

# EFFECT OF CARBONATE ON THE SOLUBILITY OF NEPTUNIUM IN NATURAL GRANITIC GROUNDWATER

B. Y. KIM<sup>1</sup>, J. Y. OH<sup>1</sup>, M. H. BAIK<sup>2</sup> and J.-I. YUN<sup>1\*</sup>

<sup>1</sup>Department of Nuclear & Quantum Engineering, KAIST  
373-1 Guseong-dong, Yuseong-gu, Daejeon, 305-701, Korea

<sup>2</sup>Radioactive Waste Technology Development Division, Korea Atomic Energy Research Institute  
P.O. Box 105, Yuseong-gu, Daejeon 305-353, Korea

\*Corresponding author. E-mail : jiyun@kaist.ac.kr

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This study investigates the solubility of neptunium (Np) in the deep natural groundwater of the Korea Atomic Energy Research Institute Underground Research Tunnel (KURT). According to a Pourbaix diagram (pH- $E_h$  diagram) that was calculated using the geochemical modeling program PHREEQC 2.0, the redox potential and the carbonate ion concentration both control the solubility of neptunium. The carbonate effect becomes pronounced when the total carbonate concentration is higher than  $1.5 \times 10^{-2}$  M at  $E_h = -200$  mV and the pH value is 10. Given the assumption that the solubility-limiting stable solid phase is  $\text{Np(OH)}_4(\text{am})$  under the reducing condition relevant to KURT, the soluble neptunium concentrations were in the range of  $1 \times 10^{-9}$  M to  $3 \times 10^{-9}$  M under natural groundwater conditions. However, the solubility of neptunium, which was calculated with the formation constants of neptunium complexes selected in an OECD-NEA TDB review, strongly deviates from the value measured in natural groundwater. Thus, it is highly recommended that a prediction of neptunium solubility is based on the formation constants of ternary Np(IV) hydroxo-carbonato complexes, even though the presence of those complexes is deficient in terms of the characterization of neptunium species. Based on a comparison of the measurements and calculations of geochemical modeling, the formation constants for the “upper limit” of the Np(IV) hydroxo-carbonato complexes, namely  $\text{Np(OH)}_y(\text{CO}_3)_z^{4-y-2z}$ , were appraised as follows:  $\log K_{122}^\circ = -3.0 \pm 0.5$  for  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$ ,  $\log K_{131}^\circ = -5.0 \pm 0.5$  for  $\text{Np(OH)}_3(\text{CO}_3)^-$ , and  $\log K_{141}^\circ = -6.0 \pm 0.5$  for  $\text{Np(OH)}_4(\text{CO}_3)^{2-}$ .

**KEYWORDS** : Neptunium, Solubility, Hydroxo-Carbonato Complexes, Granitic Groundwater, Geochemical Modeling

## 1. INTRODUCTION

Deep geological disposal is a favored method for the permanent storage of high-level radioactive waste (HLW) in a repository. Thus, fundamental knowledge of the geochemical behavior of actinides is of prime importance for ensuring the long-term safety of nuclear waste disposal when groundwater enters the repository and there is a subsequent release of radioactive waste. In general, a relatively small amount of neptunium (Np) is contained in HLW, including spent nuclear fuels. However, the amount of neptunium can build up over a prolonged discharge time through the  $\alpha$ -decay of  $^{241}\text{Am}$  ( $T_{1/2} = 432.7$  yrs) [1]. Due to its long half-life ( $^{237}\text{Np}$ :  $T_{1/2} = 2.14 \times 10^6$  yrs) and a high radiotoxicity, neptunium is an important actinide in the safety assessment of nuclear waste disposal [2].

Neptunium is likely to undergo a redox reaction and may be subject to a change in oxidation states, even under normal conditions. Owing to the different stabilities of the oxidation states, there is a noticeable difference in the

chemical properties, such as solubility, complexation, sorption, and colloid formation. For oxidizing conditions, neptunium generally remains stable in a pentavalent oxidation state. In carbonate free solutions,  $\text{NpO}_2\text{OH(s)}$  and  $\text{Np}_2\text{O}_5(\text{s})$  are considered stable solid phases [1,3-6], whereas  $\text{MNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  or  $\text{M}_3\text{NpO}_2(\text{CO}_3)_2$  ( $\text{M} = \text{Na}^+$ ,  $\text{K}^+$ ) or both are the solubility-limiting solid phases based on the X-ray powder diffraction in an equilibrium state containing carbonate. Therefore, one of the characteristics of the solubility-limiting solid phases of Np(V) is their strong reliance on the alkali carbonate concentration [1,7-12]. Additionally, many calculation studies have reported that the solubility of Np(IV) is  $5 \times 10^{-9}$  M in a neutral to highly alkaline solution [13] and  $3 \times 10^{-9}$  M for a pH range of 8.5-12.5 [14]. Yui reported that the solubility of  $\text{NpO}_2(\text{am})$  was  $2 \times 10^{-9}$  M for reducing groundwater at a relatively high pH [15]. Rees determined that the Np solubility was  $4 \times 10^{-9}$  M for a pH of 8 and an  $E_h$  value of  $-0.28$  V in deeper burial conditions [16]. The chemical form of a freshly precipitated or aged Np(IV) solid phase

is not clear. In the literature,  $\text{NpO}_2$  (am) is considered a solubility-limiting phase. In neutral to alkaline solutions that are free of carbonate ions, the solubility of  $\text{NpO}_2$  (cr) becomes consistent with that of amorphous  $\text{Np(IV)}$  hydrous solids [17,18].

As discussed in detail in a review of the OECD-NEA Thermochemical Database (TDB) [18], the presence of ternary  $\text{Np(IV)}$  hydroxo-carbonato complexes is still a controversial issue. Due to inadequate characterization of the neptunium species and the uncertainty of the solubility product of the solid phase used in the solubility experiments, the formation constants are not nominated in the OECD-NEA TDB. Nevertheless, the experimental data in the literature strongly indicates that ternary  $\text{Np(VI)}$  hydroxo-carbonato complexes, particularly  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$  [19,20],  $\text{Np(OH)}_3(\text{CO}_3)^-$  [21],  $\text{Np(OH)}_4(\text{CO}_3)^{2-}$  [19,21], and  $\text{Np(OH)}_4(\text{CO}_3)_2^{4-}$  [22], can be formed. However, data on the equilibrium constant of only one complex of either  $\text{Np(OH)}_2(\text{CO}_3)_2^{2-}$  or  $\text{Np(OH)}_3(\text{CO}_3)^-$  and either of  $\text{Np(OH)}_4(\text{CO}_3)^{2-}$  or  $\text{Np(OH)}_4(\text{CO}_3)_2^{4-}$  have been reported due to a difficulty in the chemical speciation of individual ternary complexes formed in almost the same pH range.

In this paper, the solubility of neptunium is investigated in the natural groundwater conditions of the Korea Atomic Energy Research Institute Underground Research Tunnel (KURT). A calculation with the geochemical modeling program PHREEQC 2.0 was performed on the basis of the thermodynamic data of the OECD-NEA TDB. Even though the formation constants of ternary  $\text{Np(IV)}$  hydroxo-carbonato complexes, which were not discussed in the OECD-NEA TDB due to a lack of data on the species characterization, are of low reliability, they consistently help explain the experimentally measured solubility of  $\text{Np(IV)}$ . Thus, this paper presents a discussion and evaluation of the formation constants of the ternary  $\text{Np(IV)}$  hydroxo-carbonato complexes relevant to the conditions of the KURT groundwater and in conjunction with the thermodynamic data reported in the literature.

## 2. GEOCHEMICAL CALCULATION

### 2.1 KURT Groundwater

KURT is located at the research site of the Korea Atomic Energy Research Institute in Yueseong, Daejeon, Republic of Korea. It was constructed to obtain detailed information on deep geologic environments and to demonstrate the performance of the Korean Reference System for HLW disposal under a repository-relevant condition in Korea. KURT is a small-scale underground research laboratory with one access tunnel (180 m in length) and two research modules (45 m and 30 m in length for the right and left modules) at a depth of 100 m from the surface [23,24]. The rock type is two-mica granite; it is classified as calc-alkali rock [25]. Fifteen boreholes were drilled at the KURT

site (BH-1 to BH-6, YS-1, YS-2, YS2-1, YS2-2, and YS-3 to YS-7) to investigate the hydraulic and geological characteristics of one Korean crystalline rock formation that is considered to have potential as an HLW repository in Korea. The calculations in this study are based on natural granitic groundwater sampled from the borehole YS-1 at three different depths: 169.5 m, 259.5 m, and 457.5 m [25]. The major compositions of the groundwater are presented in Table 1. The noteworthy disparity of the three groundwater samples lies mainly in the redox potential. The YS-1-3

**Table 1.** Compositions of Natural Granitic Groundwaters Sampled from a KURT Borehole

	YS-1-3	YS-1-4	YS-1-6
Depth (m)	169.5	259.5	457.5
Temp. (°C)	17.6	19.8	24.5
pH	10.71	10.23	9.93
$E_h$ (mV)	63	-109	-142
Alk. ( $\times 1000$ )	0.73	0.96	0.75
$\text{Na}^+$	25.0	35.8	36.9
$\text{K}^+$	1.14	0.60	0.58
$\text{Ca}^{2+}$	5.7	6.2	2.4
$\text{SiO}_2$	27.4	25	18.2
$\text{HCO}_3^- + \text{CO}_3^{2-}$	11.6	6.4	1.9
F <sup>-</sup>	8.1	13.9	9.0
$\text{NO}_3^-$	3.7	17.1	20.1
$\text{SO}_4^{2-}$	2.0	11.5	12.1
Cl <sup>-</sup>	3.0	2.2	3.8

conc. unit = [mg/L]

**Table 2.** The Groundwater Composition of YS-1-7 [26]

Element	Conc. (mg/L)	Element	Conc. (mg/L)
$\text{Na}^+$	17.4	$\text{CO}_3^{2-} + \text{HCO}_3^-$	78.4
$\text{Ca}^{2+}$	17.3	Cl <sup>-</sup>	2.18
$\text{Mg}^{2+}$	1.82	$\text{SO}_4^{2-}$	6.97
$\text{K}^+$	0.26	F <sup>-</sup>	3.41
$\text{Li}^+$	$1.7 \times 10^{-2}$	$\text{SiO}_2$	41.3
$\text{Sr}^+$	0.27	W	$1.9 \times 10^{-2}$
Mn	$2.2 \times 10^{-2}$	Fe	$5.0 \times 10^{-2}$
Al	$1.6 \times 10^{-2}$	$\text{Ba}^{2+}$	$9.0 \times 10^{-2}$
Mo	$3.8 \times 10^{-2}$	pH	8.44

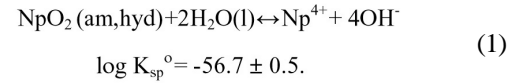
groundwater sample comprises an oxidizing condition, whereas the YS-1-4 and YS-1-6 groundwater samples reveal a reducing condition. The pH value of the groundwater ranges between 9.9 and 10.7. The temperature is increased from the surface of the earth with a geothermal gradient of +2.6 °C/100 m of depth at the KURT site.

For a comparison of the neptunium solubility with that from various experimental results, the calculation of solubility and the neptunium species was performed with the YS-1-7 groundwater [26]. The geochemical properties of YS-1-7 are analogous to other experimental conditions in the literature [19,21,22,26,27]. The  $E_h$  value of the YS-1-7 groundwater, with a higher carbonate concentration of 78.4 mg/L at a depth of 140 m to 150 m, is -200 mV. The compositions are listed in Table 2.

## 2.2 Calculation of Solubility and Chemical Species

The calculation of the solubility and chemical species of neptunium was performed with the geochemical modeling program PHREEQC 2.0 and data from the OECD-NEA TDB [18]. The chemical reactions and formation constants of the neptunium species are summarized in Table 3. The

solubility product of  $\text{NpO}_2(\text{am,hyd})$  at zero ionic strength,  $\log K_{\text{sp}}^0$ , which is selected in the OECD-NEA TDB, was used as follows [18]:



Hydrolysis and carbonate complexation may also occur in parallel to form ternary hydroxo-carbonato complexes. However, the experimental solubility data for  $\text{NpO}_2(\text{am,hyd})$  in the presence of carbonate ions are inconsistent. Moreover, a large degree of uncertainty may exist between different methods of conducting the solubility experiments (under-saturation or over-saturation) and due to the probable particle size effect of the solid phases on solubility, which has not yet been clearly elucidated [18]. Owing to the large degree of uncertainty about the solubility data and the lack of data on the species characterization [18], the equilibrium constants for ternary  $\text{Np}(\text{IV})$  hydroxo-carbonato complexes are not nominated in the OECD-NEA TDB, even though there is a strong indication of the formation

**Table 3** The Reactions and the Formation Constants of Neptunium Hydroxide and Carbonate Complexes [18]

Reaction	$\log K^0$
$\text{Np}^{4+} + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{NpOH}^{3+} + \text{H}^+$	$0.55 \pm 0.2$
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{Np}(\text{OH})_2^{2+} + 2\text{H}^+$	$0.35 \pm 0.3$
$\text{Np}^{4+} + 4\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{Np}(\text{OH})_4(\text{aq}) + 4\text{H}^+$	$-8.3 \pm 1.1$
$\text{Np}^{4+} + 2\text{H}_2\text{O} = \text{NpO}_2^+ + 4\text{H}^+ + \text{e}^-$	$-10.212$
$\text{NpO}_2^+ + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	$-11.3 \pm 0.7$
$\text{NpO}_2^+ + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{NpO}_2(\text{OH})_2^- + 2\text{H}^+$	$-23.6 \pm 0.5$
$\text{NpO}_2^{2+} + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{NpO}_2\text{OH}^+ + \text{H}^+$	$-5.1 \pm 0.4$
$2\text{NpO}_2^{2+} + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{NpO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	$-6.27 \pm 0.21$
$3\text{NpO}_2^{2+} + 5\text{H}_2\text{O}(\text{l}) \leftrightarrow (\text{NpO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	$-17.12 \pm 0.22$
$\text{NpO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{NpO}_2\text{CO}_3(\text{aq})$	$9.32 \pm 0.61$
$\text{NpO}_2^+ + \text{CO}_3^{2-} \leftrightarrow \text{NpO}_2(\text{CO}_3)^-$	$4.962 \pm 0.061$
$\text{NpO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{NpO}_2(\text{CO}_3)_2^{2-}$	$16.516 \pm 0.729$
$\text{NpO}_2(\text{CO}_3)^- + \text{CO}_3^{2-} \leftrightarrow \text{NpO}_2(\text{CO}_3)_2^{3-}$	$1.572 \pm 0.083$
$\text{Np}(\text{CO}_3)_5^{6-} + \text{e}^- \leftrightarrow \text{Np}(\text{CO}_3)_3^{3-} + 2\text{CO}_3^{2-}$	$-16.261 \pm 2.265$
$\text{NpO}_2(\text{CO}_3)_3^{5-} \leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{4-} + \text{e}^-$	$-5.72 \pm 0.095$
$\text{NpO}_2(\text{CO}_3)_2^{3-} + \text{CO}_3^{2-} \leftrightarrow \text{NpO}_2(\text{CO}_3)_3^{5-}$	$-1.034 \pm 0.11$
$\text{NpO}_2(\text{am,hyd}) + 4\text{CO}_3^{2-} + 2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{Np}(\text{CO}_3)_4^{4-} + 4\text{OH}^-$	$-17.79 \pm 0.22$
$\text{Np}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \leftrightarrow \text{Np}(\text{CO}_3)_5^{6-}$	$-1.07 \pm 0.3$
$3\text{NpO}_2(\text{CO}_3)_3^{4-} \leftrightarrow (\text{NpO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$	$-8.272 \pm 1.447$

of mixed Np(IV) hydroxo-carbonato species in alkaline carbonate-containing solutions [19,20].

### 3. RESULTS AND DISCUSSION

#### 3.1 Solubility and Chemical Speciation of Neptunium in the Granitic Groundwater of KURT

Anionic groundwater constituents are ubiquitous in natural groundwater. Tables 1 and 2 list the minor anionic ligands present in natural groundwater, including F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>. However, only the fluoride ions marginally affect neptunium speciation when the pH is less than 4.5, particularly where NpF<sub>2</sub><sup>2+</sup> is the predominant Np(IV) fluoride complex (74 %) at a pH of 4.0. Under reducing conditions and at a higher pH, NpF<sub>2</sub><sup>2+</sup> is suppressed by the strong hydrolysis reactions of Np(IV).

Fig. 1 shows the calculated solubility of Np(IV) in the YS-1 groundwater. The tetravalent neptunium complexes control the solubility of neptunium in the granitic groundwater condition of KURT. With data from the OECD-NEA TDB, the solubility of neptunium was calculated to be 2.75 × 10<sup>-9</sup> M in the YS-1-3 (pH = 10.71, E<sub>h</sub> = 63 mV) and 1.0 × 10<sup>-9</sup> M in the YS-1-4 (pH = 10.23, E<sub>h</sub> = -109 mV) and the YS-1-6 (pH = 9.93, E<sub>h</sub> = -142 mV). These values are very consistent with other calculated solubilities reported in the literature [13-16]. Beyond a pH level of 12, the solubility-limiting solid phase was transformed from NpO<sub>2</sub> (am,hyd) into Np<sub>2</sub>O<sub>5</sub>(cr) in the YS-1-3 groundwater. This transformation may be ascribed to the slightly oxidizing condition of the YS-1-3 groundwater, which allows the pentavalent neptunium species to become dominant. In a carbonate-containing solution, the solid Np(IV) hydroxo-carbonato complex, Np(OH)<sub>2</sub>(CO<sub>3</sub>)(s), is considered the most

thermodynamically stable solid phase. However, a concentration ratio of 10<sup>-9.4</sup> between Np(OH)<sub>2</sub>(CO<sub>3</sub>)(s) and Np(OH)<sub>4</sub> (am) was derived in a carbonate concentration range of 5 × 10<sup>-4</sup> M to 5 × 10<sup>-3</sup> M [22]. Therefore, Np(OH)<sub>4</sub> (am) is highly abundant and can consequently be considered a solubility-limiting phase for a carbonate concentration range of 3.1 × 10<sup>-5</sup> M to 1.3 × 10<sup>-3</sup> M in the YS-1 groundwater condition. As yet, however, there is no reliable thermodynamic and crystallographic data available for solid Np(IV) carbonate or hydroxo-carbonato ternary complexes [1].

Fig. 2 shows the chemical species distribution of neptunium in the YS-1 groundwater. The predominant species under the reducing condition is Np(OH)<sub>4</sub>(aq). At a pH level higher than that of the groundwater from the YS-1-3 sample, NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup> and NpO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> appear and help raise the solution's pH level. A Pourbaix diagram, which is shown pictorially in Fig. 3, was calculated for different groundwater conditions so that the change in solubility could be predicted for the various groundwater conditions. Initially the influence of the groundwater compositions on the distribution of the Np(IV) chemical

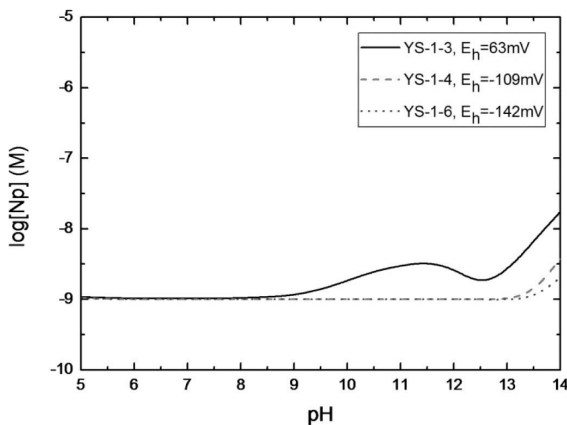


Fig. 1. Solubility Curves of Neptunium in the YS-1 Groundwater; the Calculations are Derived by Using PHREEQC 2.0 Based on the OECD-NEA TDB

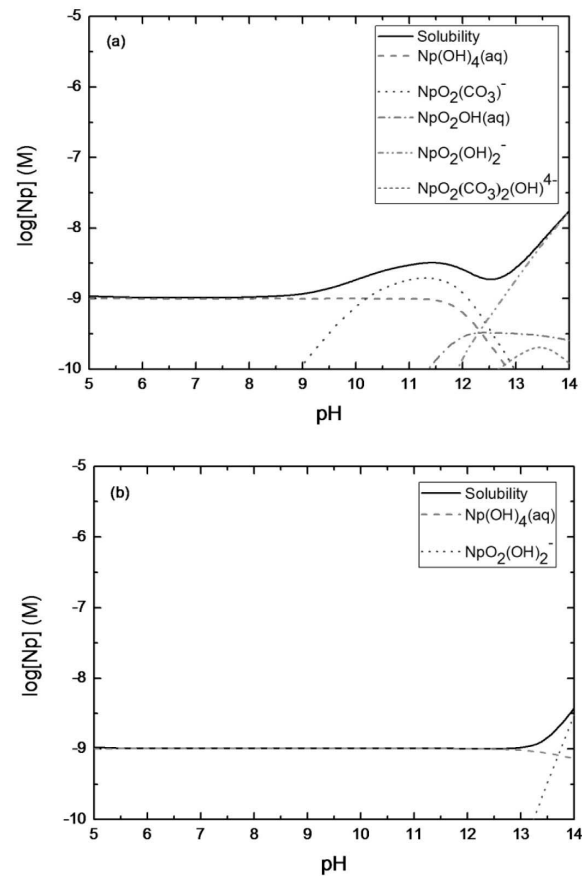


Fig. 2. Calculation of Soluble Neptunium Concentrations in the YS-1 Groundwater: (a) YS-1-3 and (b) YS-1-4

species can be neglected. Remarkably, the dominant species and its overriding pH- $E_h$  range are unchanged in the various groundwater compositions. However, the formation of the neptunium carbonate complexes varies slightly among the YS-1 groundwater samples, depending on the solution's pH and the total carbonate concentration.

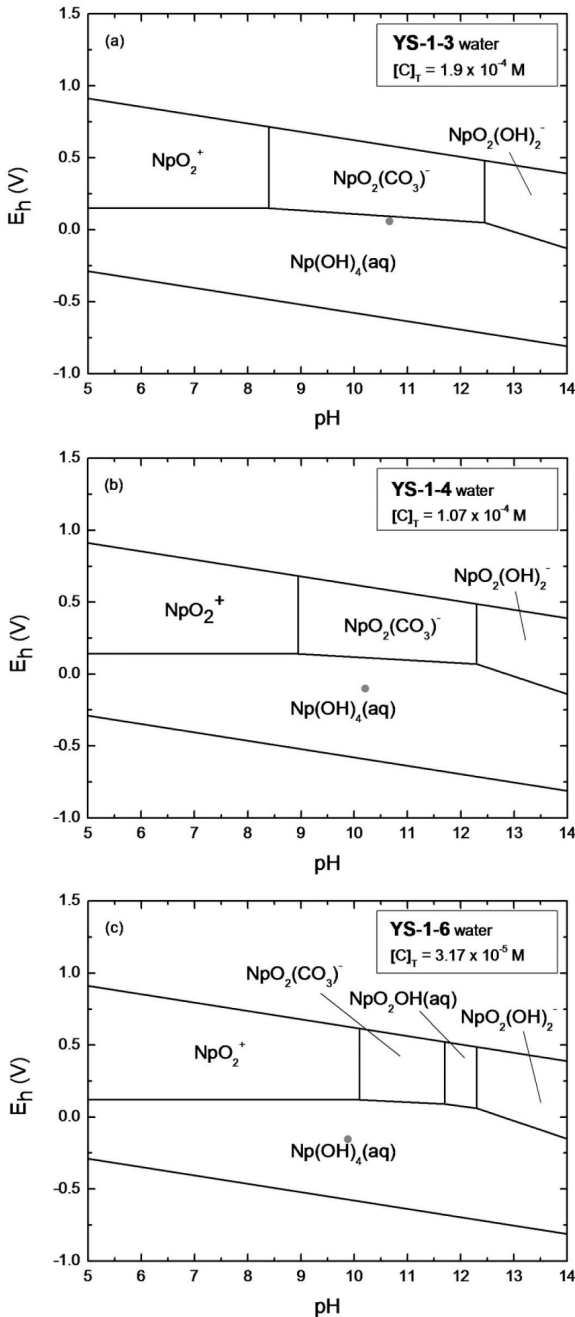


Fig. 3. Pourbaix ( $E_h$  -pH) Diagrams for Each Sample of the KURT Groundwater: (a) YS-1-3, (b) YS-1-4, and (c) YS-1-6 (closed circle)

The solubility curve was calculated as a function of the total carbonate concentration at a pH value of 9.93 to corroborate the carbonate effect on solubility. The total carbonate concentration influences the major species distribution of neptunium. As shown in Fig. 4, the solubility data differ from the total carbonate concentration and the redox potential of the groundwater. The notable influence of the carbonate effect on the solubility curve of neptunium shifts to a slightly higher carbonate concentration as the redox potential value decreases. The carbonate effect becomes pronounced when the total carbonate concentration is greater than  $2.5 \times 10^{-3}$  M at  $E_h = -100$  mV and greater than  $1.5 \times 10^{-2}$  M at  $E_h = -200$  mV. The total soluble neptunium concentration has an increasing tendency due to the carbonate complex formation of Np(V), particularly  $NpO_2(CO_3)_2^{3-}$  and  $NpO_2CO_3^-$ . However, the dominant soluble species is still  $Np(OH)_4(aq)$  when the total carbonate concentration remains lower than that of the Np(V) carbonate complexation.

### 3.2 Comparison of Solubilities by Measurements and Calculation

In the YS-1 groundwater, the total carbonate concentration is much lower the experimental value reported in the literature [19,21,22,26,27]. For the purpose of comparison between calculated and experimental solubility, the YS-1-7 groundwater, which has the highest carbonate concentration of all the groundwater samples, was used for the solubility calculation. The experimental solubility study was performed with YS-1-7 groundwater at a total carbonate concentration of about  $1.3 \times 10^{-3}$  M and a redox potential ( $E_h$ ) of -200 m [26]. Thus, a direct comparison was made between measured and calculated solubility by applying the YS-1-7 groundwater. The total carbonate concentration is defined and calculated

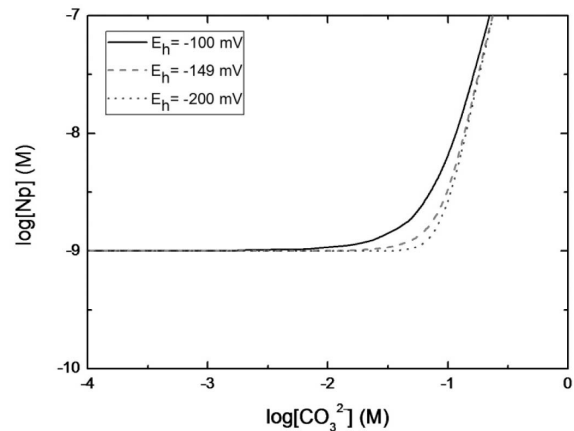


Fig. 4. Solubility Curves for  $Np(OH)_4(am)$  as a Function of the Total Carbonate Concentration at a pH Level of 9.93 and Different  $E_h$  Values

as follows [18]:

$$[C]_T = [HCO_3^-] + [CO_3^{2-}] \quad (2)$$

$$HCO_3^- = CO_3^{2-} + H^+ \quad \log K^\circ = -10.329.$$

Generally, it is difficult to perform a solubility experiment in the only tetravalent oxidation state of neptunium, particularly under conditions of a possible oxidizing geologic environment [20,22,28]. Accordingly, a reducing agent or potentiometer is used to control the  $E_h$  value throughout the experiments for the purpose of maintaining the redox environment. In the literature [20], there is a careful analysis of the effectiveness of  $NH_2OH \cdot HCl$ ,  $NH_2NH_2$ , and  $Na_2S_2O_4$  as reducing reagents, and the results reveal that  $Na_2S_2O_4$  is a highly effective reagent.

Various solubility experiments were carried out through under-saturation [20-22]. However, Kitamura and Kohara performed Np(IV) solubility experiments through both under-saturation and over-saturation methods in 2 M  $NaClO_4$  solution with a total carbonate concentration of 0.1 M and in the pH range of 9 to 13 [19]. Due to the high ionic strength of the solution, the experimental data shown in Fig. 5 were corrected to zero ionic strength according to the SIT (specific ion interaction theory). Eriksen and colleagues obtained solubility data from carbonate-containing solutions with a total carbonate concentration of  $C_T = 10^{-3} - 10^{-1}$  M in the pH range of 8.1 to 12.2 [21]. Pratopo et al. determined the solubility by evaporating an aliquot of filtrate in the carbonate concentration range of  $C_T = 5 \times 10^{-4}$  M to  $5 \times 10^{-3}$  M at pH of 8 to 12.5 [22]. Kim et al. performed the experiment with  $NpO_2$  powder put into the groundwater; the activity of  $^{237}Np$  in a filtered sample solution was measured at pH 9.5, 10.2, and 11.1 at a controlled  $E_h = -0.2$  V [26]. The calculation of solubility was made under the same groundwater conditions as those of YS-1-7 performed by Kim et al., based on the formation constants selected in OECD-NEA TDB. However, as can be seen in Fig. 5, the solubility values reported by Kim et al. [26] are higher than those calculated based on the OECD-NEA TDB. Moreover,

the wide range of scatters of the Np(IV) solubility data has been attributed particularly to the different carbonate concentrations (Fig. 5). This finding was confirmed by correction of the carbonate concentration (see Fig. 6(a)).

The formation constants of Np(IV) ternary complexes have not been selected in the OECD-NEA TDB because of the reasons stated earlier. Nevertheless, for a reasonable account of the experimentally measured solubility data from the literature, the formation of Np(IV) hydroxo-carbonato complexes needs to be considered. In contrast, spectroscopic investigations have been undertaken to ascertain the nature of Np(V) hydroxo-carbonato complexes, particularly  $NpO_2(OH)_y(CO_3)_z^{1-y-2z}$  [1,9,29]. In the case of Np(V) solubility, the calculated Np(V) solubility agrees well with the measured solubility [1]. In this study, we considered the equilibrium constants of  $Np(OH)_y(CO_3)_z^{4-y-2z}$  as reported in various studies for the PHREEQC 2.0 calculation of the soluble neptunium concentration. Table 5 lists the formation constants reported in the literature for Np(IV) hydroxo-carbonato complexes.

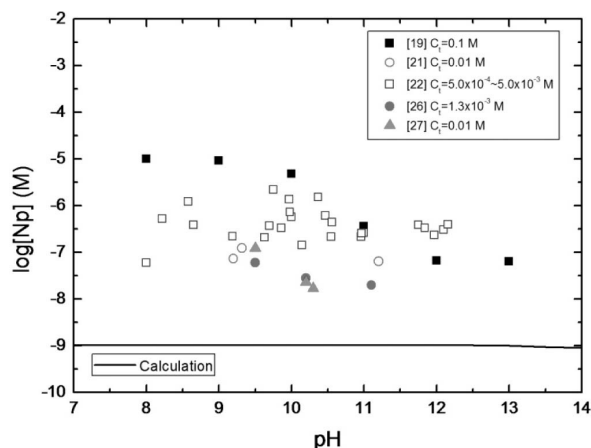


Fig. 5. Comparison of Solubility by Measurements with Calculation. Calculation was Performed Based on the Formation Constants Selected in OECD-NEA TDB

**Table 4.** The Reactions and the Formation Constants of  $NpO_2 \cdot xH_2O(am)$  and Carbonate/Bicarbonate Complexes

Reaction	$\log K^\circ$			
	[19]	[20]	[21]	[22]
$NpO_2 \cdot xH_2O(am) \leftrightarrow Np^{4+} + 4OH^- + (x-2)H_2O$	-56.7±0.5	-54.5 ± 0.3	-54.5 ± 0.3	-54.5 ± 0.3
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	-6.35	-	-6.381	-
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	-10.33	-	-10.377	-9.77

The calculation of the formation constants of neptunium was based on the equilibrium constants of  $\text{NpO}_2 \cdot x\text{H}_2\text{O}$  (am) in an aqueous carbonate system. Pratopo et al. determined the formation constants of  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  and  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  [22]. From a perspective analogous to that of the Pu(IV) experiment, they considered  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  as the dominant species at pH levels higher than 10. Using experimental data, Kitamura et al. [19] used nonlinear least-squares fitting for their numerical computations. For pH levels higher than 11,  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  and  $\text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$  were both considered for the calculation of the formation constants. Due to the high degree of uncertainty in the calculated formation constants, the contribution of  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  was neglected. However, Eriksen et al. considered only hydroxo-monocarbonato species [21]. Furthermore, in the experiment of Rai et al. [20],  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  was assumed, analogously to uranium, to be an aqueous hydroxo-carbonato species at a low bicarbonate concentration. Table 4 presents the equilibrium constants used to calculate the formation constants of the Np(IV) hydroxo-carbonato complexes in the literature.

The total soluble neptunium concentration was calculated by using the formation constants of the Np(IV) hydroxo-carbonato complexes listed in Table 5. However, when compared to the experimentally determined solubility data, the calculated solubility values of Np(IV) are largely underestimated and were not predicted even with the ternary Np(IV) formation constants reported in the literature. Therefore, the large degree of uncertainty surrounding the formation constants of  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$ ,  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$ ,  $\text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$ , and  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  must be appraised cautiously. In this study, “upper limits” of the formation constants of Np(IV) ternary complexes were calculated. The suggested dominant species are  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  or  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$  or both at a pH value of less than 10, and  $\text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$  or  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  or both at a pH value greater than 10. This suggests that the dominant species

are closely influenced by the fact that bicarbonate ions,  $\text{HCO}_3^-$ , are predominant for a pH value of less than 10 whereas carbonate ions,  $\text{CO}_3^{2-}$ , are more significant for a pH value greater than 10. The scattered neptunium solubility data from various experiments were obtained at different total carbonate concentrations and corrected to 0.01M total carbonate concentration. The solubility experiment of Pratopo et al. was performed at varied carbonate concentrations [22]: Kim et al. provided only the experimentally measured solubility [26]. Therefore, these two studies were not considered for the calculation of the formation constants of the Np(IV) ternary complexes in this study. The Boltzmann non-linear curve has been used to fit the solubility data from the various studies as the “upper limit” (Fig. 6(a)).

For the calculation of solubility when the pH is less than 10, either  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  or  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$  was selected. The task of experimentally differentiating the complexes  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  and  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$  is difficult. Therefore, for a pH value of less than 10, one hydroxo-carbonato species was selected for the calculation. In this study, the formation constant of  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$  was not included in the calculation because of its negligibly small contribution to the Np(IV) solubility and the large degree of uncertainty surrounding the formation [19]. The total concentration of the aqueous neptunium species relevant to conditions of natural groundwater was calculated by the following general expression for all possible hydroxide, carbonate, and hydroxide carbonate complexes:

$$[\text{Np}(\text{aq})]_{\text{T}} = [\text{Np}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z}] + [\text{NpO}_2(\text{OH})_y(\text{CO}_3)_z^{1-y-2z}]. \quad (3)$$

The formation constants of the Np(IV) hydroxo-carbonato species were calculated by fitting the experimental data,

**Table 5** The Reactions and the Formation Constants of the Np(IV) Hydroxo-Carbonato Complexes

Species	Reaction	log K°				
		[19]	[20]	[21]	[22] <sup>a</sup>	This study
$\text{Np}(\text{OH})_3(\text{CO}_3)^-$	$\text{Np}(\text{OH})_4(\text{am}) + \text{HCO}_3^- = \text{Np}(\text{OH})_3(\text{CO}_3)^- + \text{H}_2\text{O}$			-5.0		-5.0±0.5
$\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$	$\text{Np}(\text{OH})_4(\text{am}) + 2\text{HCO}_3^- = \text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-} + 2\text{H}_2\text{O}$	-3.0	-4.44		-0.35	-3.0±0.5
$\text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$	$\text{Np}(\text{OH})_4(\text{am}) + \text{CO}_3^{2-} = \text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$	-6.2		-5.23		-6.0±0.5
$\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$	$\text{Np}(\text{OH})_4(\text{am}) + 2\text{CO}_3^{2-} = \text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}$				-1.43	

<sup>a</sup> log K is estimated in 0.1 M  $\text{Na}_2\text{S}_2\text{O}_4$  solution. This value is not corrected to I=0 due to the lack of the ion interaction coefficients,  $\epsilon(\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}, \text{Na}^+)$  and  $\epsilon(\text{Np}(\text{OH})_4(\text{CO}_3)_2^{4-}, \text{Na}^+)$

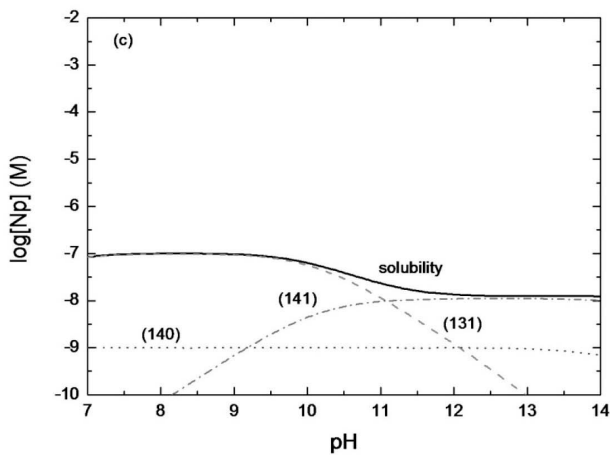
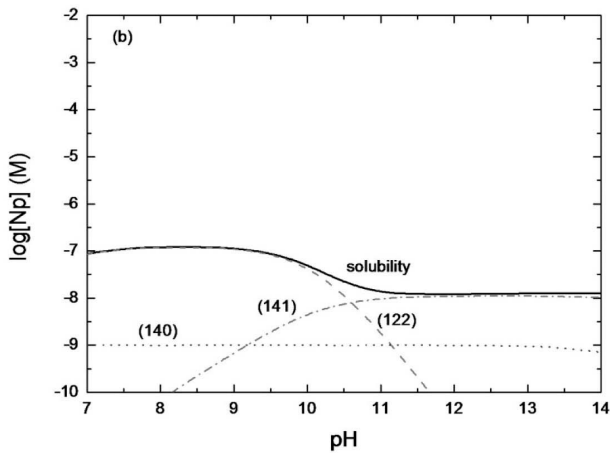
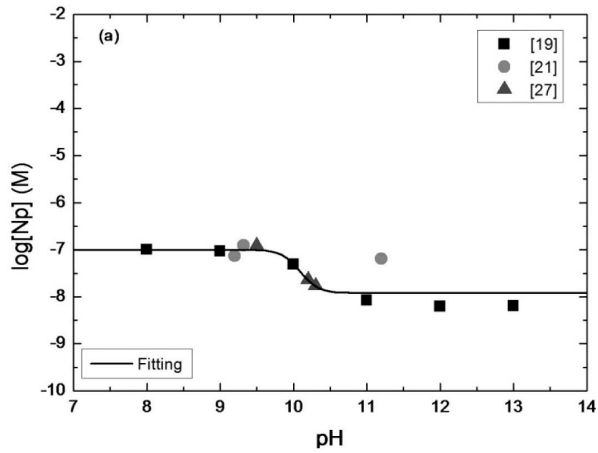


Fig. 6. Corrected Solubility Curve at  $C_T = 0.01M$  : (a) with Non-Linear Curve Fit as “Upper Limit”, (b) and (c) with Modified Formation Constants of the Np(IV) Hydroxo-Carbonato Complexes as “Upper Limit” and the Distribution of the Np(IV) Ternary Complexes

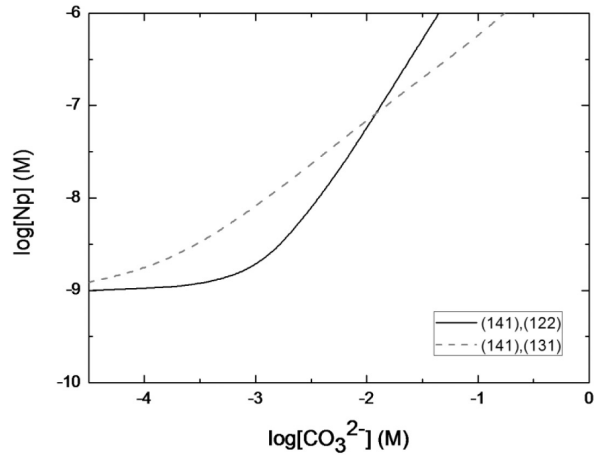
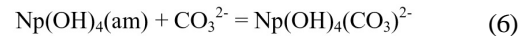
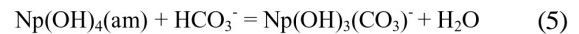
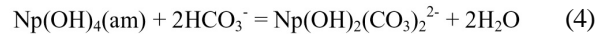


Fig. 7. Calculated Solubility Curves with the Modified Formation Constants of  $Np(OH)_y(CO_3)_z^{4-y-2z}$  as a Function of the Total Carbonate Concentration at a pH Level of 9.93

as shown in Fig. 6(a). The equilibrium reactions of  $Np(OH)_2(CO_3)_2^{2-}$ ,  $Np(OH)_3(CO_3)^-$ , and  $Np(OH)_4(CO_3)^{2-}$  are as follows:



The “upper limits” of the formation constants were estimated to be  $\log K_{122}^0 = -3.0 \pm 0.5$  for  $Np(OH)_2(CO_3)_2^{2-}$ ,  $\log K_{131}^0 = -5.0 \pm 0.5$  for  $Np(OH)_3(CO_3)^-$ , and  $\log K_{141}^0 = -6.0 \pm 0.5$  for  $Np(OH)_4(CO_3)^{2-}$ .

The solubility and the chemical species distribution are plotted in Figs. 6(b) and 6(c) with the modified equilibrium constants for the Np(IV) hydroxo-carbonato complexes at 0.01 M total carbonate concentration. Note that at a pH value less than 10.5,  $Np(OH)_2(CO_3)_2^{2-}$  or  $Np(OH)_3(CO_3)^-$  appears to be predominant, whereas  $Np(OH)_4CO_3^{2-}$  dominates at a pH value greater than 10.5.

As illustrated in Fig. 4, the effect of the carbonate ion on the Np(IV) solubility was recalculated as a function of the total carbonate concentration at a pH value of 9.93. The formation constants of the Np hydroxo-carbonato species modified in the work were taken into account for the prediction of the carbonate effect on the Np solubility. As shown in Fig. 7, the solubility steadily increases independently of  $E_h$  without any notable influence of the carbonate effect on the Np(IV) solubility. However, the solubility curve shows a large disparity depending on the species selection of



either  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  or  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$ .  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  is the dominant species at total carbonate concentration above  $1.3 \times 10^{-3}$  M and  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$  is the dominant at total carbonate concentration above  $1.4 \times 10^{-4}$  M. In summary, the solubility calculated with the modified  $K_{131}^0$  and  $K_{141}^0$  is mainly controlled by the species concentration of  $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  and  $\text{Np}(\text{OH})_3(\text{CO}_3)^-$ . The control is independent of the total carbonate concentration.

#### 4. CONCLUSION

This study investigated the solubility and aqueous species of Np in the natural granitic groundwater of KURT. The geochemical modeling program PHREEQC 2.0 was used to calculate the solubility of Np and to obtain a Pourbaix diagram for the different chemical conditions of groundwater sampled at different depths of the YS-1 borehole at KURT. The species distribution of Np(IV) in groundwater is not significantly affected by the groundwater composition. However, the pH range for the formation of the neptunium carbonate complexes differs in relation to the total carbonate concentration. The carbonate effect on the Np(IV) solubility is noticeable for carbonate concentrations greater than  $2.5 \times 10^{-3}$  M at  $E_h = -100$  mV and  $1.5 \times 10^{-2}$  M at  $E_h = -200$  mV. The solubility calculated with data from the OECD-NEA TDB is lower than the solubility values measured in various experiments. Thus, consideration of the ternary Np(IV) hydroxo-carbonate complexes is necessary for a consistent description of neptunium solubility. In the present work, the “upper limits” of the formation constants of  $\text{Np}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$  were estimated by fitting measured solubility data from the literature to the calculated solubility. Nonetheless, clear experimental evidence of the formation of the Np(IV) ternary hydroxo-carbonate complexes must be found in the future.

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