

# Review of Np(IV) in Aqueous Carbonate/Bicarbonate Solutions

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## Abstract

No reliable stability constant of Np(IV) soluble carbonate complexes is published. The experimental data are scarce. However the existing experimental information is consistent with the equilibrium constant data for the uranium system (Grenthe et al. 1992). This type of chemical analogy is used here to propose the stoichiometry of the Np(IV) complexes. Equilibrium constants are then estimated by interpreting published Np(V)/Np(IV) electrochemical and Np(IV) spectrophotometric measurements. It is proposed that f transition elements in the +4 oxidation state, M, form soluble complexes  $M(\text{CO}_3)_4^{4-}$  and  $M(\text{CO}_3)_5^{6-}$  with similar stability constants:  $\lg k_5^\circ = \lg \beta_5^\circ / \lg \beta_4^\circ = (-1.35 \pm 0.17)$  for Np,  $(-1.12 \pm 0.25)$  for U, and  $(-1.36 \pm 0.09)$  for Pu. Similar  $\lg k_5$  values are also consistent with some experimental observations in the Th and Ce(IV) carbonate/bicarbonate systems. However,  $\lg \beta_5^\circ = (38 \text{ to } 42) \pm 2$  for Np(IV) is higher than the value estimated from analogy  $(34.0 \pm 2.2)$ , and found for Th  $(32.3)$ , U  $(34.1 \pm 0.1)$ , and Pu  $(33.8 \pm 2)$ , but not for Am  $(40)$ . All the experimental information on Np(IV) in concentrated to diluted carbonate/bicarbonate media seem consistent with these proposed values. The possible formation of hydroxo-carbonate complexes is discussed, but the experimental data are not good enough to allow a unique interpretation. It is then confirmed that the most important Np(IV) complex is  $\text{Np}(\text{OH})_4^0$  in ground water systems. It is proposed that  $\text{Np}(\text{CO}_3)_4^{4-}$  might well be the only other important Np(IV) complex from quite concentrated to very diluted carbonate/bicarbonate aqueous solutions. This information can then be used to estimate Np solubility in many underground water systems.

## Introduction

$^{237}\text{Np}$  should make a significant contribution to the long term radiotoxicity of vitrified radioactive waste or spent nuclear fuel. Due to its chemical analogy with U and Pu, Np can certainly be reprocessed in the same way as U and Pu (for further transmutation); but  $^{237}\text{Np}$  will be produced from  $^{241}\text{Am}$  decay. Industrial reprocessing of Am is much more difficult if low waste production is also required. It then seems reasonable to consider the long term management of wastes containing  $^{237}\text{Np}$ , and their possible disposal in deep geologic media, where the chemical conditions are reducing, and the pH is close to neutral or alkaline. Neptunium is then expected to be in the +4 oxidation state, as Th and U, both of which should be good chemical and even geochemical analogues for Np(IV). Reliable thermodynamic data are needed to calculate the speciation that must be used to predict the solubility and transport properties of Np.

The chemistry of the carbonate systems is complicated by the fact, that the high pH of carbonate solutions results in competition between carbonate and hydroxide as ligands, and the possibility of formation of ternary complexes containing  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ligands. Experimental thermodynamic data on Np(IV) are scarce and often of moderate to low precision: the aqueous chemistry of Np(IV) in carbonate and bicarbonate media will be reviewed here. The consistency of literature information will first be checked. The stoichiometry of Np(IV) complexes in concentrated carbonate/bicarbonate aqueous solutions, will be proposed, and the corresponding formation constants will be estimated. This interpretation will provide a background for discussions of the properties at the lower carbonate concentrations typically found in ground water systems. In conclusion supplementary experimental measurements are suggested or described to check the proposed chemical model.

## 1. Methodology for reinterpretation of data

### 1.1. Activity coefficients

Details about the data and calculations are given elsewhere [9]. Activity coefficients are calculated by using the "SIT" method [10, 11]. We have re-evaluated [12] the values of the SIT parameters  $\varepsilon(\text{Na}^+, \text{HCO}_3^-)$  and  $\varepsilon(\text{Na}^+, \text{CO}_3^{2-})$ , which now are consistent with the new TDB values [11]. All equilibrium constants have been converted to the molality scale, as described in [5, 9, 12]; but all the numerical values given in the present work refer to the molar scale. The densities at high concentrations have been extrapolated, and the density for mixtures has been estimated using the approximation given in [5]; and no correction has been made for the change in water activity for reactions involving water as a reactant/product, such as  $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-$ . This induces only a small error at the highest (more than 1 M) concentrations. The concentration of cationic reactants can be neglected in the mass balance equations, but their activity must be used in the mass action law. pH is then calculated without further approximations.

### 1.2. Equilibrium constants

The notation K, K' and  $K^\circ$  in Table 1a are exemplified by  $K = [\text{Np}(\text{CO}_3)_4^{4-}] / ([\text{Np}^{4+}] [\text{CO}_3^{2-}]^4)$ ,  $K' = [\text{Np}(\text{CO}_3)_4^{4-}] / (a_{\text{Np}^{4+}} [\text{CO}_3^{2-}]^4)$ ,  $K^\circ = a_{\text{Np}(\text{CO}_3)_4^{4-}} / (a_{\text{Np}^{4+}} a_{\text{CO}_3^{2-}}^4)$ , where  $a_X$  and  $[X]$  denote the activity and concentration of X, respectively (in this example K was  $\beta_4$ ). The pH measurement usually depends also on the liquid junction potential and this correction is unknown in all published studies except [8]. This will result in a systematic error which may amount here to 0.1 pH unit. Using the SIT [10],  $\lg K^\circ = \lg K - \Delta z^2 D + \Delta \varepsilon m_{\text{Na}^+} + \Delta n \lg p$  (Table 2) where  $\Delta z^2 = 16, 0, 16$  for  $\beta_5, \beta'_5, k_5$ ,  $\Delta n = -5, -5, -1$  respectively,  $D = 0.5091 \sqrt{I} / (1 + 1.5 \sqrt{I})$ , p is the molal/molar ratio, and I the molal ionic strength.

#### 1.2.1. Redox studies

$E^\circ_{\text{V/IV}}$  is the formal potential of the  $\text{NpO}_2(\text{CO}_3)_3^{5-} / \text{Np}(\text{CO}_3)_5^{6-}$  couple recalculated at  $P_{\text{CO}_2} = 1 \text{ atm}$  from the measured potential of the Np(V)/Np(IV) carbonate solution, E (Table 1a), assuming that they were obtained at  $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ .  $E^\circ_{\text{V/IV}} = E - 0.414$ , where  $0.414 \text{ V} = 0.059_{16} \times 2 \times 3.5 (\lg P_{\text{CO}_2}(\text{atm}) = -3.5)$ . The value of  $\beta_5^\circ$

for Np(IV) (Table 2) is calculated from  $\beta'_5$  (Table 1a) and  $E^\circ_{V/IV}$ :  $\lg \beta'_{5IV} = \lg \beta'_{3V} - 2 \lg K'_p + (E^\circ_{V/IV} - E^\circ_{5/4})/0.05916$ , where the formation constant of the limiting complex of Np(IV) is  $\beta'_{5IV} = [\text{Np}(\text{CO}_3)_5^{6-}]/([\text{CO}_3^{2-}]^5 a_{\text{Np}^{4+}})$ , the Np(V) one is  $\beta'_{3V} = [\text{NpO}_2(\text{CO}_3)_3^{5-}]/([\text{CO}_3^{2-}]^3 a_{\text{NpO}_2^+})$ ,  $K'_p = a_{\text{H}^+}^2 [\text{CO}_3^{2-}]/(\text{P}_{\text{CO}_2} a_{\text{H}_2\text{O}})$ ,  $E^\circ_{5/4}$  is the standard ( $I=0$ ) potential of the  $\text{NpO}_2^+/\text{Np}^{4+}$  redox couple.

For Pu(IV) (Table 2)  $\lg \beta_{5IV} = \lg(\beta_{3VI} K_{\text{disV}}/K_{\text{P}^2}) + (E_{V/IV} - E_{\text{PuO}_2^{2+}/\text{Pu}^{4+}})/0.02958$ , where  $K_{\text{disV}} = [\text{PuO}_2(\text{CO}_3)_3^{4-}][\text{Pu}(\text{CO}_3)_5^{6-}]/([\text{PuO}_2(\text{CO}_3)_3^{5-}]^2 \text{P}_{\text{CO}_2})$  is deduced from our spectrophotometric study [18] of the disproportionation of Pu(V), our similar measurements in acidic media allowed us to calculate  $E_{\text{PuO}_2^{2+}/\text{Pu}^{4+}}$  as described in [18, 26, 27].  $E_{V/IV}$  was recalculated [27] from our data obtained by cyclic voltametry [18].

### 1.2.2. Spectrophotometric studies

Spectrophotometric measurements give (table 2) reliable  $k_5$  values and its variations with  $I$  for U [10], Np [8], Pu [5]. The equilibrium constant  $\beta_4$  is then calculated according to  $\beta_5 = k_5 \beta_4$ .  $\beta_4$  values are quite similar both for U(IV) and Pu(IV) in 3 M  $\text{NaClO}_4$ , and we then also estimate for Np(IV):  $\beta_4^{\text{Np}} \approx \sqrt{\beta_4^{\text{U}} \beta_4^{\text{Pu}}}$  (using  $\beta_5^{\text{Np}} \approx \sqrt{\beta_5^{\text{U}} \beta_5^{\text{Pu}}}$  and  $\beta_5 = k_5 \beta_4$ , gives similar numerical values).

### 1.2.3. Solubility studies

Assuming that the solid phase is  $\text{NpO}_2(\text{s})$  or  $\text{Np}(\text{OH})_4(\text{s})$ , and that the predominating soluble complex is  $\text{Np}_k(\text{CO}_3)_j(\text{OH})_i^{4k-2i-j-}$ , we have  $\lg S \approx k \lg K_s + \lg(k \beta_{ijk}) + i X_d$  where  $S$  is the Np(IV) solubility,  $X_d = \lg[\text{CO}_3^{2-}] - d \lg[\text{OH}^-]$  and  $d = (4k - j)/i$ . To discuss the published interpretations of solubility data, we then plot  $\lg S$  versus  $X_d$  for two values of  $d$  (figures 3).

## 2. Electrochemical preparation of Np(IV)

The way to prepare Np(IV) in concentrated carbonate/bicarbonate solutions, is well known [1], and the result has been controlled using spectrophotometry. However, in less concentrated carbonate media unwanted reoxidation or precipitation of Np(IV) is suspected [2].

Electrochemical preparations have been used [6, 13, 14] in concentrated carbonate solutions. The reductions of Np(V) in concentrated carbonate media must be made by using a very negative potential (-1.8 V/SHE) using a Hg electrode (and not a platinum one as in [7], where water, but not Np(V) was reduced). After electrolysis, it was observed [6, 14] that the redox potential of the solution was never stable enough to allow an accurate determination. The experimental procedure used in [16, 3, 4] probably led to the unwanted, uncontrolled and non reversible formation of Np(IV) hydroxide, that precipitates to give particles, or colloids, which may be difficult to detect. We explain these difficulties as follows : at -1.8 V/SHE water is slowly reduced even on Hg electrodes, this generates  $\text{OH}^-$  and Np(IV) can finally precipitate. The pH should therefore be measured at the end of the electrolysis, and it must not be too high. The best way to prepare a concentrated Np(IV) solution in alkaline media, is then to use mixtures of concentrated (more than 0.3 M)  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions as a buffer during the reduction. The optimal conditions for this preparation are deduced from equilibrium data of the Table 1a. We checked this experimental procedure [8]. This is already known for the preparation of Am(IV) carbonate solutions [15].

The equilibrium constants of the Table 1a are consistent with the experimental observations reported in ref.[14], and with our interpretation: due to  $\text{OH}^-$  production during the electrolysis, the limiting carbonate complex of Np(IV) is transformed into  $\text{Np}(\text{OH})_4^0$  and then the solubility is dramatically decreased. We checked this interpretation experimentally [8].

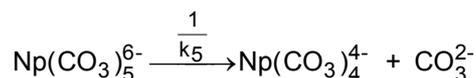
## 3. Spectrophotometry

All the published spectra [1, 7, 13, 16] of Np(IV) in concentrated carbonate/bicarbonate media (figure 2) are similar, but very different from that of the  $\text{Np}^{4+}$  aquo ion. This is evidence of the formation of carbonate complexes, which also explains the high solubility of Np(IV) in these solutions. In reference [7], one new Np(IV) spectrum is shown in a bicarbonate solution. This was not discussed in the paper and might not be consistent with reference [13]. Small differences in pH conditions typically due to water reduction in [13], might explain the contradiction between the two experimental observations. Our experimental observations [8] are consistent with those in reference [7] and not in [13]: in 1 M  $\text{NaHCO}_3$  solution, the Np(IV) spectrum is not exactly the same as in carbonate media. Spectrophotometry has been used to study the stability of the limiting complex of U [10, 17] and Pu [5, 18], and to determine the stoichiometry of the complex resulting of this dissociation reaction. We then interpreted the new spectrum in reference [7] as an evidence of the analogue reaction for Np, and we have estimated (Table 1a) the corresponding dissociation constant of the limiting complex,  $\frac{1}{k_5}$ .

We checked experimentally this estimation [8] with the same experimental methodology as for Pu [5, 18].  $\text{Na}_2\text{CO}_3$  is titrated with  $\text{CO}_2$  gas in the chemical domain shown on the figure 1. The dissociation of the limiting complex is interpreted with the loss of one  $\text{CO}_3^{2-}$ , and there is no evidence of any polymerisation or hydrolysis reaction over 3 pH units [5, 8]:



this is consistent with



The equilibrium constant,  $k_5$ , and the various activity coefficients are then calculated (Table 1a) and are found to be similar to those of U and Pu (Table 2).

Spectrophotometric techniques could also be used in (more than 0.3 M)  $\text{CO}_3^{2-}/\text{OH}^-$  aqueous solutions to check, if increasing the concentration of  $\text{OH}^-$  results in the transformation of  $\text{Np}(\text{CO}_3)_5^{6-}$  into  $\text{Np}(\text{OH})_4^0$ , and if mixed hydroxo-carbonate complexes are formed, or not. No such qualitative data are available in the literature.

#### 4. Solubility

$\text{M}_6\text{Np}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$  phases (here  $\text{M}=\text{NH}_4, \text{Na}, \text{K}, [\text{C}(\text{NH}_2)_3]_6\text{...}$ ) may control the solubility of Np(IV) in concentrated  $\text{M}_2\text{CO}_3$  solutions, and solubility measurements using this phase might then give information on the stoichiometry of the limiting complex and possibly its dissociation constant  $k_5$ . However no such data have been published. The experimental results of Moskvina in  $(\text{NH}_4)_2\text{CO}_3$  media [1] may probably be affected by the slow precipitation of this type of solid phases.

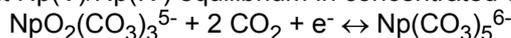
In solutions of low carbonate concentration, at most 0.01 M, prepared from NaOH and  $\text{NaHCO}_3$  [2], the  $\text{Np}(\text{OH})_{4(s)}$  solubility was found to be constant (less than 1 nM, i.e. close to the detection limit of  $^{237}\text{Np}$ ), and somewhat higher than the solubility of U(IV) and Pu(IV) under the same conditions. This is interpreted [2] with the  $\text{Np}(\text{OH})_{4(s)} \leftrightarrow \text{Np}(\text{OH})_4^0$  equilibrium, with no evidence of any other soluble complex. As shown by the authors [2], the results may be disturbed by the formation of Np(V). To avoid this, strong reductants were used: they might reduce water which induces Np(III) precipitation (Np(III) solubility is probably lower than the detection limit); but since Np(III) is probably unstable in neutral aqueous solution toward reoxidation into Np(IV), finally the interpretation and the methodology of the authors [2] was certainly correct; but additional experiments of the solubility of Np(IV) in near neutral solutions containing less than 0.01 M carbonate, and with improved detection limit for Np are needed to be able to check the  $\text{Np}(\text{OH})_{4(s)}$  solubility, preferably by using undersaturation conditions, with  $\text{Np}(\text{OH})_{3(s)}$  as starting material.

Later solubility investigations [3, 4] have a much poorer quality than those reported in [2] and cannot be interpreted quantitatively in terms of a chemical model: if  $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$  [1, 4] or  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{2-}$  [4] were predominated, that is  $d = 0$  (see § Methodology), all the experimental points should fall on the same line, c.f. Figure 3a. If instead the complexes  $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$  [4] or  $\text{Np}(\text{CO}_3)_4^{4-}$  were formed,  $d = 1$  (Figure 3b). The scattering in these later experimental results [3, 4] may be due to formation of colloidal  $\text{Np}(\text{OH})_4(s)$  which may pass through the filters used to separate the two phases. Similar problems are well-known in the corresponding Pu(IV) system.

The formation of  $\text{Np}(\text{CO}_3)_4^{4-}$  and its large stability constant (Table 1a) explains the very steep increase (Figures 3) of the Np(IV) solubility, when  $[\text{CO}_3^{2-}]$  is increased just above the values used by Rai and Ryan [2] (Figure 1). For this reason,  $\text{Np}(\text{OH})_4^0$  and  $\text{Np}(\text{CO}_3)_4^{4-}$  might well be the only two major complexes needed to interpret published solubility data, or to predict the Np(IV) solubility in most ground-waters.

#### 5. Redox equilibria

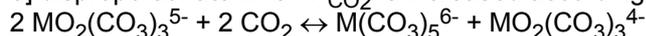
We assume that the predominant Np(V)/Np(IV) equilibrium in concentrated carbonate media is



It depends on the partial pressure of  $\text{CO}_2$ ,  $P_{\text{CO}_2}$ , which may vary from its equilibrium value, less than  $10^{-6}$  atm, to the value in the air,  $10^{-3.5}$  atm. Such a change in  $P_{\text{CO}_2}$  may result in a change of the redox potential of the solution with 360 mV. In our opinion this explains why it was difficult to prepare Np(IV) by reducing Np(V) in carbonate solution [14], and why it was difficult to measure the Np(V)/Np(IV) redox potential [6].

To check this interpretation, we have repeated [8] the redox measurements of Fedoseev and Peretrukhin [6], by using a platinum working electrode (the Hg cathode used for the electrolysis, must be completely removed). We obtained stable redox potentials,  $E^\circ_{\text{V/IV}}$ , for periods of up to several weeks at different temperatures [8].  $\beta_5$  is then estimated (Table 1a and 2) from  $E^\circ_{\text{V/IV}}$  [8]. This value of  $\beta_5$  for Np(IV) is higher than the expected one based on analogy with the other actinide(IV) complexes (Table 2); but our estimations cannot be accurate since  $P_{\text{CO}_2}$  was not properly controlled. More accurate measurements of the Np(V)/Np(IV) redox potential in carbonate/ bicarbonate should allow a check of the proposed stoichiometry of the limiting complex of Np(IV), and then a more accurate measurement of the equilibrium constant; but this experimental program is now stopped.

Pu(V) [18] and Am(V) [15, 19] disproportionate when  $P_{\text{CO}_2}$  is increased according to:



We have used this equilibrium for Pu at high ionic strength and  $\text{CO}_3^{2-}$  concentration [5, 18] to determine the equilibrium  $P_{\text{CO}_2}$  value, and then the  $\beta_5$  one (Table 2). It is not possible to study this equilibrium for Np.

Cyclic voltammetry of Am(III) in concentrated carbonate/bicarbonate solutions, is consistent with the exchange of two  $\text{CO}_3^{2-}$  [15, 11, 19]. Since the stability and stoichiometry of the Am(III) limiting complex,  $\text{Am}(\text{CO}_3)_3^{3-}$ , is well established, the stoichiometry and stability (table 2) of the limiting complex of Am(IV) are then deduced from:



For confirmation and better accuracy, these experiments should be repeated at different temperatures, with proper activity coefficient and junction potential control. This is also possible for Ce. These two results would certainly be the most reliable way to determine the stoichiometry of the limiting complex of f elements at the +4 oxidation state. This should confirm the chemical model for interpreting Np(IV) (and Pu(IV)) chemistry, assuming the analogy between the cations of the f element. It might even be possible to use this voltammetric technique in solutions of Np(IV) (and Pu(IV)) [6, 14], to check this analogy, and to measure the stability of the limiting complexes of Np(III) (and Pu(III)).

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**Table 1: Neptunium equilibria**

K' is the constant of the equilibrium, calculated in this review using concentration for anions, and activity for cations. Molar units are used for K and K'. K° is K and K' standard value, when nothing else is stated, K° is calculated in this review. E (V/SHE) is the formal potential (E° the standard one). For I corrections, we use the SIT and we assume that  $\varepsilon(M(\text{CO}_3)_4^{4-}, \text{Na}^+) = -0.09$  (M= U, Np, Pu, Am)  $\pm 0.2$ , or  $\pm 0.1$  for U. Contact with the air is assumed (where it is indicated) when the authors do not give enough information for speciation calculations, this assumption can shift the calculation of the formation constant by up to several orders of magnitude (see text) when interpreting redox measurements (see the note<sup>c</sup>).

**Table 1a: Possible equilibria**

Ref.	lg K	lg K'	lg K°	Medium (for K and K')
<b><math>\beta_4: \text{Np}^{4+} + 4 \text{CO}_3^{2-} \leftrightarrow \text{Np}(\text{CO}_3)_4^{4-}</math></b>				
[8]			39.0 $\pm$ 2.4	lg( $\beta_5^\circ / k_5^\circ$ )
			35.4 $\pm$ 2.6	lg( $\beta_5^\circ / k_5^\circ$ ) estimated from U and Pu analogy
[2]	< 38.5	< 38.4*	< 38.4*	0.01 M (HCO <sub>3</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup> ), Na
[3]	41.1 $\pm$ 1.4		39*	NaHCO <sub>3</sub> , in contact with the air
<b><math>k_5: \text{Np}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \leftrightarrow \text{Np}(\text{CO}_3)_5^{6-}</math></b>				
[8]			-0.98 $\pm$ 0.20	Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> media extrapolated to I = 0
[8]**			-1.35 $\pm$ 0.17**	Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> media extrapolated to I = 0
[7]		<1.3 <sup>a</sup> $\pm$ 0.5 <sup>a</sup>	<-1.4 <sub>5</sub> <sup>a</sup>	0.2 M Na <sub>2</sub> CO <sub>3</sub> , pH 10.8?
[8]	1.47 $\pm$ 0.08		-0.99	0.4 M Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
[8]	1.63 $\pm$ 0.05		-1.00	0.6 M Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
[8]	1.80 $\pm$ 0.04		-0.92	0.8 M Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
[8]	1.79 $\pm$ 0.10		-1.02	1.0 M Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
[8]	2.21 $\pm$ 0.03		-0.61	1.2 M Na <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
<b><math>\beta_5: \text{Np}^{4+} + 5 \text{CO}_3^{2-} \leftrightarrow \text{Np}(\text{CO}_3)_5^{6-}</math></b>				
[8]			38 <sup>b</sup> $\pm$ 2	Na <sub>2</sub> CO <sub>3</sub> media extrapolated to I = 0
			34.0 $\pm$ 2.2 = 0.5 lg( $\beta_5^{\text{U}} \beta_5^{\text{Pu}}$ ) at I = 0	
[2]	< 41.6	< 40.7*	< 40.7*	0.01 M (HCO <sub>3</sub> <sup>-</sup> + CO <sub>3</sub> <sup>2-</sup> ), Na
[8]			40.8 <sup>c</sup> $\pm$ (-1.0)	Na <sub>2</sub> CO <sub>3</sub> media extrapolated to I = 0
[8]		43.4 <sup>c</sup> (+0.5)	42.4 <sup>c</sup> (+1.0)	0.3 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air (or not)
[8]		44.6 <sup>c</sup> (+0.05)	43.2 <sup>c</sup> (+1.1)	0.6 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air (or not)
[6]		41.7 <sup>ab</sup> $\pm$ 3	40.0 <sup>ab</sup> $\pm$ 3.7	1 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air (or not) <sup>b</sup>
[8]		43.9 <sup>c</sup> (-1.8)	42.1 <sup>c</sup> (-0.1)	1 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air (or not)
[8]		43.8 <sup>c</sup> (+3)	41.6 <sup>c</sup> (+5.6)	1.5 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air (or not)
Ref	E	E*	$\Delta S$ (J/mol/K)	Medium (for E)
<b><math>\text{Np(V)/Np(IV)} \text{ redox potential: } \text{NpO}_2(\text{CO}_3)_3^{5-} + 2 \text{CO}_2 + e^- \leftrightarrow \text{Np}(\text{CO}_3)_5^{6-}</math></b>				
[8]		0.124 $\pm$ 0.06		I = 0, in contact with the air
[8]	0.46 $\pm$ 0,05		-272 $\pm$ 50	$\Delta\varepsilon = -0.03_5$ , P <sub>CO<sub>2</sub></sub> =1 atm
[8]		0.553 <sup>bc</sup> (-0.029)		
[8]	0.247			0.3 M Na <sub>2</sub> CO <sub>3</sub> , pH 10.22, in contact with the air
[8]	0.234		-133	0.6 M Na <sub>2</sub> CO <sub>3</sub> , pH = 10.28 in contact with the air
[6]	0.1 $\pm$ 0.2*			1 M Na <sub>2</sub> CO <sub>3</sub> , in contact with the air
[8]	0.244		-169	1 M Na <sub>2</sub> CO <sub>3</sub> , pH = 10.10 in contact with the air
[8]	0.228		-136	1.5 M Na <sub>2</sub> CO <sub>3</sub> , pH = 11.54 in contact with the air
<b><math>\text{Np(IV)/Np(III)} \text{ redox potential: } \text{Np}(\text{CO}_3)_5^{6-} + e^- \leftrightarrow \text{Np}(\text{CO}_3)_3^{3-} + 2 \text{CO}_3^{2-}</math></b>				
[6]	-1.32 $\pm$ 0.1			1 M K <sub>2</sub> CO <sub>3</sub>
[14]	-1.3 $\pm$ 0.1			1 M K <sub>2</sub> CO <sub>3</sub>
[14]	-1.2 $\pm$ 0.1			2 M Na <sub>2</sub> CO <sub>3</sub>

**Table 1b: No evidence of the following complexes**

Ref	lg K	*lg K'	Conditions
<b><math>Np^{4+} + 2 OH^- + 2 CO_3^{2-} \leftrightarrow Np(OH)_2(CO_3)_2^{2-}</math></b>			
[2]		< 42*	0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
[4]	45.69±0.44		0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
<b><math>Np^{4+} + 4 OH^- + CO_3^{2-} \leftrightarrow Np(OH)_4CO_3^{2-}</math></b>			
[1]	53.04 <sub>5</sub> ±0.01 <sub>5</sub>		0.15 to 2.2 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
[2]		< 46*	0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
[4]	53.05±0.02		0.1 to 2.2 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
<b><math>Np^{4+} + 4 OH^- + 2 CO_3^{2-} \leftrightarrow Np(OH)_4(CO_3)_2^{4-}</math></b>			
[2]		< 48*	0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
[4]	53.07±0.44		0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
<b><math>Np^{4+} + 3 CO_3^{2-} \leftrightarrow Np(CO_3)_3^{2-}</math></b>			
[2]	< 33,2	< 36*	0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na
[3]	37±1.2		NaOH, in contact the with air
<b><math>Np^{4+} + 6 CO_3^{2-} \leftrightarrow Np(CO_3)_6^{8-}</math></b>			
[2]		< 42*	0.01 M (HCO <sub>3</sub> + CO <sub>3</sub> ), Na

\* Recalculated or estimated in this review or in reference [5]. We therefore slightly change some of our previous preliminary values [8] (see \*\*).

\*\* Best re-evaluated value and not a mean of those deduced from different treatment of the same experimental data (see\*).

<sup>a</sup> Calculated or estimated in this review: the authors do not give this qualitative interpretation of their results.

<sup>b</sup> Questionable value or interpretation: the Np(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> stability seems to be overestimated.

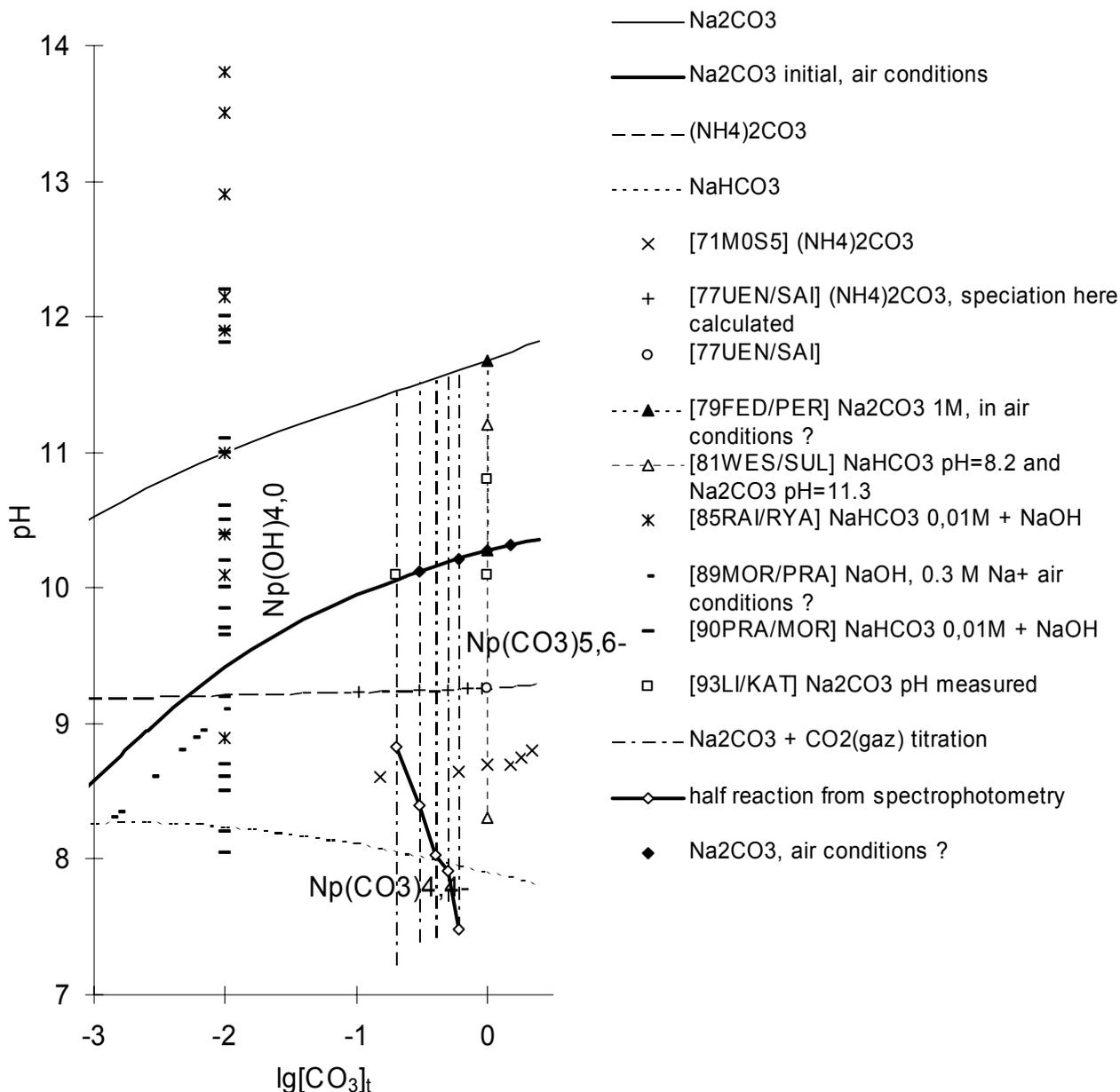
<sup>c</sup> Value calculated assuming equilibration with the air (see<sup>b</sup>), the number in parenthesis is the difference between this value and the one using the P<sub>CO<sub>2</sub></sub> calculated in [8] from pH (questionable) measurements.

**Table 2: Comparison of actinide complexation constants**

The smaller lgβ<sub>5</sub> (≈21 to 26) values for Th [21, 22] and Ce have been re-evaluated [23], to more consistent ones. Th and Ce published experimental data [24] are in qualitative agreement with U, Np and Pu k<sub>5</sub> values, and with the existence of M(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> (M = Ce or Th) as the M(IV) carbonate limiting complex, even if questionable M(CO<sub>3</sub>)<sub>6</sub><sup>8-</sup> is proposed [24], and used later [25]. Available data induce to make the comparison in 3 M NaClO<sub>4</sub> medium. A critical review suggests that the values of k<sub>5</sub> are reliable for U, Np Pu; but that the β<sub>5</sub> value is reliable only for U and Pu. See table 1 for notations and notes.

M	Ref	lg K (and not K')	lg K°	Δε	ε(Na <sup>+</sup> , M(CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup> )	
<b>β<sub>5</sub>: M<sup>4+</sup> + 5 CO<sub>3</sub><sup>2-</sup> ↔ M(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> in 3 M NaClO<sub>4</sub></b>						
Th	[21]		32.3			
U	[10]	36.86±0.55	34.1±0.10	-0.66±0.22	-0.30±0.15	
Np	[6] <sup>a</sup>	42.6±3.1	40 <sup>a</sup> ±3.7 <sup>a</sup>			
Np	[8]	41.4*±2.5	38±2	-0.89	-0.47±0.2	
Np	[8] <sup>*</sup>	42.7*±2	40.8*±4	-0.39*±0.2	0.03±0.2	
Np		36.3±2	0.5 lg(β <sub>5</sub> <sup>U</sup> β <sub>5</sub> <sup>Pu</sup> )	-0.57±0.4	-0.18±0.4	(U Np Pu analogy)
Pu	[5]	35.8±1.3	33.8*±2	-0.48*±0.2	-0.06±0.22	
Am	[19]		40±2		calculated from [15] <sup>a</sup>	
<b>k<sub>5</sub>: M(CO<sub>3</sub>)<sub>4</sub><sup>4-</sup> + CO<sub>3</sub><sup>2-</sup> ↔ M(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup></b>						
U	[10]	3.34±0.2	-1.12±0.25	-0.13±0.11	-0.30±0.15	
Np	[8]		-0.98±0.20	0.44±0.05	0.27*±0.21	
Np	[8] <sup>**</sup>	2.9±1.3	-1.35**±0.17	-0.06**±0.36	-0.23**±0.41	
Pu	[18]		-1.0±0.2	0.9±0.1	0.73*±0.21	
Pu	[5]	2.25±0.29	-1.36**±0.09	0.11**±0.08	-0.06**±0.22	

## Figures

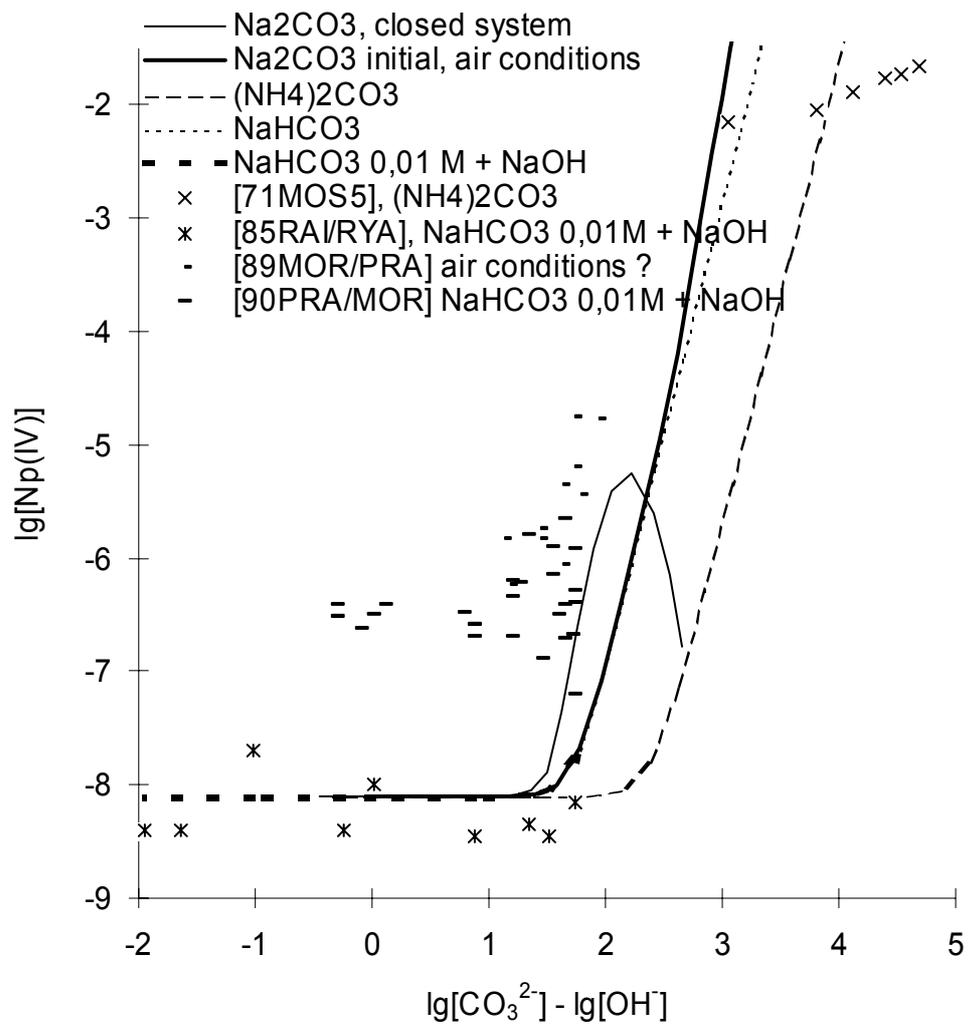


**Figure 1: Experimental conditions**

[85RAI/RYA] means publication by Rai and Ryan in 1985, i.e. reference [2], see the reference list for the other ones. In concentrated media (around 1 M and more) variations in the activity coefficients cannot be neglected: in this region, one point of the figure does not represent exactly the same chemical activity in  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions. The name of each complex is written in a region, where it predominates. Theoretical speciation in  $\text{Na}_2\text{CO}_3$  aqueous solutions, is calculated assuming either no exchange with the air or equilibration with the air ( $P_{\text{CO}_2} = 10^{-3.5}\text{atm}$ ) since these solutions are not buffered.

**Figure 2: Np(IV) spectra**

Spectra are superimposed around 700 nm; non linearity in the original publication, when photocopying or scanning it, might explain some shifting far from 700 nm wavelength. [93LI/KAT] means Li, Kato et col. 1993 reference, see the reference list for the other ones. The increase of the base line in [71MOS5] spectrum is due to precipitation (this is also a solubility study). The limiting complex is partly dissociated in 0.2 M  $\text{Na}_2\text{CO}_3$  [93LI/KAT], and the pure dissociated complex is obtained in 0.2 M  $\text{Na}_2\text{CO}_3$  solution [95DEL/VIT] titrated with  $\text{CO}_2$  gas, while the limiting one is still obtained in 0.6 M  $\text{Na}_2\text{CO}_3$  solution [95DEL/VIT]. The spectrum of the limiting complex is also shown [81WES/SUL] in 1 M  $\text{NaHCO}_3$  solution; but this was not confirmed later [95DEL/VIT].



### Figures 3: Np(IV) solubility

Solubility is calculated (line) with the numerical values of table 1a. Solubility was measured in various chemical conditions (figure 1) The shifts between calculated curves of figure 3b are mostly due to activity coefficients, and to  $\text{Np}(\text{CO}_3)_5^{6-}$  formation. Figure 3a tests the formation of  $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$  [1, 4] or  $\text{Np}(\text{OH})_4(\text{CO}_3)_2^{2-}$  [4], while figure 3b tests the formation of  $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$  [4] or  $\text{Np}(\text{CO}_3)_4^{4-}$ . It is concluded that none of these models is satisfactory (see text).  $\text{M}_6\text{Np}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$  (here  $\text{M} = \text{Na}$  or  $\text{NH}_4$ ) and other evolving solid phases certainly limit the Np(IV) solubility in [1] and [16].