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Solubility of the redox-sensitive radionuclides ^{99}Tc and ^{237}Np under reducing conditions in neutral to alkaline solutions. Effect of carbonate

Trygve E Eriksen[1], Pierre Ndalamba[1], Daqing Cui[1], Jordi Bruno[2], Marco Caceci[2], Kastriot Spahiu[2]

[1] Dept. of Nuclear Chemistry, Royal Institute of Technology, Stockholm, Sweden
[2] MBT Tecnologia Ambiental, Cerdanyola, Spain

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SVENSK KÄRNBRÄNSLEHANTERING AB
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO
BOX 5864 S-102 48 STOCKHOLM
TEL 08-665 28 00 TELEX 13108 SKB S
TELEFAX 08-661 57 19

SOLUBILITY OF THE REDOX-SENSITIVE RADIONUCLIDES ^{99}TC AND ^{237}NP UNDER REDUCING CONDITIONS IN NEUTRAL TO ALKALINE SOLUTIONS. EFFECT OF CARBONATE

Trygve E Eriksen[1], Pierre Ndalamba[1], Daqing Cui[1], Jordi Bruno[2], Marco Caceci[2], Kastriot Spahiu[2]

1 Dept. of Nuclear Chemistry, Royal Institute of Technology, Stockholm, Sweden
2 MBT Tecnologia Ambiental, Cerdanyola, Spain

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Trygve E Eriksen, Pierre Ndalamba, Daqing Cui
Dept. of Nuclear Chemistry. Royal Institute of Technology, S-100 44, Stockholm (Sweden)
Jordi Bruno, Marco Caceci and Kastriot Spahiu
MBT Tecnologia Ambiental, Parc Tecnològic del Vallés, E-08290, Cerdanyola (Spain)

1 Abstract

We have studied the solubility of Tc(IV) and Np(IV) hydrous oxides in aqueous solution as a function of pH and carbonate concentration. The solid phases used were prepared by electro-reduction and precipitation on platinum electrodes.
The experimental data are explained by the following equilibria and equilibrium constants,

Equilibrium	log K
Hydrolytic equilibria	
$TcO_2 \cdot nH_2O(s) = TcO(OH)_2(aq)$	-8.17 ± 0.05
$TcO_2 \cdot nH_2O(s) = TcO(OH)_3^-$	-19.06 ± 0.24
$Np(OH)_4(s) = Np(OH)_4(aq)$	-8.28 ± 0.23
$Np(OH)_4(s) = NpO_2^+ + e^- + 2H_2O$	-9.40 ± 0.5
Carbonate complexes	
$TcO_2 \cdot nH_2O(s) + CO_2(g) = Tc(OH)_2CO_3(aq)$	-7.09 ± 0.08
$TcO_2 \cdot nH_2O(s) + CO_2(g) = Tc(OH)_3CO_3^-$	-15.35 ± 0.07
$Np(OH)_4(aq) + CO_3^{2-} = Np(OH)_4CO_3^{2-}$	3.00 ± 0.12
$Np(OH)_4(aq) + HCO_3^{2-} = Np(OH)_3CO_3^-$	3.23 ± 0.12

The implications on the speciation and mobility of Tc(IV) and Np(IV) in groundwater , as well as those of U(IV) and Pu(IV), are discussed.

Abstract (Swedish)

Lösligheten av Tc(IV) och Np(IV) i alkaliska karbonatfria och karbonathaltiga vattenlösningar har studerats. De fasta faserna preparerades genom elektrokemisk reduktion och utfällning på platinaelektroder.
Modellering av de experimentella resultaten till hydrolys och bildning av karbonatkomplex ger följande jämvikter och jämviktskonstanter :

Jämvikter	log K
$TcO_2\ nH_2O(s) = TcO(OH)_2(aq)$	-8.17 ± 0.05
$TcO_2\ nH_2O(s) = TcO(OH)_3^-$	-19.06 ± 0.24
$Np(OH)_4(s) = Np(OH)_4(aq)$	-8.28 ± 0.23
$Np(OH)_4(s) = NpO_2^+ + e^- + 2H_2O$	-9.40 ± 0.50
$TcO_2\ nH_2O(s) + CO_2(g) = Tc(OH)_2CO_3(aq)$	-7.09 ± 0.08
$TcO_2\ nH_2O(s) + CO_2(g) = Tc(OH)_3CO_3^-$	-15.35 ± 0.07
$Np(OH)_4(aq) + CO_3^{2-} = Np(OH)_4CO_3^{2-}$	3.00 ± 0.12
$Np(OH)_4(aq) + HCO_3^{2-} = Np(OH)_3CO_3^-$	3.23 ± 0.12

Jämvikternas inverkan på speciering och mobilitet av Tc(IV), Np(IV) samt V(IV) och Pu(IV) i naturliga vatten diskuteras.

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Dept. of Nuclear Chemistry. Royal Institute of Technology, S-100 44, Stockholm (Sweden)
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1. INTRODUCTION

The fission product ^{99}Tc and the actinide ^{237}Np constitute a potential long term environmental hazard due to their long half-lives and abundance in nuclear wastes. The assessment of the release and migration of such redox-sensitive radionuclides from a nuclear waste repository is complicated as their solubility, speciation, and consequently sorption behaviour is dependent on the redox state. Under the reducing conditions expected to prevail in a deep bedrock repository, the solubility of these nuclides is controlled by the precipitation of the tetravalent hydrous oxides $NpO_2 \cdot n\ H_2O$ (=$Np(OH)_4(s)$) and $TcO_2 \cdot n\ H_2O$ (=$Tc(OH)_4(s)$). In oxic granitic groundwaters the solubility of these elements is largely increased as technetium and neptunium are oxidized to NpO_2^+ and TcO_4^- respectively . Therefore, the determination of the redox cycling and predominant speciation of these nuclides under granitic groundwater conditions is critical to assess the long term safety of HLW repositories.

The solubility of technetium in a deep bedrock repository for spent fuel has recently been discussed by Lemire and Garisto [1]. Most of the data used in their calculations had to be inferred, due to lack of experimentally determined thermodynamic data. Whereas there is strong evidence for the nature of hydrolyzed Tc(IV) species in aqueous solution at pH<5 [2] less is known about the hydrolyzed species in neutral and alkaline solutions (pH ranges of most natural waters). Meyer et al [3-6] have carried out extensive studies on the solubility of precipitated and electrodeposited Tc(IV) oxide. The concentration of dissolved Tc(IV) in neutral to basic solution was found to be

in the range 10^{-9}-10^{-8} mol·dm^{-3}, with a slight increase above pH= 8.5. Meyer et al [5,6] explained their data by taking into account the formation of the neutral aqueous species $TcO(OH)_2(aq)$. However, they speculated about the possible formation of anionic complexes, to explain the slight increase of solubility with pH. According to Vikis et al [7] the solubility of Tc(IV) hydrous oxide increases by approximately one order of magnitude per pH unit above pH=8.5. It is not clear if these results are in agreement with the data of Meyer et al. as the latter results are from experiments carried out at pH<9.7

The solubility of Np(IV) hydrous oxide has recently been reported by Rai and Ryan [8] to be pH independent and less than $5\cdot10^{-9}$ mol·dm^{-3} in neutral to very basic solution. Ewart et al [9] report an invariant Np(IV) concentration of $8\cdot10^{-9}$ mol·dm^{-3} in cement suspensions in the pH range 10-13. Pratopo et al. [10] determined the solubility of $Np(OH)_4(s)$ to be approximately $3\cdot10^{-9}$ mol·dm^{-3} in the pH range 8.5-12.5. These authors also found that the solubility of $Np(OH)_4(s)$ was larger below pH 8 due to the formation of NpO_2^+.

There is a fair agreement about the solubility behaviour of $Np(OH)_4(s)$ and the formation of Np(IV) hydroxo species. However, there is a large uncertainty concerning the critical redox reaction, and its corresponding redox equilibrium constant:

$$NpO_2.nH_2O = NpO_2^+ + e^- + n\ H_2O. \qquad (1)$$

$$K_{redox} = [NpO_2^+]/\{e^-\} \qquad (2)$$

Rai et al [11] report a value of log K_{redox} = -8.2 ± 0.12 based on the measurements of the equilibrium concentration of NpO_2^+ over $NpO_2\cdot nH_2O$ in acid solutions (pH 0.2-2.4), and in the presence of Cu(I)/Cu(II) as redox buffer. Moriyama et al [12] report log K_{redox} = - 6.7±0.4 at pH<6. But the experimental methodology and data treatment used by these authors are extremely doubtful.
Based on thermodynamic cycles Fuger and Oetting [13] estimate log $K_{4/5}$ = -10.9 ± 1.2 for the reaction

$$NpO_2^+ + e^- + 4\ H^+ = Np^{4+} + 2\ H_2O \qquad (3)$$

with

$$K_{4/5}=[Np^{4+}]/[NpO_2^+][H^+]^4\{e^-\} \qquad (4)$$

By combining this with the constant for the reaction

$$Np(OH)_4(s) + 4\ H^+ = Np^{4+} + 4\ H_2O \qquad (5)$$

$$K_{s0} = [Np^{4+}]/[H^+]^4 \qquad (6)$$

reported by Rai et al [8] to be log K_{s0} = 1.5 ± 0.3, we obtain log K_{redox} = -9.4 ± 1.2 for the $NpO_2^+/NpO_2 \cdot nH_2O$ equilibrium.
Carbonate is one of the most abundant ligands in granitic groundwaters As all O-containing ligands it has a strong tendency to form aqueous complexes with hard cations as Tc(IV) and the actinides in general. This will affect their speciation and consequently their redox cycling, solubility and sorption properties.
In some exploratory experiments, Paquette et al [14] and Paquette and Lawrence [15] reported that precipitation of $TcO_2 \cdot nH_2O$ is prevented in solutions with the ratio $[CO_3^{2-}]_{tot}/[Tc(IV)]_{tot} > 30$.
Meyer et al [3] measured the overall concentration of Tc(IV) in equilibrium with $TcO_2 \cdot nH_2O$ to be $1.8 \cdot 10^{-8}$ mol·dm^{-3} in 10^{-2} mol·dm^{-3} carbonate solution at pH 9.6. Lemire and Garisto [1] briefly discussed carbonato complexes and, on the basis of Meyer's results, assumed the formation of $Tc(OH)(CO_3)^{3-}$ in neutral, carbonate containing solutions. However, the Tc(IV) concentrations measured by Meyer et al [3] are at least two orders of magnitude lower than the ones calculated using the equilibrium constants given by Lemire and Garisto.
Nevertheless,it has been previously established that cations that have a strong tendency to hydrolyze, like Tc(IV) and Np(IV), build stable mixed hydroxo-carbonato complexes which may dominate the speciation of these metal ions in carbonate waters [16].
The carbonate complexation of Np(IV) has been discussed in several publications [12,17,18] . Moskvin [17] studied Np(IV)-carbonate complexation in 0.15-2.2 mol·dm^{-3} $(NH_4)_2CO_3$ solutions and reported the stability constant for the formation of the complex $Np(OH)_4CO_3^{2-}$ to be log β_{141} = 53.1, for the reaction:

$$Np^{4+} + 4\ OH^- + CO_3^{2-} = Np(OH)_4CO_3^{2-} \qquad (7)$$

This result has been questioned by Rai and Ryan [8], who in their study of the Np(IV) hydrous oxide under reducing conditions (0.05 mol·dm^{-3} $Na_2S_2O_4$) observed no increase in solubility on addition of 10^{-2} mol·dm^{-3} total carbonate in the pH range 6-14.2.
On the other hand, Moriyama et al [12] observed a sharp increase in Np(IV) concentration on air saturation of their solutions and interpreted their data by taking into the account the formation of $Np(CO_3)_3^{2-}$ and $Np(CO_3)_4^{4-}$ complexes with formation constants of the same order as reported for Pu(IV). In a later work the same authors [18] studied the solubility of Np(IV) in $5\cdot10^{-4}$-$5\cdot10^{-3}$ mol·dm^{-3} carbonate solutions in the pH range 8-12.5. They explained their highly scattered experimental data by assuming the following equilibria:

$$Np(OH)_4(am) + 2\ HCO_3^- = Np(OH)_2(CO_3)_2^{2-} + 2\ H_2O$$

with $\log K_1 = -0.35 \pm 0.33$

and

$$Np(OH)_4(am) + 2\ CO_3^{2-} = Np(OH)_4(CO_3)_2^{4-}$$

with $\log K_2 = -1.43 \pm 0.33$

There is, as we pointed out, a considerable scatter in their experimental data and their modeling and conclusions are highly questionable.
The purpose of the present work is to study the solubility of Tc(IV) and Np(IV) hydrous oxides as a function of pH, pe and carbonate concentration and thereby establish the stability of the hydroxo and hydroxo-carbonato complexes which predominate in neutral to alkaline pH range. This is achieved by using an experimental technique developed at the Nuclear Chemistry Department of KTH, which allows the precipitation of the M(IV) oxides under well controlled conditions. This electrodeposition technique simulates the precipitation of the fresh hydrous metal(IV) oxides at the redox transition. This is a situation very likely to be encountered when the potential oxidizing waters transporting the nuclides will mix with the undisturbed reducing groundwaters.
The thermodynamic information obtained will be used to discuss the redox cycling of Tc and Np and the implications for the mobility of Tc(IV) and Np(IV) under nuclear wastes repository conditions.

2. EXPERIMENTAL

2.1 Materials

The experiments were carried out at ambient temperature in a controlled atmosphere box flushed with argon to minimize the oxidation of Tc(IV) and Np(IV).

All chemicals used were of analytical grade. The water used was deionized, triple distilled in quartz and purged with argon (AGA 5.7 quality) containing less than 0.5 ppm oxygen.

The pH measurements were made with a Radiometer model pHM84 pH meter and a GK2321 combined glass/reference electrode and the redox potentials were monitored with a Metrohm Pt electrode and a saturated calomel electrode or a Yokogawa SR 20/AR 24 (Ag/AgCl) reference electrode connected to a Metrohm 632 pH meter. The electrodes were standardized using saturated quinhydrone buffers at pH 4 and 7.

^{99}Tc was purchased from Amersham as TcO_4^- in 0.1 mol·dm^{-3} NH_4OH aqueous solution. A stock solution of ^{237}Np was obtained by dissolving 2.8 mg $^{237}NpO_2$(cr) in 4 cm^3 concentrated HNO_3 solution.

TcO_4^- and Np(V) solutions were prepared by diluting aliquots of the stock solutions.

Hydrous Tc(IV) and Np(IV) oxides were prepared by electro-reduction and precipitation on platinum electrodes [19]. The reduction potential was controlled by an IM-K5 potentiostat.

Solution samples were analyzed for ^{99}Tc and ^{237}Np respectively in a Beckman model 5801 Liquid scintillation system using Ready Safe liquid scintillation cocktail (Beckman). The counter was calibrated with standard solutions containing known ^{99}Tc and ^{237}Np concentrations.

2.2 $TcO_2 \cdot nH_2O$ experiments

Solutions at the desired pCO_2 and pH were prepared with CO_2/N_2 mixtures. The total carbonate concentration was adjusted by adding appropriate amounts of Na_2CO_3. The gas mixtures were prepared and analyzed by AGA Special Gas.

The electroreduction was carried out in a $5 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ TcO_4^- solution. The reduction potential was - 250 mV relative to the saturated calomel electrode. A black solid phase was gradually formed on the electrode and the deposition was stopped after 5 hours. The electrode was thereafter carefully rinsed with distilled water and transferred to a vessel containing the solution to be studied.

In a typical experiment, the attainment of equilibrium was monitored as follows. After measuring the pH, 5 cm^3 samples were removed from the solution .The aliquots were added to equivalent volumes chloroform containing 0.1 $mol \cdot dm^{-3}$ tetraphenyl arsenium chloride. The organic phase removes TcO_4^- quite efficiently leaving the Tc(IV)-species in the aqueous phase. The TcO_4^- / Tc(IV) ratio was less than 20 and two to three consecutive extractions were carried out to assure complete removal of TcO_4^- from the aqueous phase. After each extraction 0.5 cm^3 samples were drawn from each phase and analyzed for ^{99}Tc .Solution samples were taken daily until constant ^{99}Tc concentration within the counting statistics was obtained. At this point, solubility equilibrium was assumed to prevail.

2.3 $NpO_2 \cdot nH_2O$ experiments

Solutions containing 10^{-4} - 10^{-5} $mol \cdot dm^{-3}$ $^{237}Np(V)$ were prepared by diluting aliquots of the stock solution in argon purged water.

The pH was adjusted to 6 and Np(IV) oxide prepared by electroreduction and precipitation on a platinum electrode. The electrode was kept at approximately -500 mV relative to the saturated calomel electrode. A dark solid phase was gradually formed on the Pt-electrode and the reduction was stopped after approximately 12 hours.

The electrode was thereafter carefully rinsed with distilled water and transferred to a vessel containing the solution to be studied. 2 cm^3 samples of the solution were drawn through a 0.1 µm preconditioned Anotec filter, acidified to 1 $mol \cdot dm^{-3}$ HCl and mixed with equal volumes of a 0.5 $mol \cdot dm^{-3}$

solution of 2-theonyltrifluoroacetone (TLA) in xylene [11]. The phases were analyzed for ^{237}Np as previously described.
The experiments were carried out in a closed system (no gas flushing through the solutions) in order to avoid loss of carbon dioxide. The hydrogen ion concentration was changed by small additions of oxygen and carbonate free stock solutions of $HClO_4$ or NaOH. The total carbonate concentration was changed by addition of small volumes of oxygen free solutions of $NaHCO_3$ or Na_2CO_3. The attainment of equilibrium was monitored in a similar way as it has been described for the Tc(IV) system. The equilibration time was normally 3-4 days.
The NpO_2^+ / $NpO_2 \cdot nH_2O$ redox-experiments were carried out in 0.5 $mol \cdot dm^{-3}$ $NaClO_4$ solutions containing low concentrations of non-interfering redox buffers ($S_2O_4^{2-}/SO_3^{2-}$;$S_4O_6^{2-}/S_2O_3^{2-}$). The hydrogen ion concentration was changed by adding small volumes of oxygen-free $HClO_4$ or NaOH solutions. The redox potentials were measured by using Pt-electrodes and saturated calomel or Ag/AgCl as reference electrodes.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The analysis of the experimental results , given in Tables 1A-5A in Appendix, is divided into three parts. The solubility data obtained in carbonate free solutions are discussed first. Secondly, the redox data are evaluated and discussed. Finally, the data obtained in carbonate solutions is analyzed.

3.1 Solubility data in carbonate-free solutions

3.1.1 $TcO_2 \cdot nH_2O$

The data (Table 1A) are shown in a log[Tc(IV)] *vs* pH plot in Figure 1. The solubility of $TcO_2.nH_2O$ is pH independent in the range 6<pH<9.5. This is in agreement with previous findings and can be explained by the equilibrium:

$$TcO_2 \cdot nH_2O = TcO(OH)_2(aq) + (n-1)H_2O \qquad (9)$$

$$\text{with} \quad \log K_{s1} = \log[TcO(OH)_2(aq)] = -8.22 \pm 0.06 \qquad (10)$$

In the pH range 9.5-12, the solubility of $TcO_2 \cdot nH_2O$ increases with pH. In the pH range 11-12, the log[Tc(IV)] *vs* pH function is linear with a slope of 1.01 ± 0.02. This indicates the formation of predominant aqueous complexes with charge -1 [20]. It may be safely assumed that only mononuclear

complexes are formed at such low concentrations. In this case, the solubility data in the pH range 11-12 may be explained by the equilibrium:

$$TcO_2 \cdot nH_2O(s) = TcO(OH)_3^- + H^+ + (n-2)\ H_2O \qquad (11)$$

and the equilibrium constant

$$K_{s2} = [TcO(OH)_3^-][H^+]. \qquad (12)$$

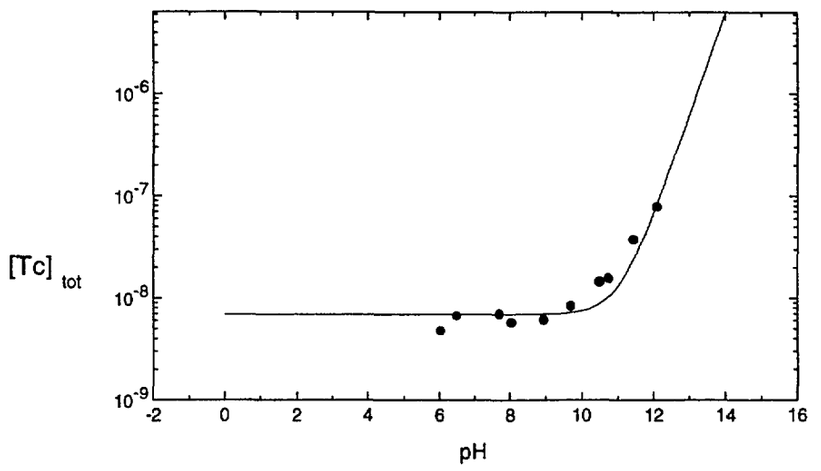

Fig 1 Plot of log [Tc(IV)] vs pH for carbonate free solutions. The solid line has been calculated using the constants log K_{s1} = - 8.16 and log K_{s2} = - 19.2 for the formation of $TcO(OH)_2(aq)$ and $TcO(OH)_3^-$ respectively.

The total concentration of Tc(IV) in equilibrium with $TcO_2 \cdot nH_2O$ in the entire pH range studied is thus given by the equation

$$[Tc(IV)]_{tot} = K_{s1} + K_{s2}/[H^+] \qquad (13)$$

Linear regression of the experimental data to equation (13) gives log K_{s1} = -8.16 ± 0.06 and log K_{s2} = -19.2 ± 0.3 . The errors are given as one standard deviation of the best linear fit.

3.1.2 $NpO_2 \cdot nH_2O$

The data obtained in carbonate free solution (Table 2A) are depicted in a log [Np(IV)] *vs.* pH plot in Figure 2.

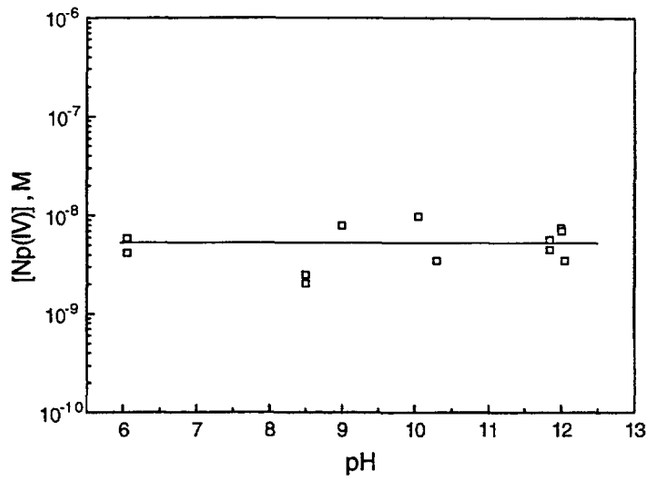

Fig. 2 Np(IV) concentration in aqueous solution equilibrated with $Np(OH)_4(s)$ plotted vs. pH.

The plot clearly demonstrates that the solubility of $NpO_2 \cdot nH_2O$ is invariant in the pH range 6-12.3, which is in agreement with previous findings [8-10]. The solubility data can be explained by assuming the following equilibrium reaction:

$$Np(OH)_4(s) = Np(OH)_4(aq) \qquad (14)$$

with $\log K_s = \log [Np(OH)_4(aq)] = -8.28 \pm 0.23$

The hydrolysis formation constants for $Np(OH)_4(aq)$ may be obtained by combining equations 5 and 14. We obtain in this way the formation constant $\log \beta_{14} = -9.8$ for the reaction:

$$Np^{4+} + 4\ H_2O = Np(OH)_4(aq) + 4\ H^+ \qquad (15)$$

Previous estimates by Allard et al [22] from linear free energy relationships are in good agreement with this experimental determination.

The solubility data from experiments carried out at various pH and pe are given in Table 3A. In neutral to moderately alkaline solutions the neptunyl cation NpO_2^+ is the predominant Np(V) species. Consequently, the Np(V) concentration in aqueous solution equilibrated with $Np(OH)_4(s)$ is determined by the redox reaction:

$$Np(OH)_4(s) = NpO_2^+ + e^- + 2\ H_2O \qquad (16)$$

In more alkaline solutions the hydrolysis of NpO_2^+ must be considered. The solubility of the Np(V) hydroxide $NpO_2(OH)(s)$ and the Np(V) hydrolysis have been extensively studied [13,23-31]. There is, however, considerable scatter in the published solubility and hydrolysis constants. In a recent publication Neck et al [30] reported the following formation constants in 0.5 mol·dm^{-3} $NaClO_4$ solution.

$$[NpO_2(OH)]/[NpO_2^+][OH^-] \qquad \log \beta_1 = 2.48 \qquad (17)$$

$$[NpO_2(OH)_2^-]/[NpO_2^+][OH^-]^2 \qquad \log \beta_2 = 4.1 \qquad (18)$$

The data in Table 3 are depicted in a log $[NpO_2^+]$ vs pe plot in Figure 3. Linear regression analysis give log K_{redox} = -9.35 ± 0.4.

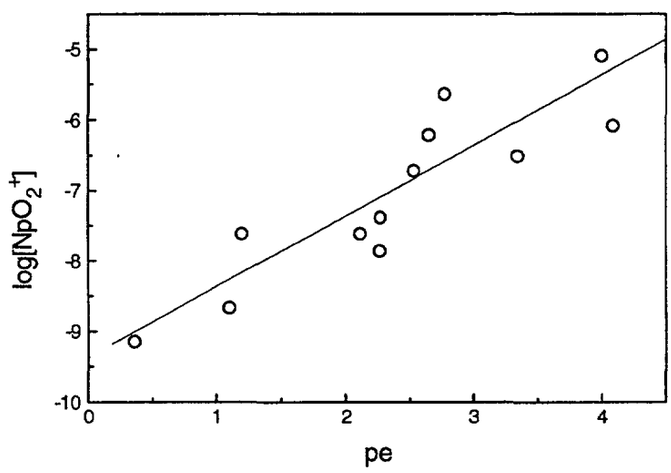

Fig. 3 Plot of the concentration of NpO_2^+ as a function of pe.

3.2 Carbonate Solutions

3.2.1 $TcO_2 \cdot nH_2O$

The solubility data obtained in solutions equilibrated with CO_2 at constant pCO_2 (Table 3) are displayed in a log[Tc(IV)] vs pH plot in Figure 3.The data obtained in carbonate free solutions are included for comparison.

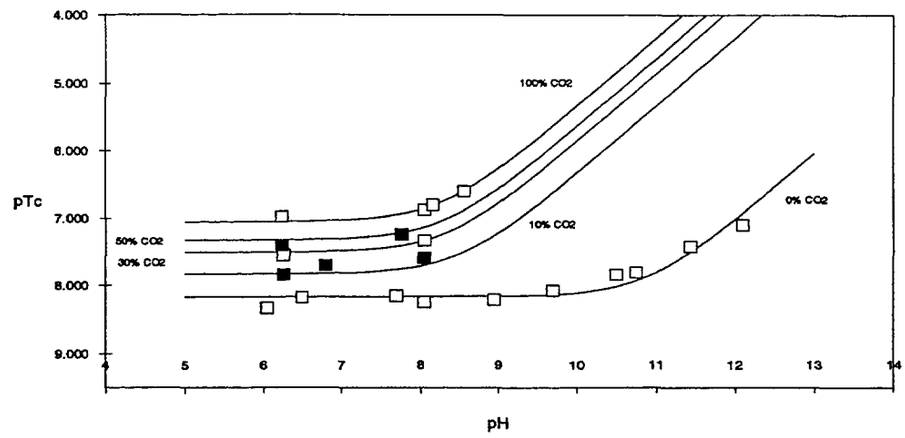

Fig. 4 Plot of -log[Tc(IV)] vs. pH for different pCO_2: 0%, 10%, 30%, 50%, 100% CO_2. The lines have been calculated using the speciation scheme and stability constants given in Table 1.

The plot clearly indicates a sizable effect of CO_2 on the solubility of $TcO_2{\cdot}nH_2O$. This suggests the formation of aqueous Tc(IV)-hydroxo-carbonato complexes that are responsible for the increase in solubility in carbonate containing solutions.

As has previously been shown, mixed hydroxo-carbonato complexes are normally the result of the addition of CO_2 groups to metal ion hydrolysis complexes [16,32].

Taking into account the predominant hydroxo complexes $TcO(OH)_2(aq)$ and $TcO(OH)_3^-$ the formation of mixed $Tc(OH)_2(CO_2)_{r1}(aq)$ and $TcO(OH)_3(CO_3)_{r2}^-$ (where $(OH)_2CO_2 = CO_3^{2-}$ and $(OH)CO_2 = HCO_3^-$) was tested.

The experimental data in Table 4A [Tc(IV)], pH, $p(CO_2)$ were checked against functions of the general type

$$[Tc(IV)]_{calc} = K_{s1r1}{\cdot}pr1(CO_2) + K_{s2r2}{\cdot}pr2(CO_2) / [H^+] \qquad (18)$$

where K_{s1r1} and K_{s2r2} are the solubility constants for the general equilibria

$$TcO_2{\cdot}nH_2O(s) + r1CO_2 = TcO(OH)_2(CO_2)_{r1} + (n-1)\ H_2O \qquad (19)$$

with $K_{r1s1} = [TcO(OH)_2CO_2)_{r1}] / pr1(CO_2)$ (20)

and r1 equal to 1 or 2

$$TcO_2{\cdot}nH_2O(s) + r2CO_2 = TcO(OH)_3(CO_2)_{r2}^- + H^+ + (n-2)\ H_2O \qquad (21)$$

and r2 equal to to either 1, 2 or 3 and $K_{r2s2}=[TcO(OH)_3(CO_2)_{r2}^-][H+]/pr2\ (CO_2)$. The best fit of theoretical functions to experimental data was obtained for r1 = r2 = 1, log K_{s1} = -7.04 and log K_{s2} = -15.00.

Nonlinear least squares calculations were carried out on the complete solubility data set using a modified version of the SIMPLEX algorithm, including jackknife and bootstrap capabilities [33]. In Table 1 the reactions and equilibrium constants obtained are compared with the results obtained by linear modelling .

The experimental and calculated solubilities are plotted in Figure 4. The standard deviation between the experimental and calculated solubilities is ± 0.08 logarithmic units. The residuals, depicted in Figure 5, are randomly (gaussian) distributed.

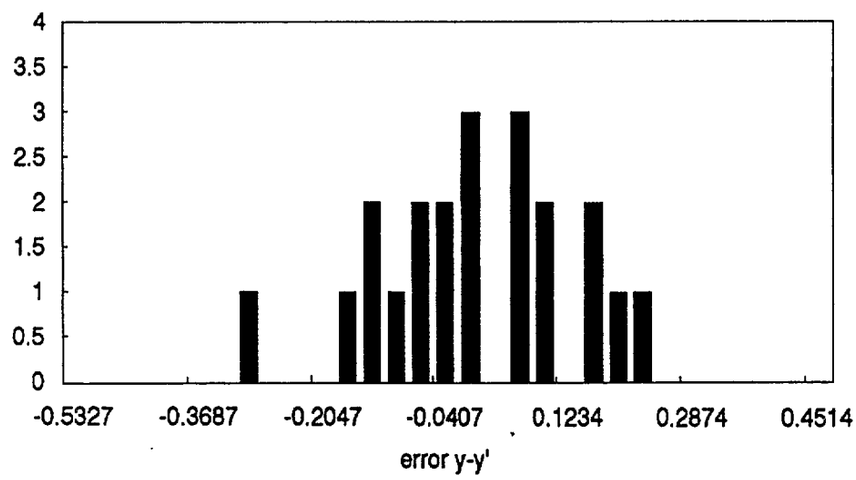

Fig. 5 Plot of residuals log [Tc(IV)]calc - log [Tc(IV)]exp calculated from the model proposed in this work. The plot clearly shows a gaussian distribution.

3.2.2 $NpO_2 \cdot nH_2O$

The carbonate experiments were carried out in 0.5 M $NaClO_4$ solutions containing low concentrations of $Na_2S_2O_4$ as redox buffer (the redox potential was kept » -630 mV vs. SCE). The solubility data obtained in carbonate solutions with total carbonate concentration 10^{-3} - 10^{-1} mol dm^{-3} in the pH range 8.1 - 12.2 are given in Table 5A.

The first and second dissociation constants for carbonic acid:

$$^*K_{a1} = \{H^+\}\{HCO_3^-\}/\{CO_2\} \quad (22) \qquad K_{a2} = \{H^+\}\{CO_3^{2-}\}/\{HCO_3^-\} \quad (23)$$

at 20°C and infinite dilution are, according to Stumm and Morgan [34].

$$\log {}^*K_{a1} = -6.381 \qquad \log K_{a2} = -10.377.$$

These values were recalculated at 0.5 M $NaClO_4$ using S.I.T. approach [35]. The density of $NaClO_4$ was taken from the Landolt-Börnstein compilation [36], the interaction coefficients from Biedermann et al [37], while the value of $K_H = a_{H2CO3^*} / P_{CO2}$ was calculated at 20 °C and 0.5 M ionic strength according to Edmond et al [38]. The concentrations of carbonate and bicarbonate ions at each experimental point have been calculated using the constants thus obtained.

Prapoto et al [18)] have evaluated the solubility product of the solid phase $Np(OH)_2(CO_3)(s)$, suggested by analogy with the corresponding solid of plutonium, and ruled out the possibility of its formation. The same applies to our experimental conditions. Furthermore, the plutonium solid was suggested by analogy with a thorium solid [39], which, according to a recent study by Östhols et al [40] of thorium oxide solubility in carbonate media, does not seem to be formed.

Owing to the very low concentration of Np(IV) in solution, only monomeric species were considered. In the pH interval under consideration the reacting species are $Np(OH)_4(aq)$, carbonate and bicarbonate, and we have therefore checked for carbonate addition complexes formed according to:

$$Np(OH)_4(aq) + n\ CO_3^{2-} = Np(OH)_4(CO_3)_n^{2n-} \qquad (24)$$

with generic constants:

$$K_n = [Np(OH)_4(CO_3)_n^{2n-}] / [Np(OH)_4][CO_3^{2-}] \quad (25)$$

and complexes formed by reactions with bicarbonate according to:

$$Np(OH)_4(aq) + m\ HCO_3^- = Np(OH)_{4-m}(CO_3)_m^{m-} + mH_2O \quad (26)$$

which can be written also with carbonate as the reacting species:

$$Np(OH)_4 + m\ CO_3^{2-} = Np(OH)_{4-m}(CO_3)_m^{m-} + m\ OH^- \quad (27)$$

with constants:

$$K_m = [Np(OH)_{4-m}(CO_3)_m^{m-}][OH^-]^m / [Np(OH)_4][CO_3^{2-}]^m \quad (28)$$

Reactions written with carbonate as the reactant were preferred since this simplified the treatment of data (see below). It is not possible to discriminate between bicarbonate complexes of the type $Np(OH)_{4-m}(HCO_3)_m$ or $Np(OH)_4(HCO_3)_n^{n-}$ and the corresponding carbonate complexes obtained by water elimination. At this pH range the formation of carbonate complexes only was assumed, following the arguments presented in [41].

Neptunium carbonate complexes may also form according to:

$$Np(OH)_4 + p\ CO_3^{2-} = Np(CO_3)_p^{4-2p} + 4\ OH^- \quad (29)$$

Thus the part of Np(IV) complexed by carbonate may be expressed:

$$[Np(IV)]_{tot} - [Np(OH)_4] = [Np(OH)_4]\ [CO_3^{2-}]\ \{K_{n=1} + K_{n=2}.[CO_3^{2-}] + \ +K_{m=1}[OH^-]^{-1} +K_{m=2}[CO_3^{2-}][OH^-]^{-2} + ...+K_{p=1}[OH^-]^{-4} + K_{p=2}\ [OH^-]^{-4}[CO_3^{2-}] +...\} \quad (30)$$

First, a graphical treatment of the data was performed:
In Figure 6 the left hand side of Eq. 14 is plotted against $[CO_3^{2-}]$ for the data obtained at pH = 9.2, where bicarbonate is the dominating carbonate species and at pH = 11.2, where carbonate dominates. The plot demonstrates the predomination of monocarbonate species with pH dependent formation constants.

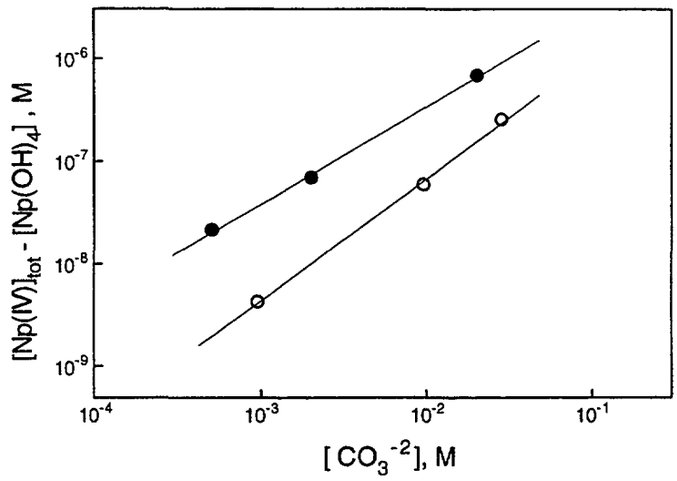

Fig. 6. The fraction of Np(IV) complexed by carbonate as a function of the carbonate concentration for data at pH = 9.2 (filled) and at pH = 11.2 (open circles).

In Figure 7 the function $F = \{ [Np(IV)]_{tot} - [Np(OH)_4] \}/[Np(OH)_4] [CO_3^{2-}]$ is plotted against $[OH]^{-1}$. As can be seen, the plot is linear, giving evidence for the formation of n=1 and m=1 complexes.

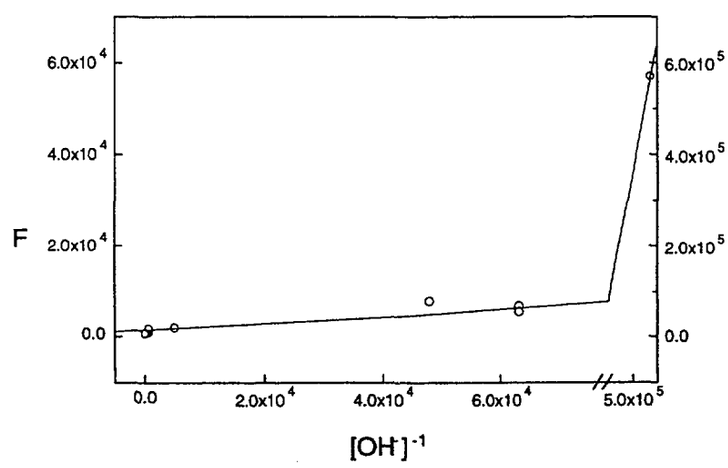

Fig. 7 Plot of the function $F = \{[Np(IV)]tot-[Np(OH)_4]\}/[Np(OH)_4] [CO_3^{-2}]$ vs. $[OH^-]^{-1}$. The line represents $10^{3.07} + 10^{-1.12} [OH^-]^{-1}$

Preliminary values of the constants were obtained by comparison of experimental data with the model function y (log u), where

$$y = \log F - \log K_{n=1} = \log (1+u) \text{ and } \log u = \log \{K_{m=1}/K_{n=1}\}[OH]^{-1}. \quad (31)$$

The constants were evaluated from the difference y -log F and log u + log [OH-], read off in the position of the best fit (see Figure 8).

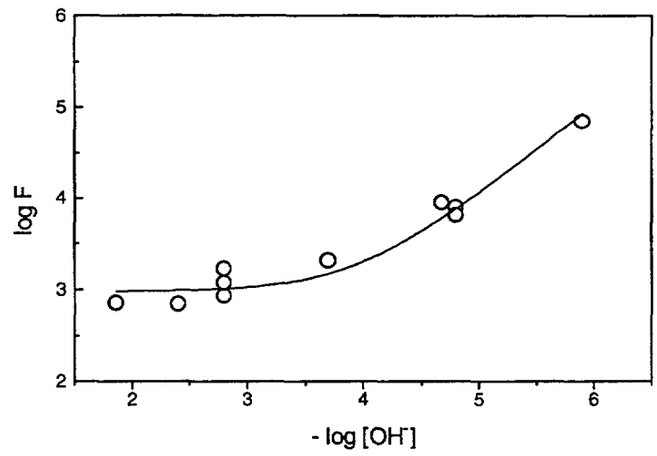

Fig. 8. log F as a function of -log [OH-]. The curve represents 2.98 + log(1+u), with log u = 3.96 - log [OH-]

Then nonlinear least squares calculations using a Simplex routine [42] have been performed. The calculated constants log $K_{n=1}$=3.00 and log $K_{m=1}$= -0.98 with st.dev.= 0.12, indicate a good agreement between the calculated and measured solubilities. The fit of the experimental data to the model function calculated with these values is presented in Figure 9.

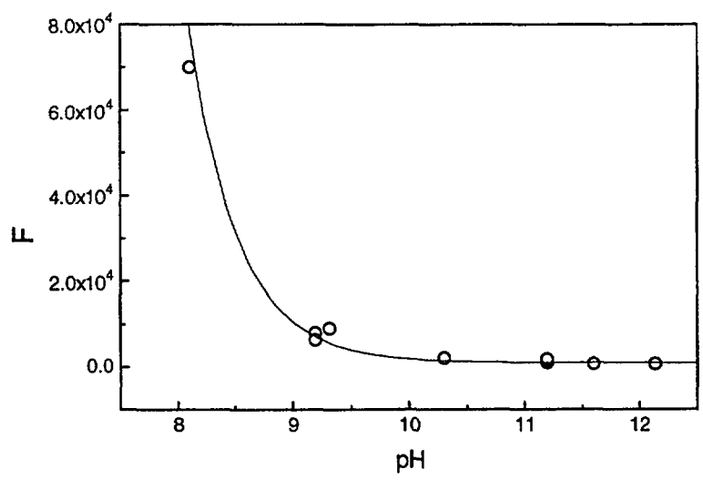

Fig. 9 Plot of the function F, representing the fraction of Np(IV) complexed by carbonate divided by the concentrations of the "reactants", vs. pH. The curve has been calculated with log K_1 = 3.00 and log K'_2 = -0.98

Since the points measured at high pH and carbonate concentration have very small ordinates, we have compared the experimental data with Equation (30) written with bicarbonate as the reactant in Figure 10, where the fit of these points to the model function is displayed more clearly.

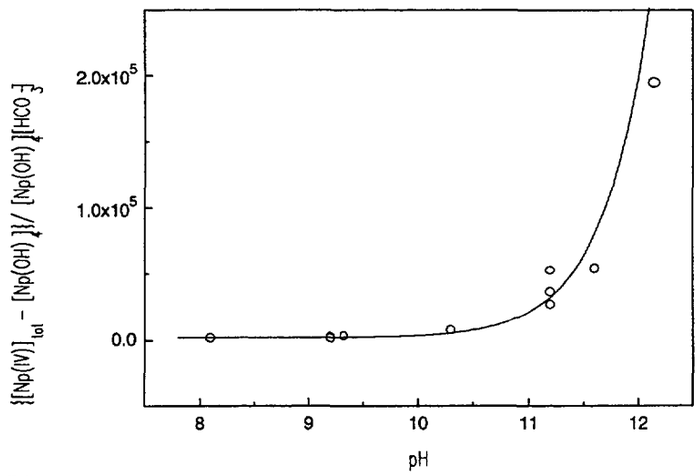

Fig. 10 Plot of the neptunium carbonate data with bicarbonate as the reactant.

The results from the calculations with a bootstrap procedure [33] for 2000 sets are shown in Figures 11-13. From these calculations it follows that the correlation between the two constants is weak (Figure 11). The values of $K_1=K_{n=1}$ have a more or less symmetrical Gaussian distribution, which makes it more reliable (Figure 12). The same does not quite hold for the values of $K_{2'}=K_{m=1}$ (Figure 11 and 13), for which the asymmetry is manifest.

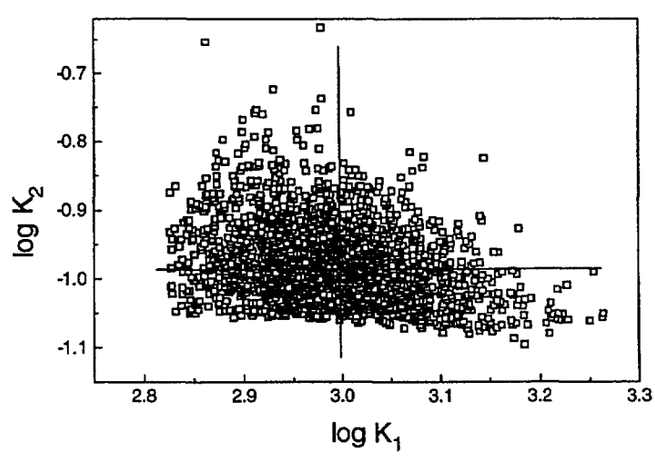

Fig. 11 Joint probability distribution of log K_1 - log K'_2 values for the Np(IV) - carbonate system.

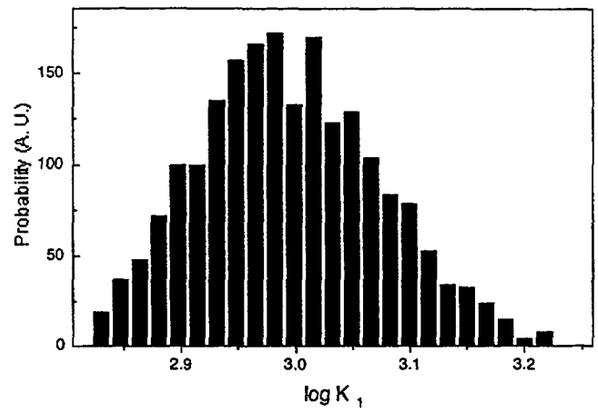

Fig. 12 Distribution of probable values of log K_1.

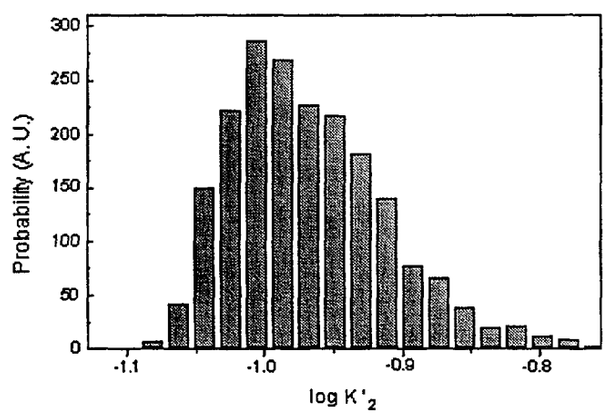

Fig. 13 Distribution of probable values of log K'_2

In conclusion, the experimental data are best explained by the following equilibria and constants:

$$Np(OH)_4 + CO_3^{2-} = Np(OH)_4(CO_3)^{2-} \quad (32)$$

$$\log K_{n=-1} = \log K_1 = 3.00 \pm 0.12 \quad (33)$$

$$Np(OH)_4 + CO_3^{2-} = Np(OH)_3CO_3^- + OH^- \quad (34)$$

$$\log K_{m=-1} = \log K'_2 = -0.98 \pm 0.12 \quad (35)$$

For reaction (32), written with bicarbonate as the reacting species and m = 1, we obtain from the values of $K_{2'}$ and K_{a2} the values of the constant K_2:

$$Np(OH)_4 + HCO_3^- = Np(OH)_3CO_3^- + H_2O \quad (36)$$

$$\log K_2 = 3.23 \pm 0.12 \quad (37)$$

The values of K_1 and K_2, determined in an ionic medium of 0.5 M ionic strength, can be considered as a good approximation of the corresponding values at infinite dilution for the following reasons: For both reactions (34) and (36) the Debye-Huckel term in the expression for the activity coefficients cancels out, since on both sides of the reactions we have ions of the same charge. Within the frame of S.I.T. [37], the change in the values of the constants extrapolated to zero ionic strength will be very small.
To a reasonable approximation this value is expected to be less than 0.1 log units for the constant of reaction (34) and less than 0.05 log units for the constant of reaction (36), since interaction coefficients for ions of charge -2 with Na^+ are in the range (-0.15)-(-0.05), while for ions of charge -1 are in the range (-0.08)-0.05 and the salting effect for $Np(OH)_4$ is expected to be even smaller [35].

$$\log K_o = \log K + \Delta\varepsilon . 0.5, \quad (38)$$

$$\Delta\varepsilon._1 = \varepsilon(Na^+, Np(OH)_4CO_3^{2-}) - \varepsilon(Na^+, CO_3^{2-})(=-0.05) \quad (39)$$

$$\Delta\varepsilon._2 = \varepsilon(Na^+, Np(OH)_3CO_3^-) - \varepsilon(Na^+, HCO_3^-)(=-0.03) \quad (40)$$

Combining the values of the constants of carbonate and bicarbonate complexes with the formation constant of $Np(OH)_4(aq)$ as calculated in the previous section, we obtain the following values for the formation constants of the carbonate and bicarbonate complexes:

$$Np^{4+} + 4\ OH^- + CO_3^{2-} \Leftrightarrow Np(OH)_4CO_3^{2-} \quad (41)$$

$$\log \beta_{141} = 49.2 \pm 0.5 \quad (42)$$

$$Np^{4+} + 3\ OH^- + CO_3^{2-} \Leftrightarrow Np(OH)_3CO_3^- \quad (43)$$

$$\log \beta_{131} = 45.8 \pm 0.5 \quad (44)$$

The value of the second constant is in fair agreement with the value 44.9 predicted by Brown and Wanner [43]. On the other hand, the formation constant for the complex $Np(OH)_4HCO_3^-$ (assumed here as $Np(OH)_3CO_3^-$ + H_2O, as discussed above) results log β_{141} = 49.4, quite similar to the value for the corresponding carbonate complex (49.2), showing that carbonate and bicarbonate ligands should form complexes of comparable stability.

For mononuclear hydrolytic complexes of actinides the logarithms of the step-wise stability constants can be described by the relationship log $K_n = a + b\,n$ where a and b are constants [22,44]. Assuming that the same holds for the hydroxy-carbonate complexes of neptunium, the values for the number of "hydroxyl" groups are n = 3.95 for $Np(OH)_3CO_3^-$ and n = 4.56 for $Np(OH)_4CO_3^{-2}$. From these values it follows that carbonate is a slightly weaker ligand as compared to hydroxyl ions, while the fifth ligand is coordinated in a much weaker way, probably because of sterical hindrance.

4. THE BEHAVIOUR OF Tc(IV) AND Np(IV) IN GROUNDWATER.

4.1 Tc(IV)

From the analysis of the solubility data it may be concluded that the formation of mixed hydroxy-carbonate complexes are important for the solubility of $TcO_2 \cdot nH_2O$ in carbonate waters.

This is clearly demonstrated in Figure 14, where the predominant speciation of Tc at various pH and redox potential has been calculated in 10^{-8} mol·dm^{-3} Tc-solution equilibrated with CO_2 at P_{CO_2} = 0.02 atm.

In hydrocarbonate groundwaters, under reducing conditions the solubility is pH-dependent. At 5 < pH < 7.5 the Tc(IV) solubility is less than 10^{-8} mol·dm^{-3} and the neutral $TcO(OH)_2$ aq is the predominant species. In the pH range 8-11 the solubility increases and the anionic complex $TcO(OH)_3CO_3^-$ is predominant.

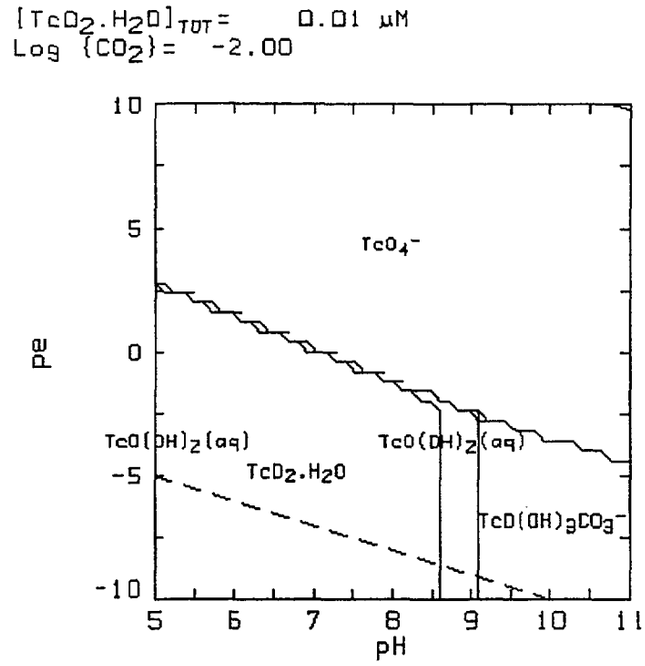

Fig. 14 Predominance diagram showing the dominant Tc speciation at natural water conditions as function of pH and pe (pe=Eh(mV)/59.16) at T=25 ^{o}C, $Tc_{tot}=10^{-8}$ mol.dm^{-3}, $P_{CO2}=0.01$ atm.

This study indicates that, as for the cations formation of mixed complexes is relevant for the speciation and probably also the migration of Tc(IV). However, it ought to be emphasized that the redox-potential remains the key variable defining the solubility of technetium in natural waters.

4.2 Np(IV)

As can be seen from Figure 15, the solubility of $Np(OH)_4(s)$ in reducing conditions and in the presence of total carbonate concentrations of the order of 1 mM, typical for granitic ground waters, increases around 3 times (0.5 logarithmic units). In the case of bentonite saturated ground waters, (pH = 9.3 and total carbonate concentrations of the order of 7-10 mM) [45], the solubility increases by more than one order of magnitude.

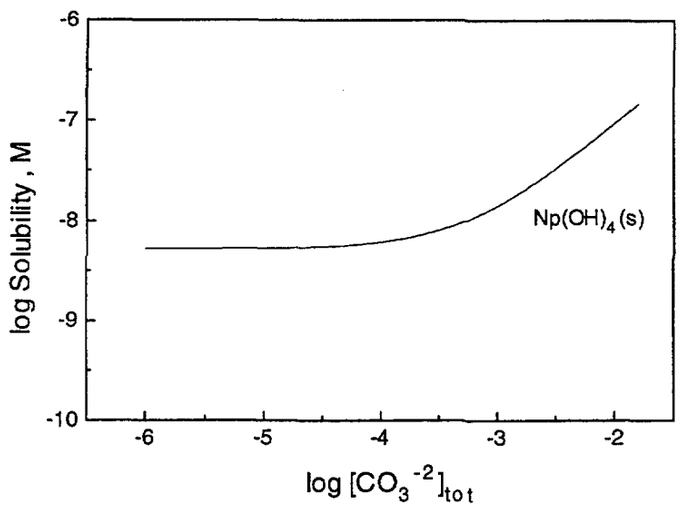

Fig. 15 Solubility of the Np(IV) hydrous oxide as a function of the carbonate concentration, calculated at pH=8 with the values of the constants reported in this work.

On the other hand, the Np(IV) speciation in neutral to alkaline ground waters and in the presence of carbonate changes. The anionic carbonate species become the dominant ones as the carbonate concentrations increases (Figures 16 and 17). This means that the sorption of negatively charged species should be taken into account, together with the neutral one. Since the surface of the most oxides and calcite will be negatively charged under these conditions, the sorption of Np(IV) may be affected, which means a higher mobility. On the other hand, similar carbonate and hydroxycarbonate species of uranyl are reported by Ho and coworkers [46, 47] to be the ones responsible for the adsorption of U(VI) on hematite and magnetite.

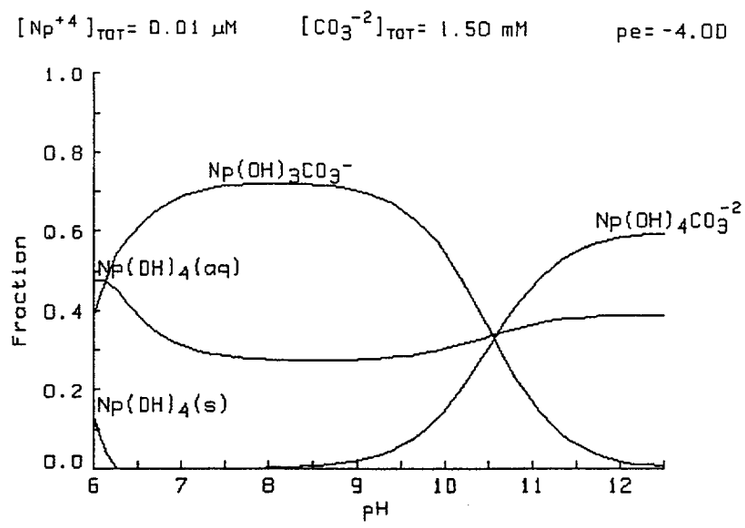

Fig. 16 Distribution of the species in solution calculated for Np(IV)tot=10^{-8} M and 1.5 mM total carbonate, reducing conditions.

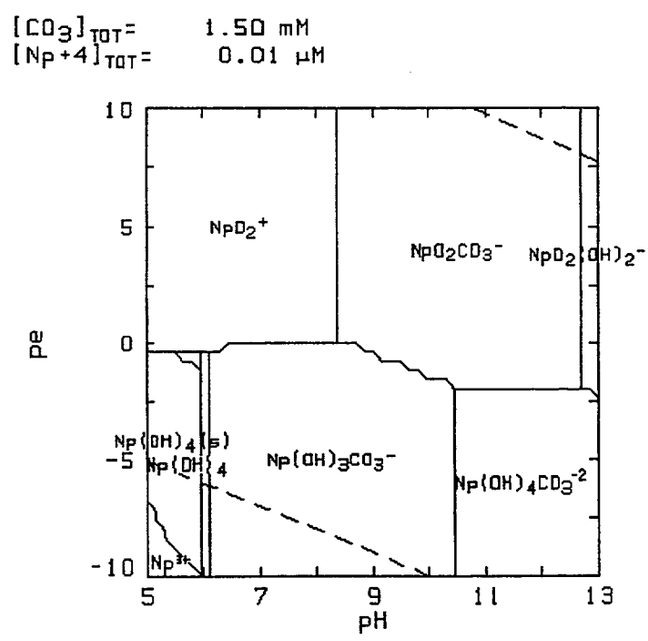

Fig. 17 Predominance area diagram for the Np-H_2O-CO_3^{2-} system.

4.3 Implications on Ac(IV) speciation in ground waters.

Owing to the analogies in the actinide series, a similar behavior should be expected for U(IV) and Pu(IV) in typical granitic ground waters. Thus, preliminary estimates of the stability constants for equivalent complexes of uranium give log β_{131}=44.7 and log β_{141}=48.8, while the respective constants for plutonium should be log β_{131}=45.7 and log β_{141}=49.8. It is worthwhile to carry out a sensitivity analysis of the influence of the Ac(IV) mixed hydroxycarbonate complexes on the solubility of these actinides and reducing conditions. In order to do this, we have calculated the solubility of $Pu(OH)_4(s)$ and $UO_2(s)$, using the corresponding SKB-databases [48,49], with and without including the mixed hydroxy-carbonate complexes and their estimated constants. The results of theses calculations are represented in Figure 18 and 19. Owing to the formation of Pu(III) and U(VI) species of these conditions, the effect of the mixed complexes in the solubility seems to be much less pronounced as compared to neptunium, which is much more stable in the Np(IV) oxidation state.

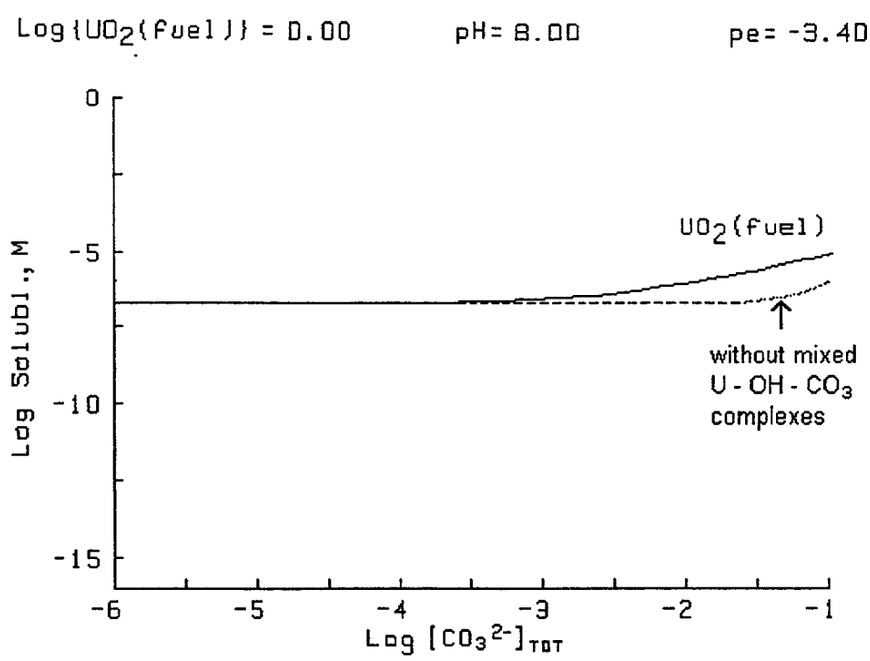

Fig. 18 Solubility of the UO_2(fuel) as a function of the carbonate concentration, calculated at pH=8, with and without mixed hydroxy carbonate complexes (the values of the constants reported in this work).

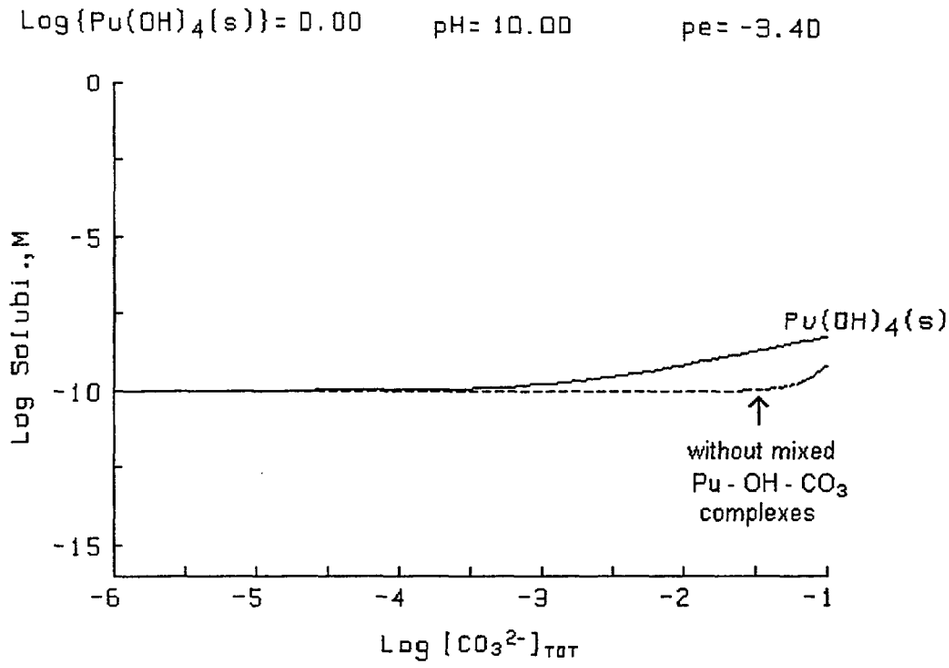

Fig. 19 Solubility of the $Pu(OH)_4(s)$ as a function of the total carbonate concentration, calculated at pH=10 with and without mixed hydroxy-carbonate complexes (the values of the constants reported in this work).

However, these calculations should be regarded as a first estimate of the potential influence of the hydroxy-carbonate complexation for the actinides. Preferably an experimental determination of their stability should be carried out, to asses their existence and their impact on Ac(IV) solubility.

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A P P E N D I X

Tables of Experimental Data

Table 1A
Tc(IV) concentration in aqueous solution equilibrated with $TcO_2 \cdot nH_2O$.

log [Tc(IV)]	pH
-8.33	6.05
-8.178	6.5
-8.161	7.7
-8.251	8.05
-8.218	8.95
-8.081	9.70
-7.842	10.5
-7.81	10.75
-7.425	11.45
-7.105	12.1

Table 2A
Np(IV) concentration in aqueous solution equilibrated with $Np(OH)_4$ s.

pH	[Np(IV)] mol.dm^{-3}
6.05	4.15E-009
6.05	5.85E-009
8.5	2.03E-009
8.5	2.47E-009
9	7.90E-009
10.05	9.76E-009
10.3	3.50E-009
11.85	4.50E-009
11.85	5.68E-009
12	7.43E-009
12.01	6.90E-009
12.05	3.50E-009

Table 3A
Np(V) concentration in 0.5 mol.dm^{-3} $NaClO_4$ solution equilibrated with $Np(OH)_4$ at various pH and Eh.

Potential*) mV	pH	[Np(V)] mol dm^{-3}	Comments
-176	12.05	2.08E-8	SCE (241 mV)
-116	11.1	3.87E-8	
-107	10.5	4.58E-8	
-107	12.3	3.30E-7	
-220	11.2	1.20E-9	
-170	11.1	3.90E-8	
-43	9.2	3.02E-7	
1.3	10.3	8.80E-7	
11	8.5	8.00E-6	
-76	10.4	2.02E-7	Ag/AgCl (226 mV)
-69	9.8	6.10E-7	
-62	9.8	2.30E-6	

Table 4A
Tc(IV) concentration in aqueous solution equilibrated with $TcO_2 \cdot nH_2O$ at various pCO_2.

log [Tc(IV)]	pH	% CO_2(g)
-7.839	6.26	10
-7.701	6.80	10
-7.60	8.05	10
-7.549	6.26	30
-7.337	8.05	30
-7.398	6.24	50
-7.247	7.76	50
-6.979	6.24	100
-6.889	8.05	100
-6.810	-8.16	100
-6.611	-8.56	100

Table 5A
Np(IV) concentration in equilibrium with $Np(OH)_4(s)$
at different pH and carbonate concentration
Eh ≈ -630 mV vs SCE, 0.5 M $NaClO_4$

pH	$[CO_3^{2-}]_{tot}$ mol dm^{-3}	[Np(IV)] mol dm^{-3}
8.1	10^{-1}	$7.30 \cdot 10^{-7}$
9.2	$2.5 \cdot 10^{-3}$	$2.66 \cdot 10^{-8}$
9.2	10^{-2}	$7.45 \cdot 10^{-8}$
9.2	10^{-1}	$6.96 \cdot 10^{-7}$
9.32	10^{-2}	$1.24 \cdot 10^{-7}$
10.3	$5 \cdot 10^{-2}$	$4.14.10^{-7}$
11.2	10^{-3}	$9.56 \cdot 10^{-9}$
11.2	$1 \cdot 10^{-2}$	$6.42 \cdot 10^{-8}$
11.2	$3 \cdot 10^{-2}$	$2.60 \cdot 10^{-7}$
11.6	10^{-1}	$3.60 \cdot 10^{-7}$
12.14	10^{-1}	$3.76 \cdot 10^{7}$

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[1] Division of Solid Mechanics, Chalmers University of Technology, Göteborg, Sweden
[2] Division of Computer Aided Design, Luleå University of Technology, Luleå, Sweden
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[2] CEA, France
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[1] KEMAKTA Konsult AB
[2] SKB
[3] Conterra AB
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