THE MIGRATION CHEMISTRY OF NEPTUNIUM

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ABSTRACT

The chemistry of neptunium, including redox properties, complex chemistry and chemistry of neptunium in its five oxidation states, III, IV, V, VI and VII has been reviewed with special emphasis on factors, which may be of importance in controlling the environmental behavior of this element. Under environmental conditions neptunium should exist predominantly in oxidation state V in the form NpO_2^+ and to some extent also as Np(IV) in the form of Np^{4+} and Np(VI) in the form of NpO_2^{2+}, whereas the other oxidation states Np(III) and Np(VII) can not exist in the environment. However, experimental evidence is lacking as is any knowledge about the mobility of neptunium in the environment.

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I INTRODUCTION /1, 2/

I.1 History of Neptunium

Element number 92 in the periodic table: uranium, was for a long time considered to be the final element in the periodic table. However, according to theory, the periodic table appeared incomplete, and it was suggested, that elements of higher atomic numbers than 92 might at one time have existed, although such elements would long since have disappeared due to short half-lifes and intense radioactivity. In 1932 the neutron was discovered, and following this event, many different elements were bombarded with neutrons. Fission of nuclei into radioactive fragments was the usual result, but then in 1940 the existence of an isotope with an atomic number higher than 92 was established by McMillan and Abelson /3/. They showed, that thermal neutron capture in ^{238}U could produce a short-lived isotope of element 93, and they called the new element, neptunium after the planet beyond Uranus namely the planet Neptun. With the discovery of neptunium (Z = 93), the first member of the group of artificial radioactive elements called the transuranium elements, had been found.

I.2 Isotopes of Neptunium

The neptunium isotope, which established the existence of an element number 93, was the β-emitting isotope ^{239}Np with a half-life of 56.4 hours, and it had been formed according to the reaction scheme,

$$^{238}U + n \rightarrow {}^{239}U \rightarrow {}^{239}Np + \beta^-$$

Since then about 18 isotopes of neptunium have been identified. Tables listing these isotopes and giving half-lives and modes of decay can be found in e.g. /2, 4/.
The neptunium isotopes all have short half-lives except for ^{236}Np ($T_{½} = 1.55 \times 10^5$ years) and ^{237}Np ($T_{½} = 2.14 \times 10^6$ years).
^{236}Np is extremely rare, being formed only in very small amounts in thermonuclear explosions, but the α-emitting ^{237}Np is of special interest because of its long half-life, its relative aboundance and the nature of the daughter products.

I.3 Formation of Neptunium

The isotope ^{237}Np is a normal product in nuclear reactors. It is currently formed in kilogram amounts as a by-product, when neutrons from the fission of ^{235}U react with ^{238}U, and in a two-step process yield ^{237}Np,

$$^{238}U + n \rightarrow {}^{237}U + 2n$$

$$^{237}U \rightarrow {}^{237}Np + \beta^-$$

^{237}Np is also formed by two-step neutron capture in ^{235}U with gamma energy being released in the process,

$$^{235}U + n \rightarrow {}^{236}U + n \rightarrow {}^{237}U \rightarrow {}^{237}Np + \beta^-$$

Thus, ^{237}Np is a normal constituent in the radioactive waste from power reactors and is also formed during the production of plutonium.

^{237}Np can be isolated during the reprocessing of uranium and plutonium, and is of practical use, because ^{238}Pu formed from ^{237}Np in the following reaction,

$$^{237}Np + n \rightarrow {}^{238}Np \rightarrow {}^{238}Pu$$

is being used for power sources in e.g. space vehicles and terrestrial navigation beacons.

I.4 Occurrence of Neptunium

Man-made actinides mostly in the form of plutonium isotopes have been introduced into the environment /5/ primarily through the atmospheric nuclear weapons tests, which took place in the period between 1950 and 1963. Disintegration of ^{238}Pu power sources has also yielded some actinides, and finally a very small amount originates from the processing of uranium fuel. In addition to the plutonium isotopes, americium- and curium isotopes are also present having been formed by multiple neutron capture.

These various transuranic isotopes will decay with very differing half-lives by their individual pathways and as a function of time, different isotopes will dominate as environmental hazards. It has been estimated /6/, that ^{241}Am will be the most important transuranic isotope in the environment for a period of 10^1 to 10^3 - 10^4 years after the formation and introduction of these transuranic isotopes into nature. For the following span of years from 10^4 to 10^5 years after formation, the nuclides ^{239}Pu, ^{240}Pu and ^{243}Am will be the principal isotopes, and for the period after 10^6 years, ^{237}Np with a contribution from ^{229}Th will be the dominant isotope.

The predicted accumulation of long-lived ^{237}Np has lead to an increased interest in studying the environmental distribution and possible behavior of neptunium in nature. From a chemical point of view, neptunium is almost unique in the periodic table, because of the very wide range of chemical properties based on the fact that neptunium can exist in five well-established oxidation states from III to VII. Thus, the chemistry of neptunium indicates that this element is capable of a varied behaviour by forming very different-behaving species, if exposed to the involved and complicated chemistry of the environment. For these reasons, the speciation of neptunium is a topic of great interest in connection with radioactive waste disposal as well as in the interpretation of the environmental impact.

II THE CHEMISTRY OF NEPTUNIUM

II.1 General

Neptunium is one of the 14 actinide elements constituting the 5f-transition series, which is a series of elements in the periodic system characterized by having unfilled lower orbitals. The actinide series starts with element number 89, actinium and electrons are then added successively to the 5f orbitals. The first electrons entering the 5f shell are not well shielded, and as their energy is fairly high, they tend to participate in bonding in competition with the 6d electrons.

For element number 93, neptunium the energy difference between the 5f and the 6d shells are of the size of ordinary bonding energies, and for this reason neptunium is able to exhibit the following oxidation states: Np(VII), Np(VI), NP(V), NP(IV) and Np(III), in the solid state as well as in aqueous solution.

The actual electron configuration of a particular neptunium species will differ being dependent on the nature of the atoms bound to the actinide as well as on the surrounding medium.

Np(VII), which is the highest oxidation state of Neptunium, is a strong oxidizing agent especially in acid media. Np(VI) is also strongly oxidizing, while Np(V) appear to be the most stable state and not particularly prone to disproportionation. Np(IV) is a mild reductant and Np(III) a more powerful reductant though not capable of decomposing water.

The ions of the neptunium oxidation states III, IV, V, VI form with great ease solvated cations in nucleophilic solvents e.g. in H_2O /7/, and the bonding is strong as shown by the enthalpies of solvation /8/. The neptunium aquo-cations will act as acids,

$$Np^{n+}(H_2O)_x \rightarrow [Np(OH)^{(n-1)+}](H_2O)_{(x-1)} + H^+$$

and the tendency of the different neptunium cations to hydrolyze decreases as follows,

$$Np^{4+} \rightarrow NpO_2^{2+} \rightarrow Np^{3+} \rightarrow NpO_2^{+}$$

The neptunium hydroxy-compounds especially those formed from the tetravalent Np^{4+} may, given sufficiently high Np^{4+} concentration, polymerize further under acid and neutral conditions to form highly polymerized positively charged products /9/.

In the following, the individual oxidation states of the neptunium species will be treated seperately.

II.2 Oxidation state III.

In the absence of complexing ions, Np(III) exists in acidic solution as the hydrated Np^{3+}-ion and is then violet of color. $Np^{3+}(aq)$ possess a spherical symmetry and has a large radius (~1.01 Å) in comparison to the charge, and for this reason it is a fairly weak acid. The pK has not been measured directly, but comparison with similar aquo-ions indicate a pK-value, which is higher than 7 /10/. A theoretical pK-value has been calculated to be 7.8 /11/. $Np^{3+}(aq)$ will precipitate out as the insoluble hydroxide in alkaline solution and does not react with water to form soluble hydroxy anions in basic solution /8/. Neptunium(III) is susceptible to oxidation and the insoluble Np(III)hydroxide will quickly be oxidized to the IV state in the presence of O_2.

II.3 Oxidation state IV.

In the absence of complexing ions, Np(IV) will exist as the spherical $Np^{4+}(aq)$-ion (radius~0.913 Å) in strong acidic solution and is then yellow-green of color. However, $Np^{4+}(aq)$ is a fairly strong acid with a measured pK value of 2.30 /10/ and a calculated value of 2.0 /11/, and in acid and neutral solution it will hydrolyze water forming first hydroxy-polymers, then colloids. $Np^{4+}(aq)$ will precipitate as the insoluble, metastable hydroxide $Np(OH)_4$, which slowly changes to the stable form NpO_2 in alkaline solution. $Np^{4+}(aq)$ does not react with water to form soluble hydroxy anions in basic solution.

II.4 Oxidation state V.

Np(V) is stable in both acidic and basic solution, but the $Np^{5+}(aq)$-ion is too acidic to exist in aqueous solution. It will immediately react with the water forming the very stable NpO_2^+-ion, which is present in acidic solution as $NpO_2^+(aq)$ (green of color) and in alkaline solution as the soluble hydroxy-anion, $NpO_2(OH)_2^-$ (yellow of color). The linear, rod-shaped $NpO_2^+(aq)$-ion is a weak acid with a pK value estimated at 8.85 /10/ and a calculated value of 10.9 /11/.

II.5 Oxidation state VI.

Np(VI) is stable in both acidic and basic solution, but the $Np^{6+}(aq)$-ion is too acidic to exist in aqueous solution. It will immediately react with the water forming NpO_2^{2+}, which is present in acid solution as $NpO_2^{2+}(aq)$ (pink/red of color). In alkaline solution it is uncertain whether the pink-colored species present is $NpO_4^{2-}(aq)$ or $NpO_2(OH)_4^{2-}(aq)$. The linear, rod-shaped $NpO_2^{2+}(aq)$-ion is a fairly strong acid (pK = 5.17, calculated value = 5.5), which hydrolyze even in dilute solution /12/. If the concentration of NpO_2^{2+} is less than 10^{-7} M only monomeric hydroxy species are formed /9/, but at higher cation concentrations polymer species may form often polynuclear of nature.

II.6 Oxidation state VII.

Np(VII) is stable only in alkaline solution and the formular for the green-colored species is believed to be NpO_5^{3-}(aq) or more likely $NpO_2(OH)_6^{3-}$(aq) /10/. Np(VII) is a strong oxidizing agent in acidic solution and water is rapidly oxidized, although indirect evidence has indicated the existance of Np(VII) under acidic conditions in the form of NpO_3^+ (brownish-red of color) /13/.

III REDOX PROPERTIES OF NEPTUNIUM

III.1 Thermodynamic data

The present knowledge about the thermodynamic properties of neptunium species is limited. The most recent compilation can be found in the series of reviews titled, 'The Chemical Thermodynamics of Actinide Elements and Compounds' /14/. The enthalpy of formation, ΔH°, and the free energy of formation, ΔF°, for the neptunium ions given in Table III-1, are taken from these reviews part 2, which is authored by Fuger and Oetting /15/.

Table III-1 Thermodynamic data for aqueous neptunium species

Species	State	ΔH° kJ mole^{-1}	ΔF° kJ mole^{-1}	S° J(K mole)$^{-1}$
Np^{3+}	aq	-527.2	-517.1	-179.1
Np^{4+}	aq	-556.1	-502.9	-389
NpO_2^+	aq	-978	-915	- 21
NpO_2^{2+}	aq	-861	-796	- 94
NpO_3^+	aq 1 M H^+		-836	
NpO_5^{3-}	aq 1 M NaOH		-1065	

III.2 Redox Properties

It is not possible to determine directly the standard electrode potentials for the neptunium species of Np(III), Np(IV), Np(V) and Np(VI), due to the lack of stability of aqueous neptunium ions in anything but acid or complexed solution. Instead the published redox potentials have been calculated by thermodynamic means or have been inferred from measured formal potentials (1 M $HClO_4$ or 1 M NaOH) /16/.

In a recent comprehensive review by Martinot and Fuger /17/, critically evaluated standard electrode potentials for neptunium couples are presented, and representative values are given in Table III-2.

Table III-2 Standard electrode potentials for neptunium couples

Reaction	Volt	Oxidation States
ACID SOLUTION		
$NpO_3^+ + e^- + 2H^+ \rightarrow NpO_2^{2+} + H_2O$	+2.04	VII → VI
$NpO_2^{2+} + e^- \rightarrow NpO_2^+$	+1.24	VI → V
$NpO_2^{2+} + 2e^- + 4H^+ \rightarrow Np^{4+} + H_2O$	+0.94	VI → IV
$NpO_2^+ + e^- + 4H^+ \rightarrow Np^{4+} + 2H_2O$	+0.64	V → IV
$Np^{4+} + e^- \rightarrow Np^{3+}$	+0.15	V → III
$Np^{4+} + 4e^- \rightarrow Np^0$	-1.30	IV → 0
$Np^{3+} + 3e^- \rightarrow Np^0$	-1.79	III → 0
BASIC SOLUTION		
$NpO_5^{3-} + e^- + H_2O \rightarrow NpO_4^{2-} + 2OH^-$	+0.6	VII → VI
$NpO_2(OH)_2 + e^- \rightarrow NpO_2(OH) + OH^-$	+0.6	VI → V
$NpO_2(OH) + e^- + 2H_2O \rightarrow Np(OH)_4 + OH^-$	+0.3	V → IV
$Np(OH)_4 + e^- \rightarrow Np(OH)_3 + OH^-$	-2.1	IV → III
$Np(OH)_3 + 3e^- \rightarrow Np(s) + 3OH^-$	-2.2	III → 0

The redox potentials given for the neptunium species in basic solution are especially uncertain, since they have been derived using poorly determined solubility equilibrium constants.

The redox interrelationship between the five oxidation states of neptunium in aqueous solution, III, IV, V, VI and VII, represented by the ionic aquo-ions of Np^{3+}, Np^{4+}, NpO_2^+, NpO_2^{2+} and NpO_3^+/NpO_5^{3+} is presented below in the form of 'Latimer' diagrams /18/, which relates solely redox potentials and oxidation states.

The redox potentials given are for the half-reactions in which the left-hand species is reduced to the right-hand species. The appropriate number of electrons, H^+ and H_2O to balance the half reaction have been left out for reasons of simplicity.

pH = 0

$$\begin{tikzcd}
NpO_3^{+} \arrow[r, "+2.04"] & NpO_2^{2+} \arrow[r, "+1.24"] \arrow[rr, bend left, "+0.94"] & NpO_2^{+} \arrow[r, "+0.64"] & Np^{4+} \arrow[r, "+0.15"] \arrow[rrr, bend right, "-1.30"'] & Np^{3+} \arrow[r, "-4.7"] \arrow[rr, bend left, "-1.79"] & (Np^{2+}) \arrow[r, "-0.3"] & Np
\end{tikzcd}$$

pH = 14

$$NpO_5^{3-} \xrightarrow{+0.6} NpO_2(OH)_2 \xrightarrow{+0.6} NpO_2(OH) \xrightarrow{+0.3} NpO_2 \xrightarrow{-2.1} Np(OH)_3 \xrightarrow{-2.23} Np$$

The $Np^{3+} \leftrightarrow Np^{4+}$ couple is reversible as is the $NpO_2^{+} \leftrightarrow NpO_2^{2+}$ couple, but the $Np^{4+} \leftrightarrow NpO_2^{+}$ couple is not readily reversible, since the latter reaction involves the breaking of neptunium-oxygen bonds.

Redox potentials of the neptunium ions, NpO_3^{+}, NpO_2^{2+}, NpO_2^{+} and Np^{4+} in different mineral acids have been determined /19/ and are shown in Table III-3. The redox potentials are similar to each other for HCl, HNO_3 and $HClO_4$ whereas the SO_4^{2-} values differ, indicating a complexing tendency of the sulfate ion especially for Np(IV).

Table III-3 Standard electrode potentials (in volt) of neptunium couples in 1 M solutions of different mineral acids

Reaction	$HClO_4$	HCl	H_2SO_4	HNO_3
$NpO_3^{+} + e^{-} + 2H^{+} \rightarrow NpO_2^{2+} + H_2O$	+2.04	-	-	>+2.0
$NpO_2^{2+} + e^{-} \rightarrow NpO_2^{+}$	+1.14	+1.14	+1.08	+1.14
$NpO_2^{+} + e^{-} + 4H^{+} \rightarrow Np^{4+} + 2H_2O$	+0.74	+0.74	+0.99	-
$Np^{4+} + e^{-} \rightarrow Np^{3+}$	+0.155	+0.14	+0.1	-

Because neptunium can exist in acidic solution in the four stable oxidation states, III, IV, V and VI, there is an distinct possibility of disproportionation reactions taking place. In Table III-4 are given equilibrium constants measured in 1 M acid (HCl or $HClO_4$) solutions for the disproportionation of Np(III) and of Np(V).

It is apparent that the tendency towards disproportionation of Np(V) to form Np(IV) and Np(VI) is small.

The disproportionation of two NpO_2^{+}-ions to form Np^{4+} and NpO_2^{2+} involves four H^{+}-ions and, thus, should be strongly pH-dependent. However, potential relations are such as to render NpO_2^{+} moderately stable with respect to disproportionation even in solutions containing high concentrations of H^+. On the other hand, in the presence of 1 M sulfuric acid, the equilibrium constant for the disproportionation of two Np(V)-species to form Np(IV) and Np(VI) is increased by a factor of 6 x 10^4 due to the complexing effect of the SO_4^{2-}ion /19/. Disproportionation reactions involving neptunium species in alkaline solution have not yet been established.

Table III-4 Disproportionation equlibria of neptunium ions

Reaction	log K
2 * Np(IV) → Np(III) + Np(V)	-10
3 * Np(IV) → 2 * Np(III) + Np(VI)	-27
2 * Np(V) → Np(IV) + Np(VI)	- 6.40

The oxidation and reduction of the different neptunium species in the presence of complexing agents as well as various oxidizing and reducing agents have been extensively studied and reported /20/. Likewise an extensive number of rate data for these processes have been compiled /21/.

IV NEPTUNIUM SPECIES

IV.1 Constants of Neptunium Species

The hydrated neptunium ions are surrounded by water molecules in the hydration shell, and it is through an exchange of the labile water molecules with nucleophilic ligands that complex formation takes place. The process is normally diffusion-controlled and highly electrostatic in nature, due to the fact that both water and the ligands are directly bound to the central metal ion. Directly measured formation constants for the many complexes of the several neptunium species are virtually impossible to obtain due to experimental difficulties. In spite of this fact, formation constants of the Np-ions with a variety of inorganic and organic ligands have been published /24/. A more limited, critically evaluated, but slightly outdated list can be found in /23/.

The need for knowledge about the possible behavior of neptunium in nature has increased efforts at obtaining 'best values' for use in environmental and geochemical modelling codes. Work towards improving the databases as a collective effort is in progress within the EEC through the ChemVal programme, which aims at validating geochemical codes, and organized within the Nuclear Energy Agency (NEA) as part of the development of the CODATA compatible thermodynamic database, expert panels, one for each actinide, are reviewing critically the relevant constants.

Lately a newly developed unified theory of metal ion complexation has been published /22/ based on which predicted formation constants of neptunium have been derived /11/.

In the following will be emphasized the complexes formed with ligands relevant to the environment, i.e. the inorganic anions to be found in the ground water: OH^-, F^-, NO_3^-, SO_4^{2-}, Cl^-, CO_3^{2-} and HCO_3^- as well as a number of low-molecular organic anions.

The ligands OH^- and HCO_3^-/CO_3^{2-} are of particular interest, because of their omni-presence in nature. It would have been desirable to include data about complexes between neptunium and humic- and fulvic acids, but no such information is available.

Table IV-1 Experimentally determined stability constants of Np^{4+} with simple inorganic ligands /23/

Reaction	log β	Temp. °C	Ionic Strength I
$Np^{4+} + OH^- \rightarrow Np(OH)^{3+}$	12.5	25	0
	11.7	25	2
$Np^{4+} + F^- \rightarrow NpF^{3+}$	8.3	20	4
$Np^{4+} + 2\,F^- \rightarrow NpF_2^{2+}$	14.5	20	4
$Np^{4+} + 3\,F^- \rightarrow NpF_3^+$	20.3	20	4
$Np^{4+} + 4\,F^- \rightarrow NpF_4$	25.1	20	4
$Np^{4+} + Cl^- \rightarrow NpCl^{3+}$	0.15	20	0.5
	-0.04	20	1
	0.04	20	2
$Np^{4+} + 2\,Cl^- \rightarrow NpCl_2^{2+}$	-0.24	25	1
	-0.15	20	2
$Np^{4+} + 3\,Cl^- \rightarrow NpCl_3^+$	-0.5	20	1
$Np^{4+} + NO_3^- \rightarrow NpNO_3^{3+}$	1.7	20	0
	0.38	25	1
	0.34	25	2
$Np^{4+} + 2\,NO_3^- \rightarrow Np(NO_3)_2^{2+}$	0.1	20	1
	0.2	25	2
$Np^{4+} + 3\,NO_3^- \rightarrow Np(NO_3)_3^+$	-0.3	20	1
$Np^{4+} + SO_4^{2-} \rightarrow NpSO_4^{2+}$	3.51	25	2
	3.41	23	3
	3.53	20	4
$Np^{4+} + 2\,SO_4^{2-} \rightarrow Np(SO_4)_2$	5.42	23	3
	5.92	20	4

The neptunium ions along with other actinide ions are classified as strong electrophiles, and they would be expected to form strong complexes with nucleophiles such as F^- and with oxygen-containing ligands, inorganic and organic alike, whereas the affinity for sulfur and the other halides should be weak.

Experimentally determined formation constants for the complexation of the selected inorganic ligands are presented in Table IV-1 for Np^{4+}, and in Table IV-2 for NpO_2^{2+}, whereas no reliable formation constants for Np^{3+} and for NpO_2^+ with the inorganic ligands are available. It can be seen that complexes are formed with F^- and SO_4^{2-}, whereas Cl^- and NO_3^- do not form complexes with the two neptunium species for which experimental data are available. Experimentally determined stability constants for the complexation between the neptunium ions and hydroxyl- and carbonate ligands are absent with the exception of the first complex of the hydroxyl ion, OH^-.

<u>Table IV-2</u> Experimentally determined stability constants of NpO_2^{2+} with simple inorganic ligands /23/

Reaction	log β	Temp. °C	Ionic Strength I
$NpO_2^{2+} + OH^- - NpO_2(OH)^+$	8.9	25	0
	8.6	25	2
$NpO_2^{2+} + F^- - NpO_2F^+$	4.6	25	0
	4.12	25	0.1
	4.04	25	0.5
	3.85	20	1
$NpO_2^{2+} + 2\,F^- - NpO_2F_2$	7.01	25	0.1
	7.00	25	0.5
	6.97	20	1
$NpO_2^{2+} + Cl^- - NpO_2Cl^+$	-0.3	25	0.5
	-0.09	10	3
$NpO_2^{2+} + 2\,Cl^- - NpO_2Cl_2$	-0.8	10	3
$NpO_2^{2+} + NO_3^- - NpO_2NO_3^+$	-0.9	25	0.5
	-0.4	25	2
$NpO_2^{2+} + SO_4^{2-} - NpO_2SO_4$	3.27	25	0
	2.20	25	0.1
	2.07	25	0.5
	1.82	20	1
$NpO_2^{2+} + 2\,SO_4^{2-} - NpO_2(SO_4)_2^{2-}$	3.8	25	0.1
	3.4	25	0.5
	2.62	20	1

In Table IV-3 are presented the predicted formation constants of the four neptunium ions to be expected in nature, Np^{3+}, Np^{4+}, NpO_2^+ and NpO_2^{2+} with the ligands, F^-, Cl^-, NO_3^- and SO_4^{2-} as calculated by the method given in /11/.

Table IV-3 Predicted stability constants of neptunium species with simple inorganic ligands given as $\log \beta_{Np,x,y}$. The over-all charge of the complex formed is also shown.

		Np^{3+}		Np^{4+}		NpO_2^+		NpO_2^{2+}	
Ligand	x,y	$\log \beta_{x,y}$		$\log \beta_{x,y}$		$\log \beta_{x,y}$		$\log \beta_{x,y}$	
F^-	1,1	4.39	+2	8.45	+3	1.60	0	4.80	+1
	1,2	7.94	+1	15.66	+2	2.14	-1	8.32	0
	1,3	10.79	0	21.77	+1	1.74	-2	10.67	-1
	1,4	12.98	-1	26.81	0	0.47	-3	11.92	-2
	1,5	14.54	-2	30.83	-1	-1.67	-4	12.07	-3
	1,6	15.49	-3	33.84	-2				
Cl^-	1,1	0.72	+2	1.29	+3	0.15	0	0.44	+1
	1,2	1.04	+1	2.27	+2	-0.03	-1	0.57	0
	1,3	1.10	0	3.07	+1	-0.43	-2	0.52	-1
	1,4	0.94	-1	3.72	0	-0.99	-3	0.34	-2
	1,5	0.60	-2	4.26	-1	-1.68	-4	0.05	-3
	1,6	0.09	-3	4.71	-2				
NO_3^-	1,1	1.01	+2	1.86	+3	0.19	0	0.64	+1
	1,2	0.92	+1	2.96	+2	-0.51	-1	0.57	0
	1,3	-0.01	0	3.57	+1	-1.84	-2	0.06	-1
	1,4	-1.68	-1	3.77	0	-3.72	-3	-0.81	-2
	1,5	-4.03	-2	3.63	-1	-6.08	-4	-1.96	-3
SO_4^{2-}	1,1	3.09	+1	5.02	+2	1.43	-1	2.60	0
	1,2	4.59	-1	8.62	0	1.28	-3	3.89	-2
	1,3	4.75	-3	11.03	-2	-0.19	-5	4.12	-4
	1,4	3.67	-5	12.37	-4	-2.88	-7	3.39	-6

It appears that the calculated values compare well with the few values which have been measured experimentally. The over-all charge of the complexes formed is also shown.

There is ample evidence, that the environmental chemistry of neptunium is strongly dominated by hydroxide- and carbonate complexation. However, due to the general insolubility of neptunium compounds especially the carbonate complexes, as shown in Table IV-4, it has not been possible to measure experimentally the formation constants for the hydroxide and carbonate complexes of any of the neptunium species. However, neptunium belong to the actinides and these elements exhibit similar behavior, when they are in the same oxidation state, and the differences in complexity constants for inorganic complexes of environmental interest between uranium, neptunium, plutonium and americium in the same oxidation state are most often within experimental error. This fact have been used among several others by Skytte Jensen /9/ and Allard et al. /6/ in their attempt at evaluating the relevant complexity constants. Another possible approach towards finding the proper complexity constants is to calculate the dicted formation constants /11, 22/.

Table IV-4 Solubility products of insoluble neptunium compunds

Reaction	$\log K_s$
Predicted Values /11/	
$Np(OH)_3 (s) \rightarrow Np^{3+} + 3 OH^-$	-25.03
$Np(OH)_4 (s) \rightarrow Np^{4+} + 4 OH^-$	-49.57
$NpO_2(OH) (s) \rightarrow NpO_2^+ + OH^-$	- 9.05
$NpO_2(OH)_2 (s) \rightarrow NpO_2^{2+} + 2 OH^-$	-23.71
$Np_2(CO_3)_3 (s) \rightarrow 2 Np^{3+} + 3 CO_3^{2-}$	-36.63
$Np(CO_3)_2 (s) \rightarrow Np^{4+} + 2 CO_3^{2-}$	-12.50
Measured Values /7/	
$Np(OH)_4 (s) \rightarrow Np^{4+} + 4 OH^-$	-55.2
$NpO_2(OH) (s) \rightarrow NpO_2^+ + OH^-$	- 9.2
$NpO_2(OH)_2 (s) \rightarrow NpO_2^{2+} + 2 OH^-$	-21.4

Table IV-5 Predicted formation constants of $Np^{3+}(aq)$ with OH^- and CO_3^{2-} (Standard conditions: 298.15 K and I=1)

Reaction	$\log \beta$		
	ref 9	ref 25	ref 11
$Np^{3+}(aq) + OH^- \rightarrow Np(OH)^{2+}(aq)$	8.0	6.60	6.23
$Np^{3+}(aq) + 2 OH^- \rightarrow Np(OH)_2^+(aq)$	-	11.00	11.46
$Np^{3+}(aq) + 3 OH^- \rightarrow Np(OH)_3 (aq)$	-	15.00	15.83
$Np^{3+}(aq) + 4 OH^- \rightarrow Np(OH)_4^-(aq)$	-	18.00	19.38
$Np^{3+}(aq) + 5 OH^- \rightarrow Np(OH)_5^{2-}(aq)$	-	-	22.14
$Np^{3+}(aq) + 6 OH^- \rightarrow Np(OH)_6^{3-}(aq)$	-	-	24.12
$Np^{3+}(aq) + CO_3^{2-} \rightarrow NpCO_3^+(aq)$	9.6	6.50	7.27
$Np^{3+}(aq) + 2 CO_3^{2-} \rightarrow Np(CO_3)_2^-(aq)$	12.9	11.00	13.12
$Np^{3+}(aq) + 3 CO_3^{2-} \rightarrow Np(CO_3)_3^{3-}(aq)$	16.2	11.50	17.82
$Np^{3+}(aq) + 4 CO_3^{2-} \rightarrow Np(CO_3)_4^{5-}(aq)$	-	-	21.47
$Np^{3+}(aq) + 5 CO_3^{2-} \rightarrow Np(CO_3)_5^{7-}(aq)$	-	-	24.12
$Np^{3+}(aq) + 6 CO_3^{2-} \rightarrow Np(CO_3)_6^{9-}(aq)$	-	-	25.80
$Np^{3+}(aq) + CO_3^{2-} + OH^- \rightarrow Np(OH)CO_3(aq)$	-	-	17.69

Table IV-6 Predicted stability constants of $Np^{4+}(aq)$ with OH^- and CO_3^{2-} (Standard conditions: 298.15 K and I=1)

Reaction	log β			
	ref 9	ref 6	ref 25	ref 11
$Np^{4+}(aq) + OH^- \rightarrow Np(OH)^{3+}(aq)$	13.45	12.5	12.5	12.04
$Np^{4+}(aq) + 2\ OH^- \rightarrow Np(OH)_2^{2+}(aq)$	26.8	25	25	23.50
$Np^{4+}(aq) + 3\ OH^- \rightarrow Np(OH)_3^{+}(aq)$	37.5	36	36	31.13
$Np^{4+}(aq) + 4\ OH^- \rightarrow Np(OH)_4(aq)$	-	46	47	45.13
$Np^{4+}(aq) + 5\ OH^- \rightarrow Np(OH)_5^{-}(aq)$	-	50*	45.3	55.38
$Np^{4+}(aq) + 6\ OH^- \rightarrow Np(OH)_6^{2-}(aq)$	-	-	-	65.27
$Np^{4+}(aq) + CO_3^{2-} \rightarrow Np(CO_3)^{2+}(aq)$	-	-	-	11.89
$Np^{4+}(aq) + 2\ CO_3^{2-} \rightarrow Np(CO_3)_2(aq)$	-	-	-	22.81
$Np^{4+}(aq) + 3\ CO_3^{2-} \rightarrow Np(CO_3)_3^{2-}(aq)$	-	-	-	33.01
$Np^{4+}(aq) + 4\ CO_3^{2-} \rightarrow Np(CO_3)_4^{4-}(aq)$	-	-	-	42.58
$Np^{4+}(aq) + 5\ CO_3^{2-} \rightarrow Np(CO_3)_5^{6-}(aq)$	-	36.5*	-	51.59
$Np^{4+}(aq) + 6\ CO_3^{2-} \rightarrow Np(CO_3)_6^{8-}(aq)$	-	-	-	60.08
$Np^{4+}(aq) + CO_3^{2-} + 3\ OH^- \rightarrow Np(OH)_3CO_3^{-}(aq)$	41	42*	41	44.84

*: assumed value

Table IV-7 Predicted stability constants of $NpO_2^{+}(aq)$ with OH^- and CO_3^{2-} (Standard conditions: 298.15 K and I=1)

Reaction	log β			
	ref 9	ref 6	ref 25	ref 11
$NpO_2^{+}(aq) + OH^- \rightarrow NpO_2(OH)(aq)$	4.3	5.1	0.87	3.10
$NpO_2^{+}(aq) + 2\ OH^- \rightarrow NpO_2(OH)_2^{-}(aq)$	-	-	3.22	5.43
$NpO_2^{+}(aq) + 3\ OH^- \rightarrow NpO_2(OH)_3^{2-}(aq)$	-	-	-	7.12
$NpO_2^{+}(aq) + 4\ OH^- \rightarrow NpO_2(OH)_4^{3-}(aq)$	-	-	-	8.22
$NpO_2^{+}(aq) + 5\ OH^- \rightarrow NpO_2(OH)_5^{4-}(aq)$	-	-	-	8.76
$NpO_2^{+}(aq) + CO_3^{2-} \rightarrow NpO_2(CO_3)^{-}(aq)$	-	5.9	4.89	4.31
$NpO_2^{+}(aq) + 2\ CO_3^{2-} \rightarrow NpO_2(CO_3)_2^{3-}(aq)$	-	11.1	7.11	7.44
$NpO_2^{+}(aq) + 3\ CO_3^{2-} \rightarrow NpO_2(CO_3)_3^{5-}(aq)$	-	16.3	7.34	9.63
$NpO_2^{+}(aq) + 4\ CO_3^{2-} \rightarrow NpO_2(CO_3)_4^{7-}(aq)$	-	-	-	10.99
$NpO_2^{+}(aq) + 5\ CO_3^{2-} \rightarrow NpO_2(CO_3)_5^{9-}(aq)$	-	-	-	11.58

Table IV-8 Predicted stability constants of $NpO_2^{2+}(aq)$ with OH^- and CO_3^{2-}
Standard conditions: 298.15° K and I=1)

Reaction	log B			
	ref 9	ref 6	ref 25	ref 11
$NpO_2^{2+}(aq) + OH^- \rightarrow NpO_2(OH)^+(aq)$	8.7	8.9	8.90	8.53
$NpO_2^{2+}(aq) + 2\ OH^- \rightarrow NpO_2(OH)_2(aq)$	17.0	17.8*	16.48	16.58
$NpO_2^{2+}(aq) + 3\ OH^- \rightarrow NpO_2(OH)_3^-(aq)$	21.3	23 *	20.30	24.25
$NpO_2^{2+}(aq) + 4\ OH^- \rightarrow NpO_2(OH)_4^{2-}(aq)$	-	-	-	31.61
$NpO_2^{2+}(aq) + 5\ OH^- \rightarrow NpO_2(OH)_5^{3-}(aq)$	-	-	-	38.68
$NpO_2^{2+}(aq) + CO_3^{2-} \rightarrow NpO_2(CO_3)(aq)$	10	10.1*	10.0	8.18
$NpO_2^{2+}(aq) + 2\ CO_3^{2-} \rightarrow NpO_2(CO_3)_2^{2-}(aq)$	17	16.7*	17.0	15.49
$NpO_2^{2+}(aq) + 3\ CO_3^{2-} \rightarrow NpO_2(CO_3)_3^{4-}(aq)$	21	23.8*	21.0	22.18
$NpO_2^{2+}(aq) + 4\ CO_3^{2-} \rightarrow NpO_2(CO_3)_4^{6-}(aq)$	-	-	-	28.35
$NpO_2^{2+}(aq) + 5\ CO_3^{2-} \rightarrow NpO_2(CO_3)_5^{8-}(aq)$	-	-	-	34.05
$NpO_2^{2+}(aq) + CO_3^{2-} + OH^- \rightarrow NpO_2(OH)CO_3^-(aq)$	-	-	-	16.18
$NpO_2^{2+}(aq) + CO_3^{2-} + 2\ OH^- \rightarrow NpO_2(OH)_2(CO_3)^{2-}(aq)$	-	-	-	23.81

*: assumed value

In Table IV-5 for Np^{3+}, in Table IV-6 for Np^{4+}, in Table IV-7 for NpO_2^+ and in Table IV-8 for NpO_2^{2+} are shown the values used by Skytte Jensen /9/, by Allard et al /6/, and calculated in /11, 22/ as well as the values currently in use for the geochemical modelling code, PHREQUE /25/. Comparison between the values for the different neptunium species show agreement within order af magnitude.

The complexing ability of the neptunium ions varies markedly among the oxidation states. For a given ligand, the stability of the complexes generally increases with the order of the effective charge on the Np-atom i.e. $NpO_2^+ < NpO_2^{2+} \sim Np^{3+} < Np^{4+}$.

IV.2 Complexes of Neptunium

In the following the complexation reactions of each neptunium ion will be treated seperately.

Complexes of Np^{3+}

Np^{3+} is very susceptible to oxidation, and no complexing constants involving Np^{3+} have been published except at extremely high ionic strength, where the following formation constants have been recorded in 7 M LiCl,

$Np^{3+} + Cl^- \rightarrow NpCl^{2+}$ log $\beta = -2.40$

$Np^{3+} + 2Cl^- \rightarrow NpCl_2^+$ log $\beta = -4.98$

Table IV-5 shows the predicted formation constants /11/ for OH^- and CO_3^{2-}, and the potential at forming strong complexes with these in nature omni-present ligands is evident. In Table IV-3 the predicted formation constants for Np^{3+} with other environmental inorganic anions can be found. It appears as expected that, F^- is able to complex strongly, whereas the other ligands form weak or no complexes. The predicted formation constants for Np^{3+} with low-molecular organic acids is presented in Table IV-9 but none of these values have been measured experimentally.

Table IV-9 Predicted stability constants of neptunium species with simple organic ligands given as log $\beta_{x,y}$.

		Np^{3+}	Np^{4+}	NpO_2^+	NpO_2^{2+}
Ligand	x,y	log $\beta_{x,y}$	log $\beta_{x,y}$	log $\beta_{x,y}$	log $\beta_{x,y}$
$HCOOH$ Formate	1,1	2.74	5.24	0.70	2.34
	1,2	3.88	9.12	-0.13	3.46
	1,3	3.66	11.91	-2.24	3.59
	1,4	2.20	13.69		2.86
	1,5	-0.46	14.54		1.30
	1,6		14.47		
CH_3COOH Acetate	1,1	3.08	5.91	0.85	2.79
	1,2	4.67	10.73	0.40	4.61
	1,3	5.00	14.73	-1.10	5.72
	1,4	4.18	18.00	-3.55	6.22
	1,5	2.28	20.60		6.16
	1,6	-0.69	22.57		
CH_2NH_2 $COOH$ Glycine	1,1	6.24	10.92	1.45	4.72
	1,2	10.71	20.38	1.28	8.02
	1,3	14.50	29.56		
CH_2OH $COOH$ Glycol	1,1	2.77	5.29	0.71	2.38
	1,2	3.99	9.43	0.05	3.72
	1,3	3.92	12.67	-1.73	4.29
	1,4	2.65	15.11	-4.53	4.19
	1,5	0.25	16.81		3.46
	1,6		17.80		
$COOH$ $COOH$ Oxalate	1,1	7.30	12.63	3.02	6.60
	1,2	11.45	22.46	2.94	10.58
	1,3	13.81	30.87		

Complexes of Np^{4+}

The experimentally determined stability constants of Np^{4+} with some inorganic ligands is given in Table IV-1, and it supports the qualitative evidence, that Np^{4+} forms stable complexes with F^- and SO_4^{2-}. The complexation between Np^{4+} and SO_4^{2-}, which proceeds due to favourable entropy changes, has been studied in detail /26/ to the extent that thermodynamic values have been determined /27/. The Np^{4+} ions show a limited tendency at forming complexes with Cl^- and NO_3^-, but in the concentrated acid solutions negatively charged 6-ligand complexes, $[Np(Cl)_6]^{2-}$ and $[Np(NO_3)]^{2-}$ have been found /28/.

In Table IV-6 are presented the calculated stability constants for Np^{4+} complexes with hydroxide and carbonate ligands, and it is evident that Np^{4+} is capable of complexing very strongly with both hydroxide and carbonate. Again, no experimental values have been measured.

Table IV-10 Experimentally determined stability constants of $Np(IV)^{4+}$, $Np(V)O_2^+$ and $Np(VI)O_2^{2+}$ with organic ligands /23,29/

Np-specie		Organic Ligand		log β
$Np(IV)^{4+}$	+	1 * oxalic acid	HOOC-COOH	7.47
$Np(IV)^{4+}$	+	2 * oxalic acid	"	13.69
$Np(IV)^{4+}$	+	3 * oxalic acid	"	19.37
$Np(V)O_2^+$	+	1 * glycolic acid	$CH_2OH-COOH$	1.51
$Np(V)O_2^+$	+	1 * lactic acid	$CH_3-CHOH-COOH$	1.75
$Np(V)O_2^+$	+	1 * oxalic acid	HOOC-COOH	4.04 3.74
$Np(V)O_2^+$	+	2 * oxalic acid	"	7.36 6.31
$Np(V)O_2^+$	+	1 * malonic acid	$HOOC-CH_2-COOH$	2.75
$Np(V)O_2^+$	+	1 * succinic acid	$HOOC-CH_2-CH_2-COOH$	1.72
$Np(V)O_2^+$	+	1 * maleic acid	HOOC-CH=CH-COOH	2.20
$Np(VI)O_2^{2+}$	+	1 * acetic acid	CH_3COOH	2.31
$Np(VI)O_2^{2+}$	+	2 * acetic acid	"	4.23
$Np(VI)O_2^{2+}$	+	3 * acetic acid	"	6.30
$Np(VI)O_2^{2+}$	+	1 * glycolic acid	HOH_2CCOOH	2.37
$Np(IV)O_2^{2+}$	+	2 * glycolic acid	"	3.95
$Np(IV)O_2^{2+}$	+	3 * glycolic acid	"	5.00

In Table IV-9 are given the predicted formation constants of the neptunium species with selected organic carboxylate ligands /23, 29/. It is apparent, that Np^{4+} is able to complex very strongly with such ligands, but experimental evidence is limited to a study of the complexation with oxalic acid as shown in Table IV-10 in which case a chelate structure seems to be formed. Np^{4+} complexes strongly with EDTA and with NTA as can be seen in Tabel IV-11.

<u>Table IV-11</u> Experimentally determined Formation Constants of Neptunium Species with EDTA and NTA

Np-Specie	Ligand		log β
Np^{4+} +	1 * Ethylene-dinitrilo-acetic acid	(EDTA)	24.6
Np^{4+} +	1 * Nitrilo-tri-acetic acid	(NTA)	17.28
Np^{4+} +	2 * Nitrilo-tri-acetic acid	(NTA)	32.06
NpO_2^+ +	1 * Ethylene-dinitrilo-acetic acid	(EDTA)	5.3
NpO_2^+ +	1 * Nitrilo-tri-acetic acid	(NTA)	6.8

Complexes of NpO_2^+

NpO_2^+ is a large ion carrying one single positive charge. 'A priori' NpO_2^+ should not be able to complex very strongly with anions, and indeed it is not the case if the predicted formation constants for complexation with the simple inorganic ligands given in Table IV-3 are to be trusted. The values given in Table IV-7 indicate that complexation of OH^- and CO_3^{2-} with NpO_2^+ is likely to take place, but the values are smaller than for the other neptunium species. No experimental values are available.

The NpO_2^+-ion is a linear entity with the oxygens carrying a net negative charge, so although NpO_2^+ is a large ion carrying the one single positive charge, the effective charge on the Np atom itself is considerably higher, and as a consequece the coordination field is stronger. For this reason NpO_2^+ does form complexes although weak with organic carboxylate ions as indicated in Table IV-9, and complexity constants have been measured experimentally as shown in Table IV-10. The complexation is particular strong in case of oxalate, where a chelate structure is formed. NpO_2^+ also complexes with EDTA and with NTA. and the complexity constants are given in Tabel IV-11.

Complexes of NpO_2^{2+}

Table IV-2 presents the experimentally determined formation constants for NpO_2^{2+}, and again it appears, that complexes are formed with F^- and SO_4^{2-}, but not with Cl^- and NO_3^- and that the measured complexation constants agree reasonably well with the predicted values given in Table IV-3. The calculated complexation constants for NpO_2^{2+} with OH^- and CO_3^{2-} are given in Table IV-8. No experimental values are available for the formation of these environmentally important species. NpO_2^{2+} form complexes with organic carboxylate ligands /23, 29/ although these are not particularly strong as can be seen in Tables IV-9 and IV-10.

IV.3 Stability Diagrams

Neptunium in the four valence states III, IV, V and VI form stable compounds and in addition is capable of prolific complex formation with a large number of different ligands.

In the current context, which is the potential for migration in nature, the ligands of interest are those found in aqueous surroundings such as sweet water, sea water as well as ground water, as are F^-, Cl^-, SO_4^{2-} and above all OH^- and CO_3^{2-}. Other ligands are the low-molecular acids of the soil organic matter, and also organic chelating agents such as EDTA and similar compounds, which have been added to the environment by various artificial means. An evaluation by Skytte Jensen /9/ concluded that the effect of F^-, Cl^- and SO_4^{2-} upon neptunium complexation is negligible and that carbonate/bicarbonate together with OH^- are the only important complex-forming agents present.

It is possible on the basis of knowledge of the chemical behavior and physico-chemical values to predict the speciation of an element in given surroundings. The stability of the different chemical forms in aqueous solution is conveniently represented in a stability diagram. Such diagrams are useful in identifying predominant species under given conditions 'in casu'

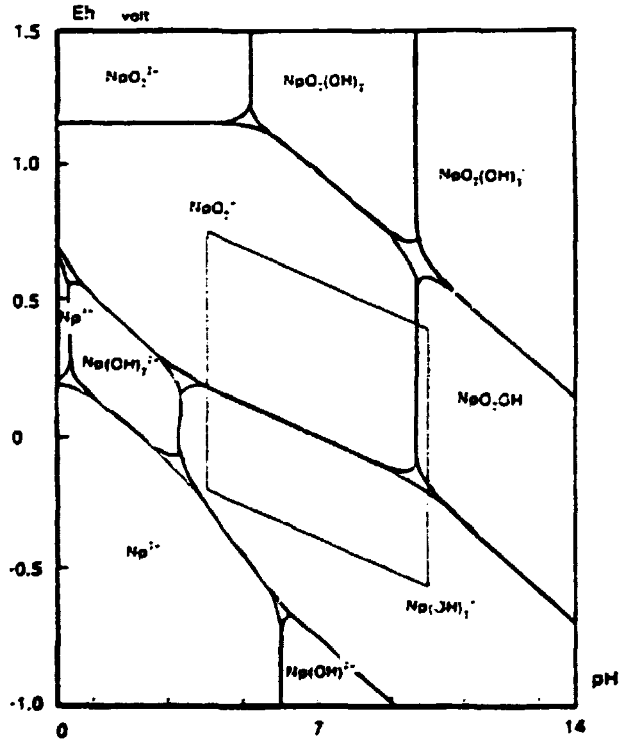


Figure 1

Neptunium speciation as a function of pH and Eh in a carbonate-free aqueous solution. The border lines denote areas within which the indicated Np-specie constitute >50% of the total amount of neptunium present.
The area defined by the parallellogram corresponds to pH/Eh conditions normally to be expected in the environment.

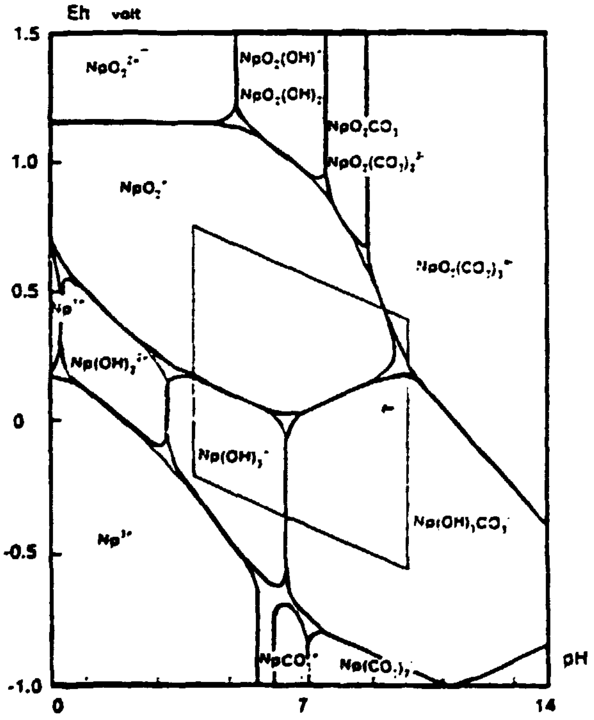
equilibrium conditions, but must be used with caution, since they often are based on estimated free-energy values. The diagrams are graphs of pH versus Eh, and they show the equilibrium occurence of species as domains relative to pH and pE or Eh, the latter two being interrelated by the equation pE = (nF/2.3RT)Eh.

The equilibrium occurrence means stability conditions of the dissolved species in aqueous environments and this means conditions of stable water. The area of geochemical interest is limited by the boundaries due to the break-down of water by either oxidation or reduction and by the environmental pH limitations 4-10.

The behavior in nature of an element such as neptunium is determined by the actual conditions of pH - Eh - temperature - pressure and also by the ionic strength and the anions present.

Figure 1, adopted from /9/, show the diagram for neptunium speciation in pure water, where only the anion OH^- is present. The hydroxy species are all formed in a stepwise manner. Figure 1 show the domains within which the indicated species constitute 50% or more of total species under the given circumstances. Within the environmental pH and Eh ranges it is the IV and V oxidation stages of neptunium, which are in existance. Np(IV) in the form of $Np(OH)_3^+$ and Np(V) in the form of NpO_2^+. Only in the higher end of the pH range is the NpO_2OH species present. Figure 1 is based on the values given in Tables IV-5 to 8. However, if the values of other origin also given in the tables are used for the calculation only negligible influence on the resulting areas of domain, can be observed /30/.

In Figure 2 are presented a similar calculation, but this time carried out in the presence of carbon dioxide at atmospheric pressure. The resulting picture is not influenced to any great



<u>Figure 2</u>

Neptunium speciation as a function of pH and Eh in an aqueous solution saturated with carbon dioxide at a partial pressure of $10^{-3.5}$ atm correspon-ding to atmospheric conditions. The border lines denotes areas within which the indicated Np-specie constitute >50% of the total amount of neptunium present.
The area defined by the parallellogram corresponds to pH/Eh conditions normally to be expected in the environment.

degree in that Np(IV) in the form of $Np(OH)_3^+$ and Np(V) in the form of NpO_2^+ still appear as the dominating species within the environmental pH and Eh ranges. In the areas outside the environmental area many carbonate species, however, have appeared.

V NEPTUNIUM IN THE ENVIRONMENT

V.1 Occurrence of neptunium

Neptunium is an actinide made by man, and it has never been found in nature, except for the extremely minute amounts of the isotopes ^{237}Np and ^{239}Np, which have been identified in close proximity to uranium ores, where they are formed continuously as the result of the bombardment of ^{238}U with neutrons from the spontaneous fission of ^{235}U /31/.

The neptunium encountered in nature originates from weapons detonation tests and from nuclear fuel facilities. As a consequence of the introduction into the environment, many efforts have been made at measuring the concentration and the distribution of neptunium in nature. However, analytical problems and very low concentrations of neptunium have limited the number of environmental samples, that have been measured.

^{237}Np and ^{239}Np are the isotopes of interest in connection with the environmental behaviour of neptunium, but there is a great difference between these isotopes in their impact on the environment /32/.

The ^{239}Np-isotope is a component of fresh fall-out and it is also discharged from nuclear facilities, but ^{239}Np has the short half-life of 56.4 hours, and is of no long-term consequence in nature. ^{239}Np has been identified following weapons testing in the soils of the immediate surroundings and also in the water and sediments downstream from nuclear fuel facilities /33/.

^{237}Np, on the other hand, has a very long half-life of 2.14×10^6 years and it will accumulate in time, since ^{237}Np is being continuously formed through the pathway,

$$^{241}Pu\ (T_{½} = 14.4\ yr) \rightarrow\ ^{241}Am\ (T_{½} = 433\ yr) \rightarrow\ ^{237}Np$$

from ^{241}Pu, which was introduced into the environment primarily through the atmospheric nuclear weapons tests. In addition, ^{237}Np is a normal product of nuclear energy production. Thus, the ^{237}Np-isotope is destined to become a small but hazardous constituent of long-term nuclear waste.

^{237}Np has not been detected in soils in the environment nor has ^{237}Np been detected in aquatic ecosystems contaminated solely by fall-out. However, ^{237}Np has been identified in soil samples from the vicinity of nuclear fuel reprocessing facilities where controlled releases of transuranium elements occur, and ^{237}Np has also been detected in aquatic ecosystems contaminated by discharges from nuclear installations /33/.

V.2 Environmental Neptunium Chemistry

Chemically, neptunium can exist in five stable oxidation states, but Np(III) and Np(VII) are highly reactive and hence are not likely to be encountered in the environment. Thus, Np(IV), Np(V) and Np(VI) are the three oxidation states to consider and which may coexist in the environment /34, 35/.

Figs. 1 and 2 indicate that Np(V) is the most common oxidation state of neptunium to expect in the environmental pH range under moderately oxidizing conditions. Np(V) should be present as the hydrated NpO_2^+-ion itself, since its hydrolysis takes place only above pH 7, and because the tendency towards complex-formation is limited. Thus, the NpO_2^+-ion is the more stable form of neptunium. $NpO_2^+(aq)$ is soluble and therefore potentially the most mobile neptunium species in nature.

Np(V) does not disproportionate very easily, but in the presence of complexing agents the tendency increases, and Np(IV) and Np(VI) are formed. According to Figs. 1 and 2 neptunium in oxidation state VI is not likely to be present as the carbonate or hydroxide complexes under environmental conditions, whereas Np(VI) in the form of the NpO_2^{2+}-ion does form strong and stable complexes with e.g. organic ligands, and Np(VI) may be present in a complexed form. Neptunium in oxidation state IV may be formed by reduction, which in nature is brought about by e.g. ferrous-containing minerals. Np(IV) will also be formed by the disproportionation of Np(V). Np(IV) is present as the $Np^{4+}(aq)$-ion only under quite acidic conditions, otherwise it hydrolyzes rapidly forming a series of soluble hydrolytic products before precipitating as the nearly insoluble hydroxide. Np(IV) is capable of forming strong complexes and may be present in nature in a complexed form. Colloid formation is a possibility to be considered in connection with the hydrolysis of $Np^{4+}(aq)$ under near neutral conditions, in which case polymerized hydroxy complexes possessing over-all positive charges are formed. Since most minerals, clays and humic acids show an excess of negative charges around neutral pH, the neptunium polymers will tend to be strongly adsorbed to these surfaces, thus be immobilized and prevented from migration. The formation of polymers increases with increasing concentration of the cation so at the environmentally low concentration of neptunium, hydrolytic polymers are not likely to be formed to any great extent.

Neptunium in all three environmental oxidation stages (IV, V, VI) is capable of forming complexes with the ligands normally associated with soil organic matter such as the low-molecular carboxylic acids and humic- and fulvic acids as well as with organic chelating agents such as EDTA and similar compounds, which have been added to the environment for various artificial means. However, the presence of neptunium complexes with organic ligands ligands, has never been demonstrated.

V.3 Neptunium in the terrestrial environment

Neptunium has not been found in the terrestrial environment except around nuclear detonation sites and near nuclear facitities, in which case neptunium was identified by its radioactivity with the chemical form of Np remaining unknown. The current knowledge about the behaviour of neptunium in the terrestrial environment therefore stems from experimental studies.

Different processes may take place when neptunium-containing solutions are in contact with the solids depending on the prevailing pH and redox conditions /37/. Sorption of Np(V) without valence change may occur, or Np(V) may be reduced to Np(IV) by surface reactions, followed by adsorption, precipitation or by complexation.

In the batch equilibrium experiments the removal of neptunium from ground water solutions by a variety of rocks both silicaceous and calcareous rocks, minerals, soils and colloid particles have been studies and a variety of distribution coefficients which differ by more than four orders of magnitude have been reported. However, too many variables are at work in these studies and many more experiments have to be carried out under well-controlled conditions before conclusions about the sorption/desorption of neptunium can be drawn.

Indications are that the adsorption of neptunium to soil constituents is not a simple ion exchange phenomena. Attempts have therefore been made to correlate the sorption of neptunium (in the form of NpO_2^+) to variables such as clay content, organic matter content, metal oxide content and the soil pH /36/. However, soil factors are inter-dependant and no simple relationship could be demonstrated. The pre-1982 literature has been reviewed in /33/, which concludes that the sorption of neptunium to soil particles proceeds less rapidly than for other actinides, and that Np(V) is the most soluble and potentially the more mobile of all actinide ions. Opposite to this conclusion stands the findings that e.g. the bioavailability of Np is far smaller than should be expected.

V.4 Neptunium in the aquatic environment

The knowledge about the occurrence, distribution and behavior of neptunium in the aquatic environment has been reviewed /33/. The conclusions, based on very limited information, however, are similar to those for neptunium in terrestrial surroundings in that Np appears to be less associated to sediments and the particulate fraction when in the Np(V) state and that a greater understanding of the mechanism for the reduction of Np(V) to No(IV) under the appropriate environmental conditions are necessary to enable accurate predictions of the behavior of Np to be made.

V.5 The mobility of neptunium.

Within the geochemical limits of pH 4-10 and the redox potentials given by the breakdown of water by either oxidation or reduction, neptunium should exist in aqueous surroundings preferably in the oxidation state V in the form of NpO_2^+, which is soluble and potentially the mobile neptunium species. Only well above pH 7 does NpO_2^+ udergo hydrolysis to form the insoluble NpO_2OH.

The other oxidation states of neptunium, which could exist in nature are Np(IV) and Np(VI). The interactions between these oxidation states of neptunium are partly governed by their total concentration in solution, so given sufficient concentrations, disproportionation reactions may take place. However, such concentrations of neptunium are unlikely to be found in the environment, and the stable oxidation states will be a function of the chemical environment in the form of the presence of oxidizing and reducing agents and complexing ligands e.g. it has been found in a case where the oxidation states were measured /37/, that Np(V) was reduced to Np(IV) in the presence of igneous rocks under anaerobic conditions, although Np in oxidation state V in the form of NpO_2^+ is considered to be the mobile species.

The availability in the environment of an element such as neptunium will depend on the competition between mobilization in the form of mobile complexes and immobilization by formation of insoluble complexes and by sorption of neptunium to minerals particularly clays as well as organic matter and metal oxides.

Experimental evidence concerning the mobility of neptunium in the environment is virtually non-existant, so given the present limited information, it is not possible to predict the behavior of neptunium over the range of soil conditions that might be of environmental interest. Although often demonstrated to be relative mobile the mobility might be questioned under different environmental conditions.

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The chemistry of neptunium, including redox properties, complex chemistry and chemistry of neptunium in its five oxidation states, III, IV, V, VI and VII has been reviewed with special emphasis on factors, which may be of importance in controlling the environmental behaviour of this element. Under environmental conditions neptunium should exist predominantly in oxidation state V in the form NpO_2^+ and to some extent also as Np(IV) in the form of Np^{4+} and Np(VI) in the form of NpO_2^{2+}, whereas the other oxidation states Np(III) and Np(VII) can not exist in the environment. However, experimental evidence is lacking as is any knowledge about the mobility of neptunium in the environment.

Descriptors - INIS:
CHEMICAL STATE; NEPTUNIUM; NEPTUNIUM COMPLEXES; NEPTUNIUM ISOTOPES; OXIDATION; RADIOECOLOGICAL CONCENTRATION; RADIONUCLIDE MIGRATION; REDOX POTENTIAL; REVIEWS

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