volume case which includes Fe - Citrate aqueous species results with the equivalent case with the Fe - Citrate aqueous complexes suppressed.

	Fe – Citrate Species Allowed[1]			Fe – Citrate Species Suppressed	
Species	Molarity	Percentage	Species	Molarity	Percentage
$MgCitrate^-$	1.67E-03	94.61%	$MgCitrate^-$	1.70E-03	96.43%
$FeOHCitrate^{2-}$	3.33E-05	1.88%	$Citrate^{3-}$	3.16E-05	1.79%
$Citrate^{3-}$	3.10E-05	1.76%	$CaCitrate^-$	3.15E-05	1.78%
$CaCitrate^-$	3.09E-05	1.75%	$NpO_2Citrate^{2-}$	2.92E-09	
$FeCitrate^-$	6.60E-08		AmCitrate(aq)	1.76E-09	
$NpO_2Citrate^{2-}$	2.87E-09		$HCitrate^{2-}$	1.55E-09	
AmCitrate(aq)	1.73E-09		$H_2Citrate^-$	1.06E-14	
$HCitrate^{2-}$	1.52E-09		$ThCitrate^+$	1.86E-19	
$H_2Citrate^-$	1.04E-14		$H_3Citrate(aq)$	3.50E-21	
$ThCitrate^+$	1.82E-19		$FeCitrate^-$	NA	
$H_3Citrate(aq)$	3.43E-21		$FeOHCitrate^{2-}$	NA	
	Total:	100.00%		Total:	100.00%

1 – Baseline Solubility

Results

The actinide solubility results presented in Tables B-1 and B-3 show that the Fe – Citrate aqueous complexes did not change the actinide concentrations. The reason for this, as the speciation data in Tables B-2 and B-4 show, is that none of the actinides form strong complexes

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with citrate. Rather the citrate complex with magnesium, $MgCitrate^-$, is the dominant citrate species regardless if the Fe – Citrate species are allowed to form or not.

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