

# TECHNICAL REPORT 02-12

**Application of the  
Nagra / PSI TDB 01/01:  
Solubility of Th, U, Np and Pu**

December 2002

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

## **PREFACE**

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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## ABSTRACT

If a true thermodynamic equilibrium with a well-known solid has established, chemical equilibrium thermodynamics allows estimation of the maximum concentration of a given radionuclide in a specified pore fluid of an underground repository. In the course of the review process for the Nagra/PSI Chemical Thermodynamic Data Base 01/01 we identified important cases of insufficient chemical knowledge leading to gaps in the database. First, experimental data for the systems  $\text{ThO}_2 - \text{H}_2\text{O}$  and  $\text{UO}_2 - \text{H}_2\text{O}$  cannot be interpreted by a unique set of thermodynamic constants. There we chose a pragmatic approach by including parameters in the database that are not thermodynamic constants in a strict sense, but that reproduced relevant experimental observations. Second, potentially important thermodynamic constants are missing because of insufficient experimental data. Estimations of these missing constants led to problem specific database extensions. Especially constants for ternary hydroxide-carbonate complexes of tetravalent actinides have been estimated by the “backdoor approach”, i.e. by adjusting thermodynamic constants to maximum feasible values that are still consistent with all available experimental solubility data. We conclude that gaps in the Nagra/PSI TDB 01/01 concerning Th, U, Np and Pu data do not lead to grossly wrong estimates of their respective solubility limits in the case of a bentonite pore water defined for the planned Swiss high-level waste repository. Attempts to improve our chemical knowledge should concentrate on the key parameters identified in this study.

## ZUSAMMENFASSUNG

Wenn nachweislich ein echtes thermodynamisches Gleichgewicht mit einer wohl-bekanntesten Festphase vorliegt, sagt die Gleichgewichtsthermodynamik die maximal mögliche Konzentration eines Radionuklids in vorgegebenen Endlagerfluiden zuverlässig voraus. Während der Überarbeitung der Nagra/PSI Thermodynamischen Datenbank 01/01 identifizierten wir verschiedene Beispiele wo fehlende chemische Kenntnisse schliesslich zu Lücken in der Datenbank führten. So können beispielsweise heute vorliegende experimentelle Daten in den Systemen  $\text{ThO}_2 - \text{H}_2\text{O}$  und  $\text{UO}_2 - \text{H}_2\text{O}$  nicht mit eindeutigen und thermodynamisch konsistenten Datensätzen beschrieben werden. In diesem Fall haben wir uns für einen pragmatischen Lösungsansatz entschlossen: Die Datenbank enthält Datensätze die in strengem Sinne nicht thermodynamische Konstanten darstellen, sondern Parameter welche die experimentellen Befunde reproduzieren. Weiter identifizierten wir Lücken in der Datenbank schlicht wegen fehlenden experimentellen Daten. Die Abschätzung dieser potentiell wichtigen fehlenden Konstanten führte zu problemorientierten Datenbankerweiterungen. Hier sind speziell die ternären Actiniden(IV)-Hydroxid-Carbonate zu erwähnen. Solche Konstanten wurden durch inverse Modellierung abgeschätzt, d.h., maximal mögliche Konstanten wurden derart festgelegt, dass sie gerade noch mit allen verfügbaren experimentellen Daten konsistent sind. Mit Extrapolationen und Modellrechnungen konnte gezeigt werden, dass die Datenbank trotz identifizierten Lücken nicht zu völlig falschen Beurteilungen der Löslichkeit der Elemente Th, U, Np und Pu führt. Für den spezifischen Fall des Bentonit-Porenwassers des geplanten Schweizer Hochaktivlagers identifiziert die Studie einige Schlüsselparameter, deren Verfeinerung unsere chemischen System-Kenntnisse wesentlich verbessern sollten.

## RÉSUMÉ

Si un véritable équilibre thermodynamique avec une phase solide bien connue est établi, la thermodynamique d'équilibre chimique permet d'estimer de manière fiable la concentration maximale d'un radionucléide donné dans un fluide interstitiel spécifique d'un dépôt souterrain. Durant le processus de révision de la banque de données thermodynamiques Nagra/PSI 01/01, nous avons identifié plusieurs cas où des connaissances chimiques insuffisantes ont abouti à des lacunes dans les données. Tout d'abord, il n'est pas possible d'interpréter les données expérimentales actuelles pour les systèmes  $\text{ThO}_2\text{-H}_2\text{O}$  et  $\text{UO}_2\text{-H}_2\text{O}$  par une série unique de constantes thermodynamiques. Pour cette raison, nous avons choisi une approche pragmatique, en incluant dans la banque de données des paramètres qui ne sont pas des constantes thermodynamiques au sens strict, mais correspondent toutefois à des observations expérimentales pertinentes. En second lieu, certaines constantes thermodynamiques potentiellement importantes manquent, faute de données expérimentales suffisantes. L'estimation de telles constantes a conduit à des extensions de la banque de données pour le traitement de problèmes spécifiques. Citons à ce propos les constantes pour les complexes ternaires hydroxo-carbonates des actinides tétravalents, qui ont été estimées par "backdoor approach", c'est-à-dire en ajustant les constantes thermodynamiques aux plus hautes valeurs possibles, tout en restant compatibles avec l'ensemble des données expérimentales de solubilité à disposition. Nous parvenons à la conclusion que, malgré les lacunes, la banque de données Nagra/PSI 01/01 n'est pas la source d'erreurs majeures dans les limites de solubilité correspondantes pour les éléments Th, U, Np et Pu. En ce qui concerne l'eau interstitielle de la bentonite définie pour le dépôt de déchets de haute activité planifié en Suisse, ce rapport identifie plusieurs paramètres-clés pour lesquels une étude détaillée devrait permettre d'améliorer nos connaissances chimiques.



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## 1 INTRODUCTION

The safety of radioactive waste disposal is one of the most debated topics in the field of environmental hazards. From a scientific point of view, to be convincing, evaluations of any waste disposal project must be based on sound theories and methods. One of these sound and well-established scientific theories is chemical equilibrium thermodynamics. Due to the precipitation of sparingly soluble solids, heavy metals (i.e. most radionuclides) will not dissolve without limits in the pore fluids of an underground repository. Chemical equilibrium thermodynamics allows estimation of the maximum concentration of a given radionuclide in a specified pore fluid. The nuclide in question cannot exceed this maximum concentration when true thermodynamic equilibrium with a well-known solid phase is established. This concept of solubility limits on radionuclide concentrations constitutes one of the pillars of safety of most radioactive waste disposal concepts (HADERMANN, 1997).

Quantitative estimates of radionuclide solubilities need reliable thermodynamic equilibrium constants. These constants cannot yet be calculated *ab initio*, they have to be derived from experimental studies of appropriate chemical systems. The increasing demand of reliable solubility estimates within the scope of radioactive waste disposal projects triggered a lot of experimental studies over the last three decades. The results of these studies have been reviewed by international expert groups with the aim to recommend reliable thermodynamic equilibrium constants (GRENTHE et al., 1992; SILVA et al., 1995; RARD et al., 1999; LEMIRE et al., 2001; HUMMEL et al., 2002).

These chemical thermodynamic databases codify existing chemical knowledge. However, due to the uneven distribution of chemical knowledge, none of these databases can be used blindly for performing predictive work. The user has to check whether the database used for application contains the information necessary to describe the safety relevant processes in sufficient detail. This completeness check of a database cannot be done “in general” but only for a given application, because it always requires a certain amount of “site-specific” chemical information.

In the following we present two important cases of insufficient chemical knowledge leading to “holes” in chemical thermodynamic databases. The first case reveals insufficient process understanding: A growing number of experimental data cannot be interpreted by a unique set of thermodynamic constants. The second case concerns insufficient experimental data: Important thermodynamic equilibrium constants are missing. In both cases we discuss in detail the presently available experimental findings.

The traditional scientific approach would just stop there by concluding that further experimental work is necessary to improve our chemical knowledge. However, safety assessments of radioactive waste disposal projects cannot be postponed until all such cases are studied experimentally in sufficient detail. We have to assess the consequences of our insufficient chemical knowledge and to limit the uncertainty by estimating limiting values. As an example, we present pragmatic approaches to our two cases of insufficient chemical knowledge, suited for performance assessment of radioactive waste repositories.

**Table 1:** Bentonite reference pore water taken from CURTI & WERSIN (2002).

Component	Total concentration [mol/l]	Uncertainty range
Na	$2.74 \times 10^{-1}$	$2.5 - 2.9 \times 10^{-1}$
K	$1.55 \times 10^{-3}$	$1.4 - 1.7 \times 10^{-3}$
Mg	$7.64 \times 10^{-3}$	$6.2 - 8.9 \times 10^{-3}$
Ca	$1.32 \times 10^{-2}$	$1.32 - 1.34 \times 10^{-2}$
Sr	$1.90 \times 10^{-5}$	$0.29 - 3.7 \times 10^{-5}$
Fe	$4.33 \times 10^{-5}$	$0.8 - 7.7 \times 10^{-5}$
Mn	$2.34 \times 10^{-5}$	$0.48 - 3.7 \times 10^{-5}$
Al	$1.92 \times 10^{-8}$	$1.5 - 7.6 \times 10^{-8}$
Cl	$1.66 \times 10^{-1}$	$0.86 - 2.1 \times 10^{-1}$
F	$1.67 \times 10^{-4}$	$1.5 - 1.7 \times 10^{-4}$
Br	$2.40 \times 10^{-4}$	$1.2 - 3.0 \times 10^{-4}$
CO <sub>3</sub> <sup>a</sup>	$2.83 \times 10^{-3}$	$0.59 - 7.0 \times 10^{-3}$
SO <sub>4</sub> <sup>b</sup>	$6.16 \times 10^{-2}$	$5.6 - 6.4 \times 10^{-2}$
Si	$1.80 \times 10^{-4}$	$1.80 - 1.84 \times 10^{-4}$
Charge imbalance <sup>c</sup>	$-2.48 \times 10^{-2}$	-
pH	7.25	6.90 – 7.89
Eh	-194 mV	-131 – -283 mV
Ionic strength	0.323	0.263 – 0.356
Solid Phases		
kaolinite	saturated	
magnetite	saturated	
calcite	saturated	
quartz	saturated	
gypsum	precipitated <sup>d</sup>	

a The carbonate system was defined by assuming a CO<sub>2</sub> fugacity (partial pressure) of 10<sup>-2.2</sup>.

b The formation of reduced sulphur species (S(IV), S(0), S<sub>2</sub>(-II), S(-II)) was suppressed in the model calculation. By not doing so, traces of troilite (FeS) and/or pyrite (FeS<sub>2</sub>) would also “precipitate”.

c Charge imbalance is compensated by charged surface species at the clay-water interface (see CURTI & WERSIN, 2002, for details).

d "Precipitated" indicates that saturation with gypsum is a result of the model calculation. "Saturated" means that saturation with the corresponding solid was assumed to be a property of the chemical system definition.

Our application concerns the solubility limits of actinides (Th, U, Np, Pu, Am) in reducing, carbonate containing bentonite pore water (Table 1). Bentonite is foreseen as backfill surrounding steel canisters that contain spent fuel and vitrified high-level waste in the planned Swiss underground repository (NAGRA, 2002). The present study refers to clay as host rock of the repository, but the concept is similar to a former study relying on crystalline host rock (NAGRA, 1994).

**Table 2:** Speciation and solubility of actinides in compacted bentonite pore water.

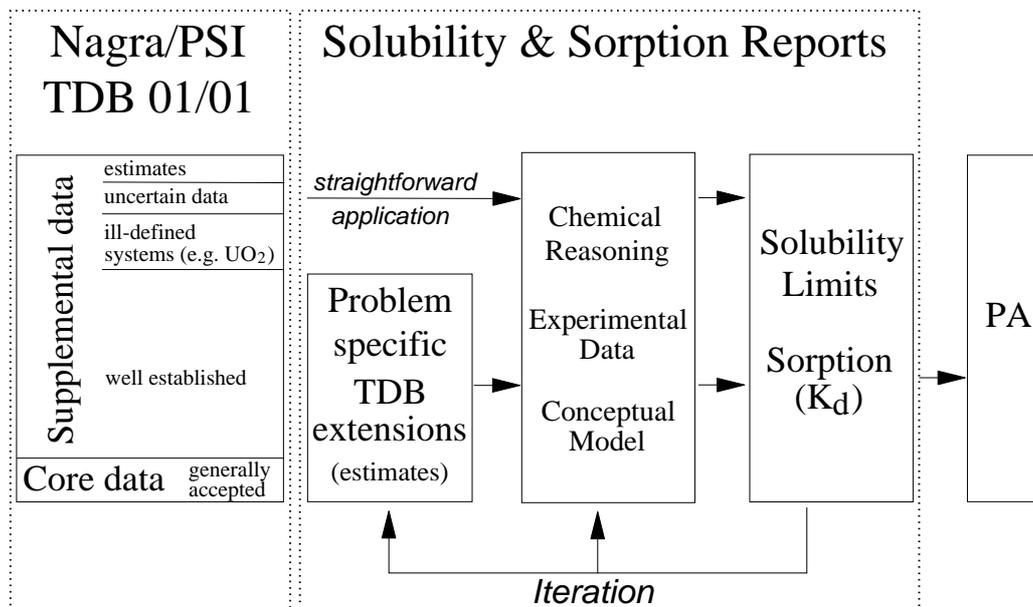
a) Calculated with data as recommended in the unaltered Nagra/PSI TDB 01/01.

Speciation (%)	Th	U	Np	Pu	Am
An <sup>III</sup> silicate					39.9
An <sup>III</sup> sulphates				87.3	28.5
An <sup>III</sup> carbonates					24.0
An <sup>III</sup> (cation, OH <sup>-</sup> , Cl <sup>-</sup> , F <sup>-</sup> )				12.5	7.6
An <sup>IV</sup> (OH) <sub>4</sub> (aq)	0.5	63.4	100.0	0.2	
An <sup>IV</sup> (OH) <sub>3</sub> CO <sub>3</sub> <sup>-</sup>	99.5				
An(V,VI)		36.6			
Total solubility (mol/l)	7·10 <sup>-7</sup>	2·10 <sup>-9</sup>	5·10 <sup>-9</sup>	2·10 <sup>-8</sup>	1·10 <sup>-6</sup>

b) Calculated with an extended problem specific TDB as discussed in this report.

Speciation (%)	Th	U	Np	Pu	Am
An <sup>III</sup> silicate				35.9	39.9
An <sup>III</sup> sulphates				35.2	28.5
An <sup>III</sup> carbonates				21.5	24.0
An <sup>III</sup> (cation, OH <sup>-</sup> , Cl <sup>-</sup> , F <sup>-</sup> )				5.3	7.6
An <sup>IV</sup> (OH) <sub>4</sub> (aq)	0.5	35.7	93.6	0.1	
An <sup>IV</sup> (OH) <sub>3</sub> CO <sub>3</sub> <sup>-</sup>	99.5	38.6	6.4	2.0	
An <sup>IV</sup> (CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>			0.02		
An(V,VI)		25.7	0.03		
Total solubility (mol/l)	7·10 <sup>-7</sup>	3·10 <sup>-9</sup>	5·10 <sup>-9</sup>	5·10 <sup>-8</sup>	1·10 <sup>-6</sup>

In a first step, solubility limits for actinides have been derived using straightforwardly the thermodynamic constants recommended in the Nagra/PSI Chemical Thermodynamic Data Base (TDB) 01/01 (HUMMEL et al., 2002). The results of these calculations are presented in Table 2a. They do not reveal the chemical analogy expected for this series of actinides. The thorium speciation is dominated by a mixed hydroxide carbonate complex, which is completely absent in all other cases. In contrast to Np, Pu is predicted to exist almost entirely in the trivalent oxidation state, but the Pu(III) speciation is rather different from the analogous Am(III). Further, the calculated solubility values are much higher for Am, Pu and Th than for U and Np.



**Figure 1:** Sketch of the iterative procedure to derive reliable solubility limits and sorption values for performance assessment (PA) of an underground repository by developing problem specific TDB extensions.

These findings indicate shortcomings in the chemical knowledge codified in our TDB. Therefore, in a second step, we go beyond the straightforward application of the Nagra/PSI TDB 01/01 (top arrows in Fig. 1) by discussing in detail the safety relevant processes in our specified chemical system. This iterative procedure leads to a problem specific extension of our TDB (bottom arrows in Fig. 1). The results of this procedure are improved estimates of actinide solubilities for performance assessment (intermediate

arrows in Fig. 1), valid for reducing, carbonate containing chemical systems at neutral to alkaline conditions. For convenience, we summarized the resulting solubilities in Table 2b.

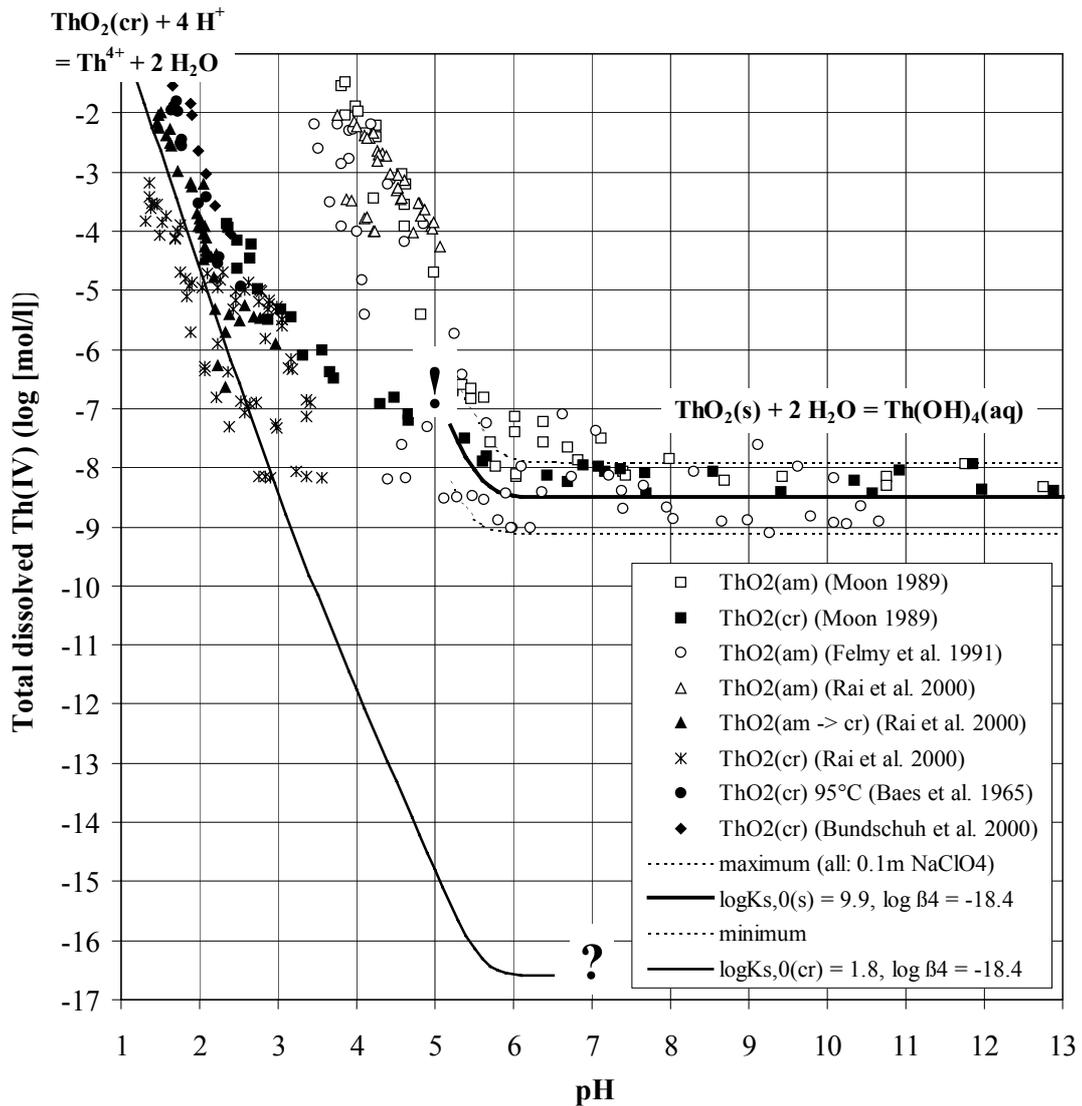
Finally, we want to remind the readers of this report that all our conclusions rely on solubility data derived from laboratory systems studied for a short time period compared with the lifetime of a repository. The solid phases studied in the laboratory may transform into thermodynamically more stable phases over long time periods. The corresponding actinide solubility then will decrease and, hence, our approach most probably over-estimates actinide solubilities that will establish at long times.

## 2 THE SYSTEM AN(IV) – H<sub>2</sub>O: THE ENIGMA OF ThO<sub>2</sub> AND UO<sub>2</sub> SOLUBILITY

The solubility of ThO<sub>2</sub> and UO<sub>2</sub> as a function of pH has been studied extensively by several groups with the aim of providing basic data for the safety assessments of planned underground repositories. The growing number of published experimental solubility data reveals a consistent but puzzling picture of the systems ThO<sub>2</sub> – H<sub>2</sub>O (Fig. 2) and UO<sub>2</sub> – H<sub>2</sub>O (Fig. 3).

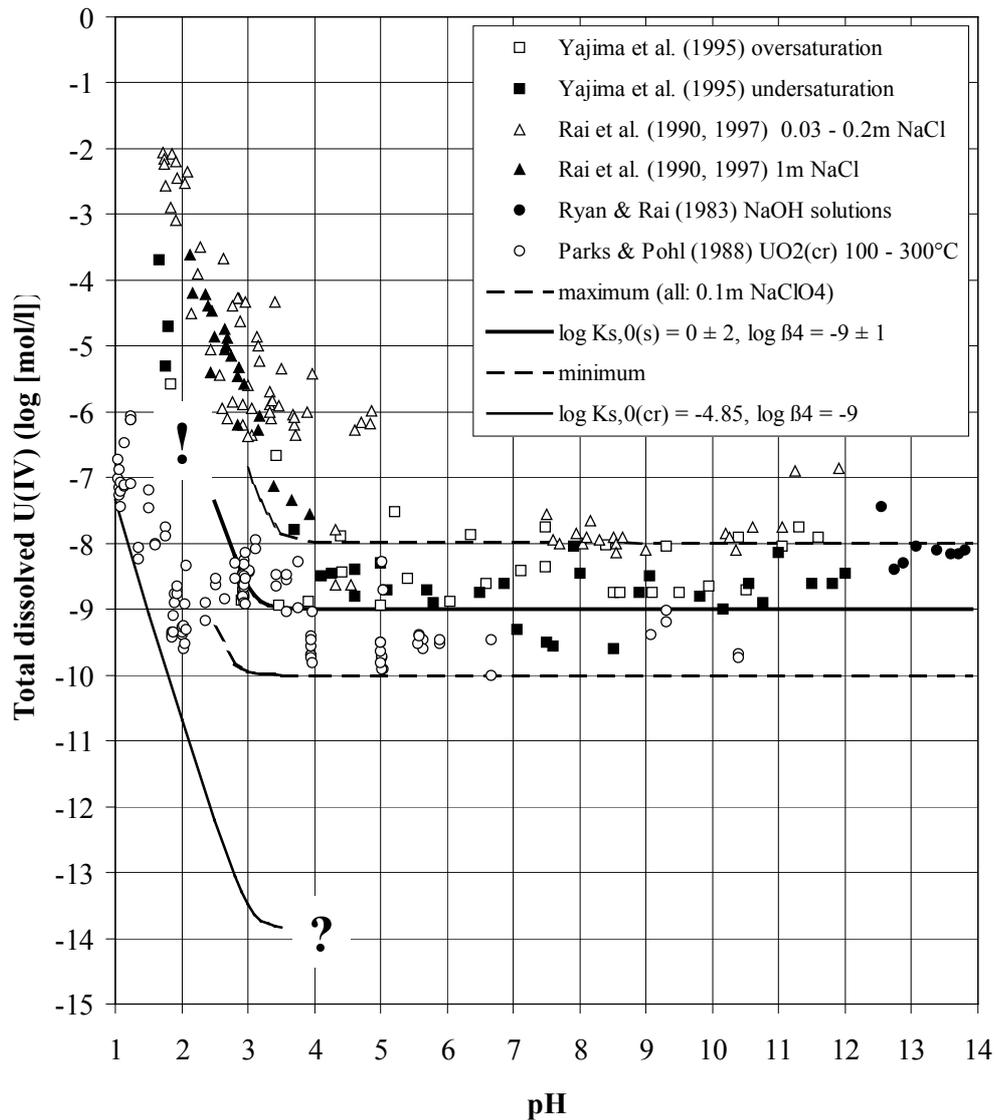
At low pH the solubility of ThO<sub>2</sub> and UO<sub>2</sub> strongly depends on the crystallinity of the solid. Differences in solubility of several orders of magnitude have been found between freshly precipitated amorphous and well crystalline solids (Figs. 2 and 3). However, with increasing pH the measured concentrations converge, and at neutral and alkaline pH the ThO<sub>2</sub> and UO<sub>2</sub> solubility is found to be independent of (bulk) crystallinity (Figs. 2 and 3). The solution always seems to “see” the same solid in neutral and alkaline solutions. We encountered the following problems by the attempt to describe all these experimental data by a unique set of thermodynamic constants:

In the system Th(IV) – H<sub>2</sub>O a set of thermodynamic quantities can be derived from experimental data: (1) The hydrolysis constant  $\log_{10}^* \beta_4^\circ$  for  $\text{Th}^{4+} + 4\text{H}_2\text{O} \Leftrightarrow \text{Th}(\text{OH})_4(\text{aq}) + 4\text{H}^+$  has been determined potentiometrically by several authors over a wide range of ionic strength (HUMMEL et al., 2002). (2) The thermodynamic properties of ThO<sub>2</sub>(cr) have been determined by calorimetry and, hence, a solubility product  $\log_{10}^* K_{s,0}^\circ(\text{cr})$  for  $\text{ThO}_2(\text{cr}) + 4\text{H}^+ \Leftrightarrow \text{Th}^{4+} + 2\text{H}_2\text{O}$  can be derived from the available thermochemical data (RAI et al., 2000).



**Figure 2:** The enigma of ThO<sub>2</sub> solubility: Data derived from the solubility of crystalline ThO<sub>2</sub> at low pH cannot describe ThO<sub>2</sub>(s) solubility above pH 6 when using independent Th(OH)<sub>4</sub>(aq) formation data (question mark). Vice versa, measured solubilities in alkaline solutions do not point back to the behaviour of ThO<sub>2</sub>(cr) at acidic conditions (exclamation mark).

Solubility data for ThO<sub>2</sub>(cr) agree fairly well with the solubility predicted by calorimetric data in the range pH < 3 (line in Fig. 2). However, combining the solubility product log<sub>10</sub>\*K<sub>s,0</sub><sup>o</sup>(cr) with the independently determined hydrolysis constant log<sub>10</sub>\*β<sub>4</sub><sup>o</sup> of Th(OH)<sub>4</sub>(aq) results in predicted Th concentrations far from any measured values in neutral and alkaline solutions. The concentration of dissolved Th(IV) should fall below any detection limit to [Th] < 10<sup>-16</sup> M (see question mark in Fig. 2).



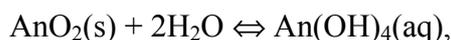
**Figure 3:** The enigma of  $\text{UO}_2$  solubility: Thermochemical data of crystalline  $\text{UO}_2$  at low pH cannot describe  $\text{UO}_2(\text{s})$  solubility above pH 4 (questions mark). Vice versa, measured solubilities in alkaline solutions do not point back to the behaviour of  $\text{UO}_2(\text{cr})$  at acidic conditions (exclamation mark).

All  $\text{ThO}_2(\text{s})$  solubility data measured in the laboratory at  $\text{pH} > 6$  have been found in the range  $10^{-7} \text{ M} > [\text{Th}] > 10^{-9} \text{ M}$ . A mean value of  $10^{-8.5 \pm 0.6} \text{ M}$  represents  $*K_{s,4}^\circ(\text{s})$  for  $\text{ThO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4(\text{aq})$ . If we combine this constant with the hydrolysis constant  $\log_{10} * \beta_4^\circ$  of  $\text{Th}(\text{OH})_4(\text{aq})$  a solubility product for  $\text{ThO}_2(\text{s})$  is calculated which produces a solubility curve somewhere in the “cloud” of solubility data for  $\text{ThO}_2(\text{am})$  and  $\text{ThO}_2(\text{cr})$  (Fig. 2). This set of parameters now describes the measured solubilities at

pH > 6 but cannot account for the solubility variation of more than 10 orders of magnitude at lower pH (see exclamation mark in Fig. 2).

The same behaviour is found in the system U(IV) – H<sub>2</sub>O (Fig. 3). At pH < 3 the solubility measured for freshly precipitated UO<sub>2</sub>(am) and the solubility of UO<sub>2</sub>(cr) derived from calorimetric data differ by 9 orders of magnitude. All measured solubility data for UO<sub>2</sub>(s) at pH > 5 have been found in the range 10<sup>-7</sup> M > [U(IV)] > 10<sup>-10</sup> M. A mean value of 10<sup>-9±1</sup> M represents \*K<sub>s,4</sub><sup>o</sup>(s) for UO<sub>2</sub>(s) + 2H<sub>2</sub>O ⇌ U(OH)<sub>4</sub>(aq).

Furthermore, this behaviour is not restricted to Th(IV) and U(IV). Similar patterns have also been found for Np(IV) and Pu(IV). In all cases the constant values measured for tetravalent actinides, An(IV), in experimental studies at neutral and alkaline pH are ascribed to the equilibrium

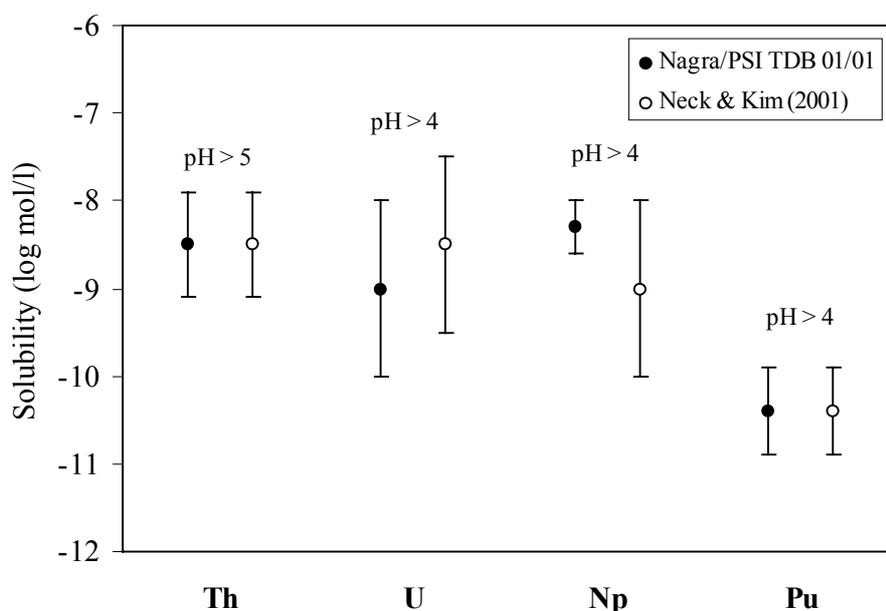


but at present the solubilities of the entire systems cannot be described by a unique set of thermodynamic constants. Since the hydrolysis constant log<sub>10</sub>\*β<sub>4</sub> is independent of the solid, we can either account for the strong variation of solubility with crystallinity at low pH by varying the solubility product from log<sub>10</sub>\*K<sub>s,0</sub>(am) to log<sub>10</sub>\*K<sub>s,0</sub>(cr), or we can describe the constant solubility at neutral and alkaline pH by an adapted log<sub>10</sub>\*K<sub>s,0</sub>(s), representing a non-specified solid with the composition AnO<sub>2</sub>(s). In both cases inconsistencies arise by extrapolating to the opposite pH range.

A more detailed discussion and comparison of An(IV) solubility and hydrolysis is given by NECK & KIM (2001). These authors conclude from the solubility data measured for ThO<sub>2</sub>(cr) and UO<sub>2</sub>(cr) that the crystalline dioxide is the solubility limiting solid only at very low pH, where An<sup>4+</sup> is the predominant aqueous species. They postulate that the bulk crystalline dioxide must be covered with an amorphous surface layer as soon as the An<sup>4+</sup> ion undergoes hydrolysis reactions, and the dissolution of AnO<sub>2</sub>(cr) seems to become quasi-irreversible. According to NECK & KIM (2001) further investigations are needed to verify this hypothesis and to ascertain the chemical form of the solubility limiting solid (or surface) in natural systems. Despite this promising qualitative model, we have to conclude that at present the systems ThO<sub>2</sub> – H<sub>2</sub>O and UO<sub>2</sub> – H<sub>2</sub>O are NOT understood in terms of quantitative equilibrium thermodynamics. The available experimental data sets cannot be described by a consistent quantitative model without ad hoc assumptions.

As a pragmatic approach suited for performance assessment of radioactive waste repositories, we decided to rely on measured solubilities of Th(IV) and U(IV) in neutral and alkaline solutions. Hence, the equilibrium constants selected for our database (Table 8) do not refer to well defined thorianite,  $\text{ThO}_2(\text{cr})$ , and uraninite,  $\text{UO}_2(\text{cr})$ , used in calorimetric measurements, but to the still poorly defined solids  $\text{ThO}_2(\text{s})$  and  $\text{UO}_2(\text{s})$  encountered in solubility studies. Furthermore, we considered independently determined hydrolysis constants in the case of Th, and adjusted the missing hydrolysis constant of  $\text{U}(\text{OH})_4(\text{aq})$  in such a way that it is compatible with all experimental solubility measurements in the system  $\text{UO}_2(\text{s}) - \text{H}_2\text{O} - \text{CO}_2$  above pH 4 (HUMMEL et al., 2002). Consequently, the equilibrium constants in the Nagra/PSI TDB 01/01 (HUMMEL et al., 2002) cannot be used to represent the widely varying solubilities of  $\text{ThO}_2$  and  $\text{UO}_2$  at low pH.

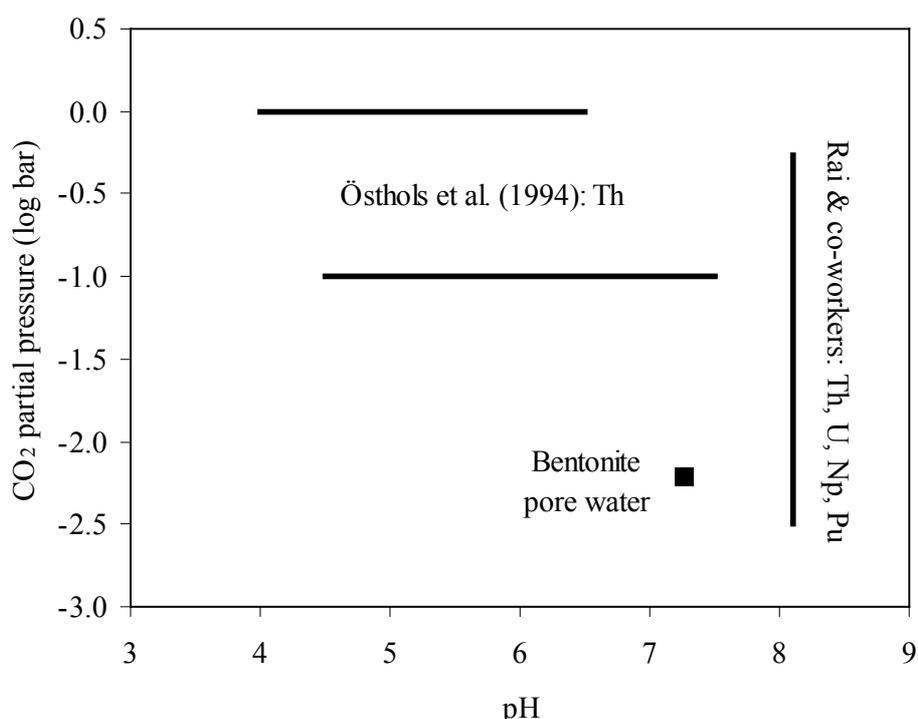
Our data selection for  $\log_{10} * K_{s,0}$  of  $\text{AnO}_2(\text{s})$  is visualised in Fig. 4. Experimental data for Th and U have been reviewed in detail by HUMMEL et al. (2002), the data for Np were taken from the NEA review (LEMIRE et al., 2001) whereas the Pu data were taken from NECK & KIM (2001). Above the threshold pH indicated in Fig. 4,  $\text{An}(\text{OH})_4(\text{aq})$  is the only hydrolysis product considered. Fig. 4 shows the solubility constants and their uncertainties as recommended in the Nagra/PSI TDB 01/01 (HUMMEL et al., 2002) and compares them to the data selection of NECK & KIM (2001).



**Figure 4:** Solubility of tetravalent actinide (hydr)oxides,  $\text{AnO}_2(\text{s})$ , in neutral and alkaline solutions in carbonate free systems. Above the indicated threshold pH the dominant (and only) aqueous species is  $\text{An}(\text{OH})_4(\text{aq})$ .

### 3 THE SYSTEM AN(IV) – H<sub>2</sub>O – CO<sub>2</sub>: MISSING TERNARY SPECIES

In neutral and alkaline solutions the An(IV) – H<sub>2</sub>O system is represented by one solid phase, AnO<sub>2</sub>(s), and one aqueous complex, An(OH)<sub>4</sub>(aq). If we need to extend this simple system to the more complicated An(IV) – H<sub>2</sub>O – CO<sub>2</sub> system, we have to add at least three more aqueous complexes, AnCO<sub>3</sub>(OH)<sub>3</sub><sup>-</sup>, An(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup>, and An(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup>. This selection follows from the experimental data available up to date, indicating that ternary hydroxide-carbonate species are most likely required to describe this extended chemical system. In the following, the origin and the reliability of these complex formation constants are discussed, and methods to estimate missing constants are evaluated. In our discussion we focus on the few solubility studies carried out at near neutral pH close to the pCO<sub>2</sub> and pH values of the reference bentonite pore water (see Fig. 5).



**Figure 5:** Parameter ranges of solubility experiments with tetravalent actinide (hydr)oxides (lines) close to the composition of the reference bentonite pore water (square) as provided in Table 1.

### 3.1 Origin of the data recommended in the Nagra/PSI TDB 01/01

The stability constants for Th recommended in the Nagra/PSI TDB 01/01 originate from ÖSTHOLS et al. (1994) (Fig. 6). FELMY et al. (1997) accepted the same constants as the best overall representation of all experimental data reported by both, FELMY et al. (1997) and ÖSTHOLS et al. (1994).

The stability constants for U in the Nagra/PSI TDB 01/01 have been taken from the NEA uranium review (GRENTHE et al., 1992), which was published several years before the more recent experimental work of RAI et al. (1998). As shown in Fig. 7, some discrepancies between the model curve for U, based on NEA recommended values, and the experimental data of RAI et al. (1998) is not yet resolved.

The stability constants for Np and Pu in the Nagra/PSI TDB 01/01 have been taken from the NEA neptunium & plutonium review (LEMIRE et al., 2001). The good agreement of the model curve for Np with the experimental data of RAI et al. (1999a) (Fig. 7) is no coincidence because exactly these Np solubility data of RAI et al. (1999a) were used by the NEA reviewers to derive the stability constants of  $\text{Np}(\text{CO}_3)_4^{4-}$  and  $\text{Np}(\text{CO}_3)_5^{6-}$ .

Rather inconsistently, the Pu solubility data of RAI et al. (1999b) have not been considered by the same NEA reviewers in their evaluation of  $\text{Pu}(\text{CO}_3)_4^{4-}$  and  $\text{Pu}(\text{CO}_3)_5^{6-}$  constants. The large discrepancy between the values recommended by NEA and the experimental results of RAI et al. (1999b) (Fig. 7) is not discussed by LEMIRE et al. (2001).

Table 3a summarizes the equilibrium constants included in the Nagra/PSI TDB 01/01 for the system  $\text{An}(\text{IV}) - \text{H}_2\text{O} - \text{CO}_2$ . Table 3b provides the speciation exclusively for An(IV) at  $\log_{10}p\text{CO}_2 = -2.2$ . In order to focus our discussion on the most important parameters, model calculations were performed for a simplified chemical system that excludes redox equilibria and complexes of minor importance for An(IV) (i.e. sulphates, chlorides, fluorides, in the present case). Total solubilities as calculated with the full geochemical model are given in the last column for comparison. The large difference in the solubility of Pu arises from the fact that 99.8 % of dissolved Pu is found as Pu(III) (51.1 %  $\text{PuSO}_4^+$ , 36.3 %  $\text{Pu}(\text{SO}_4)_2^-$ , 6.6 %  $\text{Pu}^{3+}$ , 3.2 %  $\text{Pu}(\text{OH})^{2+}$ , 2.8 %  $\text{PuCl}^{2+}$ ) at reference conditions. In the case of uranium, the distribution among the different redox states is 63.5 % U(IV), 1.3 % U(V) and 35.2 % U(VI). The difference in total dissolved

Th indicates the size of error introduced by working with a simplified chemical system instead of using the full geochemical model evaluation.

**Table 3:** Original chemical model to describe the system An(IV) - H<sub>2</sub>O - CO<sub>2</sub>.

a) Stability constants taken from the Nagra/PSI TDB 01/01 (HUMMEL et al., 2002).

	AnO <sub>2</sub> (s)	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>
	log <sub>10</sub> *K <sub>s,0</sub> <sup>o</sup>	log <sub>10</sub> *β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> *K <sup>o</sup>	log <sub>10</sub> β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> β <sub>5</sub> <sup>o</sup>
Th	9.9±0.6	-18.4±0.6	-3.1±1		29.8±1.1
U	0±2	-9±2		35.2±1.0	34.1±1.0
Np	1.5±1.1	-9.8±1.1		36.7±1.1	35.6±1.1
Pu	-2.0±1.0	-8.4±1.1		35.9±2.5	34.5±2.5

b) Speciation & solubility at log<sub>10</sub>pCO<sub>2</sub> = -2.2.

	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	An(IV) <sub>total</sub>	An <sub>total</sub>
	%	%	%	%	mol/l	mol/l
Th	0.5	99.5		0	6.3e-07	6.9e-07
U	100		0	0	1.0e-09	1.6e-09
Np	100		0	0	5.0e-09	5.0e-09
Pu	100		0	0	4.0e-11	2.2e-08

A few words to uncertainties of equilibrium constants and their propagation into the calculations:

The operational version of the underlying thermodynamic database does not include any uncertainties, although uncertainties have been assessed for most of the equilibria reported in HUMMEL et al. (2002). Thus, uncertainties are not carried through the geochemical calculations.

In many cases, the concentration of an element may be adequately approximated by a solubility constant and by the formation constants of the major complexes in solution. In general, only one complex in solution is relevant. In rare cases up to three or four different complexes need to be considered. As a first approximation, the uncertainty of a calculation may therefore be estimated from the uncertainty of the solubility product and from the uncertainty of the formation constants using an error propagation method as for example proposed by the NEA reviewers (GRENTHE et al., 1992).

Such formal error propagation is not always a straightforward procedure because uncertainties may be highly correlated. Often this reflects the difficulties to derive independent thermodynamic data from experiments that are not suited to do so. Therefore, a more detailed uncertainty analysis also requires analysing the type of available experimental data, and it is necessary to go far beyond a pure “inspection” of the database.

Consider for example the solubility of  $\text{PuO}_2(\text{s})$ . When we just concentrate on Pu(IV), the uncertainty of total dissolved Pu can formally be derived by error propagation from the uncertainty of the solubility product of  $\text{PuO}_2(\text{s})$  and of the formation constant of  $\text{Pu}(\text{OH})_4(\text{aq})$  (Table 3), i.e.  $(1.0^2+1.1^2)^{1/2} = \pm 1.5 \log_{10}$ -units. However, the uncertainties given for  $\text{PuO}_2(\text{s})$  and  $\text{Pu}(\text{OH})_4(\text{aq})$  in Table 3 are not statistically independent quantities. They are derived from experimental solubility data with an uncertainty of only  $\pm 0.5 \log_{10}$ -units (Table 8).

Under present chemical conditions  $\text{PuO}_2(\text{s})$  is predicted

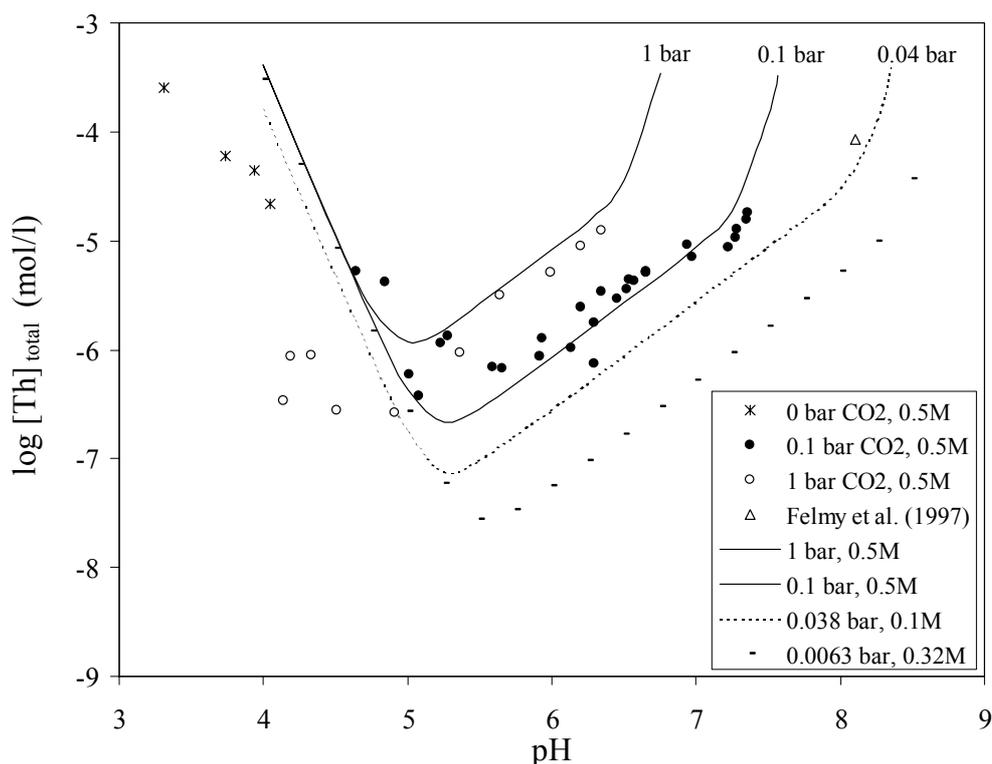
- i) to dissolve to  $\text{Pu}(\text{OH})_4(\text{aq})$ ,
- ii) to be reduced to Pu(III), and,
- iii) to form the complexes  $\text{PuCO}_3^+$ ,  $\text{PuSO}_4^+$ ,  $\text{Pu}(\text{SO}_4)_2^-$  and  $\text{PuSiO}(\text{OH})_3^{2+}$ .

From Tables 7 & 8 we see that the solubility of  $\text{PuO}_2(\text{s})$  has an uncertainty of  $\pm 0.5 \log_{10}$ -units, that the reduction equilibrium  $\text{Pu}^{4+}/\text{Pu}^{3+}$  is accurately known ( $\pm 0.04 \log_{10}$ -units), and that the uncertainty of Pu(III) complex formation ranges from  $\pm 0.2$  to  $\pm 0.8 \log_{10}$ -units (for this example,  $\pm 0.6 \log_{10}$ -units are adopted). From this we assess a maximum propagated uncertainty of  $(0.5^2+0.04^2+(\sim 0.6)^2)^{1/2} \approx \pm 0.8 \log_{10}$ -units for the solubility of Pu.

However, the redox equilibrium  $\text{Pu}^{4+}/\text{Pu}^{3+}$  was measured in very acidic  $\text{HClO}_4$ -solution and, thus, the formation of  $\text{Pu}^{4+}$  from  $\text{Pu}(\text{OH})_4(\text{aq})$  (the relevant complex at pH 7.25) needs to be included in the uncertainty assessment. Since the uncertainty of the equilibrium  $\text{Pu}(\text{OH})_4(\text{aq}) + 4\text{H}^+ \Leftrightarrow \text{Pu}^{4+} + 4\text{H}_2\text{O}$  is large ( $\pm 1.1 \log_{10}$ -units), a corrected, propagated uncertainty increases to  $(1.1^2+0.5^2+0.04^2+(\sim 0.6)^2)^{1/2} \approx \pm 1.35 \log_{10}$ -units for the total concentration of Pu (see the difference  $\text{Pu}(\text{total}) - \text{Pu}(\text{IV})$  in Table 3a).

### 3.2 Experimental basis for deducing complex formation constants

The system An(IV) - H<sub>2</sub>O - CO<sub>2</sub> has been explored by solubility and potentiometric studies mainly at high carbonate concentrations in the pH range 9 - 12. As already mentioned, we focus in this case study on the few solubility studies carried out at near neutral pH close to the pCO<sub>2</sub> and pH values of the reference bentonite pore water (Fig. 5). We have to deal with two different experimental set-ups:

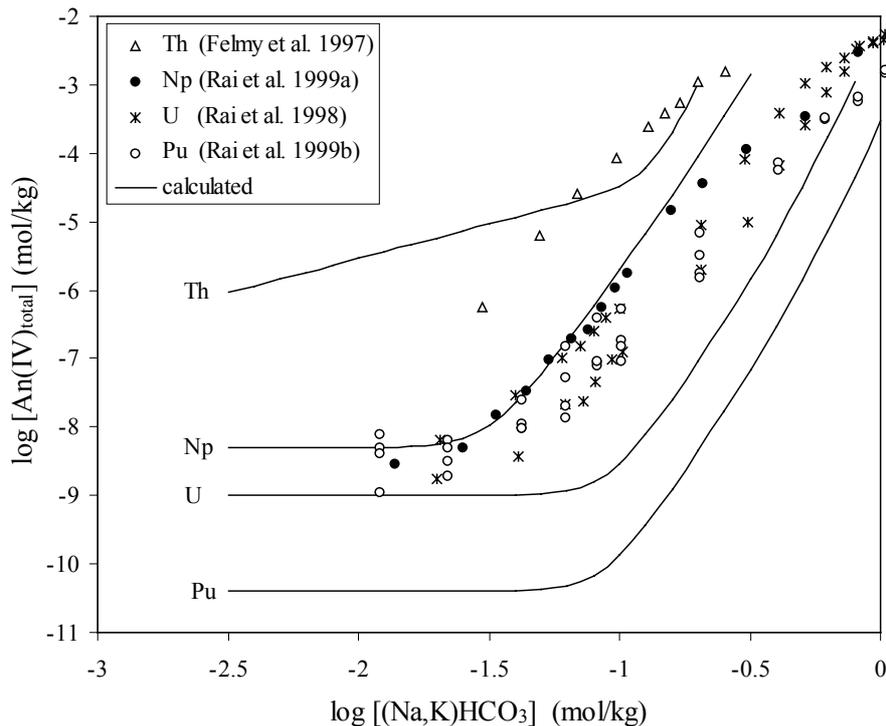


**Figure 6:** Experimental ThO<sub>2</sub> solubility data of ÖSTHOLS et al. (1994) (crosses and circles). The lines are calculated using thermodynamic data recommended in the Nagra/PSI TDB 01/01. The solid lines visualise the conditions of 1 bar and 0.1 bar CO<sub>2</sub> partial pressure at 0.5M NaClO<sub>4</sub>. The dotted line corresponds to one data point (open triangle) of FELMY et al. (1997) at 0.038 bar CO<sub>2</sub> and ionic strength 0.1M. The solubility curve that would correspond to the conditions of the reference bentonite pore water ( $10^{-2.2}$  bar = 0.0063 bar CO<sub>2</sub> and I = 0.32M) is represented by small black hyphens (note that the reference pH is at 7.25).

(1) In the Th solubility experiments of ÖSTHOLS et al. (1994) the pH was varied at constant CO<sub>2</sub> partial pressures of 0.1 and 1 bar. All experiments were carried out in 0.5 M NaClO<sub>4</sub> in order to keep the ionic strength constant. This experimental set-up, i.e. constant CO<sub>2</sub> partial pressure and constant ionic strength, provides the most reliable experimental data for deducing equilibrium constants. However, only the pH range

below 8 is accessible for experimental investigations when using  $\text{CO}_2(\text{g})$  as a modifiable component (Fig. 5). At higher pH the partial pressure of  $\text{CO}_2$  is very low and the time for equilibrium to be attained becomes very long. Note that data similar to those of ÖSTHOLS et al. (1994) do not exist for U, Np or Pu.

(2) In the solubility experiments of Rai and co-workers (FELMY et al., 1997; RAI et al., 1998, 1999a, 1999b) the concentration of  $\text{NaHCO}_3$  or  $\text{KHCO}_3$  in solution was varied. This leads to a pH buffered system ( $\text{pH} \approx 8$ ) whereas the  $\text{CO}_2$  partial pressure varies concomitantly with the bicarbonate concentration. Note that Rai and co-workers did not use a medium of constant ionic strength. They rather tried to estimate the resulting activity factor variations using the Pitzer model. This introduces additional fitting parameters in the process of deducing stoichiometry and equilibrium constants from experimental solubility data and, thus, makes a complicated solution chemical problem even more difficult.



**Figure 7:** Experimental solubility data of Rai and co-workers. The solid lines are calculated considering the varying  $\text{CO}_2$  partial pressure and ionic strength along the x-axis using thermodynamic data recommended in the Nagra/PSI TDB 01/01. In the case of Th the aqueous species  $\text{Th}(\text{OH})_4(\text{aq})$ ,  $\text{ThCO}_3(\text{OH})_3^-$  and  $\text{Th}(\text{CO}_3)_5^{6-}$  have been included, whereas for U, Np and Pu the aqueous species  $\text{An}(\text{OH})_4(\text{aq})$ ,  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  have been considered (Table 3a).

The experimental results and the model curves interpreting these two different set-ups cannot be visualised in one simple 2D graph because each line in one set-up projects to a single point in the other representation. Therefore, we show the experimental data in two different representations. However, using the same thermodynamic constants in the calculations links the model curves of both representations.

Fig. 6 shows the experimental data of ÖSTHOLS et al. (1994) at varying pH and constant  $p\text{CO}_2$ , including the model curves as obtained using data of the Nagra/PSI TDB 01/01. There is one data point ( $\text{pH} \approx 8$ ,  $p\text{CO}_2 = 0.04$  bar), which links the Östhols data to the Th solubility data of FELMY et al. (1997). An additional model curve corresponding to the reference bentonite pore water conditions ( $p\text{CO}_2 = 0.0063$  bar) is given for completeness.

In addition to the Th data of FELMY et al. (1997), Fig. 7 shows data for U(IV), Np(IV) and Pu(IV), also measured by Rai and co-workers at  $\text{pH} \approx 8$  as a function of  $\text{HCO}_3^-$  concentration. The model curves given in Fig. 7 are calculated using the chemical model and data provided in Table 3a.

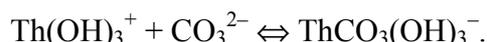
Note the difference in the speciation model for thorium, which includes the dominant ternary complex  $\text{ThCO}_3(\text{OH})_3^-$ . In fact, the absence of this complex in the case of U(IV), Np(IV) and Pu(IV), as well as the possible consequences thereof initiated the present case study.

### 3.3 The stoichiometry of hydroxide carbonate ternary species

ÖSTHOLS et al. (1994) identified the formation of at least one dominating Th hydroxide carbonate species in the parameter range of their experimental studies. However, one should note that the uncertainty in the solubility data is large; the discrepancy between the different experimental series (Fig. 6) might indicate a systematic error (in the surface area / crystallinity of the solid phase?), but there is no doubt that the Th solubility depends on the partial pressure of  $\text{CO}_2$ . ÖSTHOLS et al. (1994) interpreted this dependence as the formation of  $\text{ThCO}_3(\text{OH})_3^-$ , but the available solubility data could also be interpreted in terms of the formation of  $\text{ThHCO}_3(\text{OH})_4^-$  or  $\text{ThCO}_3(\text{O})(\text{OH})^-$ . The interpretation of ÖSTHOLS et al. (1994) is chemically reasonable because complexes with  $\text{HCO}_3^-$  are much weaker than those with  $\text{CO}_3^{2-}$ , and there is no

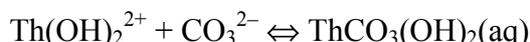
experimental evidence for the formation of monomeric Th species containing single oxygen atoms<sup>1</sup>.

It is possible to assess the validity of the equilibrium constant derived by ÖSTHOLS et al. (1994) for the mixed complex  $\text{ThCO}_3(\text{OH})_3^-$ . If we combine  $\log_{10}^*K^\circ = -3.1$  (Tab. 3a) for the equilibrium  $\text{Th}^{4+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \Leftrightarrow \text{ThCO}_3(\text{OH})_3^- + 3\text{H}^+$  with an estimate  $\log_{10}^* \beta_3^\circ = -11 \pm 1$  (NECK & KIM, 2001) for the hydrolysis reaction  $\text{Th}^{4+} + 3\text{H}_2\text{O} \Leftrightarrow \text{Th}(\text{OH})_3^+ + 3\text{H}^+$  we obtain  $\log_{10}K^\circ = 8 \pm 1$  for

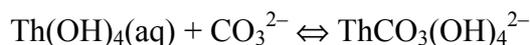


This is a reasonable value considering the equilibrium constant  $\log_{10}\beta_5^\circ = 29.8$  for the reaction  $\text{Th}^{4+} + 5\text{CO}_3^{2-} \Leftrightarrow \text{Th}(\text{CO}_3)_5^{6-}$  proposed by ÖSTHOLS et al. (1994) and the corresponding constants for U(IV), Np(IV) and Pu(IV) (Tab. 3a).

The equilibrium constant for the binding of a carbonate ligand to the hydroxide complex  $\text{Th}(\text{OH})_3^+$  is large. This observation can be used to test the effects of the addition of other ternary complexes on the speciation in the Th – H<sub>2</sub>O – CO<sub>2</sub> system. The complexes  $\text{ThCO}_3(\text{OH})_2(\text{aq})$  and  $\text{ThCO}_3(\text{OH})_4^{2-}$  have been considered in this case study. The equilibrium constant for the reaction



is certainly larger than for the corresponding reaction with  $\text{Th}(\text{OH})_3^+$  as a reactant. As an initial guess for a model calculation and for the comparison with the experimental data of ÖSTHOLS et al. (1994) we use  $\log_{10}K^\circ \approx 9$ . In the same way the potential impact of the reaction



has been tested with an initial guess of  $\log_{10}K^\circ \approx 7$ . The results of such model calculations are shown in Fig. 8.

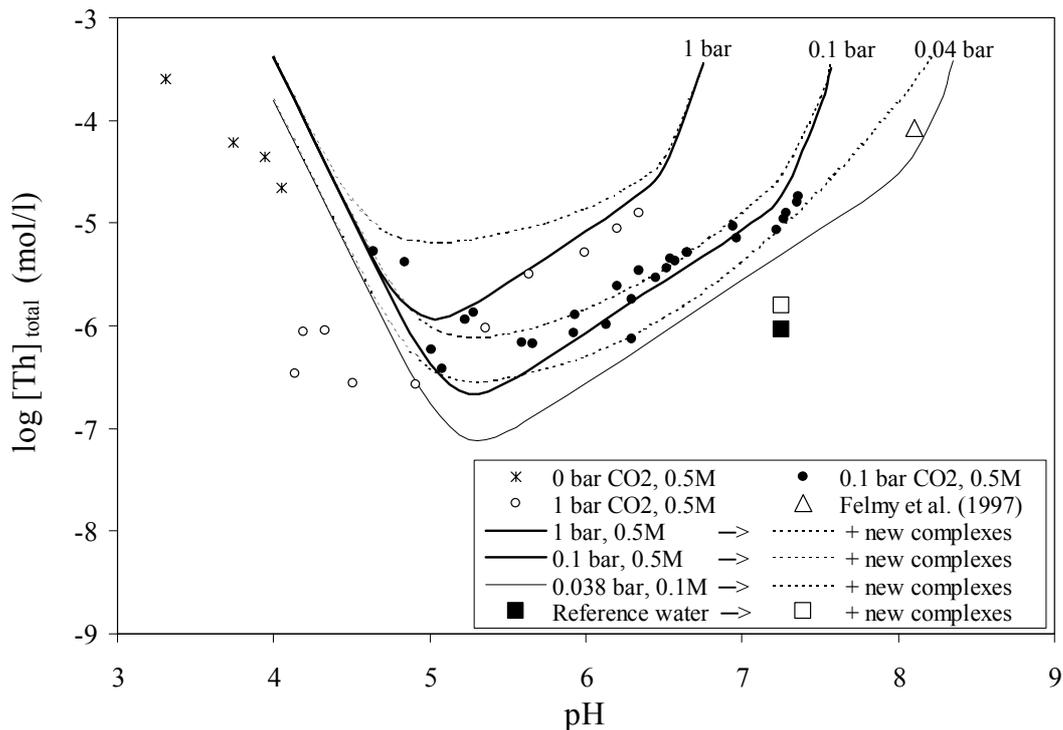
The complex  $\text{ThCO}_3(\text{OH})_2(\text{aq})$  now predominates in the region  $\text{pH} < 6$ . The experimental data of ÖSTHOLS et al. (1994) at 0.1 bar CO<sub>2</sub> partial pressure are still well represented by this model but the 1 bar curve is far off the experimental data (dotted lines below pH 6 in Fig. 8). Repeating the calculations with an equilibrium constant lowered by one order of magnitude results at  $\text{pH} < 6$  in model curves almost

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<sup>1</sup> In the case of polymeric species the situation is different: X-ray scattering data in solution indicate that the trimeric species  $(\text{UO}_2)_3(\text{OH})_5^+$  actually has the stoichiometry  $(\text{UO}_2)_3(\text{O})(\text{OH})_3^+$ . It consists of a triangular array of uranyl groups, linked by hydroxide groups bridging each pair of uranium atoms with a single oxygen atom in the middle of the triangle (see Fig. III.12 in GRENTHE et al., 1997).

identical to the original ones without considering  $\text{ThCO}_3(\text{OH})_2(\text{aq})$ . Hence, the experimental data indicate that  $\log_{10}K^\circ < 9$  and that  $\text{ThCO}_3(\text{OH})_2(\text{aq})$  is always a minor species in the Th – H<sub>2</sub>O – CO<sub>2</sub> system. In any case,  $\text{ThCO}_3(\text{OH})_2(\text{aq})$  has no influence on Th solubility in the bentonite reference pore water at pH 7.25.

The complex  $\text{ThCO}_3(\text{OH})_4^{2-}$  is on the verge of predominance in the region pH > 7 and low CO<sub>2</sub> partial pressure in our model calculations (dotted lines above pH 7 in Fig. 8). Hardly any effect is seen in the parameter range of the ÖSTHOLS et al. (1994) data by introducing  $\text{ThCO}_3(\text{OH})_4^{2-}$  with  $\log_{10}K^\circ \approx 7$ . The Th solubility at pH  $\approx 8$  and 0.04 bar CO<sub>2</sub> partial pressure is slightly overestimated but still reasonably represented, if compared with the FELMY et al. (1997) data (triangle in Fig. 8). Hence, our initial guess of  $\log_{10}K^\circ \approx 7$  for the potential ternary complex  $\text{ThCO}_3(\text{OH})_4^{2-}$  is in the right order of magnitude. However, the influence of  $\text{ThCO}_3(\text{OH})_4^{2-}$  on Th solubility in the bentonite reference pore water at pH 7.25 is small (squares in Fig. 8).

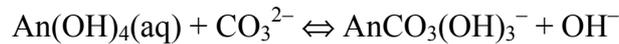


**Figure 8:** The effects of adding the complexes  $\text{ThCO}_3(\text{OH})_2(\text{aq})$  and  $\text{ThCO}_3(\text{OH})_4^{2-}$  (for guesses of equilibrium constants see text) to the model of Th solubility in the Th – H<sub>2</sub>O – CO<sub>2</sub> system (dotted lines). The solid lines refer to the original model considering  $\text{ThCO}_3(\text{OH})_3^-$  as the only ternary complex.

In summary, we believe that it is sufficient to consider  $\text{ThCO}_3(\text{OH})_3^-$  as the most important representative of ternary  $\text{Th}(\text{CO}_3)_x(\text{OH})_y^{4-2x-y}$  complexes for estimating Th solubility in the bentonite reference pore water based on available experimental data. In the following we thus focus on estimation procedures for  $\text{AnCO}_3(\text{OH})_3^-$ .

### 3.4 Estimation of missing ternary constants for U, Np and Pu by chemical analogy

For U, Np and Pu the present chemical model does not include the mixed complex  $\text{AnCO}_3(\text{OH})_3^-$ , since available experimental data are not sufficiently conclusive to unambiguously establish corresponding constants. However, in the sense of a "what if" question and based on chemical analogy among the actinides, constants for U, Np and Pu may be estimated. If we assume that the stability constant of the equilibrium



for U, Np and Pu is the same as for Th,  $\log_{10}K^\circ = 1.3$ , we derive the chemical model as provided in Table 4a. The results of this exercise are given in Table 4b and in Fig. 9. As in the former example, total solubilities as calculated with the full geochemical model are given in the last column of Table 4b. The "introduction" of mixed complexes increases the total solubility of U and Np by about two orders of magnitude. The total solubility of Pu is little affected (the major part of solutes still is Pu(III)), but the contribution of Pu(IV) to total dissolved Pu shifts from 0.2 % to 29 %.

Fig. 9 reveals that the introduction of a mixed complex, which is based on chemical analogy with Th, leads to a completely wrong description of the behaviour of the An(IV) - H<sub>2</sub>O - CO<sub>2</sub> systems as measured by Rai and co-workers. If the introduction of mixed complexes into the speciation model would cause an *underestimation* of actinide solubility in the region of low bicarbonate concentration, we could argue that other chemical species predominate this parameter region. However, the mixed complexes based on chemical analogy lead to a dramatic *overestimation* of actinide solubility in the region of low bicarbonate concentration. The general picture (dramatic overestimation) does not change when the dominant complex  $\text{An}^{(\text{IV})}\text{CO}_3(\text{OH})_3^-$  is replaced by mixed complexes exhibiting other stoichiometries (i.e.  $\text{An}^{(\text{IV})}\text{CO}_3(\text{OH})_2(\text{aq})$ ,  $\text{An}^{(\text{IV})}\text{CO}_3(\text{OH})_4^{2-}$ ). We now have the choice, either to consider the experimental data of Rai and co-workers as unreliable in the region of low bicarbonate concentration, or to admit that the principle of chemical analogy does not work in a strict sense. Considering the fact that Th hydrolysis is orders of magnitude different from U, Np and Pu hydrolysis (see

Table 4a), we preferred to rely on the experimental data of Rai and co-workers and decided to discard this attempt of applying strict chemical analogy as unsuccessful.

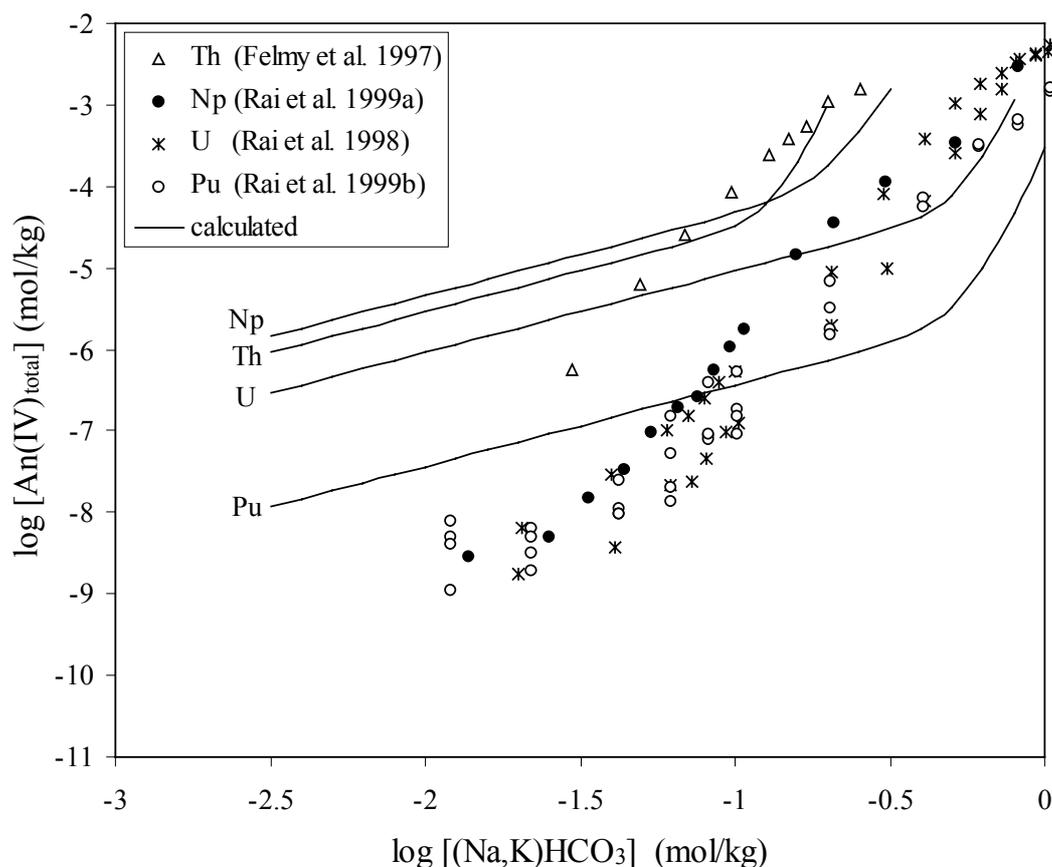
**Table 4:** Revised chemical model for the system An(IV) - H<sub>2</sub>O - CO<sub>2</sub>, assuming that a mixed hydroxide-carbonate complex identical to that of Th also exists for other An(IV).

a) Stability constants, estimates in bold face.

	AnO <sub>2</sub> (s)	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>
	log <sub>10</sub> *K <sub>s,0</sub> <sup>o</sup>	log <sub>10</sub> *β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> *K <sup>o</sup>	log <sub>10</sub> β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> β <sub>5</sub> <sup>o</sup>
Th	9.9	-18.4	-3.1		29.8
U	0	-9	<b>6.3</b>	35.2	34.1
Np	1.5	-9.8	<b>5.5</b>	36.7	35.6
Pu	-2	-8.4	<b>6.9</b>	35.9	34.5

b) Speciation & solubility at log<sub>10</sub>pCO<sub>2</sub> = -2.2. Major changes with respect to Tab. 3b in bold face.

	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	An(IV) <sub>total</sub>	An <sub>total</sub>
	%	%	%	%	mol/l	mol/l
Th	0.5	99.5		0	6.3E-07	6.9E-07
U	<b>0.5</b>	<b>99.5</b>	0	0	<b>2.0E-07</b>	<b>2.2E-07</b>
Np	<b>0.5</b>	<b>99.5</b>	0	0	<b>1.0E-06</b>	<b>1.1E-06</b>
Pu	<b>0.5</b>	<b>99.5</b>	0	0	<b>8.0E-09</b>	<b>3.0E-08</b>



**Figure 9:** Experimental solubility data of Rai and co-workers. The solid lines are calculated considering the varying  $\text{CO}_2$  partial pressure and ionic strength along the x-axis using thermodynamic data recommended in the Nagra/PSI TDB 01/01. In the case of U, Np and Pu an additional aqueous species,  $\text{AnCO}_3(\text{OH})_3^-$ , is included in the speciation model. It has been assumed that the stability constant of the equilibrium  $\text{An}(\text{OH})_4(\text{aq}) + \text{CO}_3^{2-} \rightleftharpoons \text{AnCO}_3(\text{OH})_3^- + \text{OH}^-$  for U, Np and Pu is the same as for Th (Table 4a).

### 3.5 The backdoor approach: Maximum feasible values of ternary complexes

As a next step in our quest for missing values of ternary hydroxide-carbonate complexes we apply a method called “the backdoor approach” (HUMMEL, 1992). We drop the assumption of strict chemical analogy, but we still assume that  $\text{AnCO}_3(\text{OH})_3^-$  complexes exist and are the most important mixed hydroxide-carbonate complexes for all tetravalent actinides in the region of low bicarbonate concentration. Now a special variant of the much more general “backdoor approach” consists in adjusting the formation constants of  $\text{AnCO}_3(\text{OH})_3^-$  complexes to maximum feasible values that are still consistent with the available experimental solubility data. These adjustments were

done on the basis of a "visual" fit to the data of Rai and co-workers. The chemical model and the results are provided in Table 5 and Fig. 10.

A comparison of Figs. 7 and 10 reveals that the calculated solubility curves of U, Np and Pu are solely affected below about 0.1 mol/kg (Na,K)HCO<sub>3</sub>. At higher carbonate concentrations the complexes An(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup> and An(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> still dominate, even if we include maximum feasible values for AnCO<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> complexes in our speciation model. The calculated lines for U and Pu remain below the experimental solubility data at high carbonate concentrations (Fig. 10). However, the pH – pCO<sub>2</sub> region of interest in this case study is located at the lower end of the experimental range studied by Rai and co-workers (Fig. 5). Hence, the maximum feasible values of AnCO<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> complex stability are of importance in our case study, and the actual stability constants of the complexes An(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup> and An(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> cause second order effects only (Table 5b). Note that still more than 95 % of calculated total dissolved plutonium is in the trivalent oxidation state (Table 5b).

**Table 5:** Maximum feasible formation constants of mixed hydroxide-carbonate complexes adjusted to the data of Rai and co-workers.

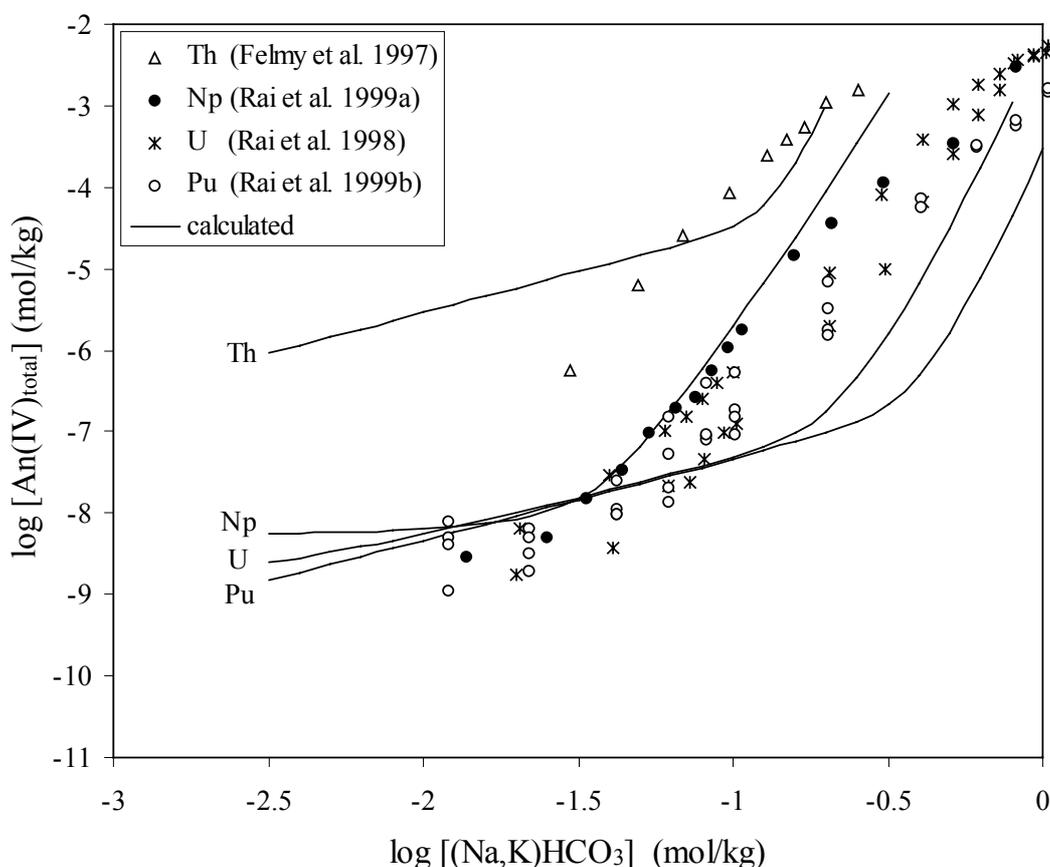
a) Stability constants, estimates in bold face.

	AnO <sub>2</sub> (s)	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>
	log <sub>10</sub> *K <sub>s,0</sub> <sup>o</sup>	log <sub>10</sub> *β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> *K <sup>o</sup>	log <sub>10</sub> β <sub>4</sub> <sup>o</sup>	log <sub>10</sub> β <sub>5</sub> <sup>o</sup>
Th	9.9	-18.4	-3.1		29.8
U	0	-9	<b>4</b>	35.2	34.1
Np	1.5	-9.8	<b>2</b>	36.7	35.6
Pu	-2	-8.4	<b>6</b>	35.9	34.5

b) Speciation & solubility at log<sub>10</sub>pCO<sub>2</sub> = -2.2. Major changes with respect to Tab. 3b in bold face.

	An(OH) <sub>4</sub> (aq)	AnCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup>	An(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>	An(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	An(IV) <sub>total</sub>	An <sub>total</sub>
	%	%	%	%	mol/l	mol/l
Th	0.5	99.5		0	6.3E-07	6.9E-07
U	<b>50</b>	<b>50</b>	0	0	2.0E-09	2.7E-09
Np	94	6	0	0	5.3E-09	5.4E-09
Pu	<b>4</b>	<b>96</b>	0	0	<b>1.0E-09</b>	2.3E-08

We are aware of the somewhat arbitrary choice of  $\text{AnCO}_3(\text{OH})_3^-$  as the most important complex, and we thus repeated the “backdoor” exercise with ternary complexes having more than one  $\text{CO}_3^{2-}$  ligand. This produces solubility curves with slopes  $> 1$  in the region of low bicarbonate concentrations. From a point of view of performance assessment those results appeared worse than those visualised in Fig. 10, because extrapolations to low bicarbonate with a slope  $> 1$  always produce non-conservative, low U, Np and Pu solubilities. The complex  $\text{AnCO}_3(\text{OH})_3^-$  chosen here ensures that we estimate maximum values for actinide solubilities which are still compatible with the experimental data of Rai and co-workers.



**Figure 10:** Experimental solubility data of Rai and co-workers. The solid lines are calculated considering the varying  $\text{CO}_2$  partial pressure and ionic strength along the x-axis using thermodynamic data recommended in the Nagra/PSI TDB 01/01. In the case of U, Np and Pu an additional aqueous species,  $\text{AnCO}_3(\text{OH})_3^-$ , is included in the speciation model. Its stability constant has been adjusted in all cases to a maximum value still compatible with the experimental data of Rai and co-workers (Table 5a).

### 3.6 “Best fit” of experimental data

As an attempt to remedy the shortcomings of the “backdoor approach”, a visual "best fit" to the data of Rai and co-workers is the last step in our exercise of data estimation. The formation constants for  $\text{An}(\text{CO}_3)_4^{4-}$ ,  $\text{An}(\text{CO}_3)_5^{6-}$  and  $\text{AnCO}_3(\text{OH})_3^-$  were varied simultaneously to obtain the best representation of the experimental data. Thereby, the complexes  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  were varied by preserving the difference in reported stabilities for  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  (about 1.0  $\log_{10}$ -units). A similar difference was used to invent a formation constant for the missing  $\text{Th}(\text{CO}_3)_4^{4-}$  complex. The results of this "best fit" are shown in Table 6 and Fig. 11.

**Table 6:** "Best fit" to the data of Rai and co-workers. Reported differences in stabilities of  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  are preserved.

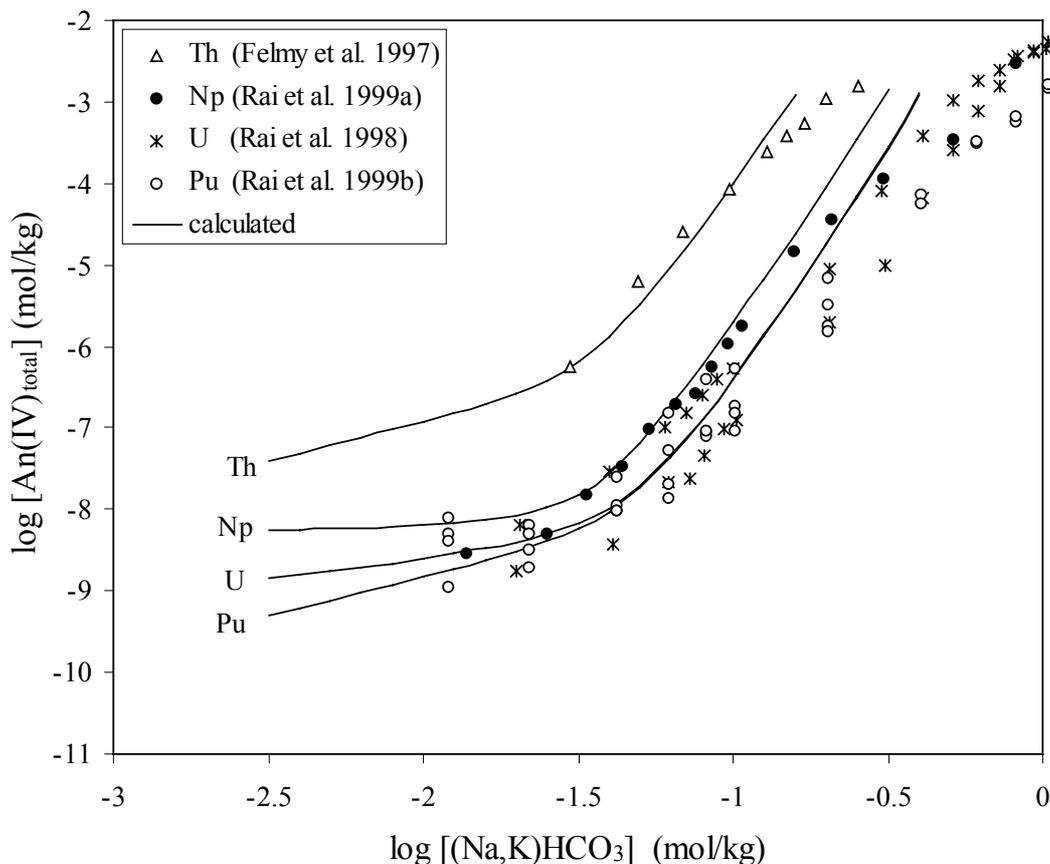
a) Stability constants, estimates in bold face.

	$\text{AnO}_2(\text{s})$ $\log_{10} * K_{s,0}^\circ$	$\text{An}(\text{OH})_4(\text{aq})$ $\log_{10} * \beta_4^\circ$	$\text{AnCO}_3(\text{OH})_3^-$ $\log_{10} * K^\circ$	$\text{An}(\text{CO}_3)_4^{4-}$ $\log_{10} \beta_4^\circ$	$\text{An}(\text{CO}_3)_5^{6-}$ $\log_{10} \beta_5^\circ$
Th	9.9	-18.4	<b>-4.5</b>	<b>30.0</b>	<b>29.0</b>
U	0	-9	<b>3.5</b>	<b>37.5</b>	<b>36.4</b>
Np	1.5	-9.8	<b>2.0</b>	36.7	35.6
Pu	-2	-8.4	<b>5.5</b>	<b>39.5</b>	<b>38.1</b>

b) Speciation & solubility at  $\log_{10} p\text{CO}_2 = -2.2$ . Major changes with respect to Tab. 3b in bold face.

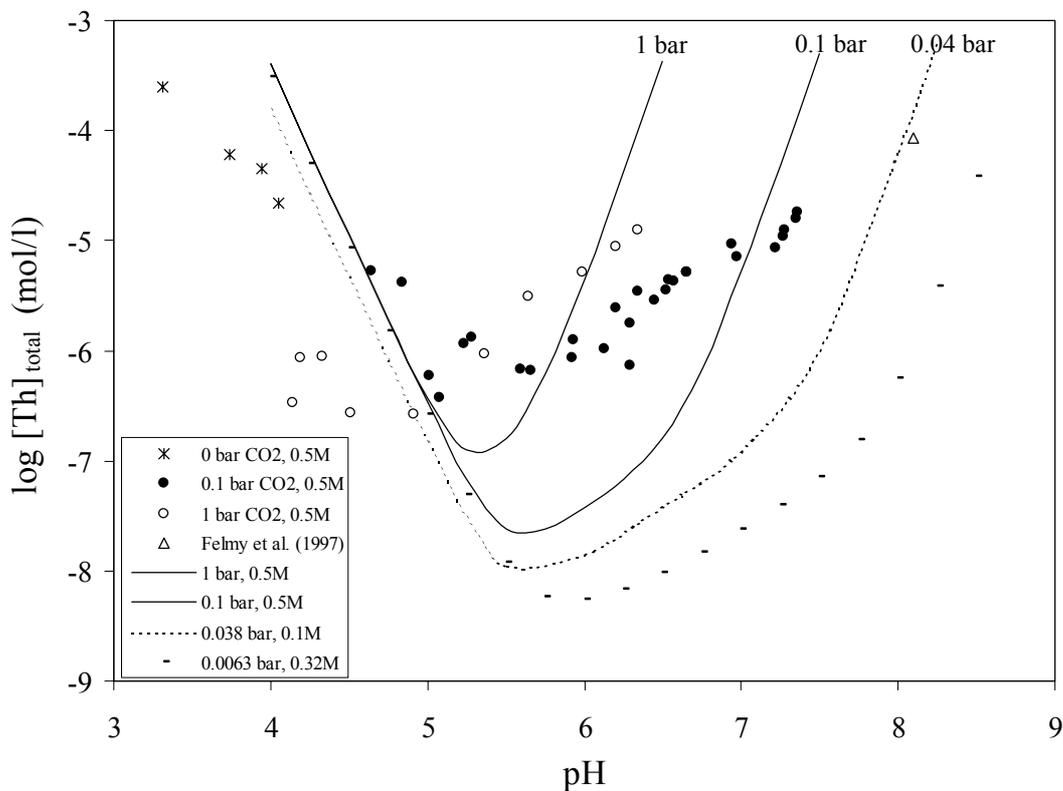
	$\text{An}(\text{OH})_4(\text{aq})$ %	$\text{AnCO}_3(\text{OH})_3^-$ %	$\text{An}(\text{CO}_3)_4^{4-}$ %	$\text{An}(\text{CO}_3)_5^{6-}$ %	$\text{An}(\text{IV})_{\text{total}}$ mol/l	$\text{An}_{\text{total}}$ mol/l
Th	<b>11.1</b>	<b>88.6</b>	0.3	0	<b>2.8E-08</b>	<b>3.0E-08</b>
U	<b>76</b>	<b>24</b>	0	0	1.3E-09	1.9E-09
Np	94	6	0	0	5.3E-09	5.4E-09
Pu	<b>11.1</b>	<b>88.8</b>	0.1	0	<b>3.6E-10</b>	2.2E-08

This "best fit" model, using a consistent set of relevant complexes for all nuclides, very well represents the Th, U, Np and Pu data from Rai and co-workers at moderate carbonate concentrations. With the exception of Th, which is an order of magnitude lower, calculated total solubilities are very similar to the original model at  $\log_{10} p\text{CO}_2 = -2.2$  (see also Table 3 and Fig. 7).



**Figure 11:** Experimental solubility data of Rai and co-workers. Solid lines are calculated considering the varying  $\text{CO}_2$  partial pressure and ionic strength along the x-axis. In all cases the same speciation model comprising the aqueous species  $\text{An}(\text{OH})_4(\text{aq})$ ,  $\text{AnCO}_3(\text{OH})_3^-$ ,  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$ , has been used and two constants have been adjusted to reach a “best fit”. The stability constant of  $\text{AnCO}_3(\text{OH})_3^-$  has been adjusted in all cases. The constants of  $\text{Th}(\text{CO}_3)_4^{4-}$ ,  $\text{U}(\text{CO}_3)_4^{4-}$  and  $\text{Pu}(\text{CO}_3)_4^{4-}$  have been adjusted/invented preserving reported differences in stability for  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  (Table 6a).

However, going back to the data of ÖSTHOLS et al. (1994), we immediately recognise that the “best fit” model for Th does no more represent these experiments (Fig. 12; see also Fig. 6)! This poses a serious dilemma, because the mixed complex  $\text{ThCO}_3(\text{OH})_3^-$  and particularly its stability was substantiated using exactly these experimental data. The mixed complexes of U(IV), Np(IV) and Pu(IV) were derived thereof using analogy principles, but the data of Rai and co-workers are not sufficiently conclusive to confirm them, and independent additional data are not available. Hence, the apparent “best fit” model actually is not best suited for extending the TDB towards bentonite pore water environments.



**Figure 12:** Consequence of the “best fit” of the  $\text{ThCO}_3(\text{OH})_3^-$  and  $\text{Th}(\text{CO}_3)_4^{4-}$  constants to the experimental Th data of FELMY et al. (1997) (Fig. 11): The experimental solubility data of ÖSTHOLS et al. (1994) are no more represented by this speciation model.

In addition, it should be noted that the formation constants for  $\text{An}(\text{CO}_3)_4^{4-}$  and  $\text{An}(\text{CO}_3)_5^{6-}$  ( $\text{An} = \text{U}, \text{Pu}$ ) in the “best fit” model strongly deviate from those selected in HUMMEL et al. (2002) on the basis of the NEA review (LEMIRE et al., 2001). This is not the case for the corresponding Np carbonate constants, since those were derived by NEA (LEMIRE et al., 2001) using the data of RAI et al. (1999a).

In summary, the only remedy of the shortcomings of the “backdoor approach” would be a complete re-analysis of all experimental data, simultaneously performed for all tetravalent actinides. Unfortunately, this is completely out of scope of this case study.

#### 4 IMPACT OF PROBLEM SPECIFIC TDB EXTENSIONS ON SOLUBILITY AND SPECIATION OF U, NP AND PU

A major uncertainty in the definition of the bentonite reference pore water (Table 1) is  $\log_{10}p\text{CO}_2$ . In order to visualise this major uncertainty we actually varied  $\log_{10}p\text{CO}_2$  from  $-3.5$  to  $-1.5$  when studying the impact of problem specific TDB extensions. This variation of  $p\text{CO}_2$  leads to a variation in pH (from 7.8 to 6.9), and, coupled to the solubility of magnetite (at least in the present concept), to a variation in system Eh (from  $-310$  to  $-100$  mV). The impact of this Eh variation is indicated in Tables 3 to 6, revealing that the total Pu concentration is much higher than the Pu(IV) concentration due to Pu(III) formation.

Hence, in our case study of compacted bentonite pore waters, TDB extensions should not be restricted to the mixed  $\text{AnCO}_3(\text{OH})_3^-$  complexes of the tetravalent actinides. The TDB extensions should also include formation constants for Pu(III) and Np(III). Table 7 gives an overview of An(III) data presently available in the Nagra/PSI TDB 01/01. Missing formation constants considered to be relevant in the present chemical environment are highlighted (shaded cells). The given values are estimates, based on chemical analogy of Np(III) and Pu(III) with Am(III). The Np(III) and Pu(III) fluoride, carbonate and silicate constants and the Np(III) sulphate and chloride data have been assumed to be the same as the corresponding Am constants. For the hydrolysis species we assumed that the stepwise stability constants of  $\text{An}^{\text{III}}(\text{OH})_2^+$  and  $\text{An}^{\text{III}}(\text{OH})_3(\text{aq})$  of Np(III) and Pu(III) are the same as the corresponding stepwise Am(III) constants.

Table 8 provides a summary of An(IV) complex formation constants. The only missing constants considered to be of relevance are those of the  $\text{AnCO}_3(\text{OH})_3^-$  complexes (shaded cells). In the light of the above addressed "serious dilemma" with the "best fit" constants, the actual values adopted in our TDB extension correspond to "maximum feasible values", taken from Table 5a.

**Table 7:** Application of the Nagra/PSI TDB 01/01 to compacted bentonite pore water: M(III) compounds and complexes. Missing formation constants considered to be relevant in this chemical environment (shaded cells) were estimated based on chemical analogy with Am(III). Eu(III) data recommended in the Nagra/PSI TDB 01/01 are included here for comparison.

M <sup>3+</sup> complexes and solids	log <sub>10</sub> K <sup>o</sup>			
	Np <sup>3+</sup>	Pu <sup>3+</sup>	Am <sup>3+</sup>	Eu <sup>3+</sup>
M(OH) <sub>3</sub> (cr) + 3 H <sup>+</sup> ⇌ M <sup>3+</sup> + 3 H <sub>2</sub> O		15.8 ± 1.5	15.2 ± 0.6	14.9 ± 0.3
M(OH) <sub>3</sub> (am) + 3 H <sup>+</sup> ⇌ M <sup>3+</sup> + 3 H <sub>2</sub> O			17.0 ± 0.6	17.6 ± 0.8
M <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> (cr) ⇌ 2 M <sup>3+</sup> + 3 CO <sub>3</sub> <sup>2-</sup>			-33.4 ± 2.2	-35.0 ± 0.3
M(OH)CO <sub>3</sub> (cr) ⇌ M <sup>3+</sup> + OH <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup>			-21.2 ± 1.4	-21.7 ± 0.1
M <sup>3+</sup> + H <sub>2</sub> O ⇌ MOH <sup>2+</sup> + H <sup>+</sup>	-6.8 ± 0.3	-6.9 ± 0.3	-7.3 ± 0.3	-7.64 ± 0.04
M <sup>3+</sup> + 2 H <sub>2</sub> O ⇌ M(OH) <sub>2</sub> <sup>+</sup> + 2 H <sup>+</sup>	-14.7	-14.8	-15.2 ± 0.8	-15.1 ± 0.2
M <sup>3+</sup> + 3 H <sub>2</sub> O ⇌ M(OH) <sub>3</sub> (aq) + 3 H <sup>+</sup>	-25.2	-25.3	-25.7 ± 0.5	-23.7 ± 0.1
M <sup>3+</sup> + 4 H <sub>2</sub> O ⇌ M(OH) <sub>4</sub> <sup>-</sup> + 4 H <sup>+</sup>				-36.2 ± 0.5
M <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> ⇌ MCO <sub>3</sub> <sup>+</sup>	7.8	7.8	7.8 ± 0.3	8.1 ± 0.2
M <sup>3+</sup> + 2 CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	12.3	12.3	12.3 ± 0.4	12.1 ± 0.3
M <sup>3+</sup> + 3 CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>	15.2	15.2	15.2 ± 0.6	
M <sup>3+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ MSO <sub>4</sub> <sup>+</sup>	3.9	3.9 ± 0.6	3.85 ± 0.03	3.95 ± 0.08
M <sup>3+</sup> + 2 SO <sub>4</sub> <sup>2-</sup> ⇌ M(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	5.4	5.7 ± 0.8	5.4 ± 0.7	5.7 ± 0.2
M <sup>3+</sup> + F <sup>-</sup> ⇌ MF <sup>2+</sup>	3.4	3.4	3.4 ± 0.4	3.8 ± 0.2
M <sup>3+</sup> + 2 F <sup>-</sup> ⇌ MF <sub>2</sub> <sup>+</sup>	5.8	5.8	5.8 ± 0.2	6.5 ± 0.5
M <sup>3+</sup> + Cl <sup>-</sup> ⇌ MCl <sup>2+</sup>	1	1.2 ± 0.2	1.05 ± 0.06	1.1 ± 0.2
M <sup>3+</sup> + 2 Cl <sup>-</sup> ⇌ MCl <sub>2</sub> <sup>+</sup>				1.5 ± 0.5
M <sup>3+</sup> + SiO(OH) <sub>3</sub> <sup>-</sup> ⇌ MSiO(OH) <sub>3</sub> <sup>2+</sup>	8.1	8.1	8.1 ± 0.2	7.9 ± 0.2
M <sup>4+</sup> + e <sup>-</sup> ⇌ M <sup>3+</sup>	3.70 ± 0.18	17.69 ± 0.04		

**Table 8:** Application of the Nagra/PSI TDB 01/01 to compacted bentonite pore water: M(IV) compounds and complexes. Maximum feasible formation constants for potentially missing mixed hydroxide carbonate complexes (shaded cells) are taken from Table 5a.

M <sup>4+</sup> complexes and solids	log <sub>10</sub> K°			
	Th <sup>4+</sup>	U <sup>4+</sup>	Np <sup>4+</sup>	Pu <sup>4+</sup>
MO <sub>2</sub> (s) + 2 H <sub>2</sub> O ⇌ M(OH) <sub>4</sub> (aq)	-8.5 ± 0.6	-9 ± 1	-8.3 ± 0.3	-10.4 ± 0.5
M <sup>4+</sup> + H <sub>2</sub> O ⇌ MOH <sup>3+</sup> + H <sup>+</sup>	-2.4 ± 0.5	-0.54 ± 0.06	-0.29 ± 1.00	-0.78 ± 0.60
M <sup>4+</sup> + 4 H <sub>2</sub> O ⇌ M(OH) <sub>4</sub> (aq) + 4 H <sup>+</sup>	-18.4 ± 0.6	-9 ± 2	-9.8 ± 1.1	-8.4 ± 1.1
M <sup>4+</sup> + 4 CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>4</sub> <sup>4-</sup>		35.22 ± 1.03	36.69 ± 1.11	35.9 ± 2.5
M <sup>4+</sup> + 5 CO <sub>3</sub> <sup>2-</sup> ⇌ M(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	29.8 ± 1.1	34.1 ± 1.0	35.62 ± 1.15	34.5 ± 2.5
M <sup>4+</sup> + CO <sub>3</sub> <sup>2-</sup> + 3 H <sub>2</sub> O ⇌ MCO <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup> + 3 H <sup>+</sup>	-3.1 ± 1.0	4	2	6
M <sup>4+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ MSO <sub>4</sub> <sup>2+</sup>	7.6 ± 0.5	6.58 ± 0.19	6.85 ± 0.16	6.89 ± 0.23
M <sup>4+</sup> + 2 SO <sub>4</sub> <sup>2-</sup> ⇌ M(SO <sub>4</sub> ) <sub>2</sub> (aq)	11.6	10.51 ± 0.20	11.05 ± 0.27	11.14 ± 0.34
M <sup>4+</sup> + 3 SO <sub>4</sub> <sup>2-</sup> ⇌ M(SO <sub>4</sub> ) <sub>3</sub> <sup>2-</sup>	12.4			
M <sup>4+</sup> + F <sup>-</sup> ⇌ MF <sup>3+</sup>	8.0	9.28 ± 0.09	8.96 ± 0.14	8.84 ± 0.10
M <sup>4+</sup> + 2 F <sup>-</sup> ⇌ MF <sub>2</sub> <sup>2+</sup>	14.2	16.23 ± 0.15	15.7 ± 0.3	15.7 ± 0.2
M <sup>4+</sup> + 3 F <sup>-</sup> ⇌ MF <sub>3</sub> <sup>+</sup>	18.9	26.1 ± 1.0		
M <sup>4+</sup> + 4 F <sup>-</sup> ⇌ MF <sub>4</sub> (aq)	22.3	25.6 ± 1.0		
M <sup>4+</sup> + 5 F <sup>-</sup> ⇌ MF <sub>5</sub> <sup>-</sup>		27.01 ± 0.30		
M <sup>4+</sup> + 6 F <sup>-</sup> ⇌ MF <sub>6</sub> <sup>2-</sup>		29.08 ± 0.18		
M <sup>4+</sup> + Cl <sup>-</sup> ⇌ MCl <sup>3+</sup>		1.72 ± 0.13	1.5 ± 0.3	1.8 ± 0.3
MO <sub>2</sub> <sup>2+</sup> + 4 H <sup>+</sup> + 2 e <sup>-</sup> ⇌ M <sup>4+</sup> + 2 H <sub>2</sub> O		9.038 ± 0.041	29.80 ± 0.12	32.28 ± 0.15

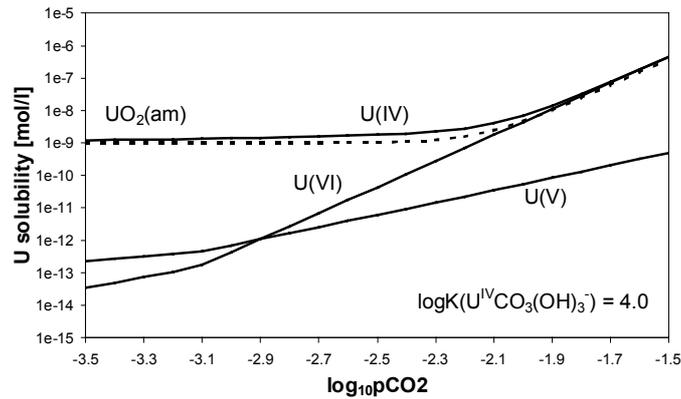
Maximum concentrations (solubilities) have been modelled for U, Np and Pu over the entire  $p\text{CO}_2$  range (which includes the mentioned ranges of pH and Eh) using data recommended in the Nagra/PSI TDB 01/01 as well as the TDB extensions provided in Tables 7 and 8. The results of this exercise are visualised in Figs. 13 to 16.

Uranium: Fig. 13a shows that the total uranium solubility is not significantly affected by introducing the complex  $\text{UCO}_3(\text{OH})_3^-$ , but the mixed complex strongly influences the speciation in solution for regions where U(IV) dominates (Figs. 13b and 13c).

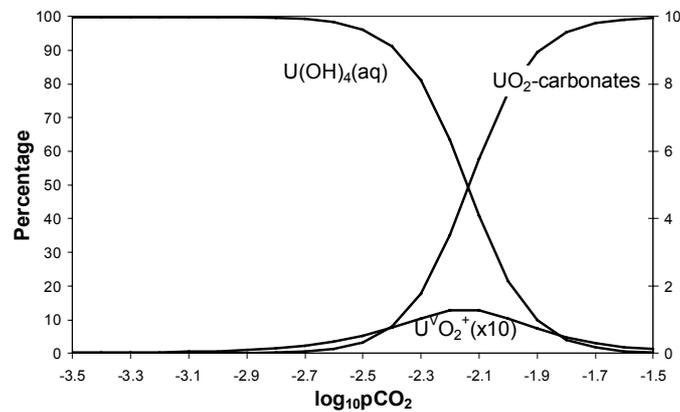
Neptunium: The estimated constants do not change the total neptunium concentration (Fig. 14a). At high  $p\text{CO}_2$  a tiny effect on speciation is observed due to formation of  $\text{NpCO}_3(\text{OH})_3^-$ . The series of estimated Np(III) complexes (Table 7) has no impact at all (Fig. 14b).

Plutonium: By introducing estimated constants into the database, the total solubility in the present  $p\text{CO}_2$  range increases by a factor of 3 to 6 (Fig. 15a). Figs. 15b and 15c clearly show that the (assumed) complex  $\text{Pu}^{\text{III}}\text{SiO}(\text{OH})_3^{2+}$  is responsible for this increase. We conclude that the Pu speciation is significantly changed by the extended TDB. The change in total solubility also is on the verge of becoming significant, particularly when we consider that the solubility of the limiting solid,  $\text{PuO}_2(\text{hyd.}, \text{aged})$ , has an uncertainty of  $\pm 0.5 \log_{10}$ -units. Note that the Pu(III)/Pu(IV) redox potential as recommended by LEMIRE et al. (2001) and subsequently included in the Nagra/PSI TDB 01/01 is far from being a well established quantity. LEMIRE et al. (2001) state (on p. 301) that “the selected thermodynamic quantities for  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{PuO}_2^+$  and  $\text{PuO}_2^{2+}$  are strongly connected, and there is a minimum amount of redundant information to provide confirmation for these values”.

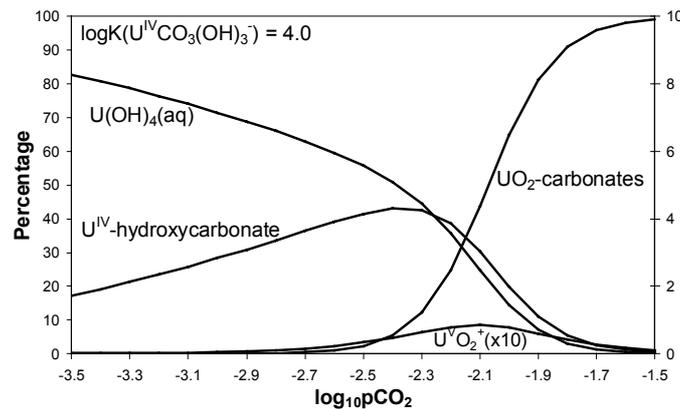
Americium: Since no TDB extensions were necessary for americium, calculated solubility and speciation reflect the unaltered contents of the Nagra/PSI TDB 01/01. Fig. 16 is provided for completeness, and to enable comparison with plutonium speciation (Fig. 15c). Provided that Pu(III) prevails in the given chemical environment, the modelled speciation in solution is very similar for both elements.



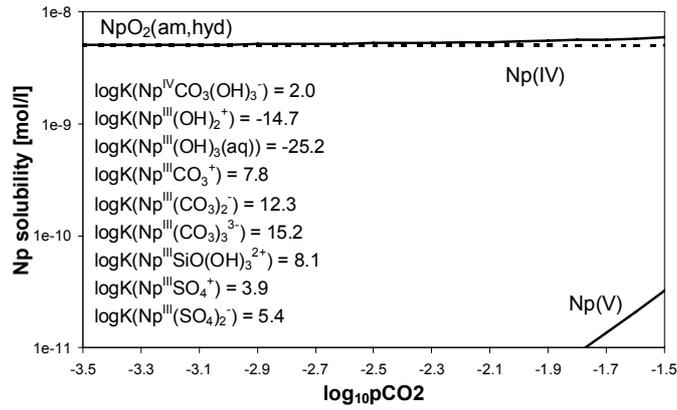
**Figure 13a:** Modelled solubility of uranium in compacted bentonite pore water using the unaltered Nagra/PSI TDB 01/01 (dotted lines), and the extended TDB from Table 8 (solid lines).



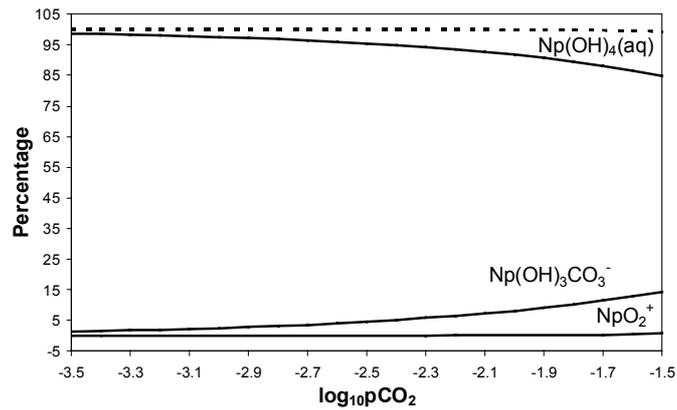
**Figure 13b:** U speciation in solution modelled with the unaltered Nagra/PSI TDB 01/01.



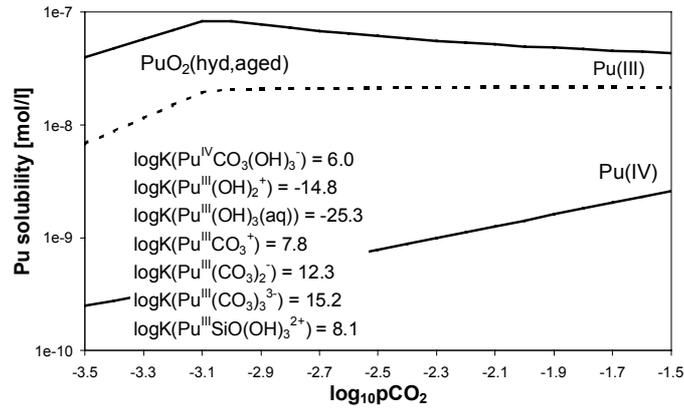
**Figure 13c:** U speciation in solution modelled with the extended, problem specific TDB (Tab. 8).



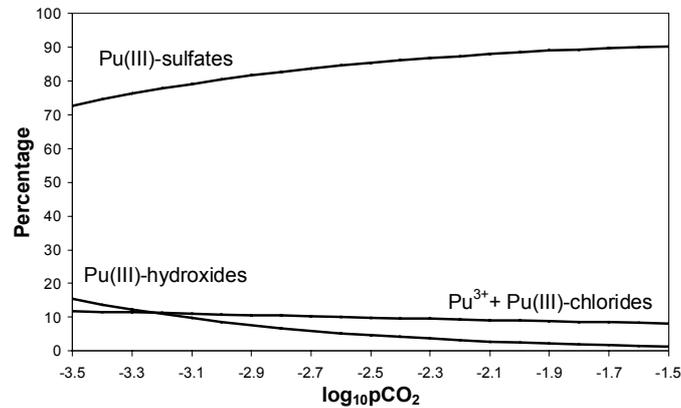
**Figure 14a:** Modelled solubility of neptunium in compacted bentonite pore water using the unaltered Nagra/PSI TDB 01/01 (dotted lines), and the extended TDB from Tables 7 and 8 (solid lines).



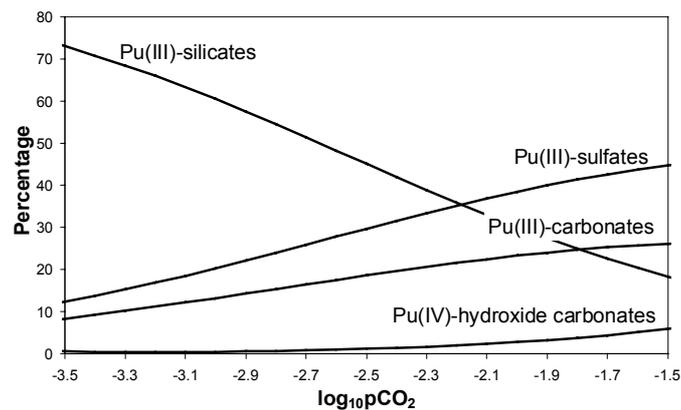
**Figure 14b:** Np speciation in solution modelled with the unaltered Nagra/PSI TDB 01/01 (dotted lines), and the extended TDB from Tables 7 and 8 (solid lines).



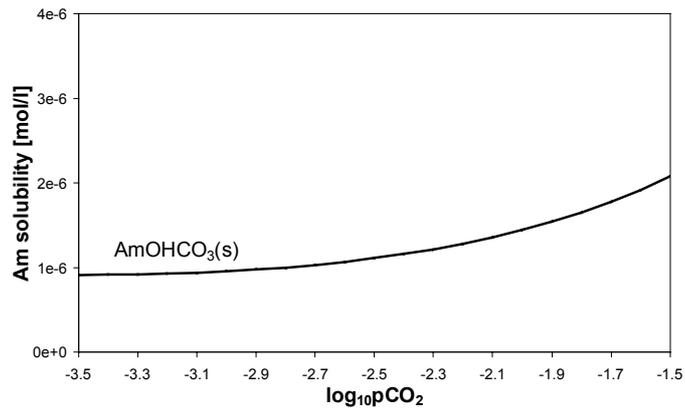
**Figure 15a:** Modelled solubility of plutonium in compacted bentonite pore water using the unaltered Nagra/PSI TDB 01/01 (dotted lines), and the extended TDB from Tables 7 and 8 (solid lines).



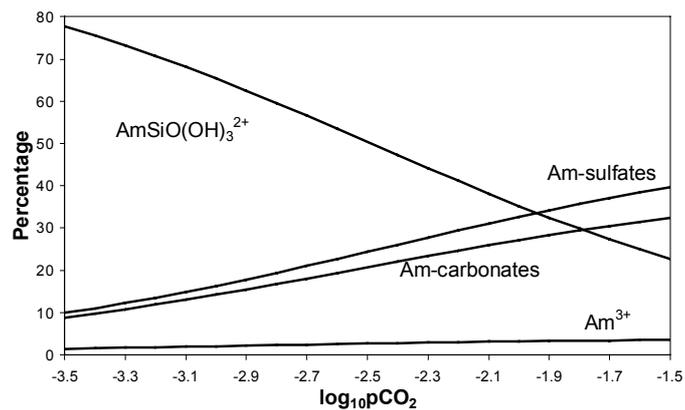
**Figure 15b:** Pu speciation in solution modelled with the unaltered Nagra/PSI TDB 01/01.



**Figure 15c:** Pu speciation in solution modelled with the extended, problem specific TDB (Tables 7 and 8).



**Figure 16a:** Modelled solubility of americium in compacted bentonite pore water using the Nagra/PSI TDB 01/01 (Table 7). We provide these results for completeness, and to enable comparison with plutonium speciation shown in Fig. 15c.



**Figure 16b:** Modelled speciation of americium in compacted bentonite pore water using the Nagra/PSI TDB 01/01 (Table 7).

## 5 CONCLUSIONS

In the course of the review process for the Nagra/PSI TDB 01/01 (HUMMEL et al., 2002) we decided to go beyond the puristic TDB (“generally accepted” and “well established” data in Fig. 1). We identified important cases of insufficient chemical knowledge, leading to gaps in the puristic TDB.

The first case reveals insufficient process understanding: A growing number of experimental data for specific systems cannot be interpreted by a unique set of thermodynamic constants (“ill-defined systems” in Fig. 1). For these systems, we chose a pragmatic approach, suited for performance assessment of radioactive waste repositories. We do this by including parameters in the Nagra/PSI TDB 01/01 that are not thermodynamic constants in a strict sense, but that reproduce relevant experimental observations (section 2).

The second case concerns insufficient experimental data: Potentially important thermodynamic equilibrium constants are missing. Estimations of these missing constants led to problem specific TDB extensions. These TDB extensions are not included in the Nagra/PSI TDB 01/01 because they are valid only for the particular applications they have been derived for.

Unknown complex formation constants can often be estimated straightforwardly by chemical analogy, e.g. using Am(III) data for Np(III) and Pu(III) complexes. However, in the case of tetravalent actinides this quick and easy estimation method failed. Our constants for  $An^{IV}CO_3(OH)_3^-$  complexes estimated based on chemical analogy (section 3.4) cause dramatic effects on solubility and speciation. Unfortunately, the results of these appraisals turned out to be completely incompatible with experimental solubility data.

Attempts to fit all carbonate complex formation constants for tetravalent actinides to series of solubility data also failed. As shown in section 3.6, fitting constants to a limited set of data leads to grossly wrong results for other data sets. Complete re-analysis of all experimental data, simultaneously for all tetravalent actinides, would be necessary to derive a chemically consistent "best fit" data set of appropriate quality. This would turn our little exercise into a very time consuming project.

The “backdoor approach”, i.e. adjusting constants for  $An^{IV}CO_3(OH)_3^-$  complexes to maximum feasible values that are still consistent with all available experimental

solubility data, turned out to be the method of choice (section 3.5). The estimated constants have no significant effects on the total solubility of U, Np and Pu in our case study (compare Tables 3 and 5). Introducing the ternary complexes has, however, a remarkable effect on the speciation in solution. Although the overall distribution among Pu(III) and Pu(IV) species does not significantly change, the fraction of  $\text{Pu}(\text{OH})_4(\text{aq})$  decreases from 100 % to about 5 %, in favour of the ternary complex.  $\text{U}(\text{OH})_4(\text{aq})$  changes from 100 % to about 50 %.

Based on our exercise in data estimation and in order to fill obvious gaps in the Nagra/PSI TDB 01/01, we propose a problem specific TDB extension for U, Np and Pu (Tables 7 and 8). Constants for mixed An(IV) hydroxide-carbonate complexes have been estimated by the backdoor approach, and various missing Np(III) and Pu(III) constants have been estimated straightforwardly by chemical analogy with Am(III).

Total uranium and neptunium solubilities modelled with these problem specific TDB extensions do not significantly deviate from calculations using solely the Nagra/PSI TDB 01/01. Deviations in Pu solubility are within those expected from associated uncertainties. However, the speciation modelled with the extended TDB significantly changes in the case of uranium at low Eh (where U(IV) prevails) and in the case of Pu. These changes can be traced back to the complexes  $\text{U}^{\text{IV}}\text{CO}_3(\text{OH})_3^-$  and  $\text{Pu}^{\text{III}}\text{SiO}(\text{OH})_3^{2+}$ .

We conclude that gaps in the Nagra/PSI TDB 01/01 due to insufficient chemical knowledge concerning Th, U, Np and Pu data do not lead to grossly wrong estimates of their respective solubility limits in the case of bentonite pore waters. Attempts to improve our chemical knowledge should concentrate on the two key complexes mentioned above, and on the confirmation of the Pu(III)/Pu(IV) redox potential.

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