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Sandia National Laboratories
Waste Isolation Pilot Plant

Uncertainty Analysis of Actinide Solubilities for the WIPP CRA-2014 PA

Work Carried Out under Task 4 of the Analysis Plan for WIPP Near-Field
Geochemical Process Modeling, AP 153, Rev. 1.
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1 INTRODUCTION

This analysis report provides the results of the new uncertainty analysis of the solubilities of Th(IV) and Am(III). 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 Waste Isolation Pilot Plant (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 element and WIPP brine under expected near-field chemical conditions. However, PA codes actually use actinide solubilities that are the products of the baseline solubilities and sampled uncertainty factors that describe possible deviations of the predicted Th(IV) and Am(III) solubilities from experimentally measured solubilities. The reason for using these uncertainty factors is to adjust the baseline solubilities up if the model underpredicts the experimentally measured solubilities, or to adjust the baseline solubilities down if the model overpredicts the measured solubilities. The baseline solubilities have been established in a separate analysis (Brush and Domski, 2013).

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

Furthermore, this analysis does not include Np(V) because PA does not sample the uncertainties in the solubilities of Np in view of the fact that releases of this element do not affect the long-term performance of the WIPP (Brush and Garner, 2005).

SNL PA personnel will use the results of this uncertainty analysis in the PA for the third recertification of the WIPP by the U.S. Environmental Protection Agency (EPA) (the 2014 Compliance Recertification Application, or CRA-2014 PA). Brush et al. (2005) describe the PA implementation of these results in detail.

We used EQ3/6, Version 8.0a, (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b) and the thermodynamic database (DB) DATA0.FMT.R2, also known as DATA0.FM1, (Xiong, 2011a) for this analysis. Wolery (2008), Wolery et al. (2010) and Xiong (2011b) completed the qualification of Version 8.0a of EQ3/6 according to Sandia National Laboratories' (SNL's) WIPP quality assurance (QA) procedures for WIPP compliance-related actinide-solubility calculations.

We carried out this analysis under Task 4 of AP-153, Rev. 1, the current analysis plan (AP) for WIPP near-field geochemical process modeling (Brush et al., 2012, Subsection 4.4). AP-153, Rev. 1, describes the modeling to be carried out from the completion of the Performance Assessment Baseline Calculations (PABC) for the second WIPP Compliance Recertification Application (CRA-2009-PABC) through the CRA-2014 PABC, if the EPA requires another PABC.

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

Table 1. Abbreviations, Acronyms, Initialisms, etc.

Abbreviation, Acronym, or Initialism	Definition
Am, Am(III)	americium, americium in the +III oxidation state
am	amorphous
AP	analysis plan
aq	aqueous (dissolved in an aqueous solution)
atm	atmosphere(s)
C, c	carbon, crystalline
Ca, Ca^{2+}	calcium, calcium ion
CAP	(SNL/WIPP QA) corrective action plan
CAR	(SNL/WIPP QA) corrective action request
CDF	cumulative distribution function
citrate	$(CH_2COO)_2C(OH)(COO)^{3-}$ or $(CH_2CO_2)_2C(OH)(CO_2)^{3-}$
Cl, Cl^-	chloride, chloride ion
ClO_4, ClO_4^-	perchlorate, perchlorate ion
Cm, Cm(III)	curium, curium in the +III oxidation state
CMS	(Sandia/WIPP software) Configuration Management System
CO_3, CO_3^{2-}	carbonate, carbonate ion
col	colloidal (suspended in an aqueous or other solution)
cr	crystalline
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
D	the difference(s) between logs (base 10) of the measured and predicted actinide solubilities (Sm and Sp)
EPA	(U.S.) Environmental Protection Agency

Table 1 continued on next page

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

Abbreviation, Acronym, or Initialism	Definition
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
f_{CO_2}	fugacity (similar to the partial pressure) of CO2
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
G-Seep	a naturally-occurring brine formerly collected from G Drift in the WIPP underground workings and used for laboratory and modeling studies
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines
H, H^+	hydrogen, hydrogen ion
HCO_3, HCO_3^-	bicarbonate, bicarbonate ion
H_2O	water
I	ionic strength, defined by $I = ½ \times \Sigma_i(M_i \times z_i^2)$, in which M_i and z_i are the molarity and charge of species i
I/O	(EQ3/6) input and output files
K, K^+	potassium, potassium ion
LIB	Library
log	the common logarithm or logarithm (base 10)
M	molar
m	molal
mcr	microcrystalline
Mg, Mg^{2+}	magnesium, magnesium ion
mM	millimolar
N	bin number (see Subsection 5.2 for explanation)
Na, Na^+	sodium, sodium ion
NaTr	sodium trifluoromethanesulfonate (also abbreviated as sodium triflate)
Nd, Nd(III)	neodymium, neodymium in the +III oxidation state
NO_3, NO_3^-	nitrate, nitrate ion
Np, Np(IV), Np(V)	neptunium, neptunium in the +IV oxidation state , neptunium in the +V oxidation state
O	oxygen
OH, OH^-	hydroxide, hydroxide ion
P	probability
PA	performance assessment

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

Abbreviation, Acronym, or Initialism	Definition
PABC	(WIPP) Performance Assessment Baseline Calculations, carried out in 2005 and 2009
pcH	the negative log (base 10) of the molar concentration of H^+
p_{CO_2}	partial pressure (similar to the fugacity) of CO_2
pmH	the negative log (base 10) of the molal concentration of H^+
ppm	parts per million
pH	the negative log (base 10) of the activity of H^+
Pu, Pu(III), Pu(IV)	plutonium, plutonium in the +III oxidation state, plutonium in the +VI oxidation state
QA	quality assurance
R	gas constant
Rev.	Revision
S_m	measured solubility
S_p	predicted solubility
SNL	Sandia National Laboratories
SO_4, SO_4^{2-}	sulfate, sulfate ion
T	temperature
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C (the sum of the dissolved species of inorganic C)
U, U(IV), U(VI)	uranium, uranium in the +IV oxidation state, uranium in the +VI oxidation state
μm	micrometer
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction
Zr, Zr(IV)	zirconium, zirconium in the +IV oxidation state
μ^0, μ^0/RT	standard chemical potential, dimensionless standard chemical potential

2 METHODS

The methods used for this analysis are similar to those used by Xiong et al. (2005, 2010, 2011). We compared experimentally measured solubilities of Th(IV), Nd(III), and Am(III) with the Th(IV) and Am(III) solubilities predicted using EQ3/6, Version 8.0a, (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b) and the thermodynamic DB DATA0.FM1 (Xiong, 2011a). We used EQ3/6, Version 8.0a, and DATA0.FM1 to recalculate all of the previous comparisons by Xiong et al. (2005, 2010, and 2011) using FMT (Babb and Novak, 1997 and addenda; Wang, 1998). We then constructed histograms and cumulative distribution functions (CDFs) of the differences between the logarithms (base 10) of the measured and predicted solubilities. We constructed separate histograms and CDFs for the Th(IV) and Am(III) models. These CDFs will be used for the CRA-2014 PA.

We established ten general criteria for including results of experimentally measured solubilities in our comparisons of measured Th(IV), Nd(III), Am(III), and Cm(III) solubilities and predicted Th(IV) and Am(III) solubilities. The general criteria are:

G1. Include only results from experimental studies published from January 1, 1990, through October 31, 2011. We deviated from this criterion by including the results of Borkowski et al. (2012) and Borkowski (2012). We included these results because we were directed to do so by our management.

G2. Include results from both papers published in peer-reviewed journals and unpublished reports (e.g., officially released reports from government laboratories such as Los Alamos National Laboratory, Lawrence Livermore National Laboratory, Pacific Northwest National Laboratory, etc.).

G3. Include only results from solubility studies. Exclude other studies that do not provide solubilities (e.g., studies of corrosion, leaching, sorption, or transport).

G4. Include only results from studies in which water was the solvent. Exclude studies in which other solvents were used (e.g., solids, molten metal or salts, or organic liquids).

G5. Include only results obtained from studies at pressures at or close to atmospheric, at temperatures at or close to those expected in the WIPP (i.e., 20-30 °C), and with posttest phase-separation methods similar to those used for the WIPP, because these were the conditions and methods used to parameterize the Th(IV) and Am(III) speciation and solubility models for WIPP compliance-related PA calculations.

G6. Include only results from studies of Th(IV); and Nd(III), Am(III), and Cm(III); because these are the elements used to parameterize the WIPP Th(IV) and Am(III) solubility models. Exclude studies of U(IV), Np(IV), and Pu(IV);

and Pu(III) because there could be systematic differences between the solubilities of these elements and those of their oxidation-state analogs used to parameterize the models; and because the difficulties inherent in maintaining these elements in these oxidation states could introduce experimental artifacts in the results obtained with these elements.

G7. Include only results from studies with a characterized solubility-controlling solid for which the value of the dimensionless standard chemical potential (μ^0/RT) is in the WIPP Th(IV) or Am(III) model (i.e., in the EPA-certified thermodynamic database), and in which the quantity of solid initially present was sufficient to prevent complete dissolution of this solid during the experiments.

G8. Include only results from studies with aqueous solutions of known composition. Exclude studies performed with groundwaters, sedimentary pore waters, and soil solutions that may contain unknown quantities of species that can be complexants or adsorbents (e.g., humic acids or other dissolved organic compounds, microbial colloids, or pseudocolloids).

G9. Include only results from studies with dissolved elements or species for which values of μ^0/RT and Pitzer ion-interaction parameters are in our models. Exclude studies with dissolved elements or species for which our models do not include values of μ^0/RT or Pitzer parameters.

G10. Include only results from studies for which the investigators provided a complete description of their experiments and the original solubilities. Exclude literature reviews and summaries, and studies in which the authors only provided average dissolved concentrations or solubility products, thus necessitating back-calculation of the solubilities.

We also continued to use the specific criterion established by Xiong et al. (2005) for the experimentally measured solubilities of Th(IV):

S1. Include only results from experiments carried out with solutions with ionic strength (I) $\geq$ 3 M or m.

Xiong et al. (2005, Subsection 5.2.3) described the reason for establishing S1.

Xiong et al. (2005, 2010, 2011) did not establish any specific criteria for experimentally measured solubilities of Nd(III), Am(III), or Cm(III). Furthermore, we did not establish any additional specific criteria for this comparison.

Domski carried out a literature search for published papers and unpublished reports on laboratory studies of Th(IV), Nd(III), Am(III), and Cm(III) solubilities. He used Search Plus, Version 2.4, operated by Los Alamos National Laboratory (LANL), Web of Science (including Science Citation Index and INSPEC), and the DOE Energy Citations Database.

This literature search identified hundreds of papers and reports on actinide chemistry. Therefore, Domski conducted preliminary evaluations of these studies by applying the criteria described above to the information provided in the abstracts of these papers and reports. Because of the large number of papers and reports identified, it was not practical to document which criteria were used to include these studies in or exclude them from the final evaluations described below. Domski excluded all papers and reports that, in his judgment, obviously failed to meet the criteria. In those cases in which it was not obvious that a paper or report should be included or excluded, Domski retained them for the final evaluations. Both Brush and Domski performed the final evaluations of the laboratory studies of actinide solubilities for this analysis.

Most of the newly acquired papers and reports did not include data tables. Therefore, we attempted to obtain numerical values for all of the experimentally measured solubilities included in this analysis, as well as the parameters required to predict these solubilities with EQ3/6. This was possible in some, but not all cases. Therefore, Domski used the open source program Engauge Digitizer (http://digitizer.sourceforge.net/) to obtain numerical values of experimental variables such as pcH or pmH, and the resulting solubilities, from the figures in the papers and reports.

Domski then set up EQ3/6 input files to predict the solubilities of Th(IV), Nd(III), and Am(III) for the conditions reported for each of the measured solubilities in the laboratory studies selected by the final evaluations. Simulations for most of the experimental data were performed using the EQ3NR code. In these runs, the pH was specified; the composition of the supporting solution was used as input, either in molar or molal units; and the radionuclide composition was calculated based on equilibrium with the solubility-controlling phase in the experiment. However, in some cases it was necessary to use both EQ3NR and EQ6 to simulate more complex experiments. In these cases, the experiments were conducted with a carbon dioxide (CO_2) atmosphere, and/or they were titrated to specific values of pH values at which the solubility measurements were made.

In many of the experiments, ionic concentrations are reported in units of moles per liter, or molarity (M); and the hydrogen ion (H^+) content of the solutions was measured in terms of the molar concentration of H^+, also known as the pcH. When using these data in EQ3/6, which uses the mass-based unit moles per kg, or molality (m); and the negative log of the hydrogen ion activity (pH), additional steps were required.

In instances in which the ionic strength is high and data are reported in molarity, it is necessary to input the following EQ3 input parameters: total dissolved solids (tdspl), solution density (rho), and the aqueous-phase scale factor (scamas). These parameters are calculated based on the fluid composition in the MS-Excel spreadsheet "Conc_density_calcs_brines.xls." This spreadsheet will be stored in the CMS in class ANALYSIS of library LIBPABC09_FMT. to the SNL/WIPP Records Center.

For those experiments that measured the pcH, a two-step approach was used to match the measured pcH. To arrive at the measured value of pcH, an initial EQ3/6 run was performed in which the input pH was referred to as pH_{init}. This resulted in an output value of pcH referred to as pcH_{init}. The difference between pcH_{init} and the measured value pcH_{exp}

was then calculated and used to calculate a new pH_{init}, and a second EQ3/6 run was performed to obtain a simulated pcH equal to pcH_{exp}.

Table 2 provides the location and run-control information for the thermodynamic database, Excel spreadsheets, and EQ3/6 I/O files for these calculations.

Table 2. Run-Control Information for the Calculations Carried Out for This Analysis.

Description or Title of File(s)	Location of File(s)
EQ3/6 DB DATA0.FMT.R2 also called DATA0.FM1	In zip file DATA0_FMT.ZIP, library LIBEQ36, class DATABASES
Excel macro GetEQData.xls	In zip file EQ36_IO_files.zip, library LIBEQ36, class AP153
EQ3/6 I/O files and Excel spreadsheets with input and extracted data	In zip file EQ36_IO_files.zip, library LIBEQ36, class AP153

Finally, Domski generated frequency distributions of differences (D) between the logs of the measured and predicted actinide solubilities (S_m and S_p, respectively) and displayed them in histograms and tables Microsoft Excel spreadsheets using Excel's "histogram" data analysis tool in this commercial spreadsheet software. Negative values of D indicate that the Th(IV) or Am(III) model implemented in EQ3/6 predicted a solubility greater than the corresponding measured value (overprediction of solubility by the model); positive values of D indicate that the model predicted a solubility less than the measured value (underprediction). The Excel files "Thorium_Uncertainty_Results_2014_PA.xls" and "Americium_Uncertainty_Results_2014_PA .xls" contain spreadsheets with S_m or S_p values (or logs thereof), frequency distributions, and histograms for this analysis. The bin numbers (N) in the histograms are defined as follows:

> Bin N contains values of D greater than $N - 0.15$ and less than or equal to N, where $D = \log_{10}(S_m) - \log_{10}(S_p)$.
>
> Examples of the definitions of bins follow:
>
> Bin -0.3 contains values of D greater than –0.45 and less than or equal to –0.3;
> Bin -0.15 contains values of D greater than –0.30 and less than or equal to –0.15;
> Bin 0 contains values of D greater than –0.15 and less than or equal to 0; and
> Bin 0.15 contains values of D greater than 0 and less than or equal to 0.15.

We will submit electronic copies of the files "Thorium_Uncertainty_Results_2014_PA.xls" "Americium_Uncertainty_Results_2014_PA.xls," and all of the other spreadsheets to the archived file EQ36_IO_files.ZIP, which is stored in the CMS in class ANALYSIS of library LIBPABC09_FMT.

3 RESULTS

This section provides the results of our new uncertainty analysis of the solubilities of Th(IV) (Subsection 3.1) and Am(III) (Subsection 3.2).

We included all of the measured solubilities included by Xiong et al. (2011) in our new uncertainty analysis of the solubilities of Th(IV) and Am(III). We also excluded all of the measured solubilities excluded by Xiong et al. (2011). Therefore, we retained for ease of reference all of the text from Xiong et al. (2011) that described their final evaluations of the papers and reports that they considered. However, we updated their text as necessary to include comparisons to our most recent predictions of the baseline solubilities of Th(IV) and Am(III), and the compositions of WIPP brines (Brush and Domski, 2012).

Each of the following subsections provides separate lists of the published papers and unpublished reports identified and evaluated previously by Xiong et al. (2005) and/or Xiong et al. (2011), and the papers and reports evaluated for this analysis. These lists appear at the beginning of each subsection.

3.1 Th(IV) Solubility Model

This subsection describes our final evaluations of experimentally measured Th(IV) solubilities from the published papers and unpublished reports that we identified for this analysis. It documents which measured solubilities we included and excluded, and why we included or excluded them. This subsection then compares the measured Th(IV) solubilities included in this analysis with those predicted using the WIPP Th(IV) speciation and solubility model in EQ3/6, and compares our results to those from previous analyses by Xiong et al. (2005, 2011) for the CRA-2004 PABC and the CRA-2009 PABC. Finally, it establishes a CDF for the differences between our measured and predicted Th(IV) solubilities for the CRA-2014 PA, and compares it to those established by Xiong et al. (2005, 2011) for the CRA-2004 PABC and the CRA-2009 PABC.

The measured Th(IV) solubilities from published papers and unpublished reports evaluated previously by Xiong et al. (2005) and/or Xiong et al. (2011) include: Altmaier et al. (2004, 2005, 2006, 2008), Baston et al. (1996), Felmy et al. (1991, 1997, 2006), Neck et al. (2002, 2003), Östhols et al. (1994), and Rai et al. (1995, 1997, 2000) (see Table 3 and the explanatory text below).

The measured Th(IV) solubilities that we evaluated for this analysis include: Borkowski (2012), Borkowski et al. (2012), Brendebach et al. (2007), Colàs et al. (2011), Fellhauer et al. (2010), Kim et al. (2010), Rai et al. (2005, 2008, 2009, 2011), Vandenborre et al. (2008, 2010), Wood (2005), and Xia et al. (2003) (Table 3 and text).

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities.

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Altmaier et al. (2004)	(A) 0.5 M NaCl (B) 5 M NaCl (C) 0.25 M $MgCl_2$ ($I = 0.75$ M) (D) 2.5 M $MgCl_2$ ($I = 7.5$ M) (E) 4.5 M $MgCl_2$ ($I = 13.5$ M)	(A) pcH = 10.4 & 11-13.5 (B) pcH = 10.8 (C) pcH = 9.0 (D) pcH = 8.9 (E) pcH = 8.8	ThO_2(cr) & $ThO_n(OH)_{4-2n}$ xH_2O(am), which they referred to as "$Th(OH)_4$(am) or $ThO_2 \cdot xH_2O$(am)"	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. Six uncentrifuged results (no duplicates) obtained at $I \geq 3$ M included by Xiong et al. (2011) and in this analysis: 01ALT04.3i – 06ALT04.3i. Ultracentrifuged results excluded by Xiong et al. (2011) and from this analysis because the posttest phase-separation method was different than those employed in the studies used to parameterize the Th(IV) model and appeared to support a different model (see text).
Altmaier et al. (2005)	(A) Mostly $NaHCO_3$-Na_2CO_3-NaCl-NaOH with $I = 0.5$ M (B) Some with 0.25-2 M Na_2CO_3 & 0.1 M NaOH	(A) pcH = 4.5-7.5 & 8.5-13.5 (B) pcH = 13	$Th(OH)_4$(am) or $ThO_2 \cdot xH_2O$(am)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. Most results excluded by Xiong et al. (2011) and from this analysis because $I < 3$ M. All other results excluded because the $Th(OH)_y(CO_3)_z^{4-y-2z}$ complex(es) found to be important by Altmaier et al. (2005) are not in the WIPP Th(IV) model. Four results (no duplicates) obtained at $I \geq 3$ M modeled but excluded by Xiong et al. (2011) and from this analysis.
Altmaier et al. (2006)	$NaHCO_3$-Na_2CO_3-NaCl with $I = 0.1$-4 M.	pcH = 8–11	$Th(OH)_4$(am) or $ThO_2 \cdot xH_2O$(am)	Most results excluded by Xiong et al. (2011) and from this analysis because $I < 3$ M. All other results excluded because the $Th(OH)(CO_3)_4^{5-}$ complex found to be important by Altmaier et al. (2006) is not in the WIPP Th(IV) model. Twelve results (no duplicates) obtained at $I \geq 3$ M modeled but excluded by Xiong et al. (2011) and from this analysis.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Altmaier et al. (2008)	(A) 0.2–5.26 m $CaCl_2$ (I = 0.6–15.78 m) (experiments with Th(IV)) (B) 2.40 m $Ca(ClO_4)_2$ (I = 7.20 m) (Th(IV))	pmH = 9.3-12.1 (all Th(IV))	Solutions with $CaCl_2$ < 1 M (entire pH range) or $CaCl_2$ > 1 M (pH < 11.5): $Th(OH)_4$(am) or $ThO_2 \cdot xH_2O$(am). Solutions with $CaCl_2$ > 1 M (pH > 11.5): unidentified, possibly a Ca-Th solid(cr).	Most results excluded by Xiong et al. (2011) and from this analysis because I < 3 M. Some results excluded because of ultracentrifugation. All other results excluded because the $Ca_4(Th(OH)_8)^{4+}$ complex found to be important by Altmaier et al. (2008) is not in the WIPP Th(IV) model.
Baston et al. (1996)	Nirex (0.02 M)	pH = 10-12	ThO_2(am)	Excluded by Xiong et al. (2005, 2011) and from this analysis because I < 3 M.
Borkowski et al. (2012)	(A) HCO_3^-/CO_3^{2-}-free & HCO_3^-/CO_3^{2-}-bearing GWB, diluted to 95% of its specified concentrations (B) HCO_3^-/CO_3^{2-}-free & HCO_3^-/CO_3^{2-}-bearing ERDA-6, diluted to 95% of its specified concentrations	(A) pcH = 6.8–10.13 (GWB: carbonate-free, or 10^{-2} or 10^{-3} M carbonate; & over- & undersaturation) (B) pcH = 7.86–11.04 (ERDA-6: carbonate-free, or 10^{-2} or 10^{-3} M carbonate; & over- & undersaturation)	Solids precipitated in oversaturation runs not reported. "Th oxyhydroxide" (composition not reported) used in undersaturation runs	Included the final results and only the final results from every solubility experiment with both GWB and ERDA-6, because the Th(IV) concentrations generally decreased with time during oversaturation experiments, and increased during undersaturation runs. However, the final results obtained from runs with ERDA-6 appear to be metastable or perhaps more metastable than those from GWB (see text). Used numerical values from Borkowski (2012) (see below). EQ3 file names: 01GWB_12.3i - 09GWB_12.3i and 01ERD_12.3i - 14ERD_12.3i.
Borkowski (2012)	Same as above	Same as above	Same as above	Same as above

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Brendebach et al. (2007)	0.2-4.5 M $CaCl_2$ (I = 0.6–13.5 M) (experiments with Th(IV))	pcH ≈ 9.3-12.1 (all Th(IV)).	Solutions with $CaCl_2$ < 1 M (entire pH range) or $CaCl_2$ > 1 M (pH < 11.5): $Th(OH)_4(am)$ or $ThO_2 \cdot xH_2O(am)$. Solutions with $CaCl_2$ > 1 M (pH > 11.5): unidentified, possibly a Ca-Th solid(cr).	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. The results of Brendebach et al. (2007) were superseded by those of Altmaier et al. (2008) (see above). Therefore, we excluded the results of Brendebach et al. (2007) from this analysis for the same reasons that Xiong et al. (2011) excluded those of Altmaier et al. (2008).
Colàs et al. (2011)	0.5 M $NaClO_4$ with 10^{-6} to 10^{-1} M gluconate	pcH ≈ 9-13	Th hydroxide ($ThO_2 \cdot xH_2O$)	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. All results excluded from this analysis because gluconate is not in the WIPP Th(IV) model.
Fellhauer et al. (2010)	1.02–5.26 m $CaCl_2$ (I = 3.06–15.78 m) (experiments with Np(IV) and Pu(IV))	pcH ≈ 11-12 (Np(IV)) pcH ≈ 10-12 (Pu(IV))	$NpO_2 \cdot xH_2O(am)$ or $PuO_2 \cdot xH_2O(am)$	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. All results excluded for the same reasons used to exclude those of Brendebach et al. (2007) and Altmaier et al. (2008). Furthermore, there could be systematic differences between the solubilities of Np(IV) and Pu(IV and Th(IV), which was used to parameterize the models; and because the difficulties inherent in maintaining Np and Pu in the +IV oxidation state could have introduced experimental artifacts in these results.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Felmy et al. (1991)	(A) 0.1 M $NaClO_4$ (B) 0.6 M NaCl (C) 1.2 M NaCl (D) 3.0 M NaCl (E) 0.6 M KCl	(A) pcH = 4.9-5.9 (B) pcH = 2.91–10.24 (C) pcH = 2.83–10.19 (D) pcH = 3.82–10.56 (E) pcH = 3.75–7.95	Th(IV) hydrous oxide (all)	Forty-five results (no duplicates) obtained at I = 3 M included in Xiong et al. (2005, 2011) and this analysis: 01FEL91.3i – 46FEL91.3i I = 3 M results obtained at pH ≤ 3.6 excluded by Xiong et al. (2005, 2011) and from this analysis because the solids dissolved before saturation was attained. File 16FEL91.3i not included because experimental pH≤ 3.6.
Felmy et al. (1997)	Information provided in previous publications	Information provided in previous publications	Information provided in previous publications	Excluded by Xiong et al. (2005, 2011) and from this analysis because this paper contains only previously published results (e.g., Felmy et al., 1991).
Felmy et al. (2006)	(A) 0.5 M $NaNO_3$ & 0.01 M citrate (B) 3.0 M $NaNO_3$ & 0.01 M citrate (C) 6.0 M $NaNO_3$ & 0.01 M citrate (D) 0.5 M $NaNO_3$ & 10^{-4} to 10^{-2} M citrate (E) 0.5 M $NaNO_3$ & 10^{-4} to 10^{-2} M citrate	(A) pcH = 5.2–12.2 (B) pcH = 5.0–11.8 (C) pcH = 4.7–12.1 (D) pcH = 6-8 (E) pcH = 9.5-10.1	Th(IV) hydrous oxide (ThO_2(am)) (all)	All results excluded by Xiong et al. (2011) and from this analysis because NO_3^- is not in the WIPP Th(IV) model.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Kim et al. (2010)	Distilled H_2O; dilute solutions with various combinations of $HClO_4$, Na_2CO_3, $NaClO_4$ and $CaCl_2$; and naturally occurring, dilute granitic groundwater; I = 0–225 mM (all solutions)	pH = 8.6–11.2 (all solutions)	ThO_2(cr) (all solutions)	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. All results excluded from this analysis because I < 3 M.
Neck et al. (2002)	0.5 M NaCl	pcH = 1.11–13.7	$Th(OH)_4$(am) or $ThO_2 \cdot xH_2O$(am)	Excluded by Xiong et al. (2005, 2011) and from this analysis because I < 3 M.
Neck et al. (2003)	(A) 0.1 M NaCl (B) 0.5 M NaCl	(A) pcH = 1.00-1.75 (B) pcH = 1.03-1.28 & 11.03-13.43	ThO_2(cr) or $ThO_2 \cdot xH_2O$(mcr)	Excluded by Xiong et al. (2005, 2011) and from this analysis because I < 3 M.
Östhols et al. (1994)	0.5 $NaClO_4$ & 0, 0.1, & 0.97 atm CO_2	pH = 3.31–7.36 (continuous titrations) & 8.21-10.45 (batch experiments)	ThO_2(mcr)	Excluded by Xiong et al. (2005, 2011) and from this analysis because I < 3 M.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Rai et al. (1995)	(A) 0.005-0.25 M $NaHCO_3$ (B) 0.1-2.0 M Na_2CO_3 (C) 0.1-2.0 M Na_2CO_3 & 0.1 M NaOH (D) 0.1-0.5 M NaOH & 1.0 M Na_2CO_3	Not provided	ThO_2(am)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. All results excluded by Xiong et al. (2011) and from this analysis because the $Th(OH)_y(CO_3)_z^{4-y-2z}$ complexes found to be important by Altmaier et al. (2005) under the conditions used by Rai et al. (1995) are not in the WIPP Th(IV) model.
Rai et al. (1997)	(A) 0.2 m NaCl (used only for U solubilities)	(A) U not included in this analysis	ThO_2(am)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. Eighty-nine results (8 duplicates) obtained at $I \geq 3$ M included by Xiong (2011) and in this analysis: 01RAI97.3i - 80RAI97.3i, although one EQ3 run did not converge, 29RAI97.3i, only eighty-eight results used. Results obtained from the most acidic solutions in each set of experiments (see Table 6) excluded by Xiong et al. (2011) and from this analysis because the solids dissolved before saturation was attained.
	(B) 1.0 m NaCl (used only for U solubilities)	(B) U not included in this analysis		
	(C) 3.2 m NaCl (data from Felmy et al., 1991)	(C) See entry for 3.0 M NaCl for Felmy et al. (1991) in this table		
	(D) 4.0 m NaCl,	(D) pcH = 3.02-5.16		
	(E) 6.0 m NaCl,	(E) pcH = 3.32-5.28		
	(F) 1.0 m $MgCl_2$ (I = 3 m),	(F) pcH = 3.84-4.94		
	(G) 1.82 m $MgCl_2$ (I = 5.46 m), &	(G) pcH = 3.17-5.46		
	(H) 3.0 m $MgCl_2$ (I = 9 m)	(H) pcH = 3.52-5.65		

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Rai et al. (2000)	(A) 0.1 M NaCl (	(A) pH = 2.0-4.7 & 1.5-2.2	(A) ThO_2(am) & ThO_2(am to cr)	Not considered by Xiong et al. 2005) because this paper came to their attention after completion of their analysis. Most results excluded by Xiong et al. (2011) and from this analysis because I < 3 M. All other results excluded because T = 90 °C.
	B) 0.1 M NaCl	(B) pH= 4.2-5.1 & 2.0-2.1	(B) ThO_2(am) & ThO_2(am to cr)	
	(C) 0.1 M NaCl	(C) pH = 1.9-4.2 & 1.9-3.0	(C) ThO_2(am) & ThO_2(am to cr)	
	(D) 0.1 M NaCl	(D) pH = 1.3-3.6	(D) ThO_2(cr)	
	(E) 0.1 M NaCl	(E) pH = 1.4-3.5	(E) ThO_2(cr)	
Rai et al. (2005)	HCO_3^-/CO_3^{2-}-free & HCO_3^-/CO_3^{2-}-bearing (up to 6.2 m) solutions with numerous other solutes dissolved from borosilicate glass	pH ≈ 0.5–12	Not determined. May have included a Th- & Si-bearing solid(s0	Not considered by Xiong et al. 2005, 2011) because this paper came to their attention after completion of their analyses. Excluded from this analysis because: (1) several components of the glass, especially SiO_2 and Al_2O_3, are not in the WIPP model; (2) the solubility-controlling solid(s) were not identified; and (3) many results were obtained from solutions with I < 3 M or m.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Rai et al. (2008)	(A) 0.0025-0.1 M Na_2SiO_3, with “carbonate impurities”	(A) pH 11, 12, or 13	ThO_2(am) containing NO_3^- impurities form preparation and SiO_2, probably sorbed to the surface (all experiments)	Not considered by Xiong et al. 2011) because this paper came to their attention after completion of their analysis. Excluded from this analysis because the $Th(OH)_3\cdot(H_3SiO_4)_3^{2-}$ complex found to be important by Rai et al. (2008) is not in the WIPP Th(IV) model.
	(B) 0.0025-0.14 M Na_2SiO_3, HCO_3^-/CO_3^{2-}-free	(B) pH = 10, 12, or 13		
	(C) 0.0356 M Na_2SiO_3, (fixed)	(C) pH = 10–13.3 (variable)		
	(D) 0.0157 M Na_2SiO_3, (fixed)	(D) pH = 10–13.3 (variable)		
Rai et al. (2009)	(A) 0.0002–0.2 m ISA	(A) pH ≈ 6 or 12 (fixed)	ThO_2(am) (all experiments)	Not considered by Xiong et al. 2011) because this paper came to their attention after completion of their analysis. Excluded from this analysis because the $Th(OH)ISA^{2+}$, $Th(OH)_3(ISA)_2^-$, and $Th(OH)_4(ISA)_2^{2-}$ complexes found to be important by Rai et al. (2009) are not in the WIPP Th(IV) model.
	(B) 0.008 or 0.08 m ISA	(B) pH = 4.5–12		
Rai et al. (2011)	Information provided in previous publications	Information provided in previous publications	Information provided in previous publications	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. Excluded from this analysis because this paper contains only previously published results.
Vandenborre et al. (2008)	0.01 M NaCl	pH = 3.0 or 4.0	ThO_2(cr) spheres with an average diameter of 500 μm	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analyses. Excluded from this analysis because I < 3 M.

Table 3 continued on next page

Table 3. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Th(IV) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pH, pcH, or pmH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Vandenborre et al. (2010)	0.01 M NaCl	pH = 0.0 to 5.2	ThO_2(cr) spheres with an average diameter of 500 μm	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. Excluded from this analysis because I < 3 M.
Wood (2005)	(A) 0.1, 1.0, & 3.0 M $NaNO_3$; 100–500 μM citrate, EDTA; & oxalate	(A) pH ≈ 2–10.5	(A) CeO_2 (crystallinity and hydration state unspecified)	Not considered by Xiong et al. (2005, 2011) because this paper came to their attention after completion of their analyses. Excluded from this analysis because NO_3^- is not in the WIPP Th(IV) model.
	(B) 0.1 M $NaNO_3$; 100–500 μM citrate, EDTA; & oxalate	(B) pH ≈ 3–12	(B) "A relatively poorly crystalline form of ThO_2"	
Xia et al. (2003)	(A) 0.5 M $NaNO_3$ & 0.01 M EDTA	pcH = 4.3–11.8	Th(IV) hydrous oxide (ThO_2(am)) (all)	Not considered by Xiong et al. (2005, 2011) because this paper came to their attention after completion of their analyses. Excluded from this analysis because NO_3^- is not in the WIPP Th(IV) model.
	(B)) 3.0 M $NaNO_3$ & 0.01 M EDTA	pcH = 6.7–12.8		
	(C)) 6.0 M $NaNO_3$ & 0.01 M EDTA	pcH = 6.8–13.2		
	(D)) 0.5 M $NaNO_3$ & 10^{-5}–10^{-2} M EDTA	pcH = 8		
	(E) 0.5 M $NaNO_3$ & 10^{-5}–10^{-2} M EDTA	pcH = 10		
	(F) 0.5 M $NaNO_3$ & 10^{-5}–10^{-2} M EDTA	pcH = 8		
	(G) 0.5 M $NaNO_3$ & 10^{-5}–10^{-2} M EDTA	pcH = 10		

Altmaier et al. (2004) measured the solubilities of $ThO_2(cr)$ and $ThO_n(OH)_{4-2n}{\cdot}xH_2O(am)$ in NaCl and $MgCl_2$ solutions with various ionic strengths (see Table 3 for additional information on these experiments). Xiong et al. (2005) did not consider the results of Altmaier et al. (2004) in their uncertainty analyses of Th(IV) solubilities for the CRA-2004 PABC because this paper came to their attention after they completed their analysis. For the CRA-2009 PABC, Xiong et al. (2011) included all six of the uncentrifuged results from solutions with $I \geq 3$ M from Altmaier et al. (2004, Figure 2) according to criterion S1 (see Section 2 above): two from their 5 M NaCl solutions, two from their 2.5 M $MgCl_2$ solutions, and two from their 4.5 M $MgCl_2$ solutions (see Table 3 for additional information on these results). However, Xiong et al. (2011) excluded the ultracentrifuged results of Altmaier et al. (2004) because this posttest phase-separation method was significantly different from those employed in the studies used to parameterize the WIPP Th(IV) solubility model (e.g., centrifugation or filtration) and appeared to support a significantly different solubility model than that established for the WIPP (i.e. ultracentrifugation showed that 99% or more of what had been interpreted as dissolved Th(IV) present as the $Th(OH)_4(aq)$ species appeared to be present as the eigencolloid $Th(OH)_4(col)$). The WIPP Th(IV) model was parameterized in the mid-1990s, before it was realized that the phase-separation methods used then might not have removed all of the $Th(OH)_4(col)$. Thus, Xiong et al. (2011) excluded the ultracentrifuged results of Altmaier et al. (2004) according to Criterion G5 (Section 2). We also excluded these results.

Although our model significantly overpredicts the solubility of Th(IV) from about pH = 6 to 13.5 in bicarbonate- (HCO_3^--) or carbonate-free (CO_3^{2-}-free) solutions, it is still adequate for WIPP compliance-related calculations because both the Th(IV) solubility and the total mobile concentration (dissolved plus colloidal) of Th(IV) predicted under these conditions are higher than they would be based on the ultracentrifuged results of Altmaier et al. (2004). This is because the concentration factors used to calculate the colloidal Th(IV) component of the WIPP mobile Th(IV) concentration are multiplied by a dissolved Th(IV) concentration (solubility) that is about 100 times higher than its actual value, based on the ultracentrifuged results of Altmaier et al. (2004).

Altmaier et al. (2005) measured the solubilities of $Th(OH)_4(am)$ and $ThO_2{\cdot}xH_2O(am)$, mostly with $NaHCO_3$-Na_2CO_3-NaCl solutions with I = 0.5 M. They also carried out some experiments with Na_2CO_3 solutions with various ionic strengths (Table 3). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. The results in Altmaier et al. (2005, Figure 4b) led Xiong et al. (2011) to suspect that, in some of their experiments, the ionic strength might have equaled or exceeded 3 M. Therefore, they used Data Thief to extract the numerical values of the plotted CO_3^{2-} concentrations from their Figure 4b, and calculated the ionic strengths of the solutions. Xiong et al. (2011) found that four of these solutions had $I \geq 3$ M. According to criterion S1 (see Section 2), Xiong et al. (2005) would have included these results in their Th(IV) uncertainty range and probability distribution. They excluded them, however, because Altmaier et al. (2005) concluded that, at high CO_3^{2-} concentrations ($\log[CO_3^{2-}]$ greater than about -0.5) in their Figure 4b, the dominant aqueous species is (are) $ThOH(CO_3)_4^{5-}$ (or $ThOH(CO_3)_4^{5-}$ and $Th(OH)_2(CO_3)_4^{6-}$), neither of which is included in the WIPP Th(IV) model. Thus, Xiong et al. (2011) used criterion G9 to exclude these results. We also excluded these results.

The WIPP Th(IV) model includes the following $Th(OH)_y(CO_3)_z^{4-y-2z}$ complexes: $Th(CO_3)_5^{6-}$, $Th(OH)_3CO_3^-$, and $Th(OH)_4(aq)$. It does not include $ThOH(CO_3)_4^{5-}$ and $Th(OH)_2(CO_3)_2^{2-}$, both of which were identified by Altmaier et al. (2005, Figure 5) as important at high CO_3^{2-} concentrations. Furthermore, it does not include $Th(OH)_2CO_3(aq)$ and $Th(OH)_4CO_3^{2-}$, which – although not identified as important in their Figure 5 – were quantified by Altmaier et al. (2005): Nevertheless, the WIPP Th(IV) model is still adequate for WIPP compliance-related calculations. This is because none of the important $Th(OH)_y(CO_3)_z^{4-y-2z}$ complexes with z > 0 approaches the $Th(OH)_4(aq)$ concentrations predicted by Brush and Domski (2013, Tables 7 and 8) for the minimum brine volume for the CRA-2014 PA (4.55×10^{-8} M for GWB and 4.75×10^{-8} M for ERDA-6) until the log of the CO_3^{2-} concentration exceeds about −1 (see Altmaier et al., 2005, Figure 4b). By contrast, the (TIC) concentrations (essentially the sum of the concentrations of HCO_3^- and CO_3^{2-}) predicted by Brush and Domski (2013, Tables 5 and 6), 0.379 mM for GWB and 0.455 mM for ERDA-6, for the minimum brine volume were more than two orders of magnitude lower than that threshold. The reason why the TIC concentrations predicted for these WIPP brines are too low to form important $Th(OH)_y(CO_3)_z^{4-y-2z}$ complexes with z > 0 is because the brucite-hydromagnesite carbonation reaction will buffer the TIC at the values given above.

Altmaier et al. (2006) determined the solubilities of $Th(OH)_4(am)$ and $ThO_2{\cdot}xH_2O(am)$ in $NaHCO_3$-Na_2CO_3-NaCl solutions with various ionic strengths (Table 3). Xiong et al. (2011) excluded most of their results according to criterion S1 (Section 2) because they were obtained using $NaHCO_3$-Na_2CO_3-NaCl solutions with ionic strengths less than 3 M. However, they found 12 results from experiments with $I \geq 3$ M (see Altmaier et al., 2006, Figure 2). Xiong et al. (2011) used criterion G9 to exclude these data because the WIPP Th(IV) model does not include the $ThOH(CO_3)_4^{5-}$ complex, which Altmaier et al. (2006) found to be the dominant aqueous species. We also excluded these results.

Nevertheless, the WIPP Th(IV) model is still adequate for WIPP compliance-related calculations for the reasons described above in the discussion of the data from Altmaier et al. (2005) (see above).

Altmaier et al. (2008) measured the solubilities of $Th(OH)_4(am)$ and $ThO_2{\cdot}xH_2O(am)$, a (possible) Ca-Th solid, and Zr(IV) or Pu(IV) solids in $CaCl_2$ with various ionic strengths and in 2.40 m $Ca(ClO_4)_2$ (Table 3). Xiong et al. (2011) used criterion G6 (Section 2) to exclude most of their results because they were obtained from experiments with Zr(IV) or Pu(IV). They used criterion S1 to exclude the Th(IV) solubilities from 0.20 and 0.51 m $CaCl_2$ solutions. Finally, Xiong et al. (2011) used criterion G9 to exclude the Th(IV) solubilities from 1.02, 2.11, and 5.26 m $CaCl_2$ solutions (I = 3.06, 6.33, and 15.78 m, respectively) because Altmaier et al. (2008) concluded that, at high $CaCl_2$ concentrations (> 0.5 m for pcH = 11-12 according to their abstract, but > 0.2 m at pH = 12 from their Figure 5), the dominant aqueous species was $Ca_4(Th(OH)_8)^{4+}$, which is not included in the WIPP Th(IV) model. We excluded these results for the same reasons.

Nonetheless, the Th(IV) model is still adequate for WIPP compliance-related calculations because the Ca concentrations predicted by Brush and Domski (2013, Tables 5 and 6) for the minimum volumes of GWB and ERDA-6 are 0.0111 and 0.0116 M, respectively. Figure 5 in

Altmaier et al. (2008) demonstrates that both the total dissolved Ca concentration and the pcH must be much higher than the values expected in WIPP brines to increase the concentration of $Ca_4(Th(OH)_8)^{4+}$ to values greater than those expected when $Th(OH)_4(aq)$ or $Th(OH)_4(col)$ is the dominant species. For example, if the $CaCl_2$ concentration is 0.51 m, the pcH must be 12 or higher to increase the $Ca_4(Th(OH)_8)^{4+}$ concentration to values greater than those expected when $Th(OH)_4(col)$ is the dominant mobile species. If the $CaCl_2$ concentration is 1.02 m, the pcH must be 11-11.5 or higher to increase the $Ca_4(Th(OH)_8)^{4+}$ concentrations greater than those expected when $Th(OH)_4(col)$ is the dominant mobile species. Therefore, the absence of $Ca_4(Th(OH)_8)^{4+}$ from the Th(IV) model does not affect its validity under expected WIPP conditions.

Although $Ca_4(Th(OH)_8)^{4+}$ and the analogous Am(III) and Cm(III) complexes described below will not be important in the WIPP, these complexes could be important in salt repositories with brines that have higher $CaCl_2$ concentrations. Brendebach et al. (2007) (see below) were, to the best of our knowledge, the first investigators to report the formation of, characterize, and assess the importance of these ternary Ca-M(IV)-OH complexes, in which the metal M can be Th(IV) or Zr(IV). Subsequently, Rabung et al. (2008) and Neck et al. (2009) reported, characterized, and evaluated analogous Ca-M(III)-OH complexes, in which M can be Am(III) or Cm(III). Subsection 3.2 and Table 8 (see below) describe the results of Rabung et al. (2008) and Neck et al. (2009).

Baston et al. (1996) studied the solubility of $ThO_2(am)$ in a low-ionic-strength solution (Table 3). Xiong et al. (2005) excluded the results of Baston et al. (1996) from their analysis, because they were obtained from solutions with $I < 3$ M (see criterion S1 in Section 2). Xiong et al. (2011) also used criterion S1 to exclude these results.

Borkowski et al. (2012) measured the solubilities of Th(IV) in the synthetic WIPP brines GWB and ERDA-6, diluted to 95% of their specified concentrations to avoid coprecipitation of Th(IV) by evaporite minerals (Table 3). (Small changes in conditions, especially temperature, during solubility experiments can cause precipitation of solids such as evaporite minerals and coprecipitation of actinide elements if the solutions are saturated with these solids under the conditions used for these tests.) Borkowski et al. (2012) used carbonate-free GWB and ERDA-6, and GWB and ERDA-6 with 10^{-3} or 10^{-2} M TIC. We considered all of the results of Borkowski et al. (2012) for inclusion in our uncertainty analysis of Th(IV) for the CRA-2014 PA according to criterion G6 (see Section 2 above). These results demonstrated that the Th(IV) concentrations generally decreased with time during their oversaturation experiments, and increased during their undersaturation runs. Therefore, we included all of the results obtained from their final samples from each experiment, and excluded those from samples taken prior to their final samples. The final results obtained from the oversaturation runs with ERDA-6 are generally greater than those from the oversaturation runs with GWB, probably because the former were carried out for 2 years and the latter for 4 years. Nevertheless, we included all of the final results from experiments with both GWB and ERDA-6. Subsequent to the release of Borkowski et al. (2012), Borkowski (2012) provided numerical values of the brine compositions, pcH, Th(IV) concentrations, and experimental durations shown graphically by Borkowski et al. (2012). We used these numerical values from Borkowski (2012) for the EQ3/6 runs for this analysis.

Brendebach et al. (2007) carried out solubility experiments with $Th(OH)_4(am)$ and $ThO_2{\cdot}xH_2O(am)$, a (possible) Ca-Th solid, and Zr(IV) solids in $CaCl_2$ solutions with various ionic strengths (Table 3). As noted above, this was the first paper to identify Ca-M(IV)-OH complexes, in which the metal M can be Th(IV) or Zr(IV). Xiong et al. (2011) did not consider the results of Brendebach et al. (2007) because this paper came to their attention after they completed their analysis. Altmaier et al. (2008) (see above) expanded the study of Brendebach et al. (2007) and presented the results at Migration 2007. Because the results of Brendebach et al. (2007) were superseded by those of Altmaier et al. (2008), we excluded the results of Brendebach et al. (2007) from our uncertainty analysis for the reasons provided for Altmaier et al. (2008) (see above).

Colàs et al. (2011) conducted solubility experiments with Th hydroxide (for which they provided the composition $ThO_2{\cdot}xH_2O$) in 0.5 M $NaClO_4$ solutions with 10^{-6} to 10^{-1} M gluconate and pcH ≈ 9–13 (Table 3). Xiong et al. (2011) did not consider this paper because it came to their attention after they completed their analysis. We used criterion G9 (Section 2) to exclude their results because gluconate is not in the WIPP Th(IV) model.

Fellhauer et al. (2010) measured the solubilities of Np(IV) and Pu(IV) solids in $CaCl_2$ solutions with various ionic strengths (Table 3). Fellhauer used 2 mM $Na_2S_2O_4$ or metallic Fe powder to establish reducing conditions and maintain Np and Pu in the +IV oxidation state. Thus, they extended the oxidation-state-analog approach of Brendebach et al. (2007) and Altmaier et al. (2008), both of whom used Th(IV), to a direct evaluation of Ca-M(IV)-OH complexes, in which the metal M was Np(IV) or Pu(IV). Xiong et al. (2011) did not consider these results because they found this paper after they completed their analysis. We excluded these results from our uncertainty analysis for the same reasons that we excluded those of Brendebach et al. (2007) and Altmaier et al. (2008). Furthermore, we used criterion G6 (Section 2) to exclude the results of Fellhauer et al. (2010), because they were obtained from experiments with Np(IV) or Pu(IV).

Felmy et al. (1991) measured the solubility of Th(IV) hydrous oxide in 0.1 M $NaClO_4$, in NaCl solutions of various ionic strengths, and in 0.6 M KCl (Table 3). Xiong et al. (2005, Subsection 5.2.3) established criterion S1 based on their comparison of the solubilities measured by Felmy et al. (1991) and those predicted using the WIPP Th(IV) solubility model, and excluded most of them because they were obtained using solutions with $I < 3$ M. Furthermore, inspection of the remaining results showed that those obtained at the most acidic values of pH were essentially independent of pH. Xiong et al. (2005, p. 12) noted that:

> [T]his behavior can be explained by noting that in … the experiments at pH ≤ ~3.6 …, the Th(IV)-bearing solids were consumed before saturation was attained (see Felmy et al., 1991, p. 298). Therefore, the constant Th(IV) concentration of slightly less than 10^{-2} M in the experiments reflects the fact that the constant quantity of Th(IV) added at the start of these experiments was insufficient to saturate these solutions under these conditions… Thus, the concentrations in the experiments at pH ≤ ~3.6 … are not solubilities. Because the concentrations measured by Felmy et al. (1991) at pH ≤ ~3.6 are not solubilities, we excluded them from the revised An(IV) comparison.

Therefore, Xiong et al. (2005) excluded these acidic results, and Xiong et al. (2011) incorporated the reason for excluding these and similar results from other studies into criterion G7 (see Section 2; the descriptions of the results of Rai et al., 1997, in Subsection 3.1 and Tables 4 and 5; and the discussions of the results of Rao et al., 1996a, in Subsection 3.2 and Table 8). After applying criteria G7 and S1, Xiong et al. (2005) included 45 results from Felmy et al. (1991) in their analysis; Xiong et al. (2011) included the same 45 results in this analysis. We also included these results.

Felmy et al. (1997) reviewed the development of models for the solubility of Th(IV) solids in high-ionic-strength solutions. Xiong et al. (2005, 2011) excluded all of the results in Felmy et al. (1997) from their analyses according to criterion G10, because this paper is a literature review and does not conduct any new data. We also excluded these results.

Felmy et al. (2006) studied the solubility of ThO_2(am) in $NaNO_3$ solutions with various ionic strengths and various concentrations of the organic ligand citrate (Table 3). Xiong et al. (2011) used criterion G9 (Section 2) to exclude their results because NO_3^- is not in the WIPP Th(IV) model. We excluded these results too.

Kim et al. (2010) measured the solubility of ThO_2(cr) in dilute solutions with various combinations of $HClO_4$, Na_2CO_3, $NaClO_4$, and $CaCl_2$ (Table 3). They also samples of a naturally occurring, dilute granitic groundwater. Xiong et al. (2011) did not consider the results of Kim et al. (2010) because this paper came to their attention after they completed their analysis. We excluded their results according to criterion S1 (Section 2), because they were all obtained using solutions with $I < 3$ M.

Neck at al. (2002) measured the solubilities of $Th(OH)_4$(am) and $ThO_2{\cdot}xH_2O$(am) in 0.5 M NaCl solutions (Table 3). Xiong et al. (2005) excluded their results according to criterion S1 (Section 2), because they were obtained using solutions with $I < 3$ M. Xiong et al. (2011) also used criterion S1 to exclude them. We excluded them too.

Neck et al. (2003) performed a solubility study with $Th(OH)_4$(am) and $ThO_2{\cdot}xH_2O$(am) in 0,1 and 0.5 M NaCl solutions (Table 3). Xiong et al. (2005, 2011) used criterion S1 (Section 2) to exclude their results. We also excluded their results.

Östhols et al. (1994) studied the solubility of ThO_2(mcr) in 0.5 M $NaClO_4$ under atmospheres with various concentrations of CO_2 (Table 3). Xiong et al. (2005, 2011) used criterion S1 (Section 2) to exclude their results. We also excluded them.

Rai et al. (1995) measured the solubilities of ThO_2(am) and UO_2(am) in a variety of $NaHCO_3$, Na_2CO_3, and Na_2CO_3 and NaOH solutions with various ionic strengths (Table 3). Xiong et al. (2005) did not consider the results of Rai et al. (1995) because this paper came to their attention after they completed their analysis. Based on their previous work and that of others, Rai et al. (1995, p. 1146) expected that "… it is probably that [sic] the dominant aqueous species of Th and U in these high-carbonate solutions are $Th(CO_3)_5^{6-}$ and $U(CO_3)_5^{6-}$, respectively." However, the response of the Th and U solubilities to concentration variations of

OH^- in their experiments led them to speculate that the complexes $U(OH)_3CO_3^-$ or $U(OH)_4CO_3^{2-}$ or, from the oxidation-state analogy, $Th(OH)_3CO_3^-$ or $Th(OH)_4CO_3^{2-}$ could be dominant (Rai et al., 1995, p. 1148). Subsequently, Altmaier et al. (2005, 2006) demonstrated that, under the conditions of Rai et al. (1995), the important $Th(OH)_y(CO_3)_z^{4-y-2z}$ complexes are actually $Th(CO_3)_5^{6-}$, $Th(OH)(CO_3)_4^{-5}$, and $Th(OH)_2(CO_3)_2^{-2}$. Although the WIPP Th(IV) model includes $Th(CO_3)_5^{6-}$, it does not include $Th(OH)(CO_3)_4^{-5}$ and $Th(OH)_2(CO_3)_2^{-2}$. Therefore, Rai et al. (1995) used conditions under which there are two important $Th(OH)_y(CO_3)_z^{4-y-2z}$ species that are not in the WIPP Th(IV) model and Xiong et al. (2011) used criterion G9 (Section 2) to exclude them. We also excluded these results.

Rai et al. (1997) carried out solubility experiments with $Th(OH)_2(am)$ in 4.0 and 6.0 M NaCl solutions and in $MgCl_2$ solutions with various ionic strengths (Table 3). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. Initially, Xiong et al. (2011) decided to include all of their results obtained at $I \geq 3$ M according to criterion S1 (Section 2). However, many of the results of Rai et al. (1997) displayed the same feature observed by Xiong et al. (2005) in the results of Felmy et al. (1991) (see above): the results obtained at the most acidic pH values were independent of pH. Therefore, Xiong et al. (2011) used criterion G7 to exclude the most acidic results (see Table 4 on the next page), which left 89 results for inclusion in their analysis. We also used these results in this analysis.

Rai et al. (2000) conducted solubility experiments with $ThO_2(am)$ and $ThO_2(cr)$ in 0.1 M NaCl solutions (Table 3). Xiong et al. (2005) did not consider these results because they found this paper later. Xiong et al. (2011) used criteria S1 and G5 (Section 2) to exclude them. Criterion G5 also applied to some of these results because they were obtained at 90 °C, a temperature higher than that expected in the WIPP. We excluded these results for the same reasons.

Rai et al. (2005) determined the concentration of Th(IV) dissolved from powdered, phosphate-free borosilicate glass in various solutions (Table 3) at 23 ± 2 °C "to determine whether the observed thorium concentrations exhibit an equilibrium phenomenon and to ascertain whether existing thermodynamic data can be used to interpret these results." The glass contained 24 components, most of which are not in the WIPP Th(IV) model. The most important of these were Al_2O_3 (5.70 wt %) and SiO_2 (48.60 wt %). The $KHCO_3$ and/or K_2CO_4 concentrations of these solutions varied from 0 to 6.2 m; the pH from about 05 to 12. Xiong et al. (2005, 2011) did not consider the results of Rai et al. (2005) because this paper came to their attention after they completed their analysis. We used criterion G9 (Section 2) to exclude the results of this study because SiO_2, Al_2O_3, and numerous other components of the glass are not in the WIPP Th(IV). We also used criterion G7, because Rai et al. (2005) were unable to identify the solubility-controlling solid(s) in their experiments. Criterion S1 also applies in many cases, because many of the results of this study were obtained from solutions with $I < 3$ M or m.

Table 4. Results from Rai et al. (1997) Excluded from Th(IV) Comparisons Because of Complete Dissolution of Solids.

Run Time (days)	Solution	Maximum pcH	Number of Results Excluded	Figure in Rai et al. (1997) with Excluded Data
7	4.0 m NaCl	3.9	7	Figure 6
51	4.0 m NaCl	4.0	5	Figure 6
91	4.0 m NaCl	4.0	5	Figure 6
8	6.0 m NaCl	3.9	3	Figure 2
125	6.0 m NaCl	3.85	3	Figure 2
159	6.0 m NaCl	3.8	5	Figure 2
7	1.8 m $MgCl_2$	4.0	5	Figure 3
73	1.8 m $MgCl_2$	4.0	4	Figure 3
8	3.0 m $MgCl_2$	3.9	2	Figure 4

Rai et al. (2008) studied the solubility of Th(IV) in basic solutions of 0.0004 to 0.14 M Na_2SiO_3 under basic conditions at 22 ± 2 °C. (Note that the range of Na_2SiO_3 concentrations given in their abstract, from which we obtained the preceding range, does not agree with that in their Table 1, from which we obtained the ranges in our Table 3). Xiong et al. (2011) did not consider this paper because it came to their attention after they completed their analysis. We used criterion G9 to exclude these data because the WIPP Th(IV) model does not include the $Th(OH)_3 \cdot (H_3SiO_4)_3^{2-}$ complex, which Altmaier et al. (2006) found to be the dominant aqueous species. Criterion G7 also applies because the solubility-controlling solid(s) in their experiments seems to contain impurities from preparation and sorbed species from their solutions that could alter its behavior from that of the ThO_2(am) used to start their runs.

Rai et al. (2009) measured the solubility of ThO_2(am) in 0.0002 to 0.2 m isosaccharinate (ISA) solutions under acidic, neutral, and basic conditions at 22 ± 2 °C (Table 3). Xiong et al. (2011) did not consider these results because they found this paper after they completed their analysis. We used criterion G9 to exclude these results because the WIPP Th(IV) model does not include the $Th(OH)ISA^{2+}$, $Th(OH)_3(ISA)_2^{-}$, and $Th(OH)_4(ISA)_2^{2-}$ complexes, which Rai et al. (2009) found to be the dominant under the conditions of their study.

Rai et al. (2011) reviewed the literature review to determine if using the solubilities of radioelements based on knowledge of the important solubility-controlling solids provides a feasible alternative to the use of numerical predictions of these solubilities based on the results of empirical leaching experiments. Xiong et al. (2011) did not consider these results because they found this paper later. We used criterion G10 to exclude these results, because Rai et al. (2011) carried out a literature review and did not conduct any new experiments.

Vandenborre et al. (2008) measured the solubility of well crystallized $^{232}ThO_2$ with reproducible surface properties in 0.01 M NaCl at a pH 3.0 or 4.0. They spiked their solutions with ^{229}Th to determine the rate of attachment of this isotope to the solid surfaces, and measured the dissolved ^{232}Th concentration to establish the rate at which this isotope dissolved. Vandenborre et al. (2010) expanded the range of pH to $0.0 < pH < 5.2$. Perhaps the most interesting results of this work are: (1) Figure 1 of Vandenborre et al. (2010), which shows the extent of the scatter in Th(IV) solubilities reported in the literature from 1964 through 2006; (2) the results of Vandenborre et al. (2010, Figure 1), which are lower than most of the values form the literature but show almost no dependence on pH over the range $0 < pH < 4$; and (3) the values of the logs of the solubility products of Th(IV) solids, which vary from −56.9 for ThO_2(cr) to −45.5 for $ThO_x(OH)_y(H_2O)_z$(s), a range of over 11 orders of magnitude. Xiong et al. (2011) did not consider the results of Vandenborre et al. (2008, 2010) because these papers came to their attention after they completed their analysis. We used criterion S1 (Section 2) to exclude the results of Vandenborre et al. (2008) and Vandenborre et al. (2010), because they were obtained from experiments carried out with solutions with $I < 3$ M.

Wood (2005) measured the solubilities of CeO_2 and ThO_2 in $NaNO_3$ solutions with and without the organic ligands citrate, desferrioxamine B, EDTA, and oxalate at 22 or 25 °C (Table 3). Xiong et al. (2005, 2011) did not consider this paper because it came to their attention after they completed their analysis. We used criterion G9 (Section 2) to exclude their results because NO_3^- is not in the WIPP Th(IV) model.

Finally, Xia et al. (2003) studied the solubility of ThO_2(am) in $NaNO_3$ solutions with various ionic strengths and various concentrations of the organic ligand EDTA (Table 3). Xiong et al. (2005, 2011) did not consider these results because they found this paper later. We used criterion G9 (Section 2) to exclude their results because NO_3^- is not in the WIPP Th(IV) model.

Figure 1 provides the histogram for our comparisons of experimentally measured and predicted Th(IV) solubilities for the CRA-2014 PA, and compares it to those obtained for the CRA-2004 PABC by Xiong et al. (2005) and the CRA-2009 PABC by Xiong et al. (2011). The current comparison includes a total of 185 measured and predicted solubilities, an increase of 45 from the 140 comparisons carried out for the CRA-2009 PABC. The current distribution peaks at Bin 1.05 with a frequency of 19 comparisons, with a secondary peak at Bin −1.2 with 19 comparisons. Table 5 summarizes the statistical parameters of the current frequency distribution and compares them to those of the previous distribution.

Inspection of Figure 1 shows that the WIPP Th(IV) model, the EQ3/6 code, and the DB Data0.FM1 overpredicted 101 of the 185 measured solubilities included in the current analysis and underpredicted 84. Therefore, Figure 1 contains more negative values (100) of the difference between the measured and predicted solubility ($D = \log_{10}(S_m) - \log_{10}(S_p)$) than positive values (84). The mean and median values of the log of the sampled uncertainty factor used to adjust the baseline Th(IV) solubilities are −0.136 and −0.189, respectively (Table 6), and the mean and median values of the sampled uncertainty factor are $10^{-0.136} = 0.732$ and $10^{-0.189} = 0.647$. (The WIPP PA codes use actinide solubilities that are the products of the baseline solubilities and the sampled uncertainty factors).

Table 6 provides values of cumulative distribution function (CDF) for Th(IV) for the CRA-2014 PA, and compares them to those obtained for the CRA-2004 PABC by Xiong et al. (2005) and the CRA-2009 PABC by Xiong et al. (2011). PA will use the current CDF to define the solubility multiplier SOLVAR for the oxidation-state IV model, material SOLMOD4 in the WIPP PA Parameter Database for the CRA-2014 PA. Brush et al. (2005) described the PA implementation of these results in detail.

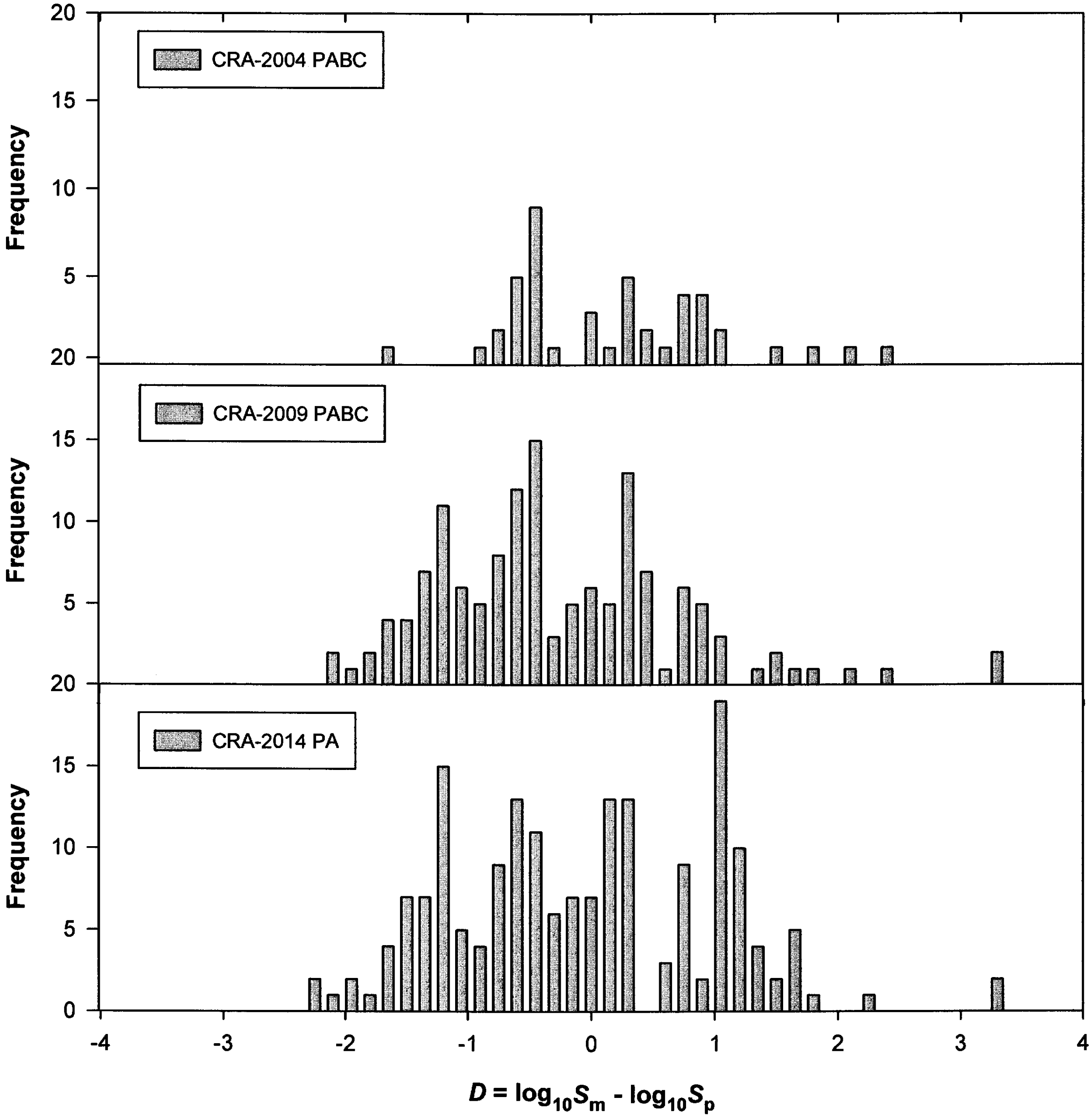

Figure 1. Comparison of the histograms of the difference $D = \log_{10} S_m - \log_{10} S_p$ for Th(IV) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

Table 5. Comparisons of Selected Statistical Properties of the Distribution of D = log10(Sm) – log10(Sp) for Th(IV) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

Analysis	Mean	Median	Standard Deviation	Minimum	Maximum
CRA-2004 PABC	0.108	0.075	0.837	−1.80	2.40
CRA-2009 PABC	−0.346	−0.520	0.995	−2.25	3.30
CRA-2014 PA	−0.136	−0.189	1.061	−2.28	3.19

Table 6. Comparisons of the CDFs of the Differences between Measured and Predicted Th(IV) Solubilities for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011). This CDF will be used to define the solubility multiplier SOLVAR for the oxidation-state IV model material SOLMOD4 in the WIPP PA Parameter Database.

X	$P(D < X)$ CRA-2004 PABC	$P(D < X)$ CRA-2009 PABC	$P(D < X)$ CRA-2014 PA
–2.40	0.0000	0.0000	0.0000
–2.25	0.0000	0.0000	0.0108
–2.10	0.0000	0.0143	0.0162
–1.95	0.0000	0.0214	0.0270
–1.80	0.0000	0.0357	0.0324
–1.65	0.0222	0.0643	0.0541
–1.50	0.0222	0.0929	0.0919
–1.35	0.0222	0.1429	0.1297
–1.20	0.0222	0.2214	0.2108
–1.05	0.0222	0.2643	0.2378
–0.90	0.0444	0.3000	0.2595
–0.75	0.0889	0.3571	0.3081
–0.60	0.2000	0.4429	0.3784
–0.45	0.4000	0.5500	0.4378
–0.30	0.4222	0.5714	0.4703

Table 6 continued on next page

Table 6. Comparisons of the CDFs of the Differences between Measured and Predicted Th(IV) Solubilities for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011) (continued). This CDF will be used to define the solubility multiplier SOLVAR for the oxidation-state IV model material SOLMOD4 in the WIPP PA Parameter Database.

X	$P(D < X)$ CRA-2004 PABC	$P(D < X)$ CRA-2009 PABC	$P(D < X)$ CRA-2014 PA
−0.15	0.4222	0.6071	0.5081
0.00	0.4889	0.6500	0.5459
0.15	0.5111	0.6857	0.6162
0.30	0.6222	0.7786	0.6865
0.45	0.6667	0.8286	0.6865
0.60	0.6889	0.8357	0.7027
0.75	0.7778	0.8786	0.7514
0.90	0.8667	0.9143	0.7622
1.05	0.9111	0.9357	0.8649
1.20	0.9111	0.9357	0.9189
1.35	0.9111	0.9429	0.9405
1.50	0.9333	0.9571	0.9514
1.65	0.9333	0.9643	0.9784
1.80	0.9556	0.9714	0.9838
1.95	0.9556	0.9714	0.9838
2.10	0.9778	0.9786	0.9838
2.25	0.9778	0.9786	0.9892
2.40	1.0000	0.9857	0.9892
2.55	1.0000	0.9857	0.9892
2.70	1.0000	0.9857	0.9892
2.85	1.0000	0.9857	0.9892
3.00	1.0000	0.9857	0.9892
3.15	1.0000	0.9857	0.9892
3.30	1.0000	1.0000	1.0000

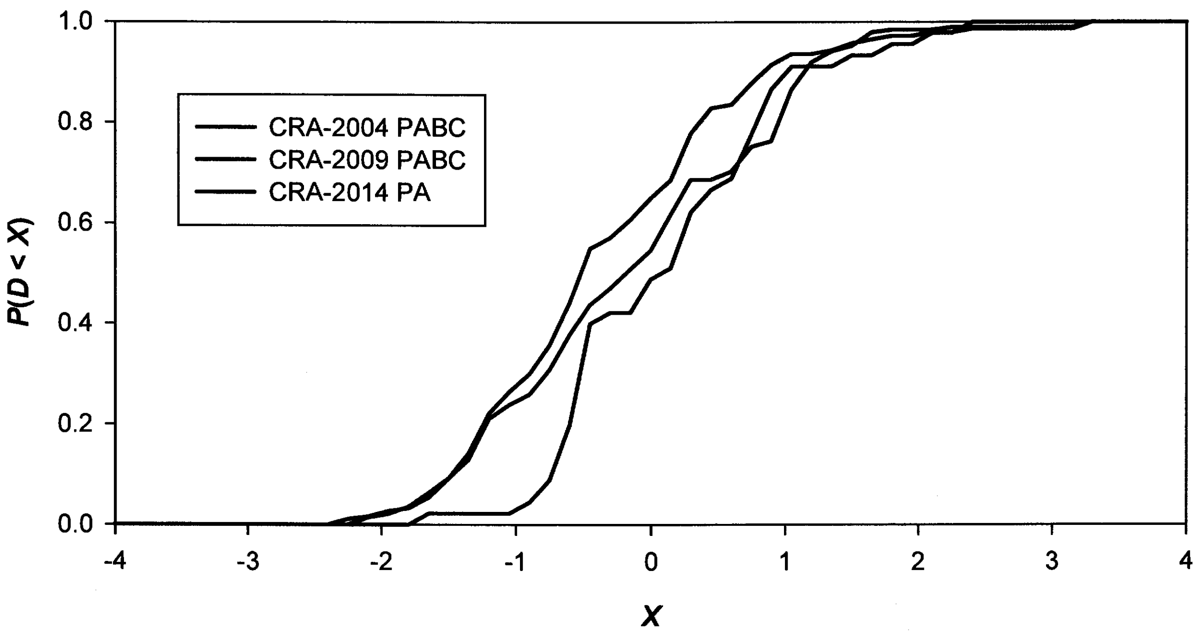

Figure 2. Comparison of plots of the CDFs for Th(IV) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

3.2 Am(III) Solubility Model

This subsection describes our comparisons of experimentally measured Am(III) solubilities with those predicted using the WIPP Am(III) speciation and solubility model in EQ3/6. It includes information similar to that provided for Th(IV) in Subsection 3.1 (see above).

The measured Am(III) solubilities from published papers and unpublished reports evaluated previously (Xiong et al., 2005; and/or Xiong et al., 2011) include: Borkowski et al. (2009), Borkowski (2010), Bunyakina and Storozhenko (2004), Khalili et al. (1994), Lucchini et al. (2007), Makino et al. (1993), Meinrath and Kim (1991), Meinrath and Takeishi (1993), Peretrukhin et al. (1996), Rao et al. (1996a, 1996b, 1999), Runde et al. (1992), Runde and Kim (1995), Silva (1982), and Wood (2002) (see Table 7 and the text below).

The measured Am(III) solubilities from published papers and unpublished reports that we evaluated for this analysis include: Borkowski et al. (2010), Borkowski (2012), Migdisov and Williams-Jones (2007), Neck et al. (2009), Rabung et al. (2008) and Vitorge and Tran The (1991) (see Table 7 and text).

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities.

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Borkowski et al. (2009)	(A) 5 m NaCl (B) GWB, diluted to 95% of its specified concentrations (C) ERDA-6, diluted to 95% of its specified concentrations	(A) pcH = 8.2–13.0 (B) pcH = 6.6–8.7 (C) pcH = 7.9–10.3	Presumably $Nd(OH)_3$, based on their thermodynamic predictions.	Superseded by Borkowski (2010) (see below).
Borkowski (2010)	(A) 5 m NaCl (B) GWB, diluted to 95% of its specified concentrations of solutes to avoid coprecipitation of Nd by evaporite minerals (C) ERDA-6, diluted to 95% of its specified concentrations of solutes to avoid coprecipitation of Nd by evaporite minerals	(A) pcH = 8.14–13.17 (B) pcH = 6.54–8.64 (C) pcH = 7.55–10.62	Presumably $Nd(OH)_3$, based on their thermodynamic predictions.	Superseded Borkowski et al. (2009). All 120 results from 5 M NaCl included by Xiong et al. (2011) and in this analysis: EQ3 input files 01Bor10.3i through 120Bor10.3i. Twenty-eight results (01BorGWB.3i through 28BorGWB.3i) with pcH ≤ 7.4 from GWB included in this analysis because Borkowski concluded that they were not affected significantly by Nd(III)-borate complexation (see the description of Borkowski et al., 2009, in the text). Fourteen results with pcH ≤ 8.1 from ERDA-6 (01BorERD.3i through 14BorERD.3i) included in this analysis because Borkowski concluded that these results were unaffected by borate. A total of 162 results (29 replicates) included.
Borkowski et al. (2010)	1, 2, 3, 4, or 5 M NaCl with 0.00. 0.01, 0.02, 0.03, or 0.04 M $Na_2B_4O_7$; all runs from undersaturation	pcH = 8.59 ± 0.04 (constant, all runs)	Presumably $Nd(OH)_3$, which was used to start these runs	Results obtained with 1, 2, 3, 4, or 5 M NaCl & 0.00 M $Na_2B_4O_7$ included in this analysis, but used numerical values from Borkowski (2012) (see below): 01bor12.3i through 05bor12.3i. All other results excluded from this analysis because the $NdHB_4O_7^{2+}$ found to be important by Borkowski et al. (2010) is not in the WIPP Am(III) model.
Borkowski (2012)	Same as above	Same as above	Same as above	Same as above

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Bunyakina & Storozhenko (2004)	Solutions saturated with $MgSO_4$ and/or $Nd_2(SO_4)_3$. Ionic strengths not provided.	Not provided	$Nd_2(SO_4)_3 \cdot 8H_2O$	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. Excluded by Xiong et al. (2011) and from this analysis because $Nd_2(SO_4)3 \cdot 8H_2O$ is not in the WIPP Am(III) model.
Khalili et al. (1994)	Synthetic brine similar to GWB	pcH = 6.4, 8.4, 10.4, & 12.4	$Nd(OH)_3 \cdot nH_2O(am)$ at pcH = 6.4 & 8.4, $Nd_2(CO_3)_3 \cdot 8H_2O$ or "uncertain" at pcH = 10.4, NdO(OH) & $Nd(OH)_3$ or "uncertain" at pcH = 12.4	Twenty-nine results for pcH = 6.4 & 8.4 included by Xiong et al. (2005) because $Am(OH)_3$ is in the WIPP Am(III) model. Results for pcH = 10.4 & 12.4 excluded by Xiong et al. (2005) because $Nd_2(CO_3)_3 \cdot 8H_2O$ and NdO(OH) are not in the model, and because it is unclear that all of the solids were identified. Twenty-four of the 29 results included by Xiong et al. (2005) excluded by Xiong et al. (2011) and from this analysis because the pcH in these runs exceeded 7.4, the pcH above which Borkowski concluded that complexation of Nd(III) by borate in GWB is significant (see text). Five results (5 duplicates) included: 01Khal94.3i.
Lucchini et al. (2007)	(A) GWB (B) ERDA-6	(A) pcH = 6.6–8.7 (B) pcH = 7.9–10.3	$Nd(OH)_3$ (both solutions), based on their thermodynamic predictions.	Excluded by Xiong et al. (2011) and from this analysis because Borkowski et al. (2009) and Borkowski (2010) superseded this paper.

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Makino et al. (1993)	0.01 M $NaClO_4$ & 0.1 ppm CO_2	pcH = 7–13	$Nd(OH)_3(cr)$ with lesser amounts of $Nd(OH)CO_3(cr)$ (unclear whether both of these solids were in equilibrium one was replacing another).	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. Excluded from by Xiong et al. (2011) and from this analysis because neither the TIC concentration of the aqueous phase nor the pCO_2 of the gaseous phase was provided, thus precluding predictions of Nd(III) solubilities for their experiments.
Meinrath & Kim (1991)	(A) 0.1 M $NaClO_4$ & 0.00031 atm CO_2 (B) 0.1 M $NaClO_4$ & 0.01 atm CO_2 (C) 0.1 M $NaClO_4$ & 1 atm CO_2	(A) pH = 4.1-4.3 (B) pH = 5.2-5.4 (C) pH = 5.7-6.2	(A) $Nd_2(CO_3)_3$ & $Nd(OH)CO_3$ initially, $Nd(OH)CO_3$ after 2 weeks (B) $Nd_2(CO_3)_3$ (C) $Nd_2(CO_3)_3$	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. All nine results (no duplicates) from (A) included by Xiong et al. (2011) and in this analysis because $Nd(OH)CO_3$ is in the WIPP Am(III) model: 01Mein91.3i and 01Mein91.6i through 09Mein91.6i. Results from (B) and (C) excluded by Xiong et al. (2011 and from this analysis because $Nd_2(CO_3)_3$ is not in the model.

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Meinrath & Takeishi (1993)	(A) 0.1 M $NaClO_4$ & 0.0003 atm CO_2	(A) pH = 5.6-6.6	(A) $Nd_2(CO_3)_3$ & $Nd(OH)CO_3$ initially, $Nd(OH)CO_3(mcr)$ after 5-7 days	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analysis. All 17 results (no duplicates) from (A) and (B) included by Xiong et al. (2011) and in this analysis because $Nd(OH)CO_3$, is in the WIPP Am(III) model: 01Mein93.3i and 01Mein93.6i through 17Mein93.6i. Results from (C), (D), and (E) excluded because $Nd_2(CO_3)_3$ is not in the model.
	(B) 0.1 M $NaClO_4$ & 0.003 atm CO_2	(B) pH = 5.4-6.3	(B) $Nd_2(CO_3)_3$ & $Nd(OH)CO_3$ initially, $Nd(OH)CO_3(mcr)$ after 30-40 days	
	(C) 0.1 M $NaClO_4$ & 0.01 atm CO_2	(C) pH = 5.2-6.2	(C) $Nd_2(CO_3)_3{\cdot}(4.5\text{-}6\ H_2O)$	
	(D) 0.1 M $NaClO_4$ & 0.08 atm CO_2	(D) pH = 4.7-5.9	(D) $Nd_2(CO_3)_3{\cdot}(4.5\text{-}6\ H_2O)$	
	(E) 0.1 M $NaClO_4$ & 1 atm CO_2	(E) pH = 4.2-5.2	(E) $Nd_2(CO_3)_3{\cdot}(4.5\text{-}6\ H_2O)$	
Migdisov and Williams-Jones (2007)	$HClO_4$ =$NaHClO_4$ (total ClO_4^- = 0.057-1.97 M	pH = 1.04-1.65 (at 25 °C)	NdF_3	Not considered by Xiong et al. (2005, 2011) because this paper came to their attention after completion of their analysis. All results excluded from this analysis because Migdisov and Williams-Jones (2007) carried out their experiments at 150, 200, and 250 °C, and because F is not in the WPP Am(IIII) model.

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Neck et al. (2009)	(A) 0.1, 0.5, 2.5, & 5.0 M NaCl; 0.1 M $NaClO_4$ (B) 0.25, 1.0, 2.5, & 3.5 M $MgCl_2$ (C) 0.25, 1.0, 2.5, & 3.5 M $CaCl_2$	(A) pcH ≈ 7 to 13, 14, or even 15 (B) pcH ≈ 7 or 7.5 to 9 (C) pcH ≈ 7-9 to 12	(A) $Nd(OH)_3$ or $Cm(OH)_3$ (5 M NaCl &1.0, 2.5, & 3.5 M $CaCl_2$)	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. All 161 results from NaCl and $MgCl_2$ solutions included in this analysis: 01NeckNa.3i through 119NeckNa.3i, and 01NeckMg.3i through 42NeckMg.3i. All 46 results from $CaCl_2$ with pcH < 10 included: 01NeckCa.3i through 46NeckCa.3i. Results with pcH> 10 excluded because the $Ca(Cm(OH)_3)^{2+}$, $Ca_2(Cm(OH)_4)^{3+}$, and $Ca_3(Cm(OH)_6)^{3+}$ complexes found to be important by Neck et al. (2009) are not in the WIPP Am(III) model.
Peretrukhin et al. (1996)	1 & 5 M NaOH (experiments with Am(III))	Not provided	$Am(OH)_3$ aged by boiling for 3 hours (undersaturation runs) or $Am(OH)_3$, crystallinity unspecified (oversaturation runs)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. Four results (two duplicates) modeled by Xiong et al. (2011) but excluded from their comparison because they predicted solubilities four to six orders of magnitude less than their measured values, possibly due to the presence of one or more $Am(OH)_x^{3-x}$ complexes with x > 4 in their experiments, but not in the WIPP Am(III) model. These results also excluded from this analysis.
Rabung et al. 2008	(A) 0.1–3.5 M $CaCl_2$	pcH ≈ 11.7	$Cm(OH)_3(am)$ (all)	Not considered by Xiong et al. (2011) because this paper came to their attention after completion of their analysis. All results excluded from this analysis because the $Ca(Cm(OH)_3)^{2+}$, $Ca_2(Cm(OH)_4)^{3+}$, and $Ca_3(Cm(OH)_6)^{3+}$ complexes found to be important by Rabung et al. (2008) are not in the WIPP Am(III) model.
	(B) 1.0 M $CaCl_2$	pcH = 10.8–11.9		
	(C) 2.5 M $CaCl_2$	pcH = 10.8–11.9		
	(D) 3.5 M $CaCl_2$	pcH = 10.8–11.9		

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Rao et al. (1996a)	0.1 M NaCl	pH = 4.8-9.0 (filtered samples in their Fig. 1) & 5.1-9.0 (41-day samples in their Fig. 2.	$Nd(OH)_3(cr)$	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. Thirty-two of the 25 °C results (no duplicates) included in Xiong et al, (2011) and in this analysis: 01RAO96.3i through 32RAO96.3i. Results obtained at $pH < 5.8$ excluded by Xiong et al. (2011) and from this analysis because the solids dissolved before saturation was attained.
Rao et al. (1996b)	(A) 0.1-1.0 M $NaHCO_3$ (B) 0.1-2.0 M Na_2CO_3	Not provided	$NaNd(CO_3)_2 \cdot 6H_2O(cr)$ (all)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. Sixty results included in Xiong et al. (2011), but seven of these did not attain equilibrium in this analysis. Therefore, fifty-three results (38 duplicates) included in this analysis: 01LR96b.3i through 22LR96.3i.

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Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Rao et al. (1999)	(A) 0.1-1.1 m $NaHCO_3$	(A) pH = 7.9-8.3	$NaNd(CO_3)_2{\cdot}6H_2O$ (all)	One-hundred-and-five results included in Xiong et al. (2005). Twenty-eight of the 105 results included by Xiong et al. (2005) excluded by Xiong et al. (2011) and from this analysis because the pcH in these runs exceeded 7.4 or 8.1, the pcH above which Borkowski concluded that complexation of Nd(III) by borate in GWB or ERDA-6, respectively, is significant (see the description of Borkowski et al., 2009, in the text). Seventy-seven results (25 duplicates) included in this analysis: 01Rao99.3i through 28Rao99.3i, and 2965Rao99.3i to generate a pickup file for 29Rao99.6i through 65Rao99.6i; and 6679Rao99.3i to generate a pickup file for 66Rao99.6i through 79Rao99.6i. Note that only 01RAO99.3i through 28RAO99.3i, 29RAO99.6i through 46RAO99.6i, and 66RAO99.6i through 72RAO99.6i are included in the analysis. Note also, that of the 77 EQ3/6 runs, six were not used because of the code failed to converge to the desired pcH value. These included the files 40Rao99.6i – 44Rao99.6i, bringing the total to 71 data points from Rao et al., 1999. A final note: the file2965Rao99.3i is 8 characters long, and is used to generate a pickup (*.3p) & output (*.3o) file, which follow MS-DOS file convention of 7 character length and thus have the final "9" truncated from their names.
	(B) 0.1-2 m Na_2CO_3	(B) pH = 10.4-10.8		
	(C) 2 M NaCl & 0.1-0.5 m $NaHCO_3$	(C) pH = 7.9-8.3		
	(D) 2 M NaCl & 0.1-2 m Na_2CO_3	(D) pH = 10.4-10.8		
	(E) 4 M NaCl & 0.1-2 m Na2CO3	(E) pcH = 10.4-10.8		
	(F) G Seep, a synthetic brine similar to GWB	(F) pcH = 5.6-7.8		
	(G) ERDA-6	(G) pcH = 6.2-10.6		
Runde et al. (1992)	0.1 M $NaClO_4$ & 0.0003, 0.01, & 1 atm CO_2	pH = 5.5 – 6.3	$Nd(OH)CO_3$ at 0.0003 atm CO_2, $Nd_2(CO_3)_3$ at 0.01 & 1 atm CO_2	Not considered by Xiong et al. (2005), because this paper came to their attention after completion of their analysis. Excluded by Xiong et al. (2011) and from this analysis because only K_{sp}'s reported, not the actual solubility data.

Table 7 continued on next page

Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Runde & Kim (1995)	(A) 5.0 M NaCl (B) 5.0 m NaCl & 0.01 atm CO2	(A) pcH = 6.7–13.8 (B) pcH = 6.6-9.3	(A) Am(OH)3(cr) (B) NaAm(CO3)3 ·xH2O(cr)	Seventy one results (18 duplicates) included in Xiong et al. (2005, 2011) and in this analysis: 01Run95.3i through 18Run95.3i; and 1953Run95.3i with 19Run95.6i through 53Run95.6i. The file 1953Run95.3i is 8 characters long, and is used to generate a pickup (*.3p) & output (*.3o) file, which both follow MS-DOS file convention of 7 character length and thus have the final "5" truncated from their names.
Silva (1982)	(A) 0.1 M $NaClO_4$ (B) 0.1 M $NaClO_4$	(A) pH = 5.7-9.5 (B) pH = 7.0-9.4	(A) $Nd(OH)_3(cr)$ (B) $Am(OH)_3(cr)$	Included in Xiong et al. (2005). Excluded from Xiong et al. (2011) and from this analysis because this paper was published prior to 1990.
Vitorge and Tran The (1991)	(A) "Lime water" (composition unspecified) with 0-10 M KOH (B) "Lime water" (composition unspecified) (C) "Cement water" (composition unspecified) with 0-10 M KOH	Unspecified for (A), (B), and (C)	$Am(OH)_3$?	Not considered by Xiong et al. (2005, 2011) because this paper came to their attention after completion of their analyses. All results excluded because the compositions of the solutions were not specified.

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Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Wood et al. (2002)	(A) 0.03 m NaTr[A] (30 °C) (B) 0.03, 0.10, & 1.0 m NaTr[A] (50 °C) (C) 0.03, 0.10, & 1.0 m NaTr[A] (100 °C) (D) 0.03, 0.010, & 1.0 m NaTr[A] (150 °C)	(A) pmH = 7.01-9.13 (B) pmH = 6.494–9.548 (I = 0.03 m) pmH = 6.653-6.711 (I = 0.10 m) pmH = 6.681-6.809 (I = 1.0 m) (C) pmH = 5.362–8.421 (I = 0.03 m) pmH = 5.739-5.744 (I = 0.10 m) pmH = 5.857-5.859 (I = 1.0 m) (D) pmH = 4.791-5.890 (I = 0.03 m) pmH = 5.017-5.021 (I = 0.10 m) pmH = 5.139-5.141 (I = 1.0 m)	Nd(OH)$_3$(cr)	Not considered by Xiong et al. (2005) because this paper came to their attention after completion of their analyses. Most results excluded by Xiong et al. (2011) and from this analysis because T > 30 °C. Fifteen results (no duplicates) obtained at 30 °C included by Xiong et al. (2011) and in this analysis: 01WO02.3i through 15WO02.3i

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Table 7. Final Evaluations of Laboratory Studies for Comparisons of Measured and Predicted Nd(III) and Am(III) Solubilities (continued).

Reference	Solution(s) and Ionic Strength(s)	pcH, pmH, or pH	Solubility-Controlling Solid	Evaluation and EQ3/6 Run Numbers for Results Included in This Analysis
Wood et al. (2002) (continued)	(E) 0.03, 0.10, & 1.0 m NaTr[A] (200 °C)	(E) pmH = 4.419-5.088 (I = 0.03 m) pmH = 4.472-4.473 (I = 0.10 m) pmH = 4.558-4.560 (I = 1.0 m)	See Wood et al. (2002) on previous page.	See Wood et al. (2002) on previous page.
	(F) 0.03, 0.10, & 1.0 m NaTr[A] (250 °C)	(F) pmH = 3.873-4.873 (I = 0.03 m) pmH = 4.050-4.068 (I = 0.10 m) pmH = 4.180-4.182 (I = 1.0 m)		
	(G) 0.03 & 0.10 m (290 °C)	(G) pmH = 3.493–6.898 (I = 0.03 m) pH = 3.406-5.221 (I = 0.10 m)		

A. Sodium trifluoromethanesulfonate, abbreviated as "sodium triflate" or "NaTr," is a noncomplexing salt used to set the ionic strength. In EQ3/6 calculations, the noncomplexing medium, sodium perchlorate, is used as the supporting solution.

B. Sodium trifluoromethanesulfonate, abbreviated as "sodium triflate" or "NaTr," is a noncomplexing salt used to set the ionic strength.

Borkowski et al. (2009) measured the solubilities of various Nd(III) solids in 5 m NaCl and the synthetic WIPP brines GWB and ERDA-6, diluted to 95% of their specified concentrations to avoid coprecipitation of Nd(III) by evaporite minerals (see Table 7). (Small changes in conditions, especially temperature, during solubility experiments can cause precipitation of solids such as evaporite minerals and coprecipitation of actinide elements if the solutions are saturated with these solids under the conditions used for these tests.) Nd(III), an oxidation-state analog of Am(III), was used along with Am(III) and Cm(III) to parameterize the WIPP Am(III) speciation and solubility model. However, Borkowski et al. (2009) stated that, in many of their experiments in GWB or ERDA-6, complexation of Nd(III) by dissolved borate probably increased the solubility of Nd(III). Because there are no Nd(III)-borate species in the WIPP Am(III) solubility model, SNL personnel asked Borkowski to select those experiments that had values of pcH low enough to preclude significant complexation of Nd(III) by borate, thereby satisfying criterion G9. Borkowski selected 18 runs with GWB (pcH ≤ 7.4) and 10 with ERDA-6 (pcH ≤ 8.1) and e-mailed them the numerical values of the results. This e-mail is in the SNL/WIPP Records Center in the records package entitled "Calculation of Actinide Solubilities for the WIPP CRA-2009 PABC," ERMS 548686. Borkowski also sent them the results of 54 runs with 5 m NaCl, because these solutions contained no borate. This e-mail is in the same records package.

Borkowski (2010) issued a report containing tables of numerical values of the final values of pcH and Nd(III) solubilities presented graphically by Borkowski et al. (2009). From the standpoint of the analysis by Xiong et al. (2011) and this analysis, Borkowski (2010) superseded Borkowski et al. (2009). However, comparisons of the numerical values in Borkowski (2010) and those e-mailed by Borkowski (see above) revealed that: (1) Borkowski (2010) contained more results than those e-mailed by Borkowski, and (2) the numerical values e-mailed by Borkowski could not be correlated with any of those in Borkowski (2010). Therefore, Xiong et al. (2011) used the numerical values from Borkowski (2010). However, they used the compositional and pcH criteria e-mailed by Borkowski (see the description of Borkowski et al., 2009, in the text above) to select these numerical values. Thus, they used the following 162 results reported by Borkowski (2010): all 120 results from the 5 M NaCl solutions, 28 results from GWB with pcH ≤ 7.4, and 14 from ERDA-6 with pcH ≤ 8.1. We used the same results in this analysis.

Borkowski et al. (2010) carried out solubility experiments with $Nd(OH)_3$ in 1, 2, 3, 4, or 5 M NaCl with 0.00, 0.01, 0.02, 0.03, or 0.04 M $Na_2B_4O_7$ at a constant pcH of 8.59 ± 0.04. Because all of these experiments were undersaturation runs and because the solutions were carbonate-free, the solubility-controlling solid in these experiments was presumably $Nd(OH)_3$. We included the results obtained from solutions with 1, 2, 3, 4, or 5 M NaCl and 0.00 M $Na_2B_4O_7$. However, we excluded all of the other results, because the $NdHB_4O_7^{2+}$ complex found to be important by Borkowski et al. (2010) is not in the WIPP Am(III) model. After the release of Borkowski et al. (2010), Borkowski (2012) provided numerical values of the Nd(III concentrations shown graphically by Borkowski et al. (2010). We used these numerical values from Borkowski (2012) for this analysis.

Bunyakina & Storozhenko (2004) conducted solubility experiments with $Nd_2(SO_4)_3{\cdot}8H_2O$ in solutions saturated with $MgSO_4$ and/or $Nd_2(SO_4)_3$ (see Table 7). Xiong et al.

(2005) did not consider the results of Bunyakina & Storozhenko (2004) because this paper came to their attention after they completed their analysis. Xiong et al. (2011) excluded these results from their analysis according to criterion G7 (see Section 2) because $Nd_2(SO_4)_3 \cdot 8H_2O$ is not in the WIPP Am(III) model. We excluded these results for the same reason.

Khalili et al. (1994) determined the solubilities of various Nd(III) solids in a synthetic brine similar to GWB (Table 7). According to criterion G7 (Section 2), Xiong et al. (2005) included 29 measured solubilities from solutions with pcH = 6.4 and 8.4 in their analysis because $Am(OH)_3$, the solubility-controlling solid in these experiments, is in the WIPP Am(III) model. However, they used the same criterion to exclude the results obtained from solutions with pcH = 10.4 and 12.4 because $Nd_2(CO_3)_3 \cdot 8H_2O$ and NdO(OH), the solubility-controlling solids in these runs, are not in the model, and because it is unclear whether all of the solids were identified at these values of pcH. After considering the results of Borkowski et al. (2009) (see text and Table 7 above), Xiong et al. (2011) used criterion G9 to exclude 24 of the 29 results included by Xiong et al. (2005), because the pcH of the solutions in these experiments exceeded 7.4, the pcH above which Borkowski concluded that complexation of Nd(III) by dissolved borate in GWB is significant. Therefore, Xiong et al. (2011) included five of the results of Khalili et al. (1994) in their analysis. We included the same five results in this analysis.

Lucchini et al. (2007) included preliminary results from Borkowski's study of the solubility of Nd(III) (see above and Table 7). Borkowski et al. (2009) and Borkowski (2010) superseded Lucchini et al. (2007). Therefore, Xiong et al. (2011) evaluated the results of Borkowski (2010) and included many of them in their analysis. We included the same results included by Xiong et al. (2011) in this analysis. See the text and the entries in Table 7 for Borkowski et al. (2009) and Borkowski (2010) for a detailed explanation of why these results were included or excluded.

Makino et al. (1993) measured the solubilities of Nd(III) solids in 0.01 M $NaClO_4$ (Table 7). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. Makino et al. (1993) stated that "the solid phase was identified as $Nd(OH)_3(c)$ by X-ray diffraction [XRD] before and after the experiments." However, both of the posttest XRD patterns in their Figure 1 show that $Nd(OH)CO_3(cr)$ was also present. Clearly, sufficient CO_3^{2-} was present in their solutions to convert at least some of the $Nd(OH)_3(cr)$ to $Nd(OH)CO_3(cr)$ during their undersaturation and/or oversaturation experiments, but it is unclear whether both of these solids were in equilibrium with the solutions or whether one solid was replacing another. It is also unclear what the TIC concentration of their solutions was, or even what the p_{CO_2} of the atmosphere in the headspace above their solutions was, because the p_{CO_2} of 0.1 ppm provided in the English summary of their paper was a detection limit (upper limit) for p_{CO_2}, not the actual concentration of CO_2 in the gaseous phase. Therefore, Xiong et al. (2011) excluded all 22 measured solubilities of Makino et al. (1993) according to criterion G8. We also excluded these results from this analysis.

Meinrath and Kim (1991) measured the solubilities of $Nd_2(CO_3)_3$ and $Nd(OH)CO_3$ in 1 M $NaClO_4$ under atmospheres with various concentrations of CO_2 (Table 7). Xiong et al. (2005) did not consider the results of Meinrath and Kim (1991) because this paper did not come to their attention until after they completed their analysis. Xiong et al. (2011) included all nine results obtained with 0.1 M $NaClO_4$ under a gaseous phase that contained 0.00031 atm CO_2 according to criterion G7 (Section 2), because $Nd(OH)CO_3$, — the solubility-controlling solid in these experiments — is in the WIPP Am(III) model. However, they used the same criterion to exclude the results obtained from 0.1 M $NaClO_4$ under 0.01 and 1 atm CO_2, because $Nd_2(CO_3)_3$ — the solubility-controlling solid in these runs — is not in the model. We included and excluded the same results from this analysis.

Meinrath and Takeishi (1993) also determined the solubilities of $Nd_2(CO_3)_3$ and $Nd(OH)CO_3$ in 1 M $NaClO_4$ under atmospheres with various concentrations of CO_2 (Table 7). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. Xiong et al. (2011) included all 17 results obtained with 0.1 M $NaClO_4$ under 0.0003 and 0.003 atm CO_2 according to criterion G7 (Section 2), because $Nd(OH)CO_3$ — the solubility-controlling solid in these experiments (Table 7) — is in the WIPP Am(III) model. However, they used the same criterion to exclude the results obtained from 0.1 M $NaClO_4$ under 0.01, 0.08, and 1 atm CO_2 because $Nd_2(CO_3)_3$ — the solubility-controlling solid in these runs — is not in the model. We included and excluded the same results from this analysis.

Migdisov and Williams-Jones (2007) performed a solubility study of NdF_3 in $HHClO_4$-$NaHClO_4$ solutions (total ClO_4^- = 0.057-1.97 M) at 150, 200, and 250 °C. Xiong et al. (2005, 2011) did not consider these results because they found this paper came to their attention after they completed their analyses. We used criterion G5 to exclude their results, because they carried out their experiments at 150, 200, and 250 °C. However, Criteria G7 and G9 also apply, because NdF_3 — the solubility-controlling solid in their experiments — and NdF^{2+} — one of the important complexes in their runs — are not in the WIPP Am(III) model.

Neck et al. (2009) measured the solubilities of $Nd(OH)_3$ and $Cm(OH)_3$ in NaCl, $MgCl_2$, and $CaCl_2$ solutions of various ionic strengths (Table 7). Xiong et al. (2011) did not consider the results of Neck et al. (2009) because this paper came to their attention after they completed their analyses. We included all of their results from experiments with NaCl solutions, because these results are consistent with the dominance of $Nd(OH)_x^{3-x}$ or $Cm(OH)_x^{3-x}$ complexes with $0 \leq x \leq 3$. Furthermore, their data from solutions with very high values of pcH ($13 \leq pcH \leq 15$) showed no evidence for $Nd(OH)_x^{3-x}$ or $Cm(OH)_x^{3-x}$ complexes with $x > 3$. (The WIPP Am(III) model contains $Am(OH)_x^{3-x}$ complexes with $0 \leq x \leq 3$, but not $x > 3$.) We also included all of their results from experiments with $MgCl_2$ solutions, because the pcH in these runs (≤ 9) was not high enough to stabilize possible $Nd(OH)_x^{3-x}$ or $Cm(OH)_x^{3-x}$ complexes with $x > 3$. Finally, we included all of their results obtained with $CaCl_2$ solutions with pcH < 10, but excluded those from $CaCl_2$ solutions with pcH > 10. The reason why we excluded the latter results is that Neck et al. (2009) provided solubility data (negative slopes of solubility versus pcH) and time-resolved laser fluorescence spectroscopic (TRLFS) results that imply that $Ca[Cm(OH)_3]^{2+}$, $Ca_2[Cm(OH)_4]^{3+}$, and $Ca_3[Cm(OH)_6]^{3+}$ and — by application of the oxidation-state analogy — $Ca[Nd(OH)_3]^{2+}$, $Ca_2[Nd(OH)_4]^{3+}$, and $Ca_3[Nd(OH)_6]^{3+}$ are the dominant species in $CaCl_2$ solutions with pcH > 10. (The WIPP Am(III) model does not contain any of the complexes $Ca[Am(OH)_3]^{2+}$, $Ca_2[Am(OH)_4]^{3+}$, or $Ca_3[Am(OH)_6]^{3+}$.)

Nevertheless, the WIPP Am(III) model is still adequate for WIPP compliance-related calculations. This is because Figures 4a through 4d of Neck et al. (2009) show that the concentrations of these $Ca_x[Am(OH)_y]^{2x+3-y}$ complexes at a pcH of 9.54 or 9.69, the values predicted by Brush and Domski (2013) for the minimum volume of GWB or ERDA-6, respectively, for the CRA-2014 PA, do not exceed ~$10^{-9.5}$ M until the $CaCl_2$ concentration exceeds ~0.25 M. This concentration of ~$10^{-9.5}$ M is several orders of magnitude less than the predicted concentrations of $AmEDTA^-$ and $Am(OH)_2^+$ (the most important Am(III) complexes in the WIPP), which are ~10^{-6} or 10^{-7} m. (Note that the numerical values of these concentrations in molal units do not differ significantly from those in molar units.) By contrast, the Ca concentrations predicted by Brush and Domski (2013) for the minimum volumes of GWB and ERDA-6 are 0.0111 and 0.0116 M. Therefore, the Ca concentrations of WIPP brines are far too low to stabilize the $Ca_x[Am(OH)_y]^{2x+3-y}$ complexes characterized by Neck et al. (2009), even after reacting with the solids in WIPP disposal rooms.

Peretrukhin et al. (1996) studied the solubilities of Tc(IV), Tc(V), Np(IV), Np(VI), Pu(III), Pu(IV), Am(III), and Am(VI) in strongly basic solutions. They carried out four experiments with Am(III), two in 1 M NaOH and two in 5 M NaOH (Table 7). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. Xiong et al. (2011) predicted Am(III) solubilities about four to six orders of magnitude less than their measured values (see their Table 9). They concluded that these differences were caused by one or more $Am(OH)_x^{3-x}$ complexes with $x > 3$ that were dominant in the experiments of Peretrukhin et al. (1996), but are not in the WIPP Am(III) model. Therefore, they used criterion G9 (Section 2) to exclude these measured Am(III) solubilities. We also excluded these results. Note, however, that other results from solutions with $13 \leq pcH \leq 15$ showed no evidence for $Nd(OH)_x^{3-x}$ or $Cm(OH)_x^{3-x}$ complexes with $x > 3$ (see Neck et al, 2009).

Rabung et al. (2008) measured the solubility of Cm in 0.1, 1.0, 2.5, and 3.5 M $CaCl_2$ solutions under basic conditions (Table 7). Xiong et al. (2011) did not consider these results because they found this paper later. We suspect that Rabung et al. (2008) was superseded by Neck et al. (2009). Our evaluation of the results of Neck et al. (2009) led us to conclude that all of their results obtained with $CaCl_2$ solutions with $pcH < 10$ are consistent with the dominance of $Cm(OH)_x^{3-x}$ complexes with $0 \leq x \leq 3$, which are included in the WIPP Am(III) model. However, their results obtained with $CaCl_2$ solutions with $pcH > 10$ imply that $Ca_x[Am(OH)_y]^{2x+3-y}$ complexes dominate. We excluded the results of Neck et al. (2009) from $CaCl_2$ solutions with $pcH > 10$ and we excluded all of the results of Rabung et al. (2008) with $pcH > 10$, because the WIPP Am(III) model does not contain any of these $Ca_x[Am(OH)_y]^{2x+3-y}$ complexes.

Rao et al. (1996a) carried out solubility experiments with $Nd(OH)_3(cr)$ in 0.1 M NaCl at 25 and 90 °C. Xiong et al. (2005) did not consider the results of Rao et al. (1996a) because this paper came to their attention after they completed their analysis. Initially, Xiong et al. (2011) decided to include the 25 °C results of Rao et al. (1996a) and exclude their 90 °C results because the latter temperature is too high to be relevant to the WIPP. However, inspection of the 25 °C results showed that those with pH values < 5.8 were essentially independent of pH. This feature is similar to that observed by Xiong et al. (2005) in the results of Felmy et al. (1991) (see the discussion of these results in Subsection 3.1 above). Therefore, according to criterion G7

(Section 2), Xiong et al. (2011) included only the 32 solubilities measured by Rao et al. (1996a) at pH values > 5.8. We included the same results in this analysis.

Rao et al. (1996b) conducted solubility experiments with $NaNd(CO_3)_2{\cdot}6H_2O(cr)$ in $NaHCO_3$ and Na_2CO_3 solutions of various ionic strengths (Table 7). Xiong et al. (2005) did not consider this paper because it came to their attention after they completed their analysis. Xiong et al. (2011) included all 60 results in their analysis. We also included these results.

Rao et al. (1999) studied the solubilities of $NaNd(CO_3)_2{\cdot}6H_2O$ in $NaHCO_3$, Na_2CO_3, NaCl-$NaHCO_3$, and NaCl-Na_2CO_3 solutions of various ionic strengths; and in synthetic G Seep (a WIPP brine similar to GWB) and ERDA-6 (Table 7). Xiong et al. (2005) included all 104 results of this study in their analyses. Xiong et al. (2011), however, excluded 28 of the 104 results included by Xiong et al. (2005) according to criterion G9 because the pcH of the solutions in these experiments exceeded 7.4 or 8.1, the pcH above which Borkowski concluded that complexation of Nd(III) by dissolved borate in GWB or ERDA-6, respectively, is significant. Therefore, Xiong et al. (2011) included 76 of the results of Rao et al. (1999) in their analysis. We included these results too.

Runde et al. (1992) measured the solubilities of $Nd(OH)CO_3$ and $Nd_2(C0_3)_3$ under atmospheres with various concentrations of CO_2 (Table 7). Xiong et al. (2005) did not consider the results of Runde et al. (1992) because this paper came to their attention after they completed their analyses. Runde et al. (1992) reported values of K_{sp}s instead of solubilities expressed as concentrations of dissolved Nd(III). Therefore, according to criterion G10 (Section 2), Xiong et al. (2011) excluded their results. We excluded them for the same reason.

Runde and Kim (1995) determined the solubility of $Am(OH)_3(cr)$ in 5.0 M NaCl and that of $NaAm(CO_3)_3{\cdot}xH_2O(cr)$ in 5.0 m NaCl under an atmosphere with 0.01 atm CO_2 (Table 7). Xiong et al. (2005, 2011) included all 71 results of this work in their analyses. We also included all 71 results in our analysis.

Silva (1982) performed solubility experiments with $Nd(OH)_3$ and $Am(OH)_3$ in 0.1 M $NaClO_4$ (Table 7). Xiong et al. (2005) included all 37 results of this study in their analyses. Xiong et al. (2011), however, included only measured solubilities from papers published or unpublished reports issued from January 1, 1990, through December 31, 2008 (criterion G1 in Section 2). Therefore, they excluded the results of Silva (1982) from their analysis. We excluded them too.

Vitorge and Tran The (1991) measured the solubilities of $Am(OH)_3$ and Am(V)-bearing solids in solutions that they referred to as “lime water” and “cement water.” They did not provide enough information on the compositions of their solutions to predict the solubilities of Am(III) in the absence of assumptions as to what solid(s) were present when samples were taken for analysis of Am concentrations, what the TIC concentration was, etc. Xiong et al. (2005, 2011) did not consider this paper because it came to their attention after they completed their analyses. We used criterion G8 (Section 2) to exclude all of their results.

Wood et al. (2002) studied the solubility of $Nd(OH)_3(cr)$ in 0.03, 0.10, and 1.0 m sodium trifluoromethanesulfonate ($NaCF_3SO_3$) solutions at 30, 50, 100, 150, 200, 250, and 290 °C. (Sodium trifluoromethanesulfonate is often abbreviated as "sodium triflate" or "NaTr.") Wood et al. (2002) used NaTr to set the ionic strength in their experiments because it dissolves to form species that do not complex Nd(III) in aqueous solutions. Xiong et al. (2005) did not consider these results because they found this paper later. Xiong et al. (2011) included the 15 results obtained at 30 °C in this revision, but excluded all results obtained at higher temperatures because they were above the acceptable temperature range of 20–30 °C specified in criterion G5 (Section 2). We included and excluded the same results.

Figure 3 provides the histogram for our comparison of experimentally measured and predicted Nd(III) and Am(III) solubilities for the CRA-2014 PA, and compares it to those obtained for the CRA-2004 PABC (Xiong et al. (2005) and the CRA-2009 PABC (Xiong et al. (2011). The current comparison includes a total of 647 measured and predicted solubilities, an increase of 206 from the 441 comparisons conducted for the CRA-2009 PABC. The current distribution peaks at Bin 0.90 with a frequency of 33, comparisons, with a secondary peak at Bins 0.15 and 0.30 with 32 comparisons each. Table 8 summarizes the statistical parameters of the current frequency distribution and compares them to those of the previous distributions.

Figure 3 shows that the WIPP Am(III) model, the EQ3/6 code, and the DB data0.FM1 overpredicted 254 of the 627 measured Nd(III) and Am(III) solubilities in this analysis, and underpredicted 393. The mean and median values of the log of the sampled uncertainty factor used to adjust the baseline Am(III) solubilities are 0.441 and 0.346, respectively (Table 8), and the mean and median values of the sampled uncertainty factor are $10^{0.441} = 2.76$ and $10^{0.346} = 2.22$. WIPP PA uses actinide solubilities that are the products of the baseline solubilities and the sampled uncertainty factors.

Table 9 provides values of the CDF for Nd(III) and Am(III) for the CRA-2014 PA and compares them to those obtained for the CRA-2004 PABC by Xiong et al. (2005) and the CRA-2009 PABC by Xiong et al. (2011). PA will use the current CDF to define the solubility multiplier SOLVAR for the oxidation-state III model, material SOLMOD3 in the WIPP PA Parameter Database for the CRA-2014 PA. Brush et al. (2005) described the PA implementation of these results in detail.

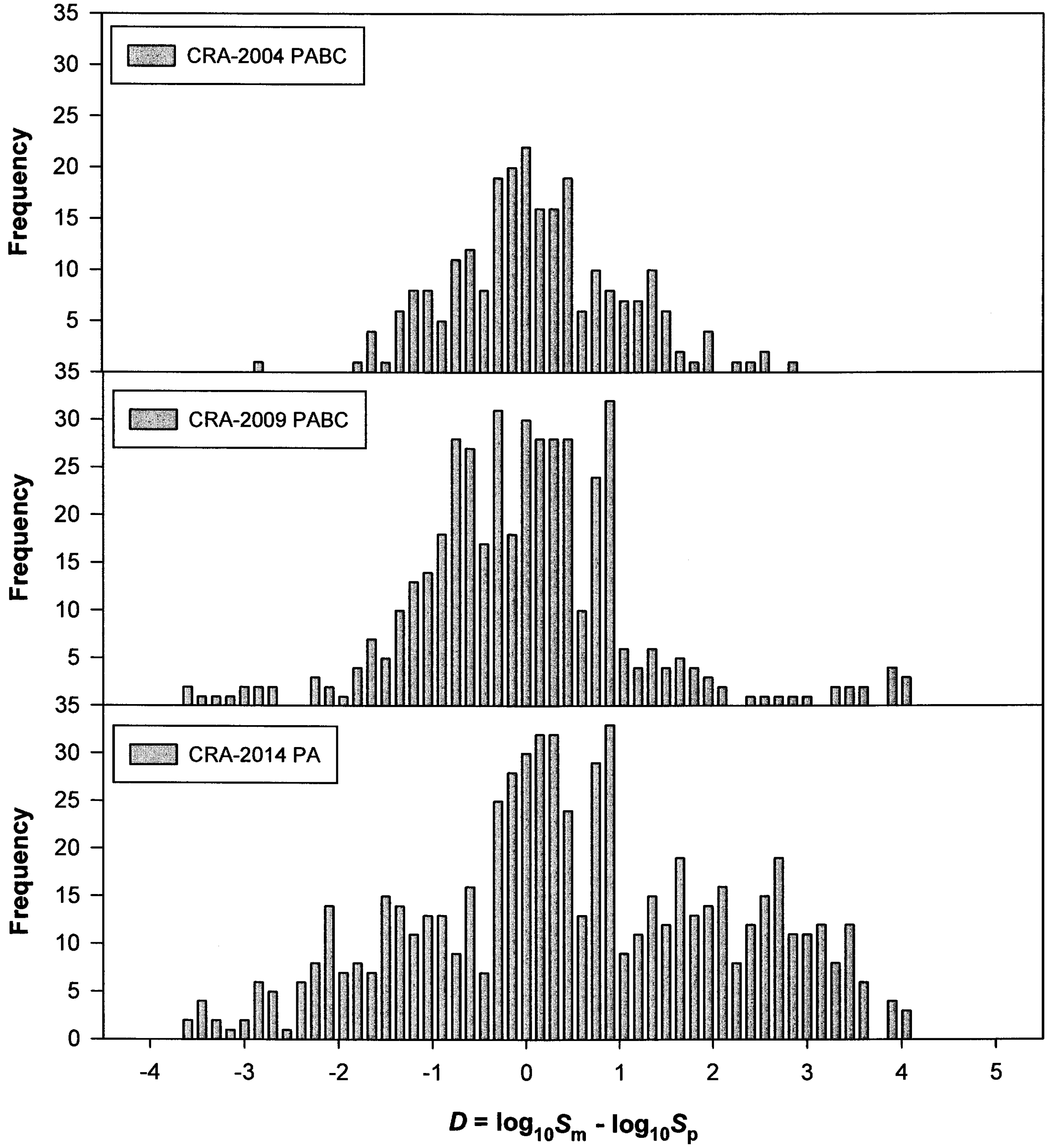

Figure 3. Comparison of the histograms of the difference $D = \log_{10} S_m - \log_{10} S_p$ for Nd(III) and Am(III) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

Table 8. Comparisons of Selected Statistical Properties of the Distribution of $D = \log_{10}(S_m) - \log_{10}(S_p)$ for Nd(III) and Am(III) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

Analysis	Mean	Median	Standard Deviation	Minimum	Maximum
CRA-2004 PABC	0.035	–0.031	0.900	–3.00	2.85
CRA-2009 PABC	–0.142	0.072	1.17	–4.20	2.70
CRA-2014 PA	0.441	0.346	1.67	-3.67	3.95

Table 9. Comparisons of the CDFs of the Differences between Measured and Predicted Nd(III) and Am(III) Solubilities for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011). This CDF will be used to define the solubility multiplier SOLVAR for the oxidation-state III model material SOLMOD3 in the WIPP PA Parameter Database.

X	$P(D < X)$, CRA-2004 PABC	$P(D < X)$, CRA-2009 PABC	$P(D < X)$, CRA-2014 PA
–3.75	0.0000	0.0000	0.0000
–3.60	0.0000	0.0045	0.0031
–3.45	0.0000	0.0068	0.0093
–3.30	0.0000	0.0091	0.0124
–3.15	0.0000	0.0113	0.0139
–3.00	0.0000	0.0159	0.0170
–2.85	0.0041	0.0204	0.0263
–2.70	0.0041	0.0249	0.0340
–2.55	0.0041	0.0249	0.0355
–2.40	0.0041	0.0249	0.0448
–2.25	0.0041	0.0317	0.0572
–2.10	0.0041	0.0363	0.0788
–1.95	0.0041	0.0385	0.0896
–1.80	0.0082	0.0476	0.1020
–1.65	0.0247	0.0635	0.1128

Table 9 continued on next page

Table 9. Comparisons of the CDFs of the Differences between Measured and Predicted Nd(III) and Am(III) Solubilities for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011) (continued). This CDF will be used to define the solubility multiplier SOLVAR for the oxidation-state III model material SOLMOD3 in the WIPP PA Parameter Database.

X	$P(D < X)$, CRA-2004 PABC	$P(D < X)$, CRA-2009 PABC	$P(D < X)$, CRA-2014 PA
−1.50	0.0288	0.0748	0.1360
−1.35	0.0535	0.0975	0.1577
−1.20	0.0864	0.1270	0.1747
−1.05	0.1193	0.1587	0.1947
−0.90	0.1399	0.1995	0.2148
−0.75	0.1852	0.2630	0.2287
−0.60	0.2346	0.3243	0.2535
−0.45	0.2675	0.3628	0.2643
−0.30	0.3457	0.4331	0.3029
−0.15	0.4280	0.4739	0.3462
0.00	0.5185	0.5420	0.3926
0.15	0.5844	0.6054	0.4420
0.30	0.6502	0.6689	0.4915
0.45	0.7284	0.7324	0.5286
0.60	0.7531	0.7551	0.5487
0.75	0.7942	0.8095	0.5935
0.90	0.8272	0.8821	0.6445
1.05	0.8848	0.8957	0.6584
1.20	0.9259	0.9048	0.6754
1.35	0.9506	0.9184	0.6986
1.50	0.9588	0.9274	0.7172
1.65	0.9630	0.9388	0.7465
1.80	0.9794	0.9478	0.7666
1.95	0.9794	0.9546	0.7883
2.10	0.9835	0.9592	0.8130
2.25	0.9877	0.9592	0.8253
2.40	0.9959	0.9615	0.8439
2.55	0.9959	0.9637	0.8671
2.70	0.9959	0.9660	0.8964

Table 9 continued on next page

Table 9. Comparisons of the CDFs of the Differences between Measured and Predicted Nd(III) and Am(III) Solubilities for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011) (continued). This CDF will be used to define the solubility multiplier SOLVAR for the oxidation-state III model material SOLMOD3 in the WIPP PA Parameter Database.

X	$P(D < X)$, CRA-2004 PABC	$P(D < X)$, CRA-2009 PABC	$P(D < X)$, CRA-2014 PA
2.85	1.0000	0.9683	0.9134
3.00	1.0000	0.9705	0.9304
3.15	1.0000	0.9705	0.9490
3.30	1.0000	0.9751	0.9614
3.45	1.0000	0.9796	0.9799
3.60	1.0000	0.9841	0.9892
3.75	1.0000	0.9841	0.9892
3.90	1.0000	0.9932	0.9954
4.05	1.0000	1.0000	1.0000

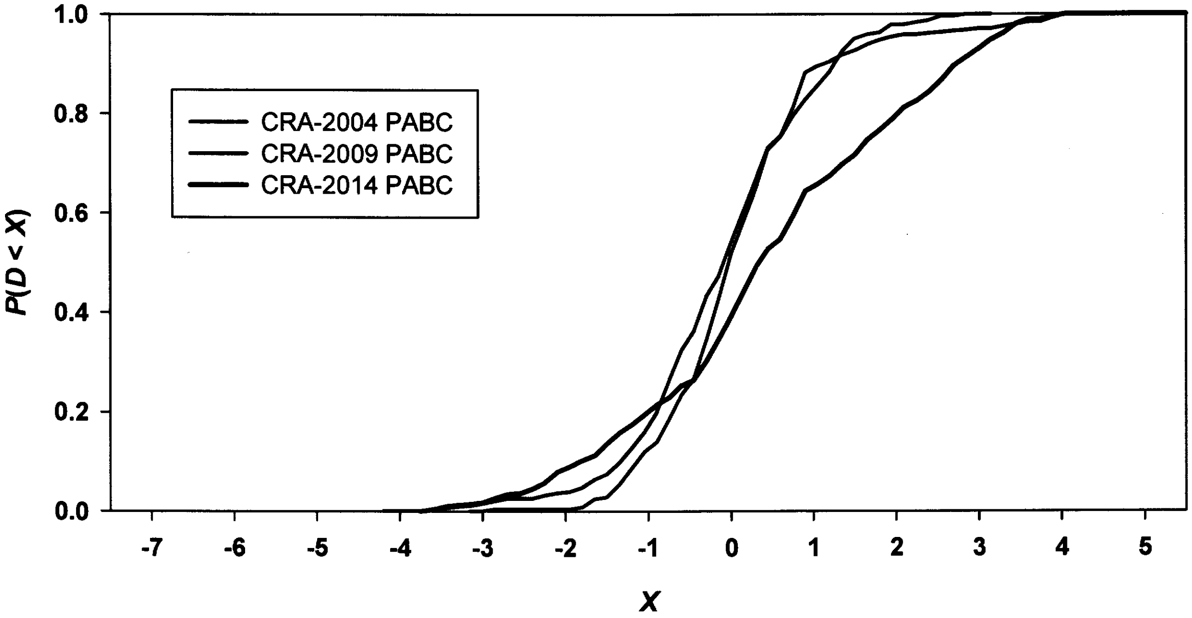

Figure 4. Comparison of plots of the CDFs for Nd(III) and Am(III) for the CRA-2014 PA (this analysis), the CRA-2004 PABC (Xiong et al., 2005), and the CRA-2009 PABC (Xiong et al., 2011).

4 CONCLUSIONS

This analysis report provides the results of the new uncertainty analysis of the solubilities of Th(IV) and Am(III). SNL PA personnel will use the results of this uncertainty analysis in the CRA-2014 PA.

We used EQ3/6, Version 8.0a, and the thermodynamic database DB DATA0.FM1 for this analysis. We carried out this analysis under Task 4 of AP-153, Rev. 1, the current analysis plan (AP) for WIPP near-field geochemical process modeling.

Our Th(IV) comparison included a total of 185 measured and predicted solubilities. The WIPP Th(IV) model overpredicted the measured solubilities in the current analysis. The mean and median values of the log of the sampled uncertainty factor used to adjust the baseline Th(IV) solubilities are –0.136 and –0.189, respectively. The mean and median values of the sampled uncertainty factor are $10^{-0.136} = 0.732$ and $10^{-0.189} = 0.647$. (The PA codes use actinide solubilities that are the products of the baseline solubilities and the sampled uncertainty factors).

Our Nd(III) and Am(III) comparison included a total of 647 measured and predicted solubilities. The WIPP Am(III) model underpredicted the measured solubilities. The mean and median values of the log of the sampled uncertainty factor used to adjust the baseline Am(III) solubilities are 0.441 and 0.346, respectively. The mean and median values of the sampled uncertainty factor are $10^{0.441} = 2.76$ and $10^{0.346} = 2.22$.

Tables 6 and 9 provide values of the CDFs for Th(IV) and for Nd(III) and Am(III) for the CRA-2014 PA.

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5 REFERENCES

Altmaier, M., V. Neck, M.A. Denecke, R. Yin, and T. Fanghänel. 2006. "Solubility of $ThO_2 \cdot xH_2O$(am) and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes in $NaHCO_3$-Na_2CO_3 solutions containing 0–4 M NaCl," *Radiochimica Acta.* Vol. 94, 495-500.

Altmaier, M., V. Neck, and T. Fanghänel. 2004. "Solubility and Colloid Formation of Th(IV) in Concentrated NaCl and $MgCl_2$ Solution," *Radiochimica Acta.* Vol. 92, 537-543.

Altmaier, M., V. Neck, and T. Fanghänel. 2008. "Solubility of Zr(IV), Th(IV) and Pu(IV) Hydrous Oxides in $CaCl_2$ Solutions and the Formation of Ternary Ca-M(IV)-OH Complexes," *Radiochimica Acta.* Vol. 96 (Migration 2007), 541-550.

Altmaier, M., V. Neck, R. Müller, and T. Fanghänel. 2005. "Solubility of $ThO_2 \cdot xH_2O$*(am)* in Carbonate Solution and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes," *Radiochimica Acta.* Vol. 93, 83-92.

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

Baston, G.M.N., M. Brownsword, A.J. Smith, and J.L. Smith-Briggs. 1996. *Further Near-Field Solubility Studies.* NSS/R357. Harwell, UK: AEA Technology plc.

Borkowski, M. 2010. *Numerical Values for Graphs Presented in the Report LCO-ACP-08, Rev. 0, Entitled: "Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations."* LA-UR 10-00898; LANL-CO ACRSP ACP-1002-05-17-01. Carlsbad, NM: Los Alamos National Laboratory — Carlsbad Operations.

Borkowski, M. 2012. *Numerical Values for Graphs Presented in Report LCO-ACP-17, Rev.), Entitled Solubility of An(IV) in WIPP Brine: Thorium Analog Studies in WIPP Simulated Brine, and for Graphs Published in Borkowski, M., et al., Radiochimicha Acta, 98 (9-11), 577–582 (2010).* LA-UR 12–26640; LANL-CO ACRSP ACP-01/2012, Rev. 0. Carlsbad, NM: Los Alamos National Laboratory — Carlsbad Operations.

Borkowski, M., J.-F. Lucchini, M.K. Richmann, and D.T. Reed. 2009. *Americium (III) Solubility in WIPP Brine: Data Summary and Recommendations.* LCO-ACP-08, Rev. 0. Carlsbad, NM: Los Alamos National laboratory – Carlsbad Operations.

Borkowski, M., M. Richmann, and J.F. Lucchini. 2012. *Solubility of An(IV) in WIPP Brine: Thorium Analog Studies in WIPP Simulated Brine*. LA-UR 12-24417. Carlsbad, NM: Los Alamos National Laboratory – Carlsbad Operations.

Borkowski, M., M. Richmann, D.T. Reed, and Y. Xiong. 2010. "Complexation of Nd(III) with Tetraborate Ion and Its Effect on Actinide(III) Solubility in WIPP Brine," *Radiochimica Acta*. Vol. 98, nos. 9-11 (Migration 2009), 577–582.

Brendebach, B., M. Altmaier, J. Rothe, V. Neck, and M.A. Denecke. 2007. "EXAFS Study of Aqueous Zr^{IV} and Th^{IV} Complexes in Alkaline $CaCl_2$ Solutions: $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$," *Inorganic Chemistry*. Vol. 46, no. 16, 6804–6810.

Brush, L.H., P.S. Domski, and Y.-L. Xiong. 2012. "Analysis Plan for WIPP Near-Field Geochemical Process Modeling." AP-153, Rev. 1, February 8, 2012. Carlsbad, NM: Sandia National Laboratories. ERMS 556960.

Brush, L.H., and P.S. Domski. 2013. "Prediction of Baseline Actinide Solubilities for the WIPP CRA-2014 PA." Analysis Report, January 21, 2013. Carlsbad, NM: Sandia National Laboratories. ERMS 559138.

Brush, L.H., and J.W. Garner. 2005. "Additional Justification of the Insignificant Effect of Np on the Long-Term Performance of the WIPP." Memorandum to D.S. Kessel, February 1, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 538533.

Brush, L.H., J.W. Garner and E. Vugrin. 2005. "PA Implementation of Uncertainties Associated with Calculated Actinide Solubilities." Memorandum to D.S. Kessel, February 2, 2005. Carlsbad, NM: Sandia National Laboratories. ERMS 538537.

Brush, L.H., and Y.-L. Xiong, 2009. "Analysis Plan for the Calculation of Actinide Solubilities for the WIPP CRA-2009 PABC." AP-143, May 6, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 551179.

Bunyakina, N.V., D.A. Storozhenko. 2004. "$MgSO_4$-$Ln_2(SO_4)_3$-H_2O (Ln = Pr, Nd, Gd) Systems at 25 °C," *Russian Journal of Inorganic Chemistry*. Vol. 49, no. 11, 1772-1774.

Colàs, E., M. Grivé, I.Rojo, and L. Duro. 2011. "Solubility of $ThO_2.xH_2O$(am) in the Presence of Gluconate," *Radiochimica Acta*. Vol. 99, no. 5, 269–273.

Fellhauer, D., V. Neck, M. Altmaier, J. Lützenkirchen and T. Fanghänel. 2010. "Solubility of Tetravalent Actinides in Alkaline $CaCl_2$ Solutions and Formation of $Ca_4[An(OH)_8]^{4+}$ Complexes: A Study of Np(IV) and Pu(IV) under Reducing Conditions and the Systematic Trend in the An(IV) Series," *Radiochimica Acta*. Vol. 98, nos. 9-11 (Migration 2009), 541–548.

Felmy, A.R., H. Cho, D.A. Dixon, Y. Xia, N.J. Hess, and Z. Wang. 2006. The Aqueous Complexation of Thorium with Citrate under Neutral to Basic Conditions," *Radiochimica Acta*. Vol. 94, 205-212.

Felmy, A.R., D. Rai, and M.J. Mason. 1991. "The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model," *Radiochimica Acta*. Vol. 55, 177-185.

Felmy, A.R., D. Rai, M.S. Sterner, M.J. Mason, N.J. Hess, and S.D. Conradson. 1997. "Thermodynamic Models for Highly Charged Aqueous Species: Solubility of Th(IV) Hydrous Oxide in Concentrated $NaHCO_3$ and Na_2CO_3 Solutions," *Journal of Solution Chemistry*. Vol. 26, no. 3, 233-248.

Khalili, F.I., V. Symeopoulos, J.-F. Chen, and G.R. Choppin. 1994. "Solubility of Nd in Brine," *Radiochimica Acta*. Vol. 66/67, 51-54.

Kim, S.S., M.H. Baik, J.W. Choi, H.S. Shin, and J.I. Yun. 2010. "The Dissolution of ThO_2(cr) in Carbonate Solutions and a Granitic Groundwater," *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 286, 91–97.

Krumhansl, J.L., K.M. Kimball, and C.L. Stein. 1991. *Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico*. SAND90-0584. Albuquerque, NM: Sandia National Laboratories.

Lucchini, J.-F., M. Borkowski, M.K. Richmann, S. Ballard, and D.T. Reed. 2007. "Solubility of Nd^{3+} and UO_2^{2+} in WIPP Brine as Oxidation-State Invariant Analogs for Plutonium," *Journal of Alloys and Compounds*. Vol. 444–445, 506–511.

Makino, H., T. Yajima, H. Yoshikawa, M. Yui, and N. Sasaki. 1993. "Nd(III) Hydrolysis Constants and Solubilities of Nd(III) Hydroxide," *Nippon Kagaku Kaishi*. Vol. 5, 445-450.

Meinrath, D., and J.I. Kim. 1991. "Solubility Products of Different Am(III) and Nd(III) Carbonates," *European Journal of Solid State and Inorganic Chemistry*. Vol. 28, 383-388.

Meinrath, G., and H. Takeishi. 1993. "Solid-Liquid Equilibria of Nd^{3+} in Carbonate Solutions," *Journal of Alloys and Compounds*. Vol. 194, no. 1, 93–99.

Migdisov, A.A., and A.E. Williams-Jones. 2007. "An Experimental Study of the Solubility and Speciation of Neodymium (III) Fluoride in F-Bearing Aqueous Solutions," *Geochimica et Cosmochimica Acta*. Vol. 71, no. 12, 3056–3079.

Neck, V., M. Altmaier, R. Müller, A. Bauer, T. Fanghänel, and J.I. Kim. 2003. "Solubility of Crystalline Thorium Dioxide," *Radiochimica Acta*. Vol. 91, 253-262.

Neck, V., M. Altmaier, T. Rabung, J. Luetzenkirchen, and T. Fanghänel. 2009. "Thermodynamics of Trivalent Actinides and Neodymium in NaCl, $MgCl_2$, and $CaCl_2$ Solutions: Solubility, Hydrolysis, and Ternary Ca-M(III)-OH Complexes," *Pure and Applied Chemistry*. Vol., 81, no. 9, 1555—1568.

Neck, V., R. Muller, M. Bouby, M. Altmaier, J. Rothe, M.A. Denecke, and J.I. Kim. 2002. "Solubility of Amorphous Thorium(IV) Hydroxide – Application of LIBD to Determine the Solubility Product and EXAFS for Aqueous Speciation," *Radiochimica Acta*. Vol. 90, 484-494.

Östhols, E., J. Bruno, and I. Grenthe. 1994. "On the Influence of Carbonate on Mineral Dissolution. III. "The Solubility of Microcrystalline ThO_2 in CO_2-H_2O Media," *Geochimica et Cosmochimica Acta*. Vol. 58, 613-623.

Peretrukhin, V.F., S.V. Kryutchkov, V.I. Silin, and I.G. Tananaev. 1996. *Determination of the Solubility of Np(IV)-(VI), Pu(III)-(VI), Am(III)-(VI), and Tc(IV), (V) Hydroxo Compounds in 0.5-14 M NaOH Solutions*. WHC-EP-0897, Rev. 0. Richland, WA: Westinghouse Hanford Co.

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

Rabung, T., M. Altmaier, V. Neck, and T. Fanghänel. 2008. "A TRLFS Study of Cm(III) Hydroxide Complexes in Alkaline $CaCl_2$ Solutions," *Radiochimica Acta*. Vol. 96, nos. 9-11 (Migration 2007), 551–559.

Rai, D., A.R. Felmy, D. Moore, and M.J. Mason. 1995. "The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated $NaHCO_3$ and Na_2CO_3 Solutions," *Scientific Basis for Nuclear Waste Management XVIII, Materials Research Society Symposium Proceedings, Symposium Held October 23-27, 1994, Kyoto, Japan.* Eds. T. Murakami and R.C. Ewing. Pittsburgh, PA: Materials Research Society. Vol. 353, 1143-1150.

Rai, D., A.R. Felmy, M.S. Sterner, D.A. Moore, M.J. Mason, and C.F. Novak. 1997. "The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaCl and $MgCl_2$ Solutions," *Radiochimica Acta*. Vol. 79, 239–247.

Rai, D., D.A. Moore, C.S. Oakes, and M. Yui. 2000. "Thermodynamic Model for the Solubility of Thorium Dioxide in the Na^+-Cl^--OH^--H_2O System at 23 °C and 90 °C," *Radiochimica Acta*. Vol. 88, 297-306.

Rai, D., M. Yui, N.J. Hess, A.R. Felmy, and D.A. Moore. 2005. "Thorium Reactions in Borosilicate-Glass/Water Systems," *Radiochimica Acta*. Vol. 93, no. 8, 443-455.

Rai, D., M. Yui, A. Kitamura, and B. Grambow. 2011. "Thermodynamic Approach for Predicting Actinide and Rare Earth Concentrations in Leachates from Radioactive Waste Glasses," *Journal of Solution Chemistry*. Vol. 40, 1473-1504.

Rai, D., M. Yui, D.A. Moore, G.J. Lumetta, K.M. Rosso, Y. Xia, A.R. Felmy, and F.N. Skomurski. 2008. "Thermodynamic Model for ThO_2(am) Solubility in Alkaline Silica Solutions," *Journal of Solution Chemistry*. Vol. 37, no. 12, 1725-1746.

Rai, D., M. Yui, D.A. Moore, and L. Rao. 2009. "Thermodynamic Model for ThO_2(am) Solubility in Isosaccharinate Solutions," *Journal of Solution Chemistry*. Vol. 38, no. 12, 1573-1587.

Rao, L., D. Rai, and A.R. Felmy. 1996a. "Solubility of $Nd(OH)_3$(c) in 0.1 M NaCl Aqueous Solution at 25 ºC and 90 ºC," *Radiochimica Acta*. Vol. 72, no. 3, 151–155. ERMS 243171.

Rao, L., D. Rai, A.R. Felmy, R.W. Fulton and C.F. Novak. 1996b. "Solubility of $NaNd(CO_3)_3 \cdot 6H_2O$(c) in Concentrated Na_2CO_3 and $NaHCO_3$ Solutions," *Radiochimica Acta*, Vol. 75, 141–147.

Rao, L., D. Rai, A.R. Felmy, and C.F. Novak. 1999. "Solubility of $NaNd(CO_3)_2 \cdot 6H_2O$(c) in Mixed Electrolyte (Na-Cl-CO_3-HCO_3) and Synthetic Brine Solutions," *Actinide Speciation in High Ionic Strength Media: Experimental and Modeling Approaches to Predicting Actinide Speciation and Migration in the Subsurface. Proceedings of an American Chemical Society Symposium on Experimental and Modeling Studies of Actinide Speciation in Non-Ideal Systems, Held August 26-28, 1996, in Orlando, Florida.* Eds. D.T. Reed, S.B. Clark, and L. Rao. New York, NY: Kluwer Academic/Plenum Publishers. 153-169.

Runde, W., and J.I. Kim. 1995. *Untersuchungen der Übertragbarkeit von Labordaten natürliche Verhältnisse: Chemisches Verhalten von drei- und fünfwertigem Americium in salinen NaCl-Lösungen (Study of the Extrapolability of Laboratory Data to Natural Conditions: Chemical Behavior of Trivalent and Pentavalent Americium in Saline NaCl Solutions)*. RCM-01094. Munich, FRG: Institute for Radiochemistry, Technical University of Munich. ERMS 241862.

Runde, W., G. Meinrath and J.I. Kim. 1992. "A Study of Solid-Liquid Phase Equilibria of Trivalent Lanthanide and Actinide Ions in Carbonate Systems," *Radiochimica Acta*. Vol. 58/59, 93–100.

Silva, R.J. 1982. *The Solubilities of Crystalline Neodymium and Americium Trihydroxides*. LBL-15055. Berkeley, CA: Lawrence Berkeley National Laboratory.

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

U.S. EPA. 2006. "Technical Support Document for Section 194.24: Evaluation of the Compliance Recertification – Actinide Source Term and Culebra Dolomite Distribution Coefficient Values." EPA Air Docket A 98-49, Item II B1-3. Washington, DC: U.S. Environmental Protection Agency Office of Air and Radiation.

Vandenborre, J., A. Abdelouas, and B. Grambow. 2008. "Discrepancies in Thorium Oxide Solubility Values: A New Experimental Approach to Improve Understanding of Oxide Surface at Solid/Solution Interface," *Radiochimica Acta*. Vol. 96, 515–520.

Vandenborre, J., B. Grambow, and A. Abdelouas. 2010. "Discrepancies in Thorium Oxide Solubility Values: Study of Attachment/Detachment Processes at the Solid/Solution Interface," *Inorganic Chemistry*. Vol. 49, no. 19, 8736–8748.

Vitorge, P., and P. Tran The. 1991. *Solubility Limits of Radionuclides in Interstitial Water: Americium in Cement. Task 3: Characterization of Waste Forms. A Series of Final Reports (1985-89): N. 34.* EUR 13664. Luxembourg: Commission of the European Communities.

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

Wolery, T.J. 2008. "Analysis Plan for EQ3/6 Analytical Studies." AP-140, Rev. 0, May 15, 2008, Carlsbad, NM: Sandia National Laboratories. ERMS 548930.

Wolery, T.W., and R.L. Jarek. 2003. "Software User's Manual: EQ3/6, Version 8.0." Software Document Number 10813-UM-8.0-00. Albuquerque, NM: Sandia National Laboratories.

Wolery, T.J., Y.-L. Xiong, and J.J. Long. 2010. "Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10." Carlsbad, NM: Sandia National laboratories. ERMS 550239.

Wood, S.A. 2005. *Understanding the Chemistry of the Actinides in High Level Waste Tank Systems: The Impact of Temperature on Hydrolysis and Complexation with Organics*. DOE/ER/14935-3A. Washington, DC: U.S. Department of Energy.

Wood, S.A., D.A. Palmer, D.J. Wesolowski, and P. Bénézeth. 2002. "The Aqueous Geochemistry of the Rare Earth Elements and Yttrium. Part XI. The Solubility of $Nd(OH)_3$ and Hydrolysis of Nd^{3+} from 30 to 290 °C at Saturated Water Vapor Pressure with In-Situ pH_m Measurement," *Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar*. Eds. R. Hellmann and S.A. Wood. St. Louis, MO: The Geochemical Society, Special Publication N. 7, 229-256.

Xia, Y., A.R. Felmy, L. Rao, Z. Wang and N.J. Hess. 2003. "Thermodynamic Model for the Solubility of ThO_2(am) in the Aqueous Na^+-H^+-OH^--NO_3^--H_2O-EDTA System," *Radiochimica Acta.* Vol. 91, 751-760.

Xiong, Y.-L. 2011a. "Release of EQ3/6 Database DATA0.FM1." E-mail to Jennifer Long, March 9, 2011. Carlsbad, NM: Sandia National Laboratories. ERMS 555152.

Xiong, Y.-L., 2011b. "WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1. Supersedes ERMS 550239." May 12, 2011. Carlsbad, NM. Sandia National Laboratories. ERMS 555358.

Xiong, Y.L., L.H. Brush, P.S. Domski, and J.J. Long. 2011. "Uncertainty Analysis of Actinide Solubilities for the WIPP CRA-2009 PABC, Rev. 1, Supersedes ERMS 552500. Analysis report, January 24, 2011. Carlsbad, NM: Sandia National Laboratories. ERMS 554875.

Xiong, Y.L., L.H. Brush, J.W. Garner, and J.J. Long. 2010. "Responses to Three EPA Comments Pertaining to Comparisons of Measured and Predicted Dissolved and Colloidal Th(IV) and Am(III) Concentrations, Revision 1. Supersedes ERMS 553409." Analysis report, May 19, 2010. Carlsbad, NM: Sandia National Laboratories. ERMS 553595.

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