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Solubility of An(IV) in WIPP Brine:

Thorium Analog Studies in WIPP Simulated Brine

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Executive Summary

The solubility of thorium (IV) in carbonate-free and carbonate-containing Waste Isolation Pilot Plant (WIPP) simulated brine was determined as a function of pH and time. These experiments correspond to the Task Implementation Plan ACP-TIP-06 entitled "Solubility of An(IV) in WIPP Brine, Studies Using Thorium Analog" being performed under Task III of the LCO-ACP-05 Test Plan entitled "Plutonium Speciation and Solubility in the WIPP". These experiments were conducted to establish the effects of carbonate, pC_{H+} and time on thorium solubility. All experiments we report were performed under the Los Alamos National Laboratory – Carlsbad Operations (LANL-CO) Quality Assurance program and are compliant with the requirements of the US Department of Energy Carlsbad Field Office, DOE/CBFO, Quality Assurance Program Document, QAPD.

The results obtained are summarized in the Figure below. After 2 years of equilibration in carbonate-free brine the measured solubility of thorium was $6\text{-}7\times10^{-7}$ M and was essentially independent of pH and brine composition over the 6.5 to 11.5 pC_{H+} range investigated (blue/black points). Sequential filtration to ~ 10 nm pore size had little effect on the measured concentration. Subsequent ultracentrifugation up to 1,000,000 g resulted in up to a 40% colloidal fraction indicating that there was relatively little intrinsic colloid formation. The steady-state thorium concentrations we measured are consistent with literature reports for simplified brine systems [Altmaier et al. 2004] but show a significantly lower extent of aggregation to form intrinsic colloids.
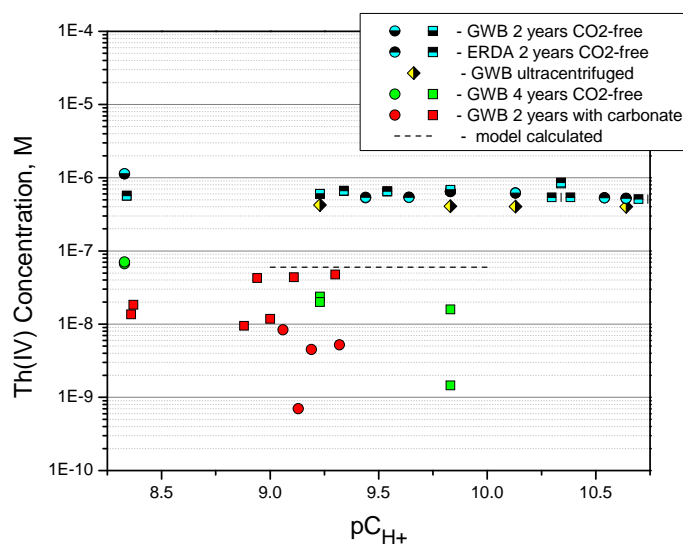

Figure. The concentrations of thorium measured in WIPP simulated brines(both ERDA-6 and GWB) as a function of time, filtration and the presence of carbonate (circles - oversaturation, squares - undersaturation). Although high, but meta-stable, concentrations were initially present, in time the measured concentrations decreased and are conservatively below the WIPP model-predicted values.

After an additional 2 years of equilibration the thorium concentrations in GWB brine carbonate-free significantly decreased (green points in the figure) and overlap the thorium concentration measured after 2 years of equilibration in brines containing carbonate (red points).

The presence of carbonate had little/no effect on the measured thorium concentrations. After two years of equilibration the thorium concentrations measured from under- and oversaturation in GWB brine did not depend on carbonate concentration. Concentrations measured from oversaturation were 2.5 orders of magnitude greater than those measured from undersaturation indicating that metastable states can last a long period of time. The trend of oversaturation data is consisted with the literature data [Altmaier 2005] presented (see Figure). In the undersaturation experiments which are more relevant to the WIPP situation, the average thorium concentration was 2×10^{-8} M and continued to decrease at $pC_{H+} > 9$. The oversaturation experiments showed a similar trend and at $pC_{H+} > 9$ the thorium concentrations decreased to below 10^{-8} M. These results reproduce, to some extent, the trends reported in the literature [Altmaier 2005], but the much higher ionic strength solutions used in our experiments shift our data to a lower pC_{H+} value by approximately 1 pH unit.

At the expected WIPP repository $pC_{H+}(\sim 9.5)$, in the presence of carbonate, the thorium concentrations in GWB brine were 2×10^{-8} M or lower. This concentration trend suggests that the mixed hydroxyl-carbonato complexes do not play any role in the thorium solubility at $pC_{H+} > 9$.

The sequential filtration of thorium in the carbonate system, led to dissolved thorium concentrations in GWB in the range of $2-6\times10^{-8}$ M. In ERDA-6 brines, however, the dissolved thorium concentrations were about 10 fold greater, but a steady state thorium concentration was achieved. The colloidal thorium species appear to be very small, less than 10 kDa. Overall, the truly dissolved thorium concentration was $3(\pm2)\times10^{-8}$ M. The average total thorium concentration consists of 30 - 60% dissolved fraction and 40 - 70% colloidal fraction.

The thorium solubility results summarized in this report support the ongoing WIPP recertification effort in three important ways:

1) they provide empirical solubilities over a broad range of conditions that improve the robustness of the WIPP Performance Assessment (PA) model,

2) they resolve and address published literature data in simplified brine systems that appeared to disagree with the current WIPP PA approach, and

3) they provide an input that will help establish the intrinsic colloidal enhancement factors for IV actinides.

There is general agreement between our data and results reported in the literature for simplified brine systems, although we are seeing a far lower colloidal fraction in the total concentrations measured. After 4 years of equilibration our measured solubilities are slightly lower (by a factor of ~ 2) than the Performance Assessment, PA, calculated solubilities but are well within the order of magnitude agreement typically observed between calculated and measured solubilities in complex brine systems.

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Acronyms and Abbreviations

Acronym	Abbreviation
Ac	Acetate
An(III)	Generic actinide in the +3 oxidation state
An(IV)	Generic actinide in the +4 oxidation state
An(V)	Generic actinide in the +5 oxidation state
β	Stability constant
Citr	Citrate
CRA	Compliance Recertification Application
DOE/CBFO	U.S. Department of Energy/Carlsbad Field Office
EDTA	Ethylenedinitrilotetraacetate
EPA	U.S. Environmental Protection Agency
ERDA-6	Energy Research and Development Administration Well 6
FMT	Fracture-Matrix Transport model
g	Standard acceleration due to gravity at the Earth's surface
GWB	Generic Weep Brine
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ISA	Isosaccharinic acids
K	Solubility Constant
kDa	Kilodaltons
LANL-CO	Los Alamos National Laboratory - Carlsbad Operations
M	Molar (mole per liter)
NIST	National Institute of Standards and Technology
Ox	Oxalate
PA	Performance Assessment
PABC	Performance Assessment Baseline Calculations
pCH+	Negative logarithm of the hydrogen ion concentration
pH	Negative logarithm of the hydrogen ion activity
QA	Quality Assurance
QAPD	Quality Assurance Program Document
rpm	Revolutions-per-minute
SIT	Specific Ion Interaction Theory
WIPP	Waste Isolation Pilot Plant

Solubility of An(IV) in WIPP Brine:
Thorium Analog Studies in WIPP Simulated Brine

A summary of the experiments performed to measure the solubility of thorium in simulated WIPP brine is provided in this report. Thorium is used in the WIPP performance assessment as the analog for An(IV) to establish the solubility of Pu(IV), Np(IV) and U(IV) under WIPP-relevant conditions. These data are part of a larger study devoted to Pu behavior in WIPP where other effects, such as redox conditions (Eh, microbial activity, presence of iron and competitors), complexation, colloid formation will also be established.

The experiments we summarize in this report correspond to all Subtasks of the Task Implementation Plan entitled "Solubility of Thorium in WIPP Brine", which is performed under Task III of the Test Plan entitled "Plutonium Speciation and Solubility in the WIPP" and designated LCO-ACP-05. All the work was performed under the LANL-CO QA program and is compliant with the QAPD.

1.0   Introduction and Literature Background

1.1. Research Goals and Overall Experimental Strategy

The most important goal of the experiments was to determine the effective solubility of thorium, which is the redox invariant analog for the tetravalent actinides used in the WIPP PA, under conditions that simulate the expected environment in the WIPP. These experiments are centered on the key scientific question related to the tetravalent actinide species:

What is the long-term solubility of Th(IV) and, by analogy, Pu(IV), U(IV) and Np(IV) in WIPP brine?

In this context, these experiments extend past results in simplified brine systems to the more WIPP-relevant simulated brines, improve the overall robustness of the WIPP model by extending the experiments in time over a broader pH range, and evaluate the colloidal enhancement factor under WIPP-relevant conditions. A secondary, but important, objective of the work was to assess the relevance and accuracy of literature results [Altmaier et al., 2004] indicating relatively high colloid formation that would suggest that the current WIPP PA assumptions are not correct with respect to the colloidal fraction of dissolved thorium.

Determining the solubility of any species in a complicated matrix such as WIPP brine is not straightforward. Our strategy, however, was to approach thorium solubility from both oversaturation and undersaturation as a function of brine composition, pH, and the presence and absence of carbonate. Solids likely to be present under these conditions were synthesized or obtained and used for the undersaturation experiments.

The An(IV) oxidation state is an important and expected oxidation state in the WIPP due to the reducing conditions present. The large quantities of reduced iron in the repository are expected to react to maintain a reducing environment in WIPP brine should inundation occur. This has been demonstrated for plutonium in WIPP-relevant brine where Pu(V/VI) were reduced

to Pu(III/IV) under a wide range of conditions [Reed et al., 2006; Reed et al. 2009]. More specifically, oxic and subsequently anoxic corrosion will lead to a hydrogen-rich atmosphere and provide available Fe^{2+} in the brine. Anaerobic microbial processes will also help sustain these reducing conditions and may impact the oxidation state of plutonium through direct and indirect bioreduction metabolic pathways.

The thorium solubility data we report provide the first solubility data, generated under the LANL-CO Quality Assurance program [QAPD 2010], for An(IV) in brine under repository-relevant conditions. These data directly support current assumptions used to model the solubility of tetravalent actinides under WIPP-relevant conditions and extend, by analogy, to Pu(IV), U(IV) and Np(IV) [Appendix Soterm 2009]. They also support the goals established in the two-year program plan for Compliance Recertification Application 2014, CRA-2014, and future 40CFR191/194 re-certifications of the WIPP.

1.2. Literature Background: Plutonium and Thorium Environmental Chemistry

Plutonium is the most important actinide from the point of view of potential release from the WIPP that speciates substantially in the An(IV) oxidation state. Plutonium can theoretically exist in the III, IV, V, VI, and VII oxidation states in aqueous systems [Katz et al. 1986], but Pu(VII) is very unstable and exists only in extremely basic solutions (for example, 7 M NaOH). Pu(VI) has been shown to form stable chloride and carbonate complexes in high ionic-strength brine when no reductants are present [Clark and Tait 1996; Reed et al., 1994; 1996]. However, Pu(VI) and Pu(V) are reduced to Pu(III/IV) under the iron-rich reducing conditions expected in the WIPP [Reed et al., 2006; Reed et al., 2009]. The expectation of reducing conditions and the reduction always noted in the presence of Fe(0/II) is why the WIPP PA makes the assumption that plutonium will predominantly exist as Pu(III) and Pu(IV) species.

Thorium exists predominantly in the IV oxidation state in the natural environment (Hobart 1990; Katz et al. 1986]. The standard reduction potential for the Th(IV)/Th(III) couple is very low at -3.8 V (relative to the standard hydrogen electrode potential). Therefore, thorium is predicted to be stable as Th(IV) in the WIPP over a wide range of conditions and, in this context, can function as a redox-invariant analog.

Solubility and hydrolysis of tetravalent actinides were critically reviewed by Neck and Kim (2001). They collected data from all important papers published before 2000 (76 papers cited) on An(IV) hydrolysis and solubility of An(IV) hydroxides and amorphous and crystalline oxides in variety of media, ionic strengths and pH. They proposed thermodynamic constants for hydrolysis and solubility of Th(IV), U(IV), Np(IV) and Pu(IV). Model calculations for amorphous $Th(OH)_4$, presented in this paper and based on the proposed thermodynamic data gave a Th(IV) solubility of 3×10^{-9} M in the pH range of 9-10 and an ionic strength below 1 M. Model plot gave a good representation of the experimental data published by Ryan and Rai (1987), Moon 1989, Rai et al. (1997), Östhols et al. (1994). Thermodynamic data published by Neck and Kim (2001) are utilized in the data base used for WIPP PA (see Appendix). The thermodynamic constants for Th(IV) and Pu(IV) solubility that are recommended in this paper are given in Table 1.

Table 1. Comparison of Thorium and Plutonium Thermodynamic Constants based on Neck and Kim (2001)		
Constant	Th(IV)	Pu(IV)
$logK_{sp}^{o}$ $AnO_2(cr)$	-54.2 ± 1.3	-64.0 ± 1.2
$logK_{sp}^{o}$ $An(OH)_4(am)$	-47.0 ± 0.8	-58.5 ± 0.7
$logK_{s(14)}^{o}An(OH)_4$ (aq)	-8.5 ± 0.6	-10.4 ± 0.5
$log\beta^{o}$ $An(OH)^{3+}$	11.8 ± 0.2	14.6 ± 0.2
$log\beta^{o}$ $An(OH)_2^{2+}$	22.0 ± 0.6	28.6 ± 0.3
$log\beta^{o}$ $An(OH)_3^{1+}$	31.0 ± 1.0	39.7 ± 0.4
$log\beta^{o}$ $An(OH)_4$	38.5 ± 1.0	48.1 ± 0.9

The key factors that define the long-term solubility of Th(IV) under WIPP-relevant conditions are expected to be pH and, to a much lesser extent, carbonate concentration. Organic ligands, including ethylenedinitrilotetraacetate (EDTA), do not affect solubility of Th(IV) at pH above 8.5. The effect of carbonate complexation to the solubility of Th(IV) was investigated in NaCl solutions of various ionic strengths [Altmaier *et al*. 2004; 2005; 2006; Neck *et al*. 2003] (see Figure 1). Significant enhancement of the solubility of thorium is noted at high carbonate concentrations but is in fact not expected in the WIPP case due to the carbonate buffering by MgO.

1.3. Literature Background: Thorium Colloids in Simplified Brine Systems

Actinides in the IV oxidation state, because of the complexity of their solution chemistry and very high tendency towards hydrolysis, form colloidal species in groundwater. The potential effect of colloid formation on the solubility of Th(IV) in concentrated NaCl and MgCl$_2$ solutions was recently published by Altmaier, Neck, and Fanghänel (2004) and is shown in Figure 2. These data indicate relatively high colloidal contributions to the measured thorium solubility.

As shown in Figure 2, in neutral-to-alkaline solutions, colloids could be formed as thorium oxy-hydroxide with log [Th]$_{Total (colloid + dissolved)}$ = -6.3 ± 0.5, independent of ionic strength and pC$_{H+}$. According to the authors, ultracentrifugation of these samples for 60 minutes at 90,000 rpm (500,000 × g) indicated that the total dissolved thorium in the solution was ~99% colloidal. Only ~1% or less was the thorium hydroxide complex. Data in Figure 2 also show that the % of thorium colloids is not constant and changes from ~90% to ~99.9% as the ionic strength is decreased. It is important to note that these experiments were conducted for relatively short times – typically two weeks up to a few months.

In solutions at high magnesium concentration and conditions conducive to colloid generation, mineral colloids can also form (i.e., Th(IV) sorbed onto $Mg_2(OH)_3Cl \cdot 4H_2O$(coll)). This led to an apparent increase of the total thorium concentration up to 10^{-5} M [Altmaier et al. 2004, Walther 2003, Degueldre and Kline 2007, Bundschuh et al. 2000].
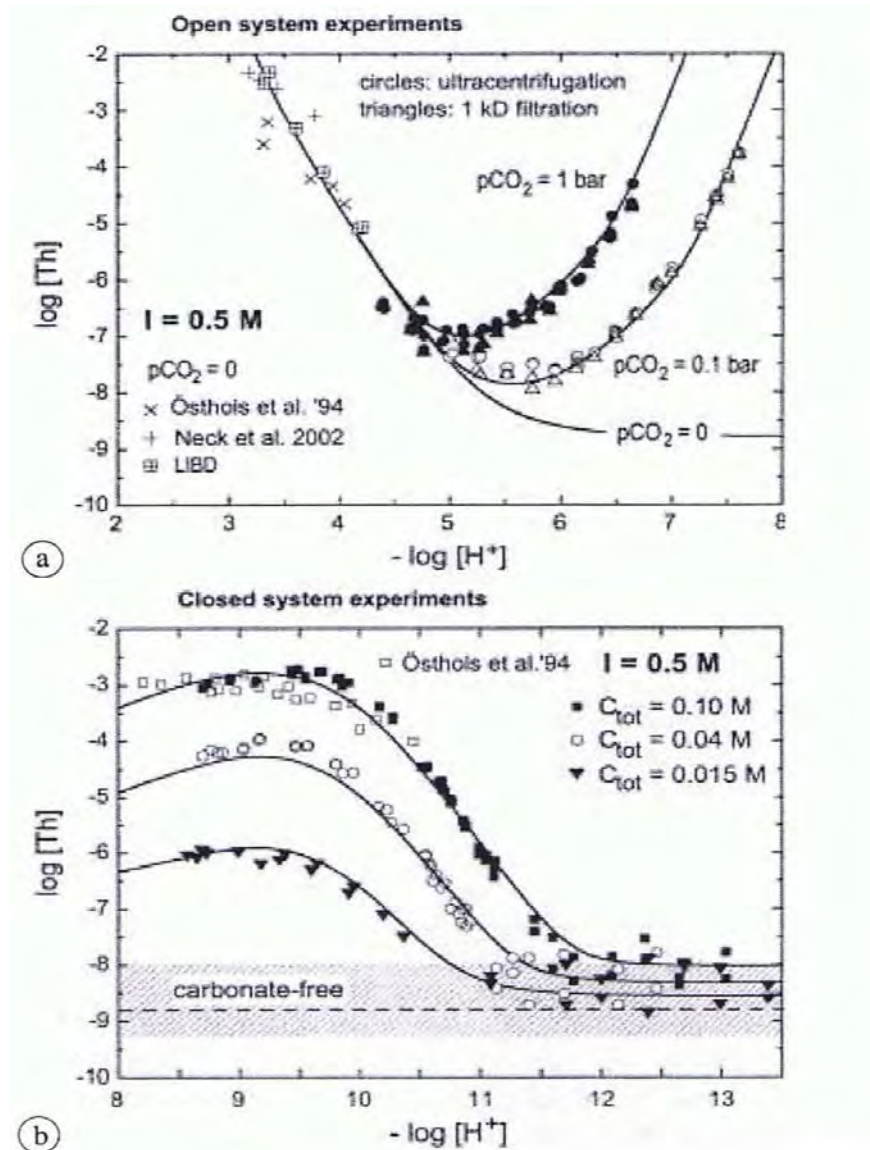
Figure 1.   Solubility of amorphous Th(IV) oxyhydroxide. Solid lines are calculated with the equilibrium constants [Altmaier 2005].
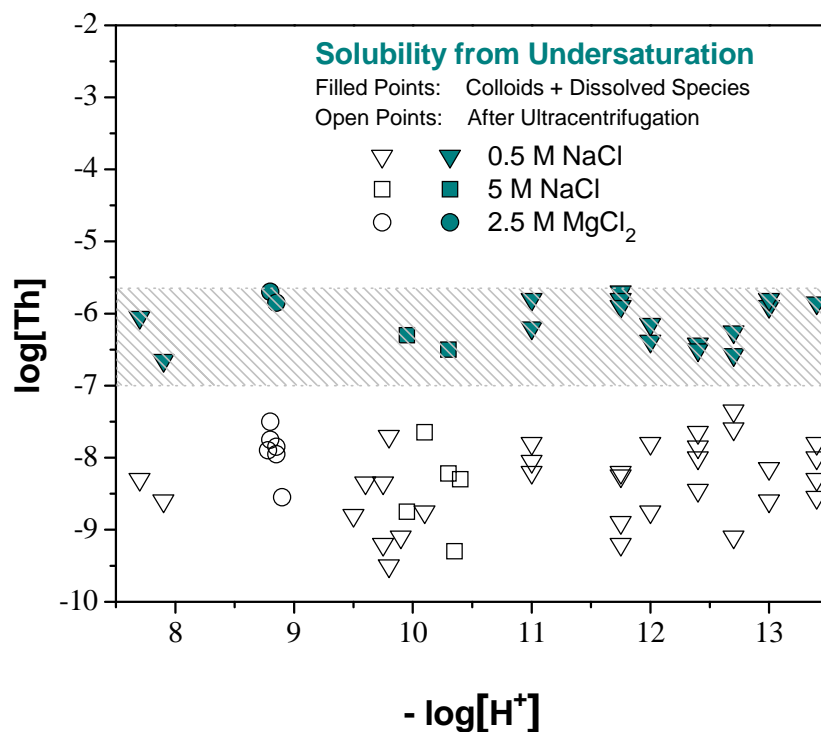
Figure 2. **Solubility of Th(OH)$_4$(am) determined from undersaturation in 0.5 M NaCl, 5.0 M NaCl, and 2.5 M MgCl$_2$. Filled points: Total thorium concentrations (including colloids). Open points: Thorium concentrations measured after ultracentrifugation at 90,000 revolutions per minute (500,000 $\times$ *g*) (based on data in Altmaier, Neck, and Fanghänel 2004).**

1.4. Th(IV) and Pu(IV) Solubility in Brine Containing Ca^{2+} and High pC$_{H+}$

The solubility of Th(IV), Pu(IV) and Zr(IV) hydrous oxides was investigated in alkaline CaCl$_2$ solutions (Altmaier et al. 2008, Brendebach et al. 2007). Significant increase of the tetravalent cation solubility was observed as a function of CaCl$_2$ concentration and pH. This effect for thorium solubility is presented in Figure 3 and for zirconium solubility in Figure 4.
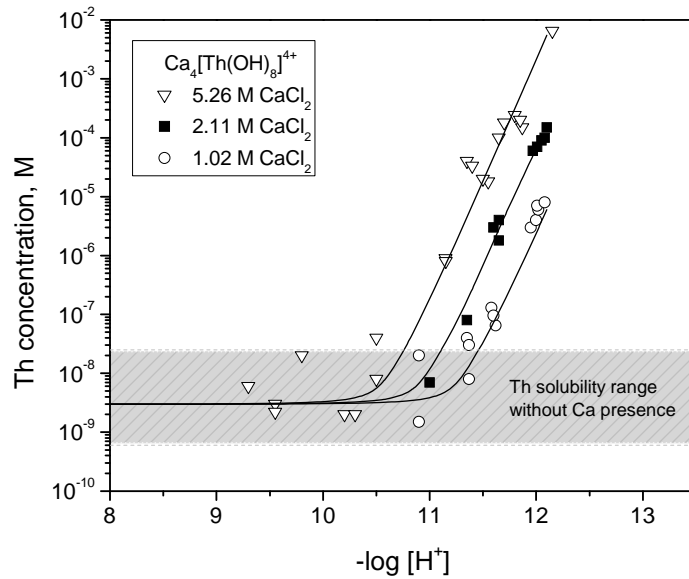
Figure 3. **Solubility of $ThO_2 \cdot xH_2O(s)$ in alkaline solutions for different $CaCl_2$ concentrations. For 1 M $CaCl_2$ solution and pH = 12 increase of thorium solubility was about 3.5 orders of magnitude.**
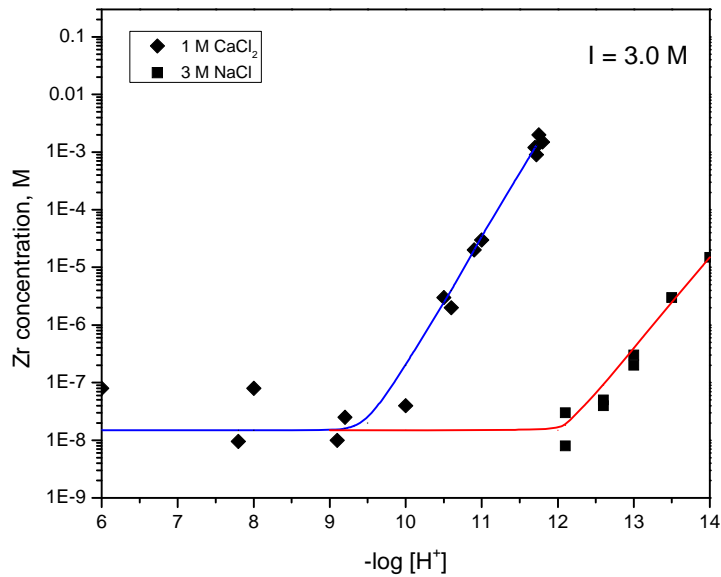
Figure 4. **Solubility of $ZrO_2 \cdot xH_2O(s)$ in alkaline solutions for ionic strength = 3 M. For 1 M $CaCl_2$ solution and pH = 12 increase of zirconium solubility about 5 orders of magnitude was observed.**

The compositions of these complex cations were established to be $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$. Similar complexes are proposed for plutonium by analogy, however in these conditions measured after 1.5-2 nm ultrafiltration the predominant oxidation state was Pu(V) and reliable analysis of the dissolved plutonium species could not be done. The data in Figure 3 reflect a stabilization of the anionic hydroxide complexes of tetravalent metals by calcium. Such stabilization in case of hydroxide and also for carbonate is a general phenomenon having significant impact on the solubility and aqueous speciation of tetravalent actinides, in particular for cementitious waste forms. For the range of conditions expected in the WIPP, a relatively low calcium concentration and a pC_{H+} of about 9.5, the formation of such complexes will have a negligible effect on An(IV) solubility.

1.5. Effect of Organic Ligands on Th(IV) and Pu(IV) Solubility in Brine

Four organic chelating agents are considered by WIPP PA and are potentially present in WIPP waste. These are acetate, oxalate, citrate and EDTA. Of these, EDTA (Log β = 23) and citrate (Log β = 11.6) are the two most important complexants of thorium and these complexants, in general, have the potential to impact actinide speciation [NIST 2004] under WIPP-relevant conditions. Oxalate (Log β = 8.2) and acetate (Log β = 4.5), are not likely to significantly impact the speciation of thorium as well as the An(III) actinides.   Model calculations indicate that for pC_{H+} greater than 8.5 even the EDTA complex does not play a significant role in solubility of tetravalent actinides. At repository conditions i.e. pC_{H+} about 9.5 and a total EDTA concentration of 10^{-5} M, the contribution of EDTA complexes to the total solubility of Th(IV) is negligibly small. To demonstrate this effect experimentally, a short-term experiment was performed to measure the solubility of thorium in brine with all four ligands present. This confirmed our hypothesis that the presence of these organics would not impact thorium solubility. Based on this, a long-term detailed set of experiments was not considered to be needed.

The possible impact of the presence of isosaccharinic acids, ISA, on thorium speciation was also considered. ISA is a chemical breakdown product of cellulosic material that has been show to occur at pH>12. The two diastereoisomers, α- and β-isosaccharinic acids are the products of chemical degradation of cellulosic materials in alkaline solutions. The alkaline degradation of different cellulosic materials was studied under the alkaline conditions existing in the initial stage of the cementitious repository (pH=13.3). They are expected to be present in cement pore water, but are strongly adsorbed to the cement surface. In the pore water, the concentration of ISA is expected to reach 10^{-4} M (Van Loom et al. 1998). The complexation data for ISA is very limited and there were no literature references for the tetravalent cations such as thorium. ISA is structurally a 2-hydroxycarboxylic acid, therefore, by analogy we can relate the complexation of thorium by ISA to the stability constants for Th(IV) with glycolic acid, lactic acid and 2-hydroxybutanoic acid (log K of 4.3, 4.2 and 3.8 respectively). Ligands with such low stability constant values cannot outcompete An(IV) hydrolysis. For WIPP-related conditions, the occurrence of the cellulosic chemical degradation pathways have a very low probability and, even if degradation occurs, the ISA formed will likely have a negligible effect on An(IV) solubility.

2.0 WIPP PA Assumptions and Site-Relevant Data

2.1. Brine Inundation and Redox Scenario

The expected scenario in the WIPP is that it will remain unsaturated throughout repository history due to the self-sealing of the salt. However, as a consequence of low-probability intrusion scenarios, brine can enter the repository and dissolve actinides leading to a potential for their release from the WIPP. In this scenario, as brine enters the repository, iron will undergo anoxic corrosion, producing Fe^{2+}. Both metallic iron (Fe^0) and Fe^{2+} have been shown to quantitatively reduce Pu(VI) in WIPP brines to either Pu(IV) or Pu(III). Clark and Tait (1996) and Felmy et al. (1997) have experimentally observed the reduction of Pu(VI) carbonates by either Fe^0 or Fe^{2+} to Pu(IV). The reduction of Pu(V/VI) to Pu(III/IV) has also been observed in WIPP-specific experiments [Reed et al., 2006; Reed et al, 2009]. Pu(III) has also been observed in WIPP experiments [Felmy et al, 1989; Reed et al., 2009] but its long-term stability under WIPP-relevant conditions has not been established.

The role of iron in the conceptual model is critical to the WIPP safety case because massive quantities of iron metal (approximately 10^9 moles) will be placed within the repository. The reaction rate of iron with the brine is relatively fast (days and weeks, not years). Therefore, iron functions as a reactive barrier that will react with brine to establish a highly reducing environment, leading to the reduction of multivalent actinides to their lower, less soluble, oxidation states. This anticipated role of iron also puts the focus of actinide speciation on the lower-valent oxidation states of An(III) and An(IV) for the multivalent actinides and these oxidation states are the most important for the calculation of potential release in WIPP PA.

2.2. Thorium as an Analog for Actinide (IV) Species

The solubility and speciation of multivalent actinides, especially plutonium, are often investigated by oxidation state analogy, which states that lanthanides and actinides that are in the same oxidation states have similar chemical behavior. Redox-invariant analogs can considerably simplify experimental design and consequently improve the reliability of experimental data. Additionally, the lanthanide analogs possess physical (charge, ionic radius) and chemical (complex formation constants) characteristics that allow them to be used to examine the chemical behavior of actinides. Formation of complexes of most ligands with *f*-elements is due to the electrostatic attraction between the metal and the electron-donating functionality of the ligand molecule.

The use of Th(IV) as an analog for U(IV), Np(IV) and Pu(IV) leads to conservatively high assumptions with respect to solubility and potential for release. The variation of the charge to radius ratio for the tetravalent actinides is greater than for actinides in other oxidation states [Cotton and Wilkinson 1988], and larger differences in the chemical behavior among the IV actinides are observed. The tetravalent analogs often require adjustment of the analog data to make the values agree more closely with those of Pu(IV) or U(IV). Such adjustments and equations for obtaining estimates of Pu(IV) data from trivalent and hexavalent analogs are reported in the literature [Choppin 1999].

The need for these kinds of adjustments is best illustrated by the relative hydrolysis constants for An(IV) species. The first hydrolysis constants for Th(IV) and Pu(IV) [NIST 2004, Neck and Kim 2001] for various ionic strengths are compared in Figure 5. The logarithms of the

solubility products for Pu(IV) and Th(IV) crystalline dioxides are equal to -64.1 and -54.2, respectively. The application of the Th(IV) model to the other IV species is more uncertain, yet still conservative, because Th(IV) is the most soluble among these elements under WIPP conditions. It is typically understood that the measured solubility of thorium will be ~ 100 times greater than the measured solubility for plutonium(IV) under the same conditions.
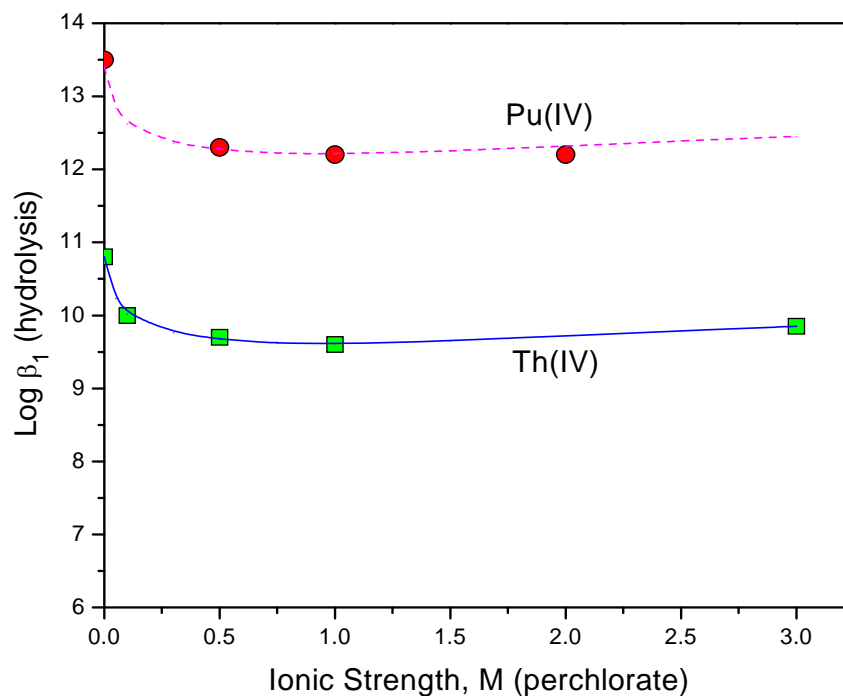
Figure 5. Comparison of the first hydrolysis constant for Th(IV) and Pu(IV). The trends in the changes noted are the same. However, due to the higher charge density of Pu(IV), the hydrolysis constants are 2.7 log units (~ 500 times) greater than Th(IV).

2.3. Actinide Oxidation State Distribution and Solubility in the WIPP PA

The oxidation state distribution of the various actinides considered in the WIPP model is given in Table 2. Thorium only persists as Th(IV) whereas the distribution of uranium and neptunium is divided between the An(IV) oxidation state and a more oxidized species (either An(VI) or An(V)). Plutonium is assumed to speciate as Pu(III) and Pu(IV) species.

Table 2. Oxidation States of the Actinides in the WIPP

Actinide		Oxidation States		
Thorium		IV		
Uranium		IV		VI
Neptunium		IV	V	
Plutonium	III	IV		
Americium	III			
Curium	III			

The following, written in terms of the thorium analog, are the principal reactions for An(IV) in the WIPP model:

$$ThO_2 \ (am) + 2H_2O = Th(OH)_4(aq) \qquad (1)$$

$$Th^{4+} + 4OH^- = Th(OH)_4 \ (aq) \qquad (2)$$

$$Th^{4+} + 3OH^- + CO_3^{2-} = Th(OH)_3CO_3^- \qquad (3)$$

$$Th^{4+} + 5CO_3^{2-} = Th(CO_3)_5^{6-} \qquad (4)$$

$$Th^{4+} + 2SO_4^{2-} = Th(SO_4)_2 \ (aq) \qquad (5)$$

$$Th^{4+} + 3SO_4^{2-} = Th(SO_4)_3^{2-} \qquad (6)$$

$$Th^{4+} + 2OH^- + SO_4^{2-} = Th(OH)_2SO_4 \ (s) \qquad (7)$$
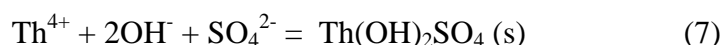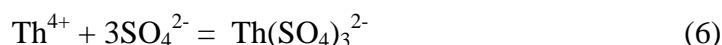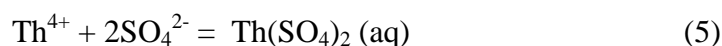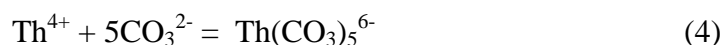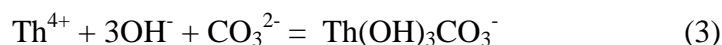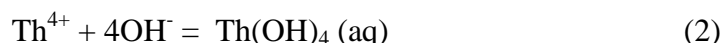
The Th(IV) dissolved concentration can be modeled using Pitzer formalism in the Na^+-K^+ -Mg^{2+}-Cl^-- SO_4^{2-}-CO_3^{2-}-HCO_3^- -OH^--H_2O system. The Pitzer interaction parameters for the following species Th^{4+}, $Th(OH)_2SO_4(s)$, $Th(SO_4)_3^{2-}$, $Th(SO_4)_2(aq)$, ThO_2, $Th(OH)_4(aq)$, $Th(OH)_3CO_3^-$, and $Th(CO_3)_5^{6-}$ are required to describe the data pertinent to the WIPP (Felmy et al. 1991; Felmy and Rai 1992; Felmy et al. 1997).

The set of Fracture-Matrix Transport, FMT, calculations of actinide solubility in the WIPP system that are performed for the PA are equilibrated with halite, anhydrite, brucite, and magnesite [Novak et al. 1996], the minerals that are present in large quantities in the repository. The effects of the MgO backfill are realized through the establishment of equilibrium of brine with brucite and magnesite. Table 3 gives the solubilities for each actinide oxidation state analog as calculated with the thermodynamic model and FMT.

Table 3. Solubilities of the oxidation state analogs, in moles/liter, with MgO backfill and organics present, calculated for the CRA-2009 Performance Assessment Baseline Calculations, PABC.

	Solubilities in brine for various oxidation state of actinides			
Brine	(III)	(IV)	(V)	(VI*)
GWB	1.66×10^{-6}	5.63×10^{-8}	3.90×10^{-7}	1×10^{-3}
ERDA-6	1.51×10^{-6}	6.98×10^{-8}	8.75×10^{-7}	1×10^{-3}

*Not calculated, established by EPA.

3.0 Results and Discussion: Thorium Solubility in Carbonate-Free Brine

Thorium solubility data generated in carbonate-free ERDA-6 and GWB brine from oversaturation (Subtask 1) and undersaturation (Subtask 3) are summarized in this section. These data provide a starting point to establish the effects of carbonate and organic complexation on the solubility of An(IV). The specific goal of this study was to establish the real-system contribution of hydrolysis to Th(IV) solubility and to measure the degree of colloid formation as a function of pC_{H+} and brine composition.

3.1. Subtask 1: Oversaturation Study of the Solubility of Thorium(IV) in Carbonate-free Brine.

The objective of this Subtask was to measure the effective solubility of thorium(IV) from oversaturation as a function of key subsurface parameters: brine composition and pH in carbonate-free brine.   Two simulated brines (GWB and ERDA-6) were prepared according to the *Brine Preparation* (ACP-EXP-001) procedure. These brines were at 95% of saturation to prevent salt precipitation during the solubility experiments. The pC_{H+} of the brine was varied as a parameter. The experimental matrix is presented in Table 4.

The samples were prepared and maintained as follows:

- pC_{H+} in brine solutions was adjusted according to Table 4

- Solutions were distributed to the washed bottles (15 mL)

- Two replicates were prepared for each data point,

- 50 μL of thorium stock solution (1000 ppm) was added to each bottle and stirred. Initial concentration of thorium was ~10^{-5} M

- Bottles were kept in a glove box with a controlled (CO_2-free) atmosphere

- Solutions were equilibrated for 1.5 years to reach steady state

Table 4.   **Experiment designation and conditions to investigate the solubility of thorium (IV) in brines versus pC_{H+} in a carbonate-free environment (Subtask 1).**

Medium / pC_{H+}	ERDA-6	GWB
~7	-	G7CF-x
~8	E8CF-x*	G8CF-x
~9	E9CF-x	G9CF-x
~10	E10CF-x	-

*where x denotes consecutive numbering of replicate experiments.

The time-dependence of the equilibration profile is shown in Figure 6. Long times were needed to achieve steady-state concentrations.
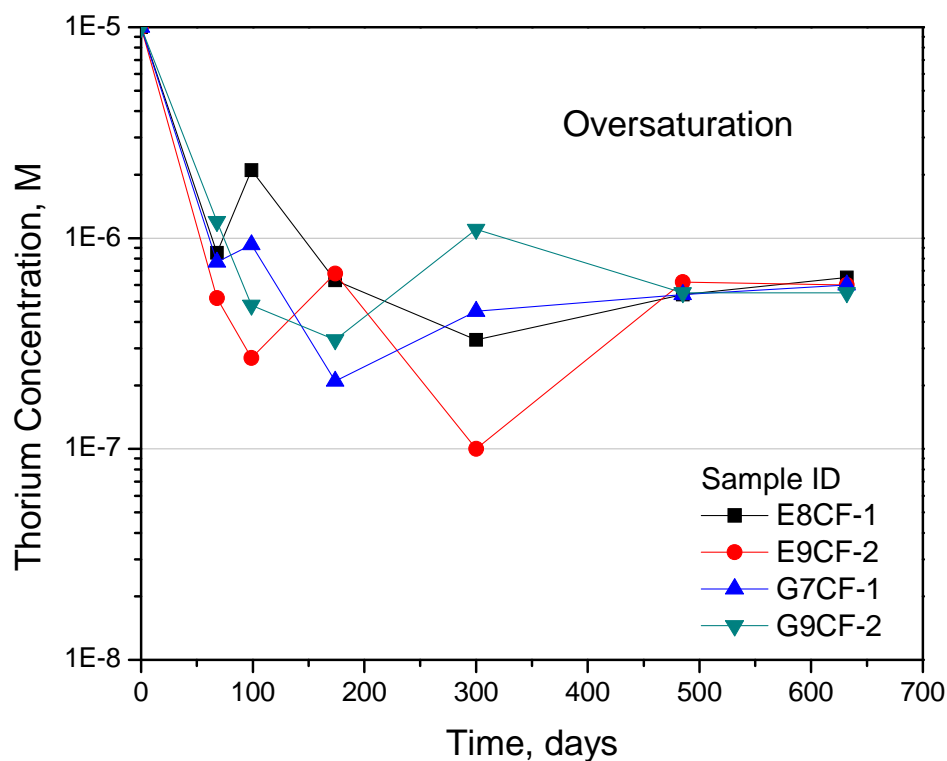
Figure 6.   **Time-dependence of thorium concentration in GWB and ERDA-6 brine from oversaturation. Over a year was needed to establish steady-state concentrations.**

3.2. Subtask 3: Undersaturation Study of the Solubility of Thorium (IV) in Carbonate- free Brine.

The solubility of thorium (IV) was measured in carbonate-free brines in which solid thorium oxy-hydroxide was slowly dissolved. These experiments were carried out in a carbon dioxide free environment. They were analogous to those performed in Subtask 1 but the concentration of thorium (IV) was approached from undersaturation. Two simulated brines (GWB and ERDA-6) were prepared according to the *Brine Preparation* (ACP-EXP-001) procedure. These brines were at 95% of saturation to prevent salt precipitation during the solubility experiments. The pC_{H+} of the brine was varied as a parameter. The experimental matrix is presented in Table 4.

The samples were prepared and maintained as follows:

- pC_{H+} in brine solutions was adjusted according to Table 5

- Solutions were distributed to the washed bottles (15 mL)

- Two replicates were prepared for each data point

- Thorium solid (thorium oxy-hydroxide prepared in our laboratory) was added to each bottle and stirred

- Bottles were kept in a glove box with a controlled (CO_2-free) atmosphere,

- Solutions were equilibrated for 1.5 years to reach steady state.

Table 5:   Undersaturation experiment designation and conditions to investigate the solubility of thorium (IV) in brines versus pC_{H+} in the carbonate free brines (Subtask 3).

Medium / pC_{H+}	ERDA-6	GWB
~7	UE7CF-x*	UG7CF-x
~8	UE8CF-x	UG8CF-x
~9	UE9CF-x	UG9CF-x
~10	UE10CF-x	-

* where x denotes consecutive numbering of replicate experiments.

The time-dependence of the equilibration profile is shown in Figure 7. Long times were needed to achieve steady-state concentrations.
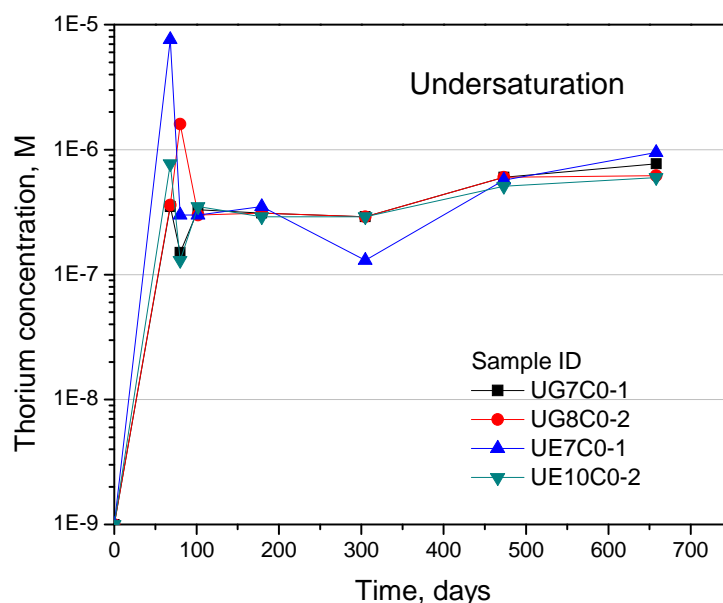
Figure 7.   Time-dependence of thorium concentration in GWB and ERDA-6 brine from undersaturation. Over a year was needed to establish steady-state concentrations.

3.3. Overall Experimental Approach, Sampling and Analysis

The bottles remained sealed during the experiment and were only open during the short duration of the sampling. Because CO_2 was at a very low concentration in the glovebox atmosphere, this short sampling time did not lead to significant carbonate uptake. Sampling was performed periodically until steady state conditions were established, i.e. the thorium concentration in solution did not change appreciably.

Samples, typically 0.2 mL in volume, were taken with a single-use pipet tip, transferred to the spin filter at 30 kDa of nominal pore size (~5nm) and centrifuged at 13400 rpm for 30 minutes. The filtrate was used for thorium analysis. Ion Coupled Plasma – Mass Spectrometry, ICP-MS, samples were diluted 100 times according to the Analysis of Solutes in Brine Using the Agilent ICP-MS (ACP-EXP-011) procedure. pH was determined periodically by direct measurement in the bottle. Hydrogen ion concentration in the brines was measured using the Determination of Hydrogen Ion Concentration in Brine (ACP-EXP-010) procedure.

The thorium concentration was analyzed by ICP-MS which is the most reliable method for thorium analysis (detection limit of 1 ppt which corresponds to $\sim 5 \times 10^{-10}$ M in the brine sample and an uncertainty of $\pm$ 20 to 100%). Ultracentrifugation was used to establish the colloidal fraction contributing to the total thorium concentration. Ultracentrifugation was performed at 120,000 rpm (1,000,000 $\times$ g) for two hours and a 15 μL aliquot was taken from the top of the solution for ICP-MS analysis. In all experiments, thorium equilibration was very slow and required a minimum of one year of equilibration – this was especially true for the undersaturation experiments (see Figures 4 and 5).

3.4. Results: Thorium Solubility in ERDA-6 and GWB Brine

The measured thorium concentrations in the thorium solubility studies performed in carbonate-free ERDA-6 brine after one year of equilibration are presented in Figure 8. After 18 months of equilibration the thorium solubilities in the carbonate-free ERDA-6 brine measured from under- and oversaturation were within experimental uncertainty and did not change with time. This indicated that a steady state concentration was achieved. The thorium concentration did not depend significantly on pC_{H+} in the pC_{H+} range investigated and was $6 - 7 \times 10^{-7}$ M. This concentrations are in agreement with those reported by Altmaier et al. (2004) (see Figure 2) and represents the sum of the dissolved and nano-colloidal fraction of thorium(IV).

Analogous experiments were conducted in GWB brine and these results are shown in Figure 9. To cover the range of pC_{H+} in the repository, thorium experiments were also performed in GWB brine for $pC_{H+} > 9$, which is above the cloud point of the brine. In this case, GWB was titrated with NaOH to a certain pC_{H+} (~9.8) leading to a significant amount of precipitate formation. The residual brine was filtered by a 0.2 μm filter and this filtrate was used in the higher pH experiments.   After 18 months of equilibration the thorium solubilities measured from under- and oversaturation in GWB brine are in agreement.
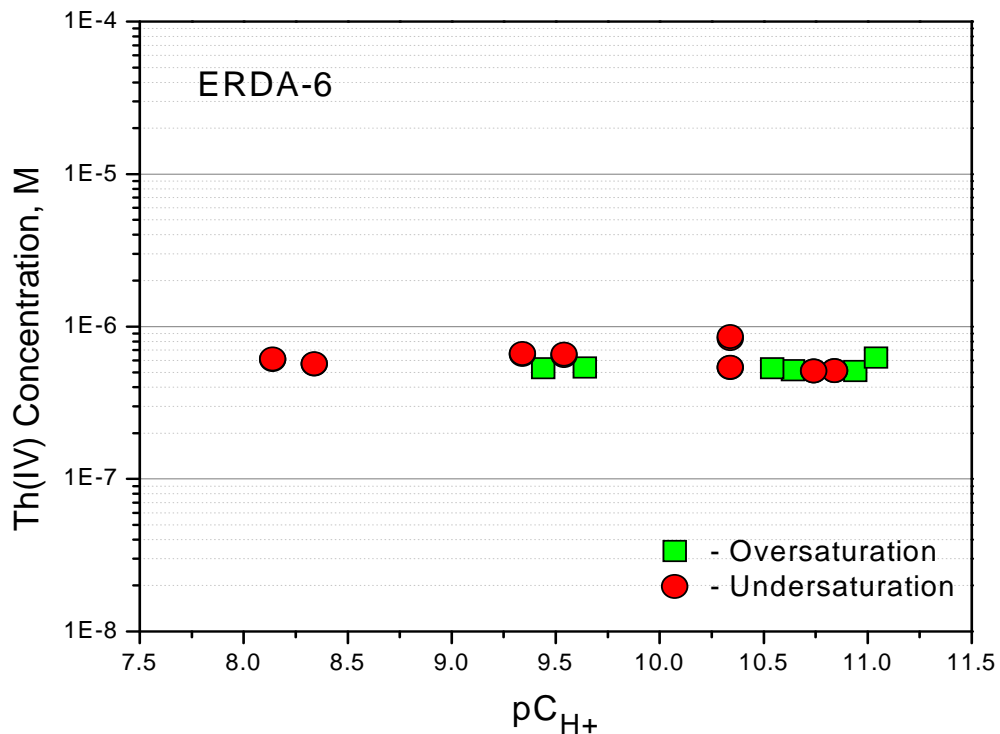
Figure 8. Thorium concentrations measured in ERDA-6 brine after a year and a half of equilibration (30 kDa filtration).
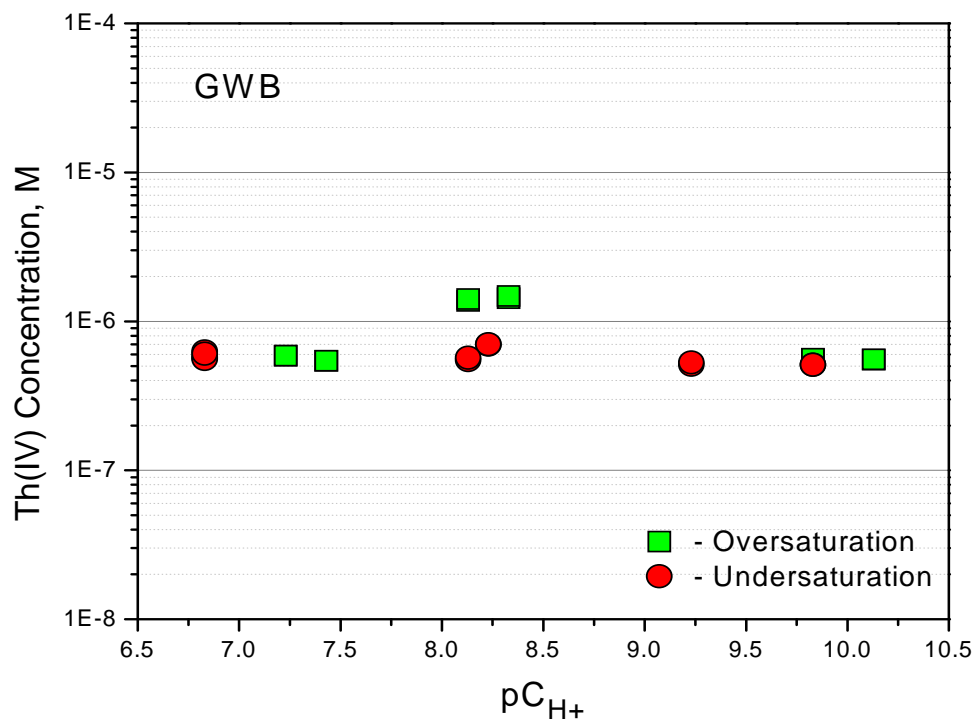
Figure 9.   The results of thorium solubility in carbonate free system measured in GWB brine after equilibration over one year.

The solubility of thorium measured in GWB brine was equal to the solubility of thorium measured in ERDA-6 brine. The thorium concentration does not depend significantly on the pC_{H+} and brine used. The solubilities of Th(IV) measured for both brines in the present work are in good agreement with the data reported in Altmaier at al. (2004) measured in simplified brine systems at variable ionic strengths (see Figure 2). For the pC_{H+} range used in this work, the concentration of thorium, on average, was $\log[Th]_{Total} = -6.25$, corresponding to a concentration of 5.6×10^{-7} M. This value compares to $\log[Th]_{Total} = -6.3 \pm 0.5$ reported in Altmaier et al. (2004). These concentrations, in both sets of data, include dissolved thorium species and intrinsic nano-colloidal contributions (<5 nm).

Our carbonate-free solutions were kept for the next 2 years after we measured steady state concentrations of thorium that was very similar to the concentrations reported in the literature. These samples were sampled and the goal of these samplings were to observe what changes happened in thorium concentrations after total of 4 years of equilibration. GWB brine solutions were sampled using the following approach: a sample of brine was filtered using 100 kDa spin filter by centrifugation at 13400 rpm for 30 minutes and then an individual sample of 15 µL was taken and entered to 1.50 mL 2% high purity nitric acid containing an indium internal standard. Thorium concentrations were measured using ICP-MS. The results of thorium measurements in carbonate-free systems in GWB brine from oversaturation and undersaturation after equilibration for additional 2 years are presented in Figure 10.
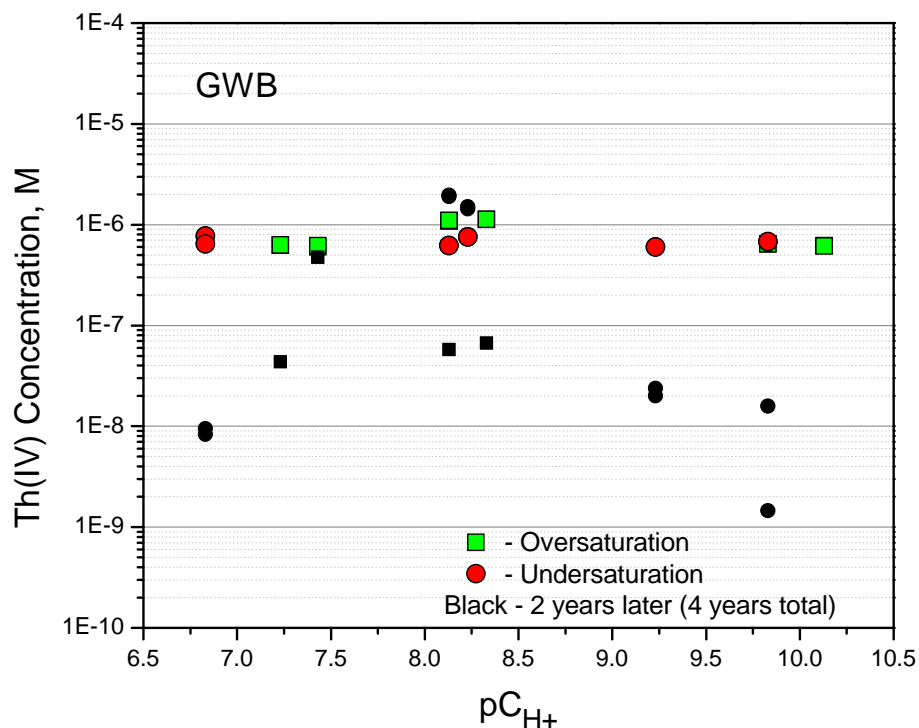
Figure 10. **After an additional 2 years of equilibration the thorium concentrations in GWB brine carbonate-free significantly decreased (black points in the figure). In the range pC_{H+} between 7.5 and 8.3 for some samples the thorium concentration was not changed for others dropped down one order of magnitude and more.**

The results of these measurements gave evidence that the equilibration process for thorium is very long and suggest that some data reported in the literature may not have reached their final steady state concentrations.

4.0 Thorium Solubility in the Presence of Carbonate

Thorium solubility data generated in carbonate containing ERDA-6 and GWB brine from oversaturation (Subtask 2) and undersaturation (Subtask 4) are summarized in this section. These data establish the effects of carbonate complexation on the solubility of An(IV). The specific goal of this study was to establish the real-system contribution of hydrolysis to Th(IV) solubility and to measure the degree of colloid formation as a function of pC_{H+} and brine composition.

4.1. Subtask 2:   Oversaturation Study of the Thorium (IV) Solubility in Brine Containing Carbonate.

The objective of this Subtask was to measure the effective solubility of thorium (IV) from oversaturation as a function of key subsurface parameters: brine composition, pH and carbonate-concentration.   Two simulated brines (GWB and ERDA-6) were prepared according to the *Brine Preparation* (ACP-EXP-001) procedure. These brines were at 95% of saturation to prevent salt precipitation during the solubility experiments. The pC_{H+} of the brine was varied as a parameter. The experimental matrix is presented in Table 6.

Table 6. Experiment designation and conditions to investigate the solubility of thorium (IV) from oversaturation as a function of pC_{H+} in carbonate containing brines (Subtask 2).

Medium pC_{H+}	ERDA-6		GWB	
~7	E7C2-x*	E7C3-x*	G7C2-x*	G7C3-x*
~8	E8C2-x	E8C3-x	G8C2-x	G8C3-x
~9	E9C2-x	E9C3-x	G9C2-x	G9C3-x
~10	E10C2-x	E10C3-x	G10C2-x	G10C3-x

*where x denotes consecutive numbering of replicate experiments, C2 – 10^{-2} M carbonate, C3 – 10^{-3} M carbonate.

The samples were prepared and maintained as follows:

- Brines were spiked with carbonate solution to obtain final concentration 10^{-2} and 10^{-3} M

- pC_{H+} in brine solutions was adjusted according to Table 5

- Solutions were distributed to the washed bottles (15 mL)

- Two replicates were prepared for each data point,

- 50 μL of thorium stock solution (1000 ppm) was added to each bottle and stirred. Initial concentration of thorium was ~2×10^{-5} M

- Bottles were kept in a hood

- Solutions were equilibrated for 2 years

The time-dependence of the equilibration profiles and pH changes are shown in Figures 11 to 13.

4.2. Subtask 4:   Undersaturation Study of the Thorium (IV) Solubility in Brine Containing Carbonate.

The solubility of thorium (IV) was measured in carbonate containing brines in which solid thorium oxy-hydroxide was slowly dissolved. They were analogous to those performed in Subtask 2 but the concentration of thorium (IV) was approached from below saturation. Two simulated brines (GWB and ERDA-6) were prepared according to the *Brine Preparation* (ACP-EXP-001) procedure. These brines were at 95% of saturation to prevent salt precipitation during the solubility experiments. The pC_{H+} of the brine was varied as a parameter. Experiments were conducted for two carbonate concentrations. The experimental matrix is presented in Table 7.

The samples were prepared and maintained as follows:

- Brines were spiked with carbonate solution to obtain final concentration 10^{-2} and 10^{-3} M

- pC_{H+} in brine solutions was adjusted according to Table 7

- Solutions were distributed to the washed bottles (15 mL)

- Two replicates were prepared for each data point

- Thorium solid (thorium oxy-hydroxide prepared in our laboratory) was added to each bottle and stirred

- Bottles were kept in a hood,

- Solutions were equilibrated for 2 years.

Table 7:   Undersaturation experiment designation and conditions to investigate the solubility of thorium (IV) in brines versus pC_{H+} and carbonate concentration (Subtask 4).

Medium / pC_{H+}	ERDA-6		GWB	
~7	UE7C2-x*	UE7C3-x*	UG7C2-x*	UG7C3-x*
~8	UE8C2-x	UE8C3-x	UG8C2-x	UG8C3-x
~9	UE9C2-x	UE9C3-x	UG9C2-x	UG9C3-x
~10	UE10C2-x	UE10C3-x	UG10C2-x	UG10C3-x

*where x denotes consecutive numbering of replicate experiments, C2 – 10^{-2} M carbonate, C3 – 10^{-3} M carbonate.

During two years of equilibration small decrease of pH in all the samples was observed. In samples at initial pC_{H+} ~ 9.6 a drop of ~0.52 pH unit was noted. The average decrease in all other samples was equal to 0.17 pH units. The trend in pH changes for GWB is presented in Figure 11 and for EDRA-6 in Figure 12.
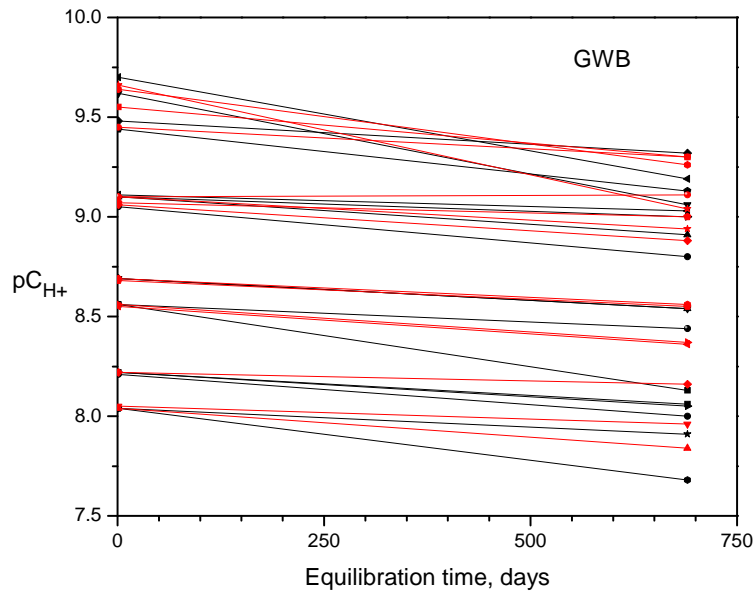
Figure 11.   **Changes of pC_{H_+} with equilibration time in carbonate containing GWB samples (oversaturation – black lines, undersaturation – red lines).**
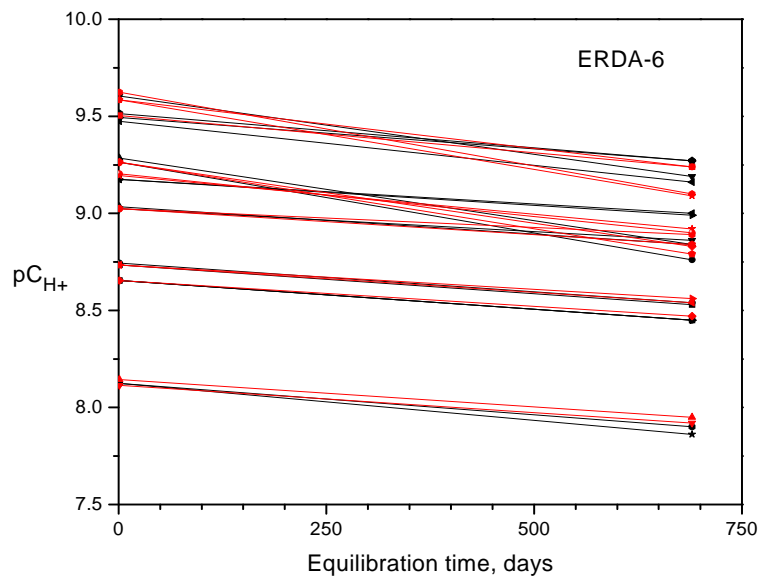
Figure 12.   **Changes of pC_{H_+} with equilibration time in carbonate containing ERDA-6 samples (oversaturation – black lines, undersaturation – red lines).**
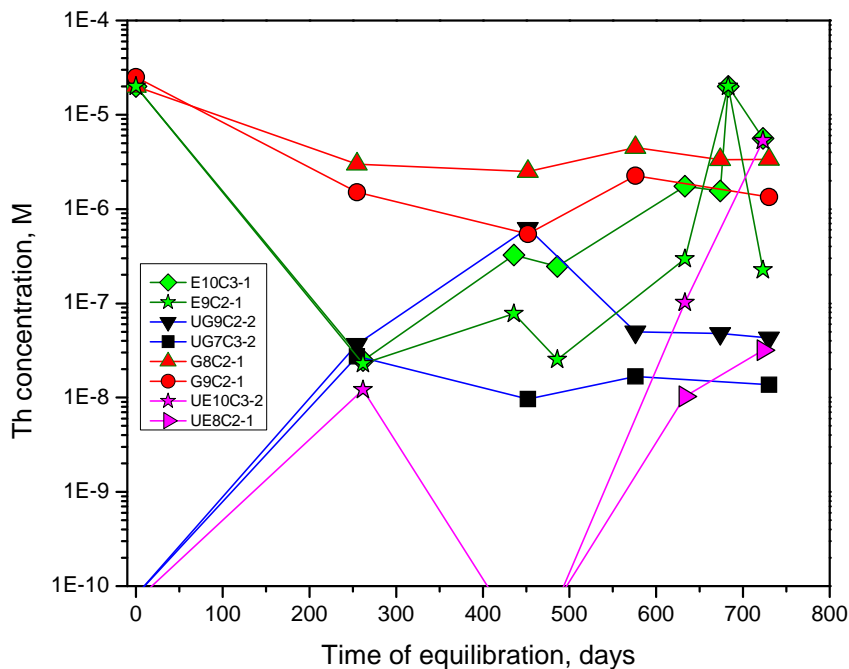
Figure 13. Time-dependence thorium concentrations in GWB and ERDA-6 brine measured from under- and oversaturation (oversaturation – blue lines, undersaturation – red lines). Long equilibration times are needed to reach the steady-state thorium concentrations.

In comparison to GWB, there was a more pronounced decrease in pH observed in ERDA-6 brine. At an initial pC_{H+} greater than 9.3 this decrease was 0.45 pH units. For all the other samples, an average decrease of 0.21 pH units was noted.

The time-dependence of the equilibration profile is shown in Figure 13. Long times are needed to achieve steady-state thorium concentrations in ERDA-6 brine.

4.3. Experimental Approach, Sampling and Analysis

The bottles remained sealed during the experiment and were only open during the short duration of the sampling. This short sampling time did not lead to a significant change in the carbonate concentration in the brines. Sampling was performed periodically until steady state conditions were established, meaning that the thorium concentration in solution did not change appreciably.

Samples, typically 0.2 mL in volume, were taken with a single-use pipet tip, transferred to a 100 kDa spin filter (nominal pore size ~20nm) and centrifuged at 13400 rpm for 30 minutes. The filtrate was used for thorium analysis. Inductively Coupled Plasma – Mass Spectrometry, ICP-MS, samples were diluted 100 times according to the *Analysis of Solutes in Brine Using the Agilent ICP-MS* (ACP-EXP-011) procedure. pH was determined on the beginning and the end of experiment by direct measurement. Hydrogen ion concentration in the brines was measured

using the *Determination of Hydrogen Ion Concentration in Brine* (ACP-EXP-010) procedure.

ICP-MS is the most reliable method for thorium analysis (detection limit of 1 ppt which corresponds to $\sim 5 \times 10^{-10}$ M in the brine sample and an uncertainty of $\pm$ 20 to 100%).   At higher concentrations the uncertainty was typically <5%.

Ultracentrifugation and sequential filtration was used to establish the colloidal fraction contributing to the total thorium concentration. Ultracentrifugation was performed at 120,000 rpm (1,000,000 $\times$ g) for two hours and a 15 μL aliquot was taken from the top of the solution for ICP-MS analysis.   In all experiments, thorium equilibration was very slow and required a minimum of two years of equilibration, especially for the undersaturation experiments.

4.4. Results: Thorium Solubility in ERDA-6 and GWB Brine Containing Carbonate

The measured thorium concentration, after almost two years of equilibration time, that were performed in ERDA-6 brine containing carbonate are presented in Figure 14A and 14B. After 20 months of equilibration, the thorium concentrations in the ERDA-6 brine measured from under- and oversaturation were not stable enough to conclude that a steady state was achieved.   In many samples where solubility is measured from undersaturation the thorium concentrations were below the detection limit.   It was possible that, in ERDA-6 brine, a significant part of thorium was adsorbed on the walls of vessels used in these experiments. For this reason, a second addition of thorium to the samples equilibrated from oversaturation was performed to continue the experiment. The results of the sampling after 40 days of equilibration after the 2nd thorium addition are presented in Figure 14B. During 20 months of experiment the changes in pH were small, similar to these observed in the neodymium solubility experiments containing carbonate.
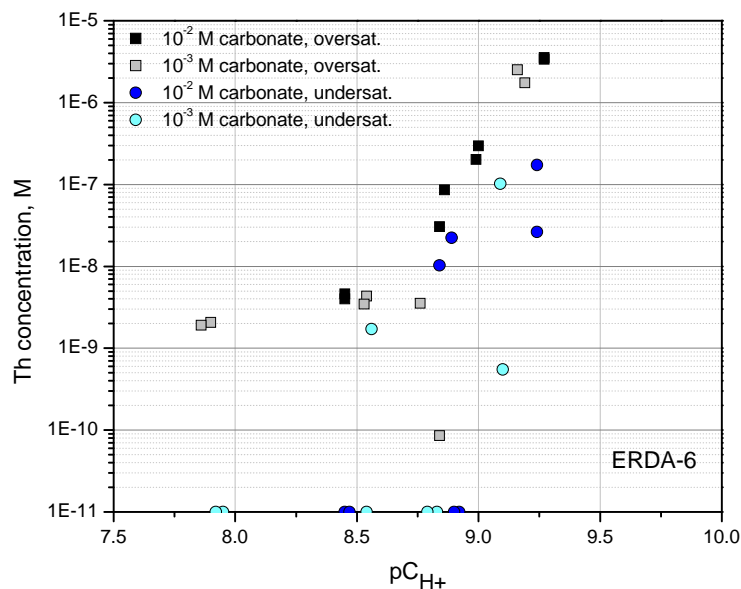
Figure 14A.   Thorium concentrations measured in ERDA-6 brine after two years of equilibration (100 kDa filtration).
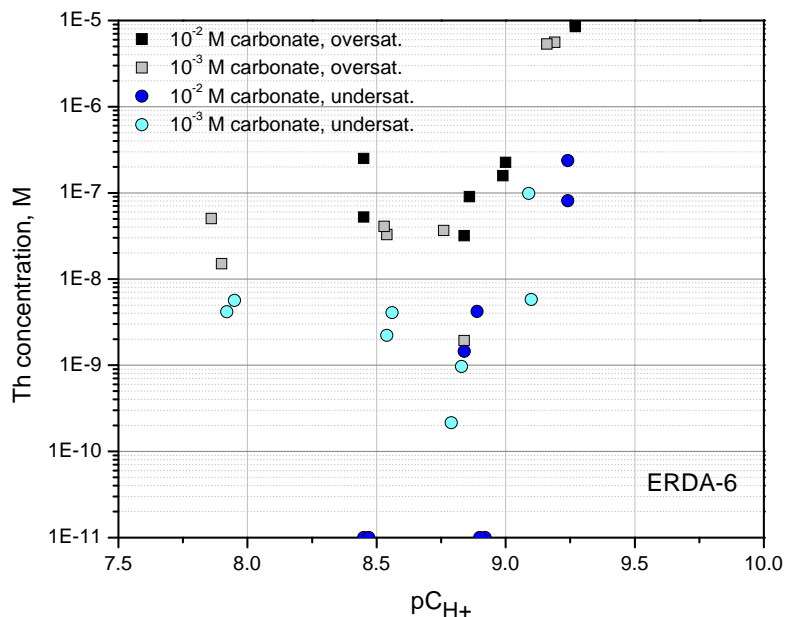
Figure 14B.   Thorium concentrations measured in ERDA-6 brine 40 days after 2nd addition of thorium (total 2×10^{-5} M) to the oversaturation samples (100 kDa filtration).

Analogous experiments were conducted in GWB brine and these results are shown in Figure 15. To cover the range of pC_{H+} expected in the repository, thorium experiments were also performed in GWB brine for $pC_{H+} > 9$, which is above the cloud point of the brine. In this case, GWB was titrated with NaOH to a certain pC_{H+} (~9.8) leading to a significant amount of precipitate formation. The residual brine was filtered through a 0.2 µm filter and this filtrate was used in the higher pH experiments. Changes in pC_{H+} after 24 months were small, similar to those observed in the neodymium solubility experiments containing carbonate. After two years of equilibration the thorium concentrations measured from under- and oversaturation in GWB brine did not depend on the carbonate concentration. Concentrations measured from oversaturation were 2.5 orders of magnitude greater than those measured from undersaturation indicating that meta-stable states can last a long period of time. The trend in the oversaturation data is consistent with the literature data [Altmaier 2005] presented in Figure 1. In the undersaturation experiments, which are more relevant to the WIPP situation, the average thorium concentration was to 2×10^{-8} M and tended to decrease above $pC_{H+} > 9$. For the oversaturation experiments, similar trends were observed and, at $pC_{H+} > 9$, the thorium concentrations decreased to below 10^{-8} M. These results reproduce, to some extent, the trends reported in the literature [Altmaier 2005], however our data were for much higher ionic-strength brines leading to an effective shift to lower pC_{H+} values of about 1 pH unit.

At the predicted WIPP repository pC_{H+}, regardless of the carbonate level, the thorium concentrations in GWB brine were 2×10^{-8} M. This suggests and confirms that the ternary hydroxy-carbonato complexes do not play a significant role in the thorium solubility at $pC_{H+} > 9$.
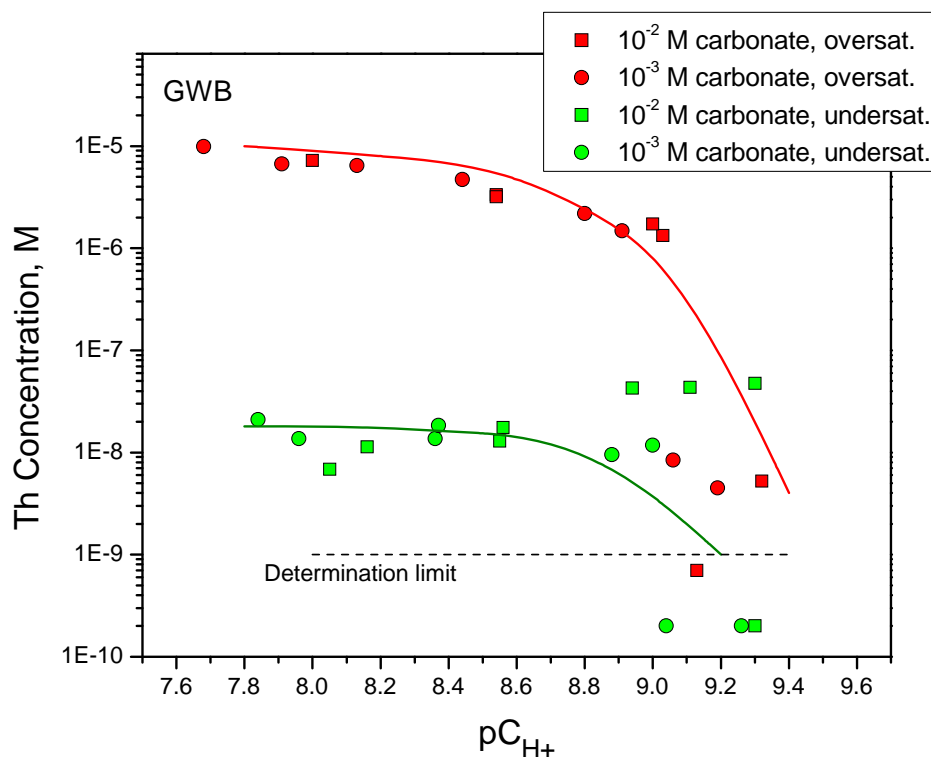
Figure 15.   The results of thorium solubility as a function of carbonate concentration measured in GWB brine after the equilibration time of two years.

Our solubility data for $pC_{H+} > 9$, measured after 4 years of equilibration, were reported in the previous section for carbonate-free GWB brine and was approximately 2×10^{-8} M.   These are consistent with the dissolved thorium concentrations reported in the literature and are slightly below the current calculated solubilities in WIPP PA.

5.0   Contribution of Colloids to the Measured Thorium Steady State Concentrations

5.1. Ultracentrifugation: Colloidal Fraction of the Measured Thorium Concentration

A representative number of samples from the carbonate free experiments were further analyzed by ultracentrifugation to establish the colloidal fraction of the thorium concentrations measured. In our procedure, ultracentrifugation was performed for 2 hours at 120,000 rpm (~ 1,000,000 × g) with a Beckmann-Coulter model Optima max-XP ultracentrifuge. This protocol exceeded the degree of separation used by Altmaier et al. (2004) where 90,000 rpm for 60 minutes was used. Thorium concentrations measured before and after ultracentrifugation are reported in Figure 16, along with the initial total concentration data. Total thorium

concentrations measured before ultracentrifugation were within the experimental uncertainty of the total concentrations measured a few months earlier (see Figures 6 and 7).
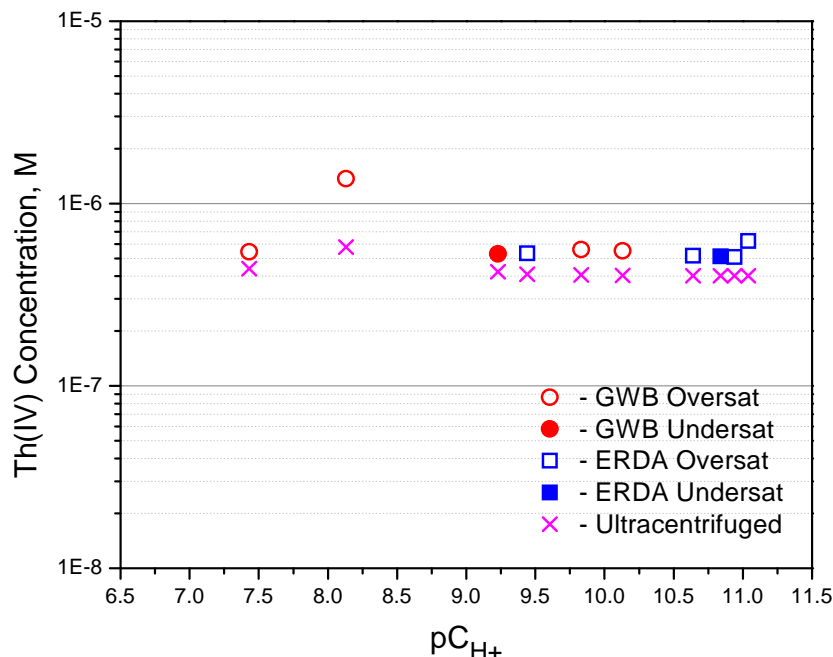
Figure 16.   Concentration of thorium measured before and after ultracentrifugation in representative ERDA-6 and GWB samples.

Although our total thorium concentration data are in agreement with Altmaier et al. (2004), our results show a different partitioning between the thorium colloidal and dissolved fraction. In our samples, the highest colloidal fraction was ~40% while Altmaier et al. (2004) reports a high colloidal fraction of at least ~99%. We do not yet fully understand what is causing this difference but their samples were equilibrated for a much shorter period of time. The newest information provided by German scientists (Xavier and Altmaier 2012) confirms our results and their new results are in contradiction to their previously-published results. The research to establish the colloidal fraction contribution in the total thorium solubility was continued for carbonate containing samples using sequential filtration. Additionally, the effect of equilibration time on this colloidal partitioning was investigated.

5.2. Sequential Filtration: Size Distribution of the Thorium Colloidal Fraction

Selected samples of solutions from the thorium solubility experiment were used for the determination of the thorium size particles distribution. To this end, samples were sequentially filtered using filters with different pore sizes. The following pore size filters were used: 0.45 µm, 0.22 µm, ~20 nm (100 kDa), ~10 nm (30 kDa), ~5 nm (10 kDa) and ~2.5 nm (3 kDa). The filtrate from a bigger pore size was used as a filtering solution for a smaller pore size. The

samples from all the filtrates were taken and measured for thorium contents using ICP-MS. The results of these experiments are presented in the Figures 17 and 18.
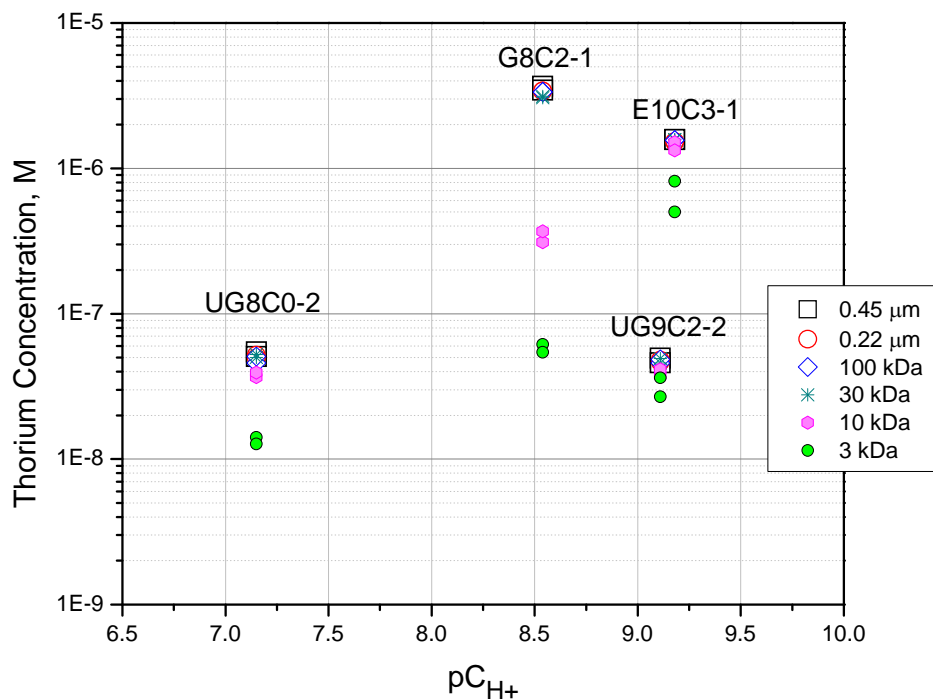
Figure 17.   **Thorium concentrations measured during sequential filtration as a function of pore size for samples with varied pC_{H+}.**

In sample G8C2-1 the colloidal fraction was the greatest, however total thorium concentration was also the greatest. The dissolved thorium concentrations in all GWB brines were in the range of 2×10^{-8} to 6×10^{-8} M. In ERDA-6 brine, the dissolved thorium concentration was about 10 fold greater, but steady state thorium concentrations were not yet achieved. Even in these partially equilibrated samples the thorium colloidal fraction was small (about 50%).

The colloidal particles of thorium appear to have very small dimensions, smaller than 10 kDa. Dissolved thorium concentration was $3(\pm2)\times10^{-8}$ M. The average total thorium concentration consists of 30-60% dissolved fraction and 40-70% colloidal fraction.
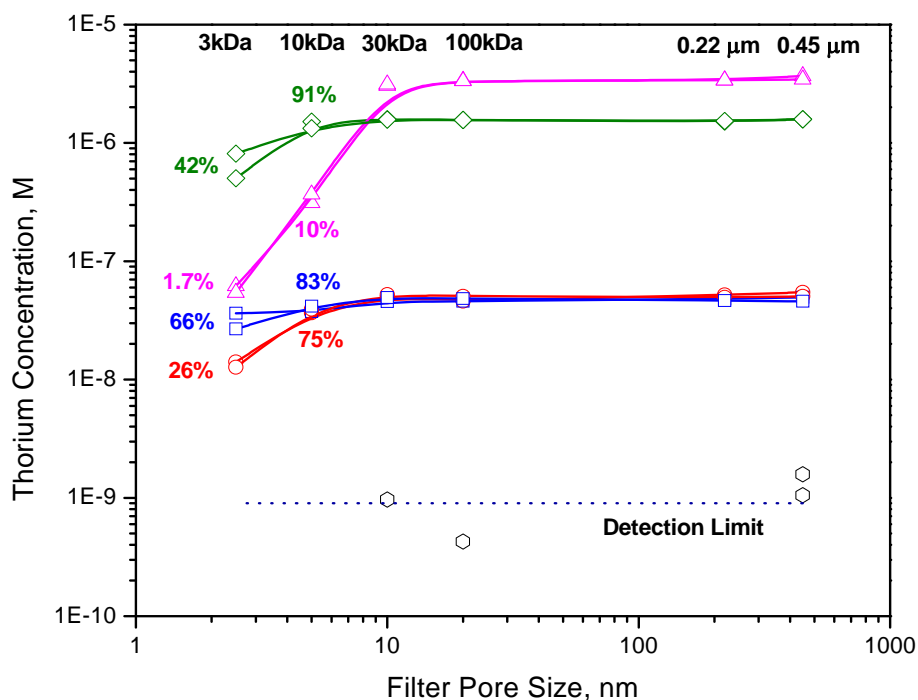
Figure 18. Distribution of thorium concentrations measured as a function of pore size for samples.

6.0 Conclusions

The solubility of thorium measured in this work provides new insight to our understanding of thorium solubility in brine systems and, by analogy, the behavior of An(IV) species in WIPP brine. Very long equilibration times are needed to obtain reliable thorium solubility data, which means that the chemical processes in this system are kinetically controlled. This is likely caused by the slow inter-conversion of colloidal and dissolved species coupled with a very slow precipitation process. This equilibration time takes much longer in ERDA-6 brine than in GWB brine.

In carbonate-free systems our data after 2 years of equilibration were in very good agreement with the data published in the literature [Altmaier et al. 2004]. However, after continuing equilibration for the next 2 years the thorium concentrations drop significantly down to the level 2×10^{-8} M, i.e. to the level of the dissolved thorium fraction. Meta-stable steady state thorium concentrations lasted for a long period of time and are far away from thermodynamic equilibrium.

The colloidal fraction found in this work using ultracentrifugation and sequential filtration is much smaller and contributes approximately 40-70% to the total thorium concentration. In this context, an average enhancement factor due to the presence of colloidal species is ~2.

After two years of equilibration the thorium concentrations measured from under- and oversaturation in GWB brine did not depend on carbonate concentration. Concentrations measured from oversaturation were 2.5 orders of magnitude greater than those measured from undersaturation indicating that metastable states can last a long period of time. The trend in oversaturation data is consistent with the literature data [Altmaier 2005] as presented in Figure 1. In the undersaturation experiments, which are more relevant to the WIPP situation, the average thorium concentration was to 2×10^{-8} M and decreased steadily at $pC_{H+} > 9$. In the oversaturation experiments, the concentration plot exhibited similar trends and at $pC_{H+} > 9$ the thorium concentrations decreased below 10^{-8} M. These results are consistent with trends reported in the literature [Altmaier 2005], except that we see a ~ 1 pH shift lower due to the higher ionic strengths in our brines that were investigated.

At the repository-relevant pC_{H+}, regardless of carbonate levels, the thorium concentrations in GWB brine was 2×10^{-8} M. This behavior of thorium suggests that the mixed hydroxy-carbonato complexes do not play a significant role in the solubility of thorium at $pC_{H+} > 9$.

7.0 References

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8.0 Appendix

Comparison of Recent Thorium Thermodynamic Data with Those Used in the WIPP FMT_050405.chemdat Database

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The goal of this review is to critically compare the new thorium thermodynamic data published recently in the literature [1,2,3] with those present in the FMT_050405.chemdat database (referred to as the FMT database in this report) used for actinide(IV) solubility modeling in WIPP brine. In this review, three areas were assessed: inorganic complexation data, Pitzer interaction parameters and organic complexation constants. As a result of this assessment we found that:

1) Thermodynamic data used in the FMT database for hydrolysis and carbonate complexation are consistent with the data reported in the recent literature [1,2],

2) Stability constants for thorium sulfate aqueous species and solids in the FMT database are greater than those reported in the literature [2],

3) The FMT database remains as the most comprehensive listing of Pitzer parameters for thorium. In the "Chemical Thermodynamic of Thorium"[2], SIT parameters were given for modeling ionic strength effects and these do not extend to WIPP-relevant ionic strengths and, in this context, are not comparable to the FMT database.

4) Published stability constants for Th(IV) complexation with selected organic ligands cannot be directly compared with those in FMT since they only relate to lower ionic strengths. The FMT database thermodynamic stability constants appear to be greater than those present in the literature [2,3] and if so, introduce additional conservatism to the WIPP model.

5) The complexation of thorium with organics and sulfate is much less important than the effects of hydrolysis and carbonate complexation in defining the solubility of Th(IV). In this context, the identified discrepancies for these data do not significantly affect the WIPP actinide(IV) solubility model.

1. Introduction

In this review the thermodynamic constants calculated on the basis of the standard chemical potentials for the appropriate species present in the FMT database were compared with those from the Critical Stability Constants NIST Database [1] and those reported in Chemical Thermodynamics of Thorium [2].

In response to Don Reed's request of April 30, 2006, L. Brush wrote "… *the FMT database does not contain formation constants. Instead, the data entered for each aqueous and solid species is the dimensionless standard chemical potential. Therefore, you will have to convert the dimensionless standard chemical potentials for the aqueous species to their formation constants, if you need them. As an example, according to Yong-Liang, consider the equilibrium constant (log K) for the second dissociation reaction of carbonic acid,*

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+.$$

Log K for the dissociation constant for HCO$_3^-$ is then given by the following equation:

$$\log K = -[(\mu^o/RT)_{CO_3^{2-}} + (\mu^o/RT)_{H^+} - (\mu^o/RT)_{HCO_3^-}] / 2.3026" \tag{1}$$

The approach suggested by Brush was used for the thermodynamic stability calculations using the FMT database. The thorium species and associated standard chemical potentials imported from the FMT_050405.chemdat database are reported in Table A-1.

2. Major thorium complexation reactions with inorganic ligands

The inorganic aqueous and solubility-limiting species for Th(IV) are listed in Table A-2 (column "Th(IV) Reactions"). Thermodynamic stability constants for the reactions listed in the column "log K^0 FMT" were calculated using standard chemical potentials for appropriate species imported from the FMT database (see Table A-1) and equation (1).

Table A-1. Thorium species and dimensionless standard chemical potentials present in FMT_050405.chemdat database used to calculate the thermodynamic stability constants shown in Table A-2.

Species	μ°_i/RT
H_2O	-95.6635
OH^-	-63.435
H^+	0
Na^+	-105.651
K^+	-113.957
SO_4^{2-}	-300.386
HSO_4^-	-304.942
HCO_3^-	-236.751
CO_3^{2-}	-212.944
Th^{4+}	-284.227
$Th(CO_3)_5^{6-}$	-1411.378
$Th(OH)_3(CO_3)^-$	-775.627
$Th(OH)_4(aq)$	-626.5853
$Th(SO_4)_2(aq)$	-911.69
$Th(SO_4)_3^{2-}$	-1214
$Th(Ac)_2^{2+}$	-604.8
$ThAc^{3+}$	-448.525
$ThCit^+$	-285.898
$ThEDTA(aq)$	-285.419
$Th(C_2O_4)^{2+}$	-297.428
$ThO_2(am)$	-451.408
$Th(SO_4)_2.9H_2O(s)$	-1775.9
$Th(SO_4)_2.8H_2O(s)$	-1680
$Th(SO_4)_2.Na_2SO_4.6H_2O(s)$	-2011.29
$Th(SO_4)_2.K_2SO_4.4H_2O(s)$	-1837.57
$Th(SO_4)_2.2K_2SO_4.2H_2O(s)$	-2181.81
$2[Th(SO_4)_2.7/2K_2SO_4(s)]$	-5581.66

Table A-2. Complexation reactions and corresponding stability constants or solubility products for thorium species expected under WIPP conditions.

Th(IV) Reactions Aqueous Species	log K^0 FMT	log K NIST[1]	log K^0 Therm. of Th [2]
$ThO_2(am) + 2H_2O \rightleftarrows Th(OH)_4(aq)$ $ThO_2(am) + 2H_2O \rightleftarrows Th^{4+} + 4OH^-$ (am) - amorphous	-7.0	 -55.6 (0.5)*	*-8.1* -46.7 ± 0.9 fresh -47.5 ± 0.9 aged
$Th^{4+} + 4OH^- \rightleftarrows Th(OH)_4(aq)$ $Th^{4+} + 4H_2O \rightleftarrows Th(OH)_4(aq) + 4H^+$	38.5 -17.5	40.2 (3.0)*	*38.6* -17.4 ± 0.7
$Th^{4+} + 3OH^- + CO_3^{2-} \rightleftarrows Th(OH)_3CO_3^-$ $Th^{4+} + CO_3^{2-} + 3H_2O \rightleftarrows Th(OH)_3CO_3^- + 3H^+$	38.3	 -0.5 (0)*	38.3 ± 0.7 (40.8 ± 0.6 include colloids)
$Th^{4+} + 5CO_3^{2-} \rightleftarrows Th(CO_3)_5^{6-}$	27.1	32.3 (0)*	31.0 ± 0.7
$Th^{4+} + 2SO_4^{2-} \rightleftarrows Th(SO_4)_2(aq)$	11.6		9.69 ± 0.27
$Th^{4+} + 3SO_4^{2-} \rightleftarrows Th(SO_4)_3^{2-}$	12.4		10.75 ± 0.076
Solids	**log K_s^0**	**log K_s**	**log K_s^0**
$Th^{4+} + 2SO_4^{2-} + 9H_2O \rightleftarrows Th(SO_4)_2 \cdot 9H_2O(s)$	13.0		11.28 ± 0.14
$Th^{4+} + 2SO_4^{2-} + 8H_2O \rightleftarrows Th(SO_4)_2 \cdot 8H_2O(s)$	12.9		11.42 ± 0.50
$Th^{4+} + 2Na^+ + 3SO_4^{2-} + 6H_2O \rightleftarrows$ $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(s)$	17.6		13.84 ± 0.17
$Th^{4+} + 2K^+ + 3SO_4^{2-} + 4H_2O \rightleftarrows$ $Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O(s)$	18.1		15.0 ± 0.05
$Th^{4+} + 4K^+ + 4SO_4^{2-} + 2H_2O \rightleftarrows$ $Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O(s)$	21.2		18.67 ± 0.22
$Th^{4+} + 7K^+ + 5.5SO_4^{2-} \rightleftarrows$ $Th(SO_4)_2 \cdot 3.5K_2SO_4(s)$	24.7		22.38 ± 0.39

* In parentheses are listed ionic strengths for constants reported in Critical Stability Constants NIST Database 46. Other constants are listed as the thermodynamic constants, i.e. extrapolated to zero ionic strength. Constants printed in italic font are calculated in this assessment using the reported constant and $pK_w = 14.0$.

Discussion of inorganic ligand interactions with thorium

The $ThO_2(am)$ dissolution constant reported in the NIST database as log K = -55.6 measured in 0.5 M $NaClO_4$ is quite different than the constants reported in Chemical Thermodynamics of Thorium and used in the FMT model. This constant was rejected from our assessment as an outlier and was also not accepted in the recently published NEA review [2]. Other constants for the formation of the hydroxy-complexes are in good agreement with those used in the FMT model. It is necessary to note that there are small differences in dissolution constants for fresh and aged $ThO_2(am)$ solids.

The constant for the formation of the pentacarbonato complex used in the FMT model is 4 orders of magnitude smaller than reported in Chemical Thermodynamics of Thorium and 5 orders of magnitude smaller than listed in the NIST database. The pentacarbonato complex is not likely the most important carbonate complex under WIPP-relevant conditions because of the low carbonate concentration expected in the WIPP. Therefore, other ternary thorium complexes with carbonate and hydroxide may play a more important role. One of these complexes, $Th(OH)_3CO_3^-$, is present in the FMT database. The stability constant for this complex is in good agreement with those reported in both the NIST database and Chemical Thermodynamics of Thorium. It may be advisable, purely as a simplification of the current model, to replace the chemical potential currently used in the FMT model with the value that includes colloid formation corresponding to log K^0 = 40.8. Such an approach could eliminate an enhancement factor for An(IV) colloids. The stability constants for other ternary hydroxy-carbonate complexes of thorium, e.g. $Th(OH)(CO_3)_4^{5-}$, $Th(OH)_2CO_3(aq)$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4CO_3^{2-}$, are also reported in this data review [2] and the presence of these species could improve the accuracy but not the conservatism of the FMT model. Additionally, Pitzer parameters for these species were not given in the review [2], but we cannot exclude the possibility of data that could provide a basis for estimating these parameters.

Other species considered in the model are the thorium sulfate complexes and solids. All of these stability constants and solubility products are about two orders of magnitude greater as used in the FMT database than reported in Chemical Thermodynamics of Thorium. In our opinion, the most important reactions for thorium speciation at $pC_{H+} \sim 9.5$ are hydrolysis and carbonate complexation. Thorium sulfate complexes and thorium sulfate solids are less important to the

WIPP chemistry. However, they may contribute to some extent to the total picture. The presence of thorium-sulfate thermodynamic data makes the FMT database more robust and extends the applicability of the FMT model to broader range of pH.

3.   Pitzer ion-interaction parameters for thorium species

Ion-interaction Pitzer parameters are not available in the NIST database. In Chemical Thermodynamics of Thorium [2], SIT (Specific Ion Interaction Theory) parameters are predominantly used for ionic strength corrections. The SIT parameters are not relevant to the FMT database, since in the FMT calculations, Pitzer ion-interaction parameters are used. In Chemical Thermodynamics of Thorium, the only Pitzer parameters listed are for the interaction of Th^{4+} with Cl^- and are taken from Roy et al. 1992 [4]. These same binary and ternary parameters are used in the FMT database. The FMT database is currently the most comprehensive collection of WIPP-relevant Pitzer interaction parameters.

4.   Complexation of thorium by organic ligands

The major source of thorium complexation with organic ligand data as a function of NaCl ionic strength is the SAND99-0943 report [3]. Thorium data published in this report is collected in Table A-3. Data for thorium complexation with EDTA is not available in this report. In Chemical Thermodynamics of Thorium, complexation with organic ligands is not discussed. Therefore, the FMT database can only be compared to the NIST database and to the data in the SAND99-0943 report. The FMT stability constants were calculated using the standard chemical potential for the appropriate species and are given in Table A-4.

Discussion of organic ligand interactions with thorium

The comparison of the thorium thermodynamic data for organic ligands is very difficult, because the calculated FMT constants are thermodynamic, but other values reported in the NIST

Table A-3. Logarithm of stability constants of thorium with different organics as a function of NaCl ionic strength published in the SAND99-0943 report [3].

Complex	0.3M NaCl	1 M NaCl	2 M NaCl	3 M NaCl	4 M NaCl	5 M NaCl
$ThAc^{3+}$	4.41 ± 0.02	3.85 ± 0.02	3.92 ± 0.03	4.26 ± 0.03	4.29 ± 0.03	4.51 ± 0.03
$ThAc_2^{2+}$	7.47 ± 0.03	6.56 ± 0.03	6.82 ± 0.03	7.19 ± 0.02	7.30 ± 0.03	7.66 ± 0.03
$ThCitr^+$	9.67 ± 0.03	9.56 ± 0.03	9.31 ± 0.04	9.55 ± 0.02	10.07 ± 0.02	10.18 ± 0.03
$ThCitr_2^{2-}$	18.72 ± 0.04	18.28 ± 0.03	17.41 ± 0.06	17.33 ± 0.04	-	19.12 ± 0.04
$ThOx^{2+}$	7.08 ± 0.04	7.07 ± 0.02	7.04 ± 0.02	7.13 ± 0.01	7.26 ± 0.03	7.47 ± 0.02
$ThOx_2$	13.63 ± 0.04	13.42 ± 0.04	13.49 ± 0.05	13.83 ± 0.06	13.95 ± 0.04	14.63 ± 0.03

- where Ac denotes acetate, Citr denotes citrate and Ox denotes oxalate ions.

Table A-4. Thermodynamic stability constants for thorium–organic complexes used in the FMT model and reported in the NIST database.

Complex ThL_n	$\log \beta_n^0$ FMT	$\log \beta_n(\mu)$ NIST [1]	$\log \beta_n^0$ Therm. of Th [2]
$ThAc^{3+}$	7.4	The same as in SAND99-0943	NA
$ThAc_2^{2+}$	11.2	The same as in SAND99-0943	NA
$ThCitr^+$	15.2	$11.61(0.1 \text{ M Na}^+)$	NA
$ThCitr_2^{2-}$	-	$21.14(0.1 \text{ M Na}^+)$	NA
$ThOx^{2+}$	11.4	$8.8(0.1 \text{ M Na}^+)$	NA
$ThOx_2(aq)$	-	$16.8(1.0 \text{ M NH}_4^+)$	NA
$ThOx_2.6H_2O(s)$	-	$-21.38(1.0 \text{ M NH}_4^+)$	NA
ThEDTA	23.6	$22.3(0.5 \text{ M Na}^+)$	NA

- where Ac denotes acetate, Citr denotes citrate, and Ox denotes oxalate ions

database and SAND99-0943 report are the apparent stability constant measured at specific ionic strengths. A very rough comparison suggests that the FMT constants are greater than those reported in the NIST database and SAND99-0943 report and, in this context, introduce additional conservatism to the model. The most important constants are for the complexation of thorium with EDTA and these are in reasonable agreement.

In our opinion, the most important reactions for thorium speciation at $pC_H \sim 9.5$ are hydrolysis and carbonate complexation. Therefore, thorium complexes with organic ligands are less important to the WIPP chemistry model and do not make a significant contribution to the total solubility of thorium.

5.   References

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