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Neptunium in the Hydrosphere and in the Geosphere

I. Chemistry of Neptunium in the Hydrosphere and Sorption of Neptunium from Groundwaters on Sediments under Aerobic and Anaerobic Conditions

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Neptunium /Neptunium in the hydrosphere /Neptunium in the geosphere /Sorption of Np/*Chemistry of* Np

Summary

The possible pathways of Np into the hydrosphere and the geosphere and the chemical reactions of Np in the hydrosphere are discussed. The sorption of Np under various conditions is investigated in batch experiments. Natural sediments and groundwaters of low, medium, and high salinity are used. The oxidation states of Np are determined by extraction and colloid formation is checked by ultrafiltration.

Under aerobic conditions (Eh > 300 mV) the carbonato complexes of Np(V) are sorbed at the surface of the sediments in reversible sorption equilibria with relatively low sorption ratios (about 1 to 6 ml/g). Under strongly anaerobic conditions (Eh < 200 mV) Np(V) is quantitatively reduced to Np(IV) and sparingly soluble hydroxo complexes or $Np(OH)_4$, respectively, are formed. Reversible sorption equilibria are not established, but the sorption ratio is given by the amount of sparingly soluble precipitates of Np(IV) to the amount of Np in the solution. At initial concentrations of about 10^{-7} mol/l of Np(V), the apparent sorption ratio is of the order of 10^3 ml/g.

1. Introduction

^{237}Np has a very long half-life ($2.14 \cdot 10^6$ y) and is produced from uranium in nuclear reactors

$$^{235}U(n,\gamma)^{236}U(n,\gamma)^{237}U \xrightarrow[6.75\,d]{\beta^-,\gamma} {}^{237}Np \qquad (1)$$

$$^{238}U(n,2n)^{237}U \xrightarrow[6.75\,d]{\beta^-,\gamma} {}^{237}Np \qquad (2)$$

The concentration of ^{237}Np in nuclear fuel of water-cooled reactors after a burn-up of 35 000 WMd is about 0.5 kg (besides about 9 kg of plutonium) per ton of uranium. The half-life of ^{237}Np is longer than that of all other radionuclides of transuranium elements, except ^{244}Pu ($8.26 \cdot 10^7$ y) and ^{247}Cm ($1.56 \cdot 10^7$ y) which are, however, produced only in very small amounts. Therefore, if the nuclear fuel elements are stored after burn-up without further reprocessing, the radioactivity of ^{237}Np is of major importance on a long time scale.

If the nuclear fuel is reprocessed, however, the possible paths of ^{237}Np depend on the special conditions of reprocessing [1 – 7]. The distribution coefficients of Np(IV) and of Np(VI) between tributylphosphate (TBP) in organic solvents and nitric acid solutions are about 2 to 3 orders of magnitude higher than the distribution coefficient of Np(V). Np(IV) and Np(VI) are extracted in form of the complexes $Np(NO_3)_4(TBP)_2$ and $NpO_2(NO_3)_2(TBP)_2$, respectively, whereas Np(V) is practically not extracted. The behaviour of Np(V) is governed by its disproportionation in acid solutions [7]

$$2\,NpO_2^+ + 4\,H^+ \rightleftharpoons Np^{4+} + NpO_2^{2+} + 2\,H_2O \qquad (3)$$

and by redox reactions [7]

$$2\,NpO_2^+ + HNO_3 + 2\,H^+ \rightleftharpoons 2\,NpO_2^{2+} + HNO_2 + H_2O \qquad (4)$$

or

$$NpO_2^+ + Fe^{2+} + 4\,H^+ \rightleftharpoons Np^{4+} + Fe^{3+} + 2\,H_2O \qquad (5)$$

or

$$2\,NpO_2^{2+} + 2\,N_2H_4 \rightleftharpoons 2\,NpO_2^+ + N_2 + 2\,NH_4^+ \qquad (6)$$

or

$$4\,NpO_2^{2+} + N_2H_4 \rightleftharpoons 4\,NpO_2^+ + N_2 + 4\,H^+ \qquad (7)$$

or

$$NpO_2^+ + U^{4+} + 4\,H^+ \rightleftharpoons 2\,Np^{4+} + UO_2^{2+} + 2\,H_2O \qquad (8)$$

The disproportionation (eq. (3)) is strongly influenced by the acid concentration. It is negligible in neutral solutions and nearly quantitative in 6 *M* HNO_3 [2]. Furthermore, by complexation of Np^{4+} and of NpO_2^{2+} the equilibrium (3) is shifted to the right. Reaction (4) is catalyzed by small concentrations of HNO_2 (10^{-5} to 10^{-2} mol/l). It is shifted to the right by high concentrations of HNO_3, and it is shifted to the left by high concentrations of HNO_2 [7]. Temperature and light also influence this redox reaction. Reduction of NpO_2^+ by Fe^{2+} (eq. (5)) is rather fast [7]. Reduction of NpO_2^{2+} by N_2H_4 is assumed to follow eq. (6) at low concentrations of N_2H_4 and eq. (7) at high concentrations of N_2H_4 [8]. Reduction of NpO_2^+ by U^{4+} is also relatively fast [7].

If the concentration of HNO_2 is adjusted exactly and if the time of equilibration between the organic and the aqueous phase is relatively short in the first cycle of the Purex process, > 99% of ^{237}Np will stay in the aqueous phase and will be found in the high activity waste (HAW). Otherwise, appreciable amounts of ^{237}Np are oxidized to NpO_2^{2+} according to eq. (4) and extracted together with U and Pu. Furthermore, disproportionation of NpO_2^+ according to eq. (3) will proceed markedly with the time of equilibration. The amounts of Np that are extracted into the organic phase may be as high as about 90% and

will accompany the uranium, if no special measures are taken in order to transform Np into NpO_2^+ in the course of the second cycle of the Purex process (reduction). In this case, separation of Np from U is necessary before the latter can be reused. Thus, depending on the conditions of the reprocessing process, variable amounts of the ^{237}Np are in the high activity waste (HAW) and the rest is in the low activity waste (LAW) solutions.

With respect to further treatment and storage of ^{237}Np, two options are feasible: a) Careful separation and isolation of ^{237}Np from HAW and/or α-waste, transformation into a most stable chemical form (e.g. NpO_2 or other ceramic compounds) and separate storage. b) Storage of ^{237}Np with HAW or with α-waste, respectively, without separation. In all cases, the long half-life of ^{237}Np has to be taken into account, and possible reactions of ^{237}Np in the hydrosphere and in the geosphere have to be considered.

2. Chemical reactions of Np in the hydrosphere

For assessment of the chemical reactions of Np in the hydrosphere the Eh-pH-diagram (Fig. 1) is very useful. This diagram has been plotted on the basis of thermodynamic data compiled by ALLARD, KIPATSI and LILJENZIN [9]. The possible actinide species that may be formed in groundwaters have been discussed by ALLARD [10]. Additionally the results published by LIERSE, TREIBER and KIM [11] with respect to the formation of $NpO_2(OH)$ and of $NpO_2(OH)_2^-$ and the results published by RAI and RYAN [12] with respect to the formation of $Np(OH)_5^-$ have been taken into account.

The most important feature of the chemistry of Np in aqueous solutions is the great range of stability of Np(V). In this respect, Np differs markedly from its neighboring elements U and Pu that exhibit only small ranges of stability in the oxidation state +5. In neutral or nearly neutral solutions NpO_2^+ ions predominate at redox potentials between about 100 and about 800 mV, that is under aerobic conditions. Np(VI) is only formed at very high redox potentials that may be created by strongly oxidizing reagents like nitric acid or by radiolysis products. Besides that, the chemical properties of Np(VI) are very similar to those of U(VI).

Two hydrolysis products of NpO_2^+ have been described, $NpO_2(OH)$ and $NpO_2(OH)_2^-$ [11] with the hydrolysis constants

$$\beta_1 = \frac{[NpO_2(OH)]}{[NpO_2^+][OH^-]} \quad (9) \quad (\log \beta_1 = 2.33 \pm 0.62 \text{ at the ionic strength } \mu = 1.0)$$

and

$$\beta_2 = \frac{[NpO_2(OH)_2^-]}{[NpO_2^+][OH^-]^2} \quad (10) \quad (\log \beta_2 = 4.89 \pm 0.05 \text{ at the ionic strength } \mu = 1.0)$$

From that it follows that the fractions of $NpO_2(OH)$ and of $NpO_2(OH)_2^-$ increase sharply near pH 11 and that at about pH 11.5 $NpO_2(OH)_2^-$ becomes the predominant species of Np(V) in carbonate-free aqueous solutions. At pH 8.5, however, less than 0.1% of Np(V) is present in form of $NpO_2(OH)$ and less than 10^{-4}% in form of $NpO_2(OH)_2$. Therefore, if these hydrolysis products are not sorbed with extremely high preference, they can be neglected in natural groundwaters. The solubility product of $NpO_2(OH)$ was determined by several authors [11, 13–16]

$$K_s = [NpO_2^+][OH^-] \quad (11) \quad (\log K_s \text{ varying between } -8.81 \text{ and } -9.73)$$

It follows that at pH 8.5 the solubility product of $NpO_2(OH)$ will not be exceeded if $[NpO_2^+] < 5 \cdot 10^{-4}$ mol/l. From solubility measurements at pH 7.0 ± 0.1 the value $4.4 \cdot 10^{-4}$ mol/l was calculated for the solubility of NpO_2^+ [17]. Consequently, at low concentrations of Np(V) precipitation of $NpO_2(OH)$ or formation of colloidal hydroxo complexes of Np(V) will not occur in groundwaters.

Np(IV) is formed in aqueous solutions at low redox potentials Eh (strongly anaerobic conditions). The most important species of Np(IV) in natural waters is $Np(OH)_4$ or $NpO_2 \cdot x\,H_2O$, respectively. No evidence was found for the existence of an anionic species of Np(IV) that has been predicted from thermodynamic data [11]. Therefore, the hypothetical species $Np(OH)_5^-$ is set in brackets in Fig. 1 and will not be considered in the following.

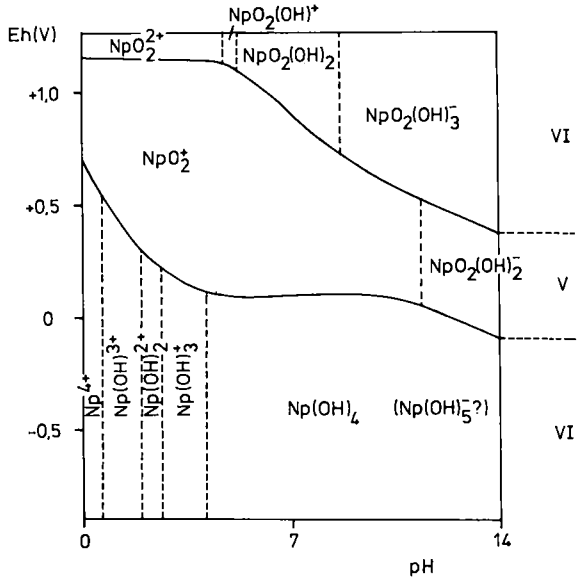


Fig. 1. Eh-pH-diagram of neptunium (plotted on the basis of thermodynamic data compiled by ALLARD, KIPATSI and LILJENZIN [9]).

Many compounds present in groundwaters influence the speciation of Np. Soluble complexes or new solids my be formed. The most important inorganic components with respect to complexation in groundwaters are carbonate, chloride, phosphate, sulfate, fluoride, and silicate. The actinides in their various oxidation states are hard acids and prefer complexation with hard bases, in

particular with oxygen-containing ligands. The stability constants of the formation of the 1 : 1 complexes of the actinide ions M^{3+}, M^{4+}, MO_2^+, and MO_2^{2+} as reported in the literature [1, 18] are plotted in Fig. 2. The first hydrolysis constants are included in this figure. Although there are variations of the values that have been measured, some general trends are obvious: The stability constants for the formation of the 1 : 1 complexes of MO_2^+ ions are relatively low, whereas those of M^{4+} ions are relatively high. With respect to the complexing ligands the following order of stability is valid: $CO_3^{2-} > OH^- > F^- > HPO_4^{2-} > SO_4^{2-} > Cl^- > Br^- > I^-$ with only difference in the sequence of HPO_4^{2-} and F^- in case of M^{4+} ions.

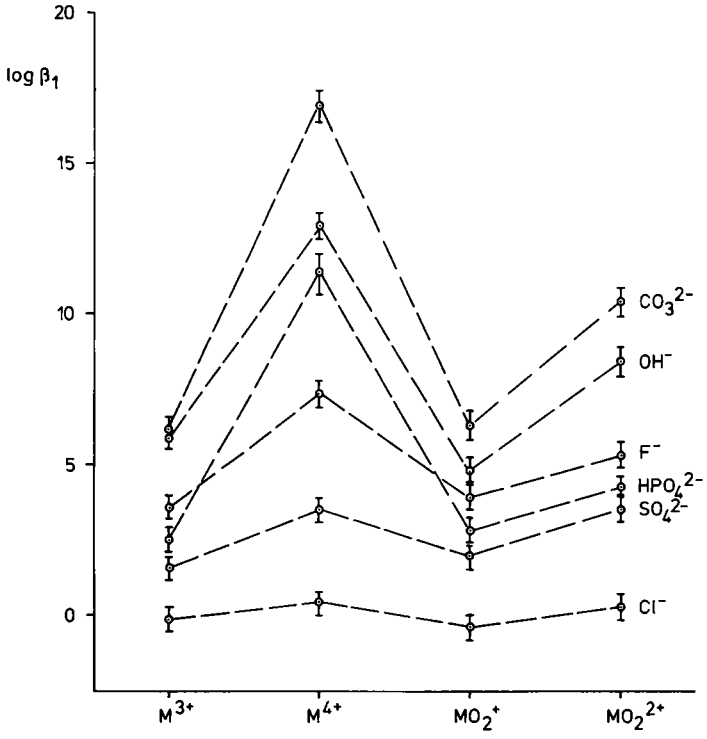


Fig. 2. Logarithms of the stability constants β_1 for the formation of 1 : 1 complexes of the actinide ions M^{3+}, M^{4+}, MO_2^+, and MO_2^{2+}.

The most important inorganic ligand is carbonate, because it has very strong complexation properties for actinide ions and it is present in all natural waters in relatively high concentrations. The total concentration of carbonate in groundwaters varies between about 1 and 10 mmol/l. Complexation of NpO_2^+ by carbonate has been investigated in several studies [19–22].

At low and medium carbonate alkalinity CA (CA = $[HCO_3^-] + 2[CO_3^{2-}]$) up to 10^{-2} mol/l 1 : 1 and 1 : 2 complexes are predominant:

$$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^- \qquad (12)$$

($\log \beta_1 = 4.13 \pm 0.03$ [22] at ionic strength $\mu = 0.02$)

$$NpO_2^+ + 2\,CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-} \qquad (13)$$

($\log \beta_2 = 7.06 \pm 0.05$ [22] at ionic strength $\mu = 0.02$)

Apparently, the triscarbonato complex $NpO_2(CO_3)_3^{5-}$ is not formed in greater amounts in this range of carbonate alkalinity [22]. Other carbonato complexes that have been reported in literature (NpO_2HCO_3 [23], $NpO_2OH(CO_3)^{2-}$ and $NpO_2OH(CO_3)_2^{4-}$ [15]) were also not observed under these conditions [22]. From the stability constants β_1 and β_2 measured by BIDOGLIO, TANET and CHATT [22] it follows that $NpO_2(CO_3)^-$ predominates at $[CO_3^{2-}] > 10^{-4}$ mol/l, whereas $NpO_2(CO_3)_2^{3-}$ predominates at $[CO_3^{2-}] > 10^{-3}$ mol/l. $[CO_3^{2-}]$ depends on the total carbonate concentration $c_{tot} = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$ and on the concentration of H^+:

$$[CO_3^{2-}] = c_{tot}\left(1 + \frac{[H^+]}{K_2F_2} + \frac{[H^+]^2}{K_1F_1K_2F_2}\right)^{-1}, \qquad (14)$$

where K_1 is the first and K_2 is the second dissociation constant of carbonic acid and F_1 and F_2 are the corresponding products of the activity coefficients.

In agreement with other authors [17, 22] it must be concluded that in groundwaters carbonato complexation of NpO_2^+ leads to the predominance of $NpO_2(CO_3)^-$ at lower carbonate alkalinity (eq. (12)) and to that of $NpO_2(CO_3)_2^{3-}$ at higher carbonate alkalinity (eq. (13)), whereas hydroxo complexes of Np(V) can be neglected.

Fluoride ions, phosphate ions and sulfate ions are generally present in groundwaters in much smaller concentrations than carbonate ions and their concentration is limited by the formation of sparingly soluble calcium compounds. Because of these low concentrations and the relatively low stability constants compared with those of the carbonato complexes (Fig. 2) their influence on the complexation of actinide ions in groundwaters can be neglected.

Chloride ions are found in high concentrations in groundwaters of high salinity and in brines. However, the stability constants of the 1 : 1 complexes with carbonate ions and with chloride ions differ by more than 6 orders of magnitude for MO_2^+ and by more than 15 orders of magnitude for M^{4+}, as can be seen from Fig. 2. Therefore, even at extreme ratios of chloride ion concentration to carbonate ion concentration of up to 10^6 and up to 10^{15}, respectively, complexation by carbonate ions will predominate in groundwaters.

A very interesting phenomenon of the chemistry of Np(V) is the formation of sparingly soluble mixed carbonato complexes with alkali or alkaline earth ions of the compositions $M^IM^{II}NpO_2(CO_3)_2 \cdot x\,H_2O$ [17] or $M^I_3NpO_2(CO_3)_2 \cdot x\,H_2O$ [17, 24] or $M^INpO_2(CO_3)$ [25], respectively. Compounds of this kind have been found to precipitate at pH 7 under aerobic conditions from 0.1 *M* $NaClO_4$ and from groundwater after addition of NpO_2^+ or NpO_2^{2+} and the concentrations of NpO_2^+ in equilibrium with these precipitates were of the order of 10^{-3} mol/l [17]. Thus, formation of these sparingly soluble compounds is possible at relatively high concentrations of Np(V) and of alkali or alkaline earth ions.

The concentration of organic compounds in groundwaters varies strongly with the depth and may depend on the special conditions. Relatively high concentrations

of dissolved organic carbon (DOC) are found near the surface. DOC values between about 0.1 and about 15 mg/l have been measured in groundwaters in the U.S. [26]. Under conditions of strong infiltration from humus soil DOC values up to about 100 mg/l may be observed. On the other hand, in deep groundwaters that are in contact with lignite-bearing sands also relatively high DOC values are found. The major part of DOC in groundwaters is present in form of humic and fulvic acids. These compounds are of various composition and the most important organic complexing agents in groundwaters. Their complexation properties are mainly due to carboxylate groups and to a smaller extent to phenolate groups. The concentration of carboxylate groups in humic and fulvic acids varies between about 3 and 7 mmol/g. The stability constants of the complexes formed between the actinide ions M^{3+}, M^{4+}, MO_2^+, and MO_2^{2+} and humic or fulvic acids are rather high [27–30]. If calculated on the basis of the mole number of carboxylate groups the stability constants are comparable to those measured for the monohydroxo and the monocarbonato complexes of the corresponding actinide ions. Taking into account the concentration of humic and fulvic acids in groundwaters and their content of carboxylate groups, the concentration of carboxylate groups in dissolved humic and fulvic acids in groundwaters varies between about $0.3 \cdot 10^{-6}$ mol/l and about 10^{-4} mol/l (at very high DOC values up to about $5 \cdot 10^{-4}$ mol/l). As the stability constants of humic and fulvic acids calculated on the basis of the mole number of carboxylate groups in these compounds are, in general, somewhat smaller than those of the monocarbonato complexes, it follows that complexation by humic and fulvic acids will only be important if the DOC values are high and at the same time the concentration of carbonate ions (eq. (14)) is low. These conditions may apply in groundwaters near the surface, particularly at relatively high acidity. It may be mentioned that increased solubility of Pu(IV) was observed in presence of humic acid at pH 7 [32].

Besides humic and fulvic acids, simpler compounds such as carboxylic acids or amino acids are also found in groundwaters, but in relatively small concentrations. The stability constants β_1 of 1 : 1 complexes formed between actinide ions and monocarboxylic acids are relatively small (for complexation of M^{3+}, M^{4+}, MO_2^+, and MO_2^{2+} by acetic acid: $\log \beta_1$ about 2.0, 4.0, 1.3, and 2.3, respectively [31]). They are higher for α-hydroxy carboxylic acids and appreciably higher for polycarboxylic acids [31], but in general below the stability constants of the monocarbonato complexes. With respect to the relatively low concentration of these acids, compared with the concentration of carbonate ions and of humic and fulvic acids, the influence of these organic compounds can usually be neglected.

The highest stability constants have been measured for chelate complexes formed with EDTA or similar compounds [1, 18]. However, these compounds are generally not found in groundwaters in measurable concentrations.

Summarizing, the following conclusions can be drawn with respect to the chemical species of Np in groundwaters:

- If there is no intensive influence of radiation, Np(VI) species can be neglected.
- Under aerobic conditions Np(V) is stable within a wide range of redox potential Eh. It may be present in form of the carbonato complexes $NpO_2(CO_3)^-$ or (at higher carbonate concentration) $NpO_2(CO_3)_2^{3-}$.
- the possibility of formation of sparingly soluble mixed carbonato complexes of NpO_2^+ has to be taken into account, in particular at relatively high concentrations of NpO_2^+ and of alkali and alkaline earth ions.
- Under strongly anaerobic conditions (below about Eh = 200 mV) Np(V) will be reduced to Np(IV) (e.g. by Fe^{2+}) and the very sparingly hydroxo complexes of Np(IV) ($Np(OH)_4$ or $NpO_2 \cdot x\,H_2O$, respectively) will regulate the solubility of Np(IV).
- Even at very high salinity appreciable dissolution of the hydroxo complexes of Np(IV) is not to be expected, as the stability of the chloro complexes in neutral solutions is low compared with the stability of the hydroxo complexes.
- Complexation of Np(V) and of Np(IV) by humic and fulvic acids may be important at high DOC values and low concentrations of carbonate.

3. Experimental part

For the sorption experiments 5 sediments and 5 groundwaters were selected, sampled from the layers covering the salt dome near Gorleben, FRG. Sampling was carried out under an inert gas atmosphere of nitrogen by the institute of applied geology of the university of Berlin*. The individual groundwaters were sampled at the same site as the sediments. The sediments and the groundwaters were filled separately into closed containers. Mineralogical and chemical analysis of the sediments was done by the institute of mineralogy of the university of Munich and chemical analysis of the groundwaters by the chemical laboratory of Dr. PICKEL**. After storage at the site of sampling and transport to Darmstadt, pH and Eh of the groundwaters were measured and the groundwaters were analyzed. Data of the sediments are given in Table 1, and analytical data of the groundwaters are summarized in Table 2.

The samples for the sorption experiments were taken from the containers in which the sediments and the groundwaters, respectively, had been stored and transported, under the same conditions as sampling itself, namely under an inert gas atmosphere of nitrogen. One set of experiments was carried out under aerobic conditions, that is in

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Table 1. Characterization of the sediments (Prof. Dr. W.-D. GRIMM, University of Munich)

Sediment no.	Depth under ground (m)	Mineralogical components	Specific surface area (m^2/g)	Main chemical components in percent							
				SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe	Mn
S 1	3 (–)	mainly quartz, small amounts of orthoklas, plagioklas, kaolinite, muskovite, calcite, chlorite, dolomite	216	88.18	5.47	1.34	0.97	0.29	0.14	0.16	0.08
S 2	54 – 57 (Miozene)		137	96.42	1.74	0.27	0.88	0.21	0.20	0.08	0.05
S 3	57 – 59 (Saale-glacial)		113	89.09	6.29	1.14	0.40	0.47	0.13	0.23	0.09
S 4	72 – 78 (Miozene)		252	92.47	3.97	0.77	1.07	0.45	0.34	0.31	0.03
S 5	200 – 204 (Elster-glacial)		142	92.85	3.22	0.76	0.66	1.12	0.32	0.20	0.02

Table 2. Characterization of the groundwaters after storage and transport

Groundwater no.	Sampled at a depth of (m)	pH	Eh (mV)	Chemical components in mg/l											
				Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	$Fe^{2+/3+}$	Mn^{2+}	Cl^-	Br^-	NO_3^-	SO_4^{2-}	HCO_3^{-*}	SiO_2
G 1	12 – 15	7.0 ±0.1	305 ±15	12.96	2.43	26.6	0.050	0.03	0.002	17.8	0.017	< 0.01	30.16	61.0	14.8
G 2	36 – 41	6.7 ±0.1	365 ±15	8.54	3.18	20.4	0.054	< 0.01	0.090	10.2	0.013	< 0.01	30.1	52.0	11.3
G 3	51 – 54	7.5 ±0.1	335 ±15	589	34.9	262	1.87	< 0.01	0.21	1354	0.49	0.18	35.6	198	14.6
G 4	68 – 70	7.5 ±0.1	340 ±15	3216	75	280	3.7	< 0.01	0.82	5670	2.1	< 0.01	188	256	17.7
G 5	193 – 221	6.8 ±0.1	230 ±15	57680	86	1861	2.6	< 0.01	4.0	97429	24.1	< 0.01	2271	147	9.6

* Total carbonate concentration $c_{tot} = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$ calculated as $[HCO_3^-]$.

the atmosphere of the laboratory. Another set of experiments was done under anaerobic conditions in inert gas boxes filled with a mixture of 99% Ar and 1% CO_2. The oxygen content in these inert gas boxes was between 0.02 and 0.05%.

In the first step of the experiments the groundwaters were equilibrated with the corresponding sediments, either under aerobic or under anaerobic conditions. For that purpose, 50 g or 250 g of the sediments were moved smoothly with 100 ml or 500 ml, respectively, of the groundwaters in closed polyethylene bottles for 1 month. Then the groundwaters were filtered through membrane filters (Millipore) of 0.45 μm pore size. pH and Eh of the groundwaters were measured again and chemical analysis was repeated.

In order to spike the groundwaters with Np(V), the filtered groundwater samples were shaken smoothly for one week with $\approx$ 0.5 mg (aerobic conditions) or $\approx$ 3 mg (anaerobic conditions) of $^{237}NpO_2$. $^{237}NpO_2$ was supplied from CEN, Fontenay aux Roses ($> 99\%$ $^{237}NpO_2$, prepared by chemical decomposition of neptunium(IV) oxalate). By the shaking a small amount of the $^{237}NpO_2$ was dissolved in form of NpO_2^+ (about 0.5% under aerobic conditions and about 0.1% under anaerobic conditions [33]) yielding initial concentrations of $^{237}NpO_2^+$ of the order of 10^{-7} mol/l in the groundwaters.

7.5 ml of the spiked groundwaters and 3 g of fresh sediment were filled in polyethylene tubes, tightly closed by polyethylene stoppers and turned slowly over head (3 revolutions per minute) to ensure good mixing. The time of equilibration was varied between 1 and 90 days. Then the mixtures were centrifuged and the supernatant groundwaters were filtered through membrane filters (Millipore) of 0.45 μm pore size. For each combination of sediment and groundwater and for each time of equilibration at least 3 independent experiments were made and another experiment as blank (groundwater without sediment) to check for wall adsorption. In the case of the experiments under anaerobic conditions, all operations were carried out in the inert gas boxes.

After separation of groundwater and sediment, 5 ml of the groundwater were brought to dryness on a tray, and the α-activity of ^{237}Np was measured in the α-plateau of a low level counter. At high salinity of the groundwaters, 5 ml were mixed with 0.5 ml of conc. HCl and 1 ml of 1 M iron(II) sulfamate and the mixture was extracted two times with 1 ml of 0.5 M thenoyltrifluoroacetone (TTA) in xylene to separate Np from the salt. The organic phase was brought to dryness and measured as above. The detection limit in the low level counter was equivalent to $1.5 \cdot 10^{-10}$ mol/l of ^{237}Np.

From the initial counting rate I_0 of the spiked groundwater and the counting rate I_L measured after equilibration the sorption ratio R_S of Np was determined,

$$R_S = \frac{I_0 - I_L}{I_L} \frac{m}{V} \qquad (15)$$

m is the mass of the dry sediment and V is the volume of the groundwater. Proper corrections were made for the difference between the mass of the wet and that of the

dry sediment and for wall adsorption, if necessary. Details of the corrections and the possible errors of R_S have been described in a previous communication [34].

In order to identify the oxidation state of Np in the groundwaters before and after equilibration with the sediments, 5 ml were taken, 0.5 ml of conc. HCl was added and the mixture was extracted two times with 1 ml of 0.5 *M* TTA in xylene. Both the aqueous and the organic phase were brought to dryness on a tray and the α-activity was measured as above.

In order to identify the oxidation state of the Np that has been sorbed, the sediments were shaken for 5 min with 5 ml of H_2O, and 5 ml of 0.5 *M* TTA in xylene. The organic phase was brought to dryness on a tray and the α-activity was measured as above. Longer treatment of the sediments with the acid solution may cause dissolution of Fe^{2+} and reduction of Np(V).

In order to check for the presence of colloidal forms of Np in the groundwaters, 5 ml were passed through an ultrafilter of 0.002 μm pore size in an ultrafiltration set (Amicon MPS-1), the filtered groundwater was brought to dryness and measured as above.

The sorption experiments were followed by desorption experiments. For that purpose, the sediments that had been equilibrated with the spiked groundwaters for 90 days were mixed with fresh non-spiked groundwaters and the equilibration was again followed as function of time for 60 days. The evaluation of the desorption experiments is described in detail in a previous communication [34].

In further experiments, some experimental conditions were varied: a) EDTA or citric acid was added in concentrations of 10^{-4} mol/l to study the influence of complexation. Citric acid was chosen because its complexation properties are near those of humic and fulvic acids, whereas complexation by EDTA is much stronger than that by any natural components of groundwaters. b) The initial concentration of Np(V) was changed to about 10^{-9} mol/l, that is by a factor of about 100 less than in the other experiments.

4. Results and discussion

The redox potentials Eh and the iron concentrations measured in the groundwaters varied markedly between the time of sampling, after storage and transport and after equilibration (conditioning) with the sediments. These changes and their influence on the chemistry of trace elements have been discussed in detail in previous communications [35, 34]. The same kind of changes were observed here in the investigations on the sorption of Np. The influence of the ratio of the concentrations of Fe^{2+} and Fe^{3+} on the ratio of the concentrations of Np^{4+} and NpO_2^+ is obvious from eq. (5) from which it follows

$$\frac{[Np^{4+}]}{[NpO_2^+]} = KF\frac{[Fe^{2+}]}{[Fe^{3+}]}[H^+]^4 , \qquad (16)$$

where K is the equilibrium constant of eq. (5) and F is the quotient of the activity coefficients. The interaction of Fe(II) with Np(V) was also proved by autoradiographic studies in which increased deposition of Np was observed on Fe(II)-bearing minerals like pyrite and biotite [36]. In the following, only the redox potentials Eh measured after equilibration with the sediments are considered.

Typical results obtained under aerobic conditions are plotted in Fig. 3 as function of time for the combinations groundwater G 2/sediment S 2 and groundwater G 4/sediment S 4. Under aerobic conditions the redox potential Eh was 480 and 420 mV, respectively, that means the systems were clearly in the range of stability of Np(V). By extraction with TTA only Np(V) was found in the groundwaters and in the sediments. No colloidal forms of Np were detected by ultrafiltration. The sorption ratios R_S ($R_S = 1.4 \pm 0.4$ ml/g and $R_S = 2.7 \pm 0.6$ ml/g) were similar for both systems. As the pH does not differ markedly in both systems, the difference of R_S may be due to the specific surface areas of S 2 and S 4 which also differ by a factor of about 2 (Table 1). In both systems the sorption equilibria were attained relatively fast (Fig. 2). This is in agreement with the concept that under aerobic conditions the sorption ratio is determined by the sorption equilibria of the carbonato complexes of Np(V), namely $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$, respectively:

$$R_S\,(\text{obs}) \approx \sum r'_{q,p} F_p \frac{m_p}{m} \qquad (17)$$

$r'_{q,p}$ are the partial sorption ratios of the species $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$ at the surface of the mineral phase p (in ml/m^2), F_p are the specific surface areas of these phases, m_p are their masses, and m is the total mass of the sediment.

Under anaerobic conditions, the sorption ratios are appreciably higher and of the order of 10^3 ml/g (Fig. 2). The redox potentials measured under anaerobic conditions were 75 mV and 80 mV, respectively. This is the range in which Np(IV) is clearly the predominating oxidation state of Np (Fig. 1). By extraction with TTA the Np in the solution was found to be > 99% Np(V) and in the sediments only Np(IV) was found. That means, under anaerobic conditions Np was reduced to sparingly soluble hydroxo complexes of Np(IV) and the observed sorption ratio is mainly determined by formation of these sparingly soluble compounds [35]:

$$R_S\,(\text{obs}) \approx \frac{n}{m\,c_L} \qquad (18)$$

n is the mole number of Np in the sparingly soluble hydroxo complexes, m is the mass of the sediment, and c_L is the residual concentration of Np in the groundwater. As Fig. 2 shows, the formation of these sparingly soluble compounds of Np(IV) is appreciably faster at high salt concentration (system G4/S4) than at low salt concentration (system G 2/S 2). By ultrafiltration of the groundwaters after 10 days of equilibration an appreciable fraction of colloidal forms of Np was found in G 2, but

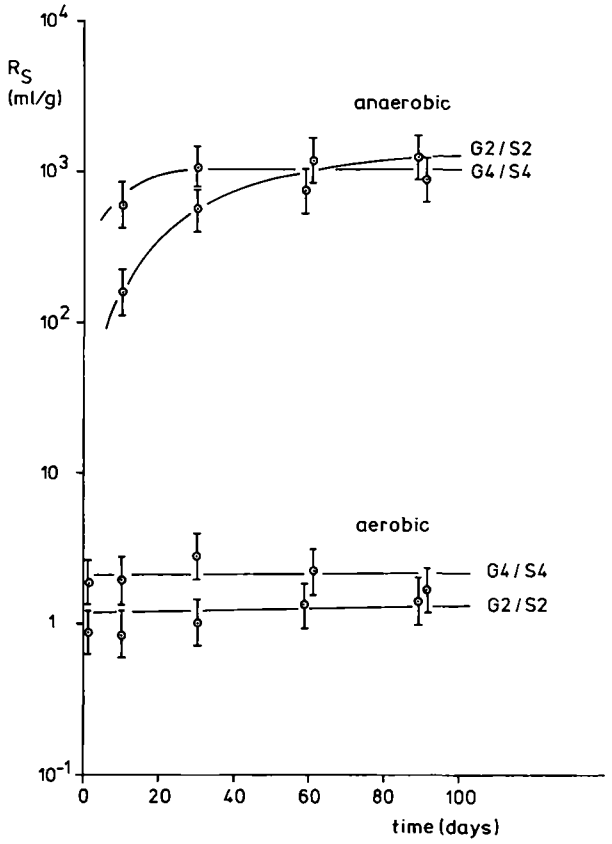


Fig. 3. Sorption ratios R_S in the systems G 2/S 2 and G 4/S 4 under aerobic and under anaerobic conditions as function of time.

not in G 4. After 90 days of equilibration, however, the colloidal fractions of Np in both groundwaters were negligible (< 1%). These observation are in agreement with the concept that at these low concentrations ($\approx 10^{-7}$ mol/l of Np) the formation of the sparingly soluble polynuclear hydroxo complexes and the hydroxide of Np are slow processes and that these processes are accelerated at high ionic strength (high salinity). The final sorption values observed after 90 days of equilibration, however, do not differ markedly and should depend mainly on the initial concentration of Np(V).

Sorption ratios measured in all 5 systems under aerobic and under anaerobic conditions after 90 days of equilibration are listed in Table 3. Under aerobic conditions the sorption ratios of Np(V) present in form of the carbonato complexes $NpO_2(CO_3)^-$ and $NpO_2(CO_3)_2^{3-}$ vary between about 1 and 4 ml/g. They are mainly due to the sorption of these anionic complexes on the surface of the sediments. As to be expected for anions of this kind, the sorption ratios are relatively low. An influence of the formation of sparingly soluble mixed carbonato complexes with alkali and/or alkaline earth ions is not observed. Such an influence is not probable with respect to the reported solubility of these complexes [17] and the low concentration of neptunyl ions used in these experiments.

Under anaerobic conditions high sorption ratios were found in the systems G 2/S 2, G 4/S 4, and G 5/S 5 (Table 3) where the redox potentials were low. The systems G 2/S 2 and G 4/S 4 were clearly in the range where Np(IV) is the prevalent oxidation state of Np (Fig. 1). In the system G 5/S 5 the redox potential was near to the 1 : 1 ratio of Np(IV) : Np(V) which corresponds to the separation line in Fig. 1. Under these conditions, appreciable amounts of Np(IV) are formed and removed from the solution due to the low solubility of the Np(IV) species, until the major part of Np is transformed into Np(IV). In the systems G 1/S 1 and G 3/S 3, however, the redox potential was relatively high and only a minor part of the Np was reduced to Np(IV) leading to intermediate values of R_S. In the groundwater G 1 that was sampled at a relatively low depth of 12 to 15 m under ground (Table 2) a high DOC value of 13 mg/l was measured, and complexation of Np(V) or Np(IV) by humic and fulvic acids may influence the sorption of Np.

The influence of the redox potential is illustrated in Fig. 4. In this figure all R_S values measured at various potentials Eh near pH 7 are plotted as function of Eh. Three ranges of sorption ratios can be distinguished: Below about Eh = 200 mV R_S is high (of the order of 10^3 ml/g at the given initial concentration of Np(V) of $\approx 10^{-7}$ mol/l). At high redox potentials > 300 mV R_S is low and varies between about 1 ml/g and about 6 ml/g. This is the range of an adsorption equilibrium between the carbonato complexes of Np(V) in solution and the sediment. Between about 200 mV and about 300 mV there is a range of intermediate values of R_S caused by the fact that Np(V) is partially reduced to Np(IV).

In the range of low sorption ratios no Np(IV) was found by extraction with TTA in the groundwaters as well as in the sediments and no colloidal forms of Np were observed by ultrafiltration. In the range of high sorption ratios, however, only Np(IV) was found in the sediments. At low salt concentrations (low salinity) vari-

Table 3. Sorption ratios R_S after 90 days of equilibration under aerobic and under anaerobic conditions (mean of 3 independent determinations)

System (groundwater/ sediment)	Aerobic conditions			Anaerobic conditions		
	pH	Eh (mV)	R_S (ml/g)	pH	Eh (mV)	R_S (ml/g)
G 1/S 1	6.0 ± 0.1	570 ± 15	1.9 ± 0.5	6.0 ± 0.1	230 ± 15	21 ± 6
G 2/S 2	7.1 ± 0.1	480 ± 15	1.4 ± 0.4	6.8 ± 0.1	75 ± 15	1290 ± 330
G 3/S 3	7.9 ± 0.1	435 ± 15	2.6 ± 0.6	7.3 ± 0.1	210 ± 15	168 ± 42
G 4/S 4	7.0 ± 0.1	420 ± 15	2.7 ± 0.6	7.3 ± 0.1	80 ± 15	1060 ± 260
G 5/S 5	7.0 ± 0.1	475 ± 15	3.7 ± 0.8	6.9 ± 0.1	110 ± 15	1600 ± 500

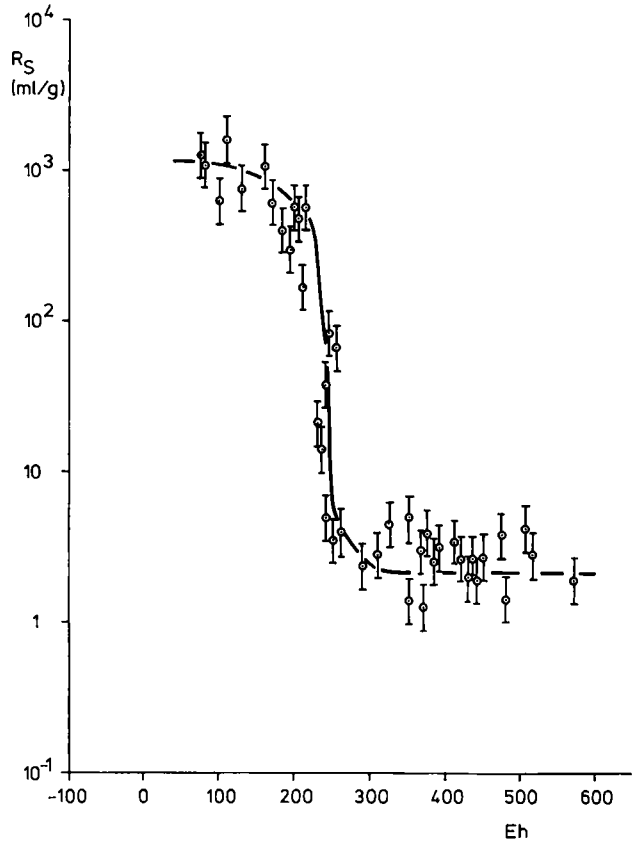


Fig. 4. Sorption ratios R_S measured in various systems at pH 7.0 ± 0.5 as function of the redox potential Eh.

able amounts of Np colloids were separated by ultrafiltration during the first periods of equilibration under anaerobic conditions. These amounts decreased with time and were appreciably lower at high salt concentrations.

The results of the desorption experiments can be summarized as follows: Under aerobic conditions the same sorption ratios were measured as in the sorption experiments within the limits of experimental errors: $R_D \approx R_S$. This also proves that sorption of Np is reversible under aerobic conditions and is in agreement with the concept that under aerobic conditions the sorption of Np is determined by the sorption equilibrium of NpO_2^+ and the carbonato complexes of Np(V) between the groundwater and the sediment.

Under anaerobic conditions, however, extremely small concentrations of Np in solution were found in the desorption experiments. Obviously, redissolution of the sparingly soluble species of Np(IV) does lead to lower concentrations in solution than that found after precipitation of these species. This observation is very common in case of sparingly soluble hydroxides [37].

The sorption experiments in presence of 10^{-4} mol/l of EDTA or of 10^{-4} mol/l of citric acid did not lead to marked changes of the sorption ratios R_S. Under anaerobic conditions somewhat smaller values of R_S were measured at low salinity, whereas at high salinity no influence was observed. Appreciably higher concentrations of complexing agents are not to be expected in deep groundwaters. As already mentioned, near the surface or in rivers relatively high concentrations of humic or fulvic acids may be found and they will compete with the carbonate ions in forming complexes with Np(V), (under aerobic conditions) or with Np(IV) (under anaerobic conditions). The sorption behaviour will be determined by that of the complexes formed, as has been observed for various trace elements in river water [38].

If the concept derived previously [35] and used here is right and the apparent sorption of Np under anaerobic conditions is due to nearly quantitative reduction of Np(V) and formation of the sparingly soluble hydroxide of Np(IV) the following relation should hold:

$$R_S = \frac{c_0 - c_L}{c_L} \frac{V}{m} \tag{19}$$

c_0 is the initial concentration of Np(V), c_L is the residual concentration of the sparingly soluble hydroxide of Np(IV) in the solution, V is the volume of the solution and m is the mass of the sediment. Eq. (19) is practically the same as eq. (15) and follows immediately from the definition of the sorption ratio R_S. If the sparingly soluble hydroxide of Np(IV) is present as a solid precipitate, c_L is given by its solubility and is constant as long as the composition or the structure of this precipitate do not change. In order to prove this relation, experiments were carried out at initial concentrations of Np(V) of about 10^{-9} mol/l instead of about 10^{-7} mol/l. Under aerobic conditions the same sorption ratios were measured within the limits of error. This confirms the existence of a sorption equilibrium under aerobic conditions. Under anaerobic conditions, however, in the system groundwater G 5/sediment S 5 the value of R_S was found to be 16 ± 3 ml/g at $c_0 = 0.5 \cdot 10^{-9}$ mol/l, whereas it was 3700 ± 500 ml/g at $c_0 = 0.7 \cdot 10^{-7}$ mol/l. This is in agreement with eq. (19) if c_L is constant and $c_L \ll c_0$. It follows that c_L, the solubility of the Np(IV) hydroxide formed under these conditions, should be of the order of 10^{-10} mol/l. However, taking into account the desorption experiments, the solubility of Np(IV) hydroxide is smaller than 10^{-10} mol/l. Accordingly, the solubility product of $Np(OH)_4$ should be of the order of 10^{-38} or less. Values varying between 10^{-34} and 10^{-75} have been estimated for the solubility product of Np(IV) hydroxide [9, 12, 15, 39, 40].

5. Conclusions

- If strongly oxidizing reagents and intensive radiation are absent, Np(VI) can be neglected.
- At Eh > 300 mV NpO_2^+ or the carbonato complexes of Np(V) are sorbed at the surface of the sediments in a reversible sorption equilibrium with sorption ratios of about 1 to 6 ml/g, depending on the specific surface area of the sediments and the prevailing carbonato complex.
- At Eh < 200 mV (Np(V) is reduced to Np(IV) and polynuclear hydroxo complexes of Np(IV) are formed.

During the first days various amounts of these hydroxo complexes are found in form of colloids, actually higher percentages at low concentrations of Np and at lower salinity. Precipitation of Np(IV) hydroxide proceeds more or less slowly. In this range a sorption equilibrium is not established, but the sorption ratio R_S is mainly given by the ratio of the amount of insoluble species of Np(IV) (hydroxide) to the amount of soluble species of Np, and the apparent sorption ratio R_S depends on the initial concentrations c_0 of Np(V) in the system. At $c_0 \approx 10^{-7}$ mol/l R_S is of the order of 10^3 ml/g.

- In the range between about 200 and 300 mV intermediate values of R_S are observed.
- The sorption ratios R_S of Np are not changed markedly by high salt concentrations or by the presence of low concentrations of organic complexing agents.

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