CHAPTER SIX

NEPTUNIUM

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6.1 HISTORICAL

The first report on the discovery of neptunium was in 1940 by McMillan and Abelson (1940), although McMillan did the preliminary work in 1939 and published his findings (McMillan, 1939). He did not claim that a new element had been discovered until confirmatory measurements had been undertaken in the following year. The production of neptunium was accomplished by placing a layer of uranium trioxide on paper with several aluminum or paper foils and then exposing this to neutrons from a cyclotron. Examination of the uranium paper sample containing the non-recoiling fraction displayed that two new radioactive components had been created. One component displayed a 23 min half-life, later identified as U-239, while the second exhibited a 2.3 day half-life. Both components decayed via β particle emission. Preliminary chemical analysis was performed to determine the behavior of the 2.3 day component and resulted in the contradictory assignment of this component as that exhibiting an atomic number of 93, but not being transuranic in nature (Segrè, 1939). Segrè noted in his paper that his conclusions were contradictory. However, the following quotation is from his paper, "The necessary conclusion seems to be that the 23 minute uranium decays into a very long-lived 93 and that transuranic elements have not yet been observed." The primary stumbling block to the proper assignment of the material as transuranic in nature was the lack of observation of any alpha decay activity that would emanate from the daughter product of the beta decay of this new material with an atomic number 93. It was this work by Segrè (1939) that led McMillan and Abelson to revisit the chemical analysis and determine its properties in greater depth.

To initiate their work they first had to generate more material. In doing this they were able to confirm the 'linked' nature of the 23 min and 2.3 day half-life materials observed. The ratio of these two materials was observed to remain constant. This also confirmed the earlier suggestion by Hahn *et al.* (Quill, 1938) that the following reaction was possible when uranium underwent neutron bombardment:

$$\mathrm{U} + \text{neutron} \rightarrow \mathrm{U}(23\,\text{minute}) \rightarrow \text{Eka-Re} \tag{6.1a}$$

$$^{238}\mathrm{U}(\mathrm{n},\gamma)^{239}\mathrm{U}(\beta^-, 23\ \text{min}) \rightarrow {}^{239}\mathrm{Np}(\beta^-, 2.3\ \ \text{day}) \rightarrow {}^{239}\mathrm{Pu} \tag{6.1b}$$

Differences between the rare earths and this element were observed immediately by McMillan and Abelson (1940) because it did not form a precipitate when exposed to HF in the presence of bromate, an oxidizing agent, in a strong acid. It did form a precipitate with HF in the presence of SO_2, a reducing agent. This bifurcated behavior in the presence of HF was thought to explain the incorrect assignment of this element as a rare earth by Segrè (1939) since the oxidizing potential of the solution had not been well controlled in earlier experiments (Segrè, 1939). Further evidence strongly suggested that the material was indeed an actinide, such as, precipitation in the reduced state with a thorium carrier by iodate and in the oxidized state with a uranium carrier by acetate. Also the precipitation with thorium carrier in the presence of H_2O_2 and precipitation in a carbonate-free basic solution indicated actinide-like behavior. Careful confirmatory measurements, which involved uranium that had undergone neutron bombardment and subsequent purification via fluoride precipitation in the presence of SO_2, showed the in-growth of the new element with a 2.3 day half-life. The new material was observed to exhibit a beta particle of energy approximately 470 keV. Further speculation by McMillan and Abelson regarding the daughter product, which would have atomic number 94 and a mass number of 239, was also recorded but will be discussed in Chapter 7 of this work. The element discovered by McMillan and Abelson was named after the planet Neptune, which is the first planet beyond Uranus in our solar system. This system was likewise followed for naming plutonium as its orbit was beyond Neptune.

6.2 NUCLEAR PROPERTIES

Twenty-two isotopes of neptunium are now known (Table 6.1). The isotope ^{237}Np has a sufficiently long half-life ($t_{1/2} = 2.144 \times 10^6$ years) that can be handled at weighable quantities. It is the most significant neptunium

Table 6.1 *Nuclear properties of neptunium isotopes.*

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
226	31 ms	EC, α	α 8.044	^{209}Bi(^{22}Ne,5n)
227	0.51 s	EC, α	α 7.677	^{209}Bi(^{22}Ne,4n)
228	61.4 s	EC, α		^{209}Bi(^{22}Ne,3n)
229	4.0 min	$\alpha \geq 50\%$ EC $\leq 50\%$	α 6.890	^{233}U(p,5n)
230	4.6 min	$\alpha > 99\%$ EC $\leq 0.97\%$	α 6.66	^{233}U(p,4n)
231	48.8 min	EC $< 99\%$ $\alpha > 1\%$	α 6.28 γ 0.371	^{233}U(d,4n) ^{235}U(d,6n)
232	14.7 min	EC	γ 0.327	^{233}U(d,3n)
233	36.2 min	EC $< 99\%$ $\alpha \sim 10^{-3}\%$	α 5.54 γ 0.312	^{233}U(d,2n) ^{235}U(d,4n)
234	4.4 d	EC 99.95% β^+ 0.05%	γ 1.559	^{235}U(d,3n)
235	396.1 d	EC $> 99\%$ α $1.6 \times 10^{-3}\%$	α 5.022 (53%) 5.004 (24%)	^{235}U(p,2n)
236[a]	22.5 h	β^- 50% EC 50%	β^- 0.54 γ 0.642	^{235}U(d,n)
236[a]	1.54×10^5 yr	EC 87% β^- 13%	γ 0.163	^{235}U(d,n)
237	2.144×10^6 yr $>1 \times 10^{18}$ yr	α SF	α 4.788 (51%) 4.770 (19%) γ 0.086	^{237}U daughter ^{241}Am daughter
238	2.117 d	β^-	β^- 1.29 γ 0.984	^{237}Np(n,γ)
239	2.3565 d	β^-	β^- 0.72 γ 0.106	^{243}Am daughter ^{239}U daughter
240	1.032 h	β^-	β^- 2.09 γ 0.566	^{238}U(α,pn)
240 m	7.22 min	β^-	β^- 2.05 γ 0.555	^{240}U daughter ^{238}U(α,pn)
241	13.9 min	β^-	β^- 1.31 γ 0.175	^{238}U(α,p) ^{244}Pu(n,p3n)
242 g or m	5.5 min	β^-	β^- 2.7 γ 0.786	^{244}Pu(n,p2n) ^{242}Pu(n,p)
242 g or m	2.2 min	β^-	β^- 2.7 γ 0.736	^{242}U daughter
243	1.85 min	β^-	γ 0.288	^{136}Xe + ^{238}U
244	2.29 min	β^-	γ 0.681	^{136}Xe + ^{238}U

[a] Not known whether ground-state nuclide or isomer.

isotope for chemists. ^{237}Np is synthesized by neutron irradiation of uranium according to the reactions (6.2) to (6.4). In conventional nuclear reactors ^{237}Np is generated as a by-product mainly through reactions (6.2) and (6.3). The latter reaction predominates in reactors with fuels of enriched ^{235}U.

$$^{238}\mathrm{U}(n,2n)\,^{237}\mathrm{U}\underset{6.75\,\mathrm{d}}{\xrightarrow{\beta^-}}\,^{237}\mathrm{Np} \qquad (6.2)$$

$$^{235}\mathrm{U}(n,\gamma)\,^{236}\mathrm{U}(n,\gamma)^{237}\mathrm{U}\xrightarrow{\beta^-}\,^{237}\mathrm{Np} \qquad (6.3)$$

$$^{238}\mathrm{U}(n,\gamma)\,^{239}\mathrm{U}\xrightarrow{\beta^-}\,^{239}\mathrm{Np}\xrightarrow{\beta^-}\,^{239}\mathrm{Pu}(n,\gamma)^{240}\mathrm{Pu}\xrightarrow{\beta^-}\,^{240}\mathrm{Am}(n,\gamma)^{241}\mathrm{Am}\xrightarrow{\alpha}\,^{237}\mathrm{Np} \qquad (6.4)$$

The isotopes ^{238}Np and ^{239}Np have relatively short half-lives and are useful as radioactive tracers for analytical applications or for fundamental chemistry research. They are synthesized by neutron irradiation of ^{237}Np and ^{238}U, respectively, through the following reactions:

$$^{237}\mathrm{Np}(n,\gamma)^{238}\mathrm{Np} \qquad (6.5)$$

$$^{238}\mathrm{U}(n,\gamma)^{239}\mathrm{U}\xrightarrow{\beta^-}\,^{239}\mathrm{Np} \qquad (6.6)$$

The isotopes ^{235}Np and ^{236}Np are synthesized by cyclotron irradiation of ^{235}U according the following reactions:

$$^{235}\mathrm{U}(d,n)^{236}\mathrm{Np} \qquad (6.7)$$

$$^{235}\mathrm{U}(p,n)^{235}\mathrm{Np} \qquad (6.8)$$

The isotopes heavier than ^{237}Np are unstable with respect to β^- decay. Isotopes lighter than ^{237}Np decay by electron capture and also are unstable with respect to alpha decay.

6.3 PRODUCTION OF PRINCIPAL NEPTUNIUM ISOTOPES

The principal isotopes of neptunium are generated by irradiation of uranium with neutrons. Of the 22 isotopes listed in Table 6.1, only ^{235}Np, ^{236}Np and ^{237}Np have half-lives long enough to permit accumulation. Neptunium-237 is generated by reactions (6.2), (6.3) and (6.4). However, by irradiating uranium, only ^{237}Np is capable of accumulating. Neptunium-239 is produced from irradiation of ^{238}U and the decay of the resulting ^{239}U, however, the half-life of ^{239}Np, 2.3565 days, is too short for accumulation. Irradiation of uranium by neutrons is unsuitable for the generation of ^{235}Np and ^{236}Np. Therefore only ^{237}Np is produced in any significant quantities. Currently, the production of plutonium is the source of ^{237}Np where the isotope is a by-product of the process. Significant quantities also reside in spent fuel, in high-level waste (HLW), and in solutions containing ^{237}Np stored at various reprocessing facilities. There are no known commercial uses for neptunium. The need for ^{238}Pu as a heat source for radioisotope thermoelectric generators (RTGs) and radioisotope heater units (RHUs) is the main reason to separate and purify ^{237}Np. RTGs are used to supply electricity to space vehicles used in the Galileo, Ulysses, and Cassini NASA missions (see Chapter 7). RHUs are used to provide heat for delicate instruments on space missions. Future needs to separate ^{237}Np and the other actinides from spent fuel and HLW may be required by the proposed transmutation of actinides residing in these materials. Removal of the transuranics, including especially ^{237}Np, has the advantage of eliminating concerns for the long-term storage of radioactive waste. A recent and rather novel use of ^{237}Np is to produce pure ^{236}Pu tracer to assess the amount of plutonium in the environment. Yamana *et al.* (2001) demonstrated that the irradiation of ^{237}Np with bremsstrahlung of an electron beam of 23 and 30 MeV produced ^{236}Pu with low ^{238}Pu impurity. Neptunium-237 could also be used in nuclear weapons; its critical mass is approximately 73 kg.

Plutonium-238 is generated by the reaction shown below:

$$^{237}\mathrm{Np}(\mathrm{n},\gamma)\ ^{238}\mathrm{Np} \xrightarrow{\beta^-} {}^{238}\mathrm{Pu} \tag{6.9}$$

To obtain ^{238}Pu, ^{237}Np is separated from spent fuel by various modifications of the well-known plutonium and uranium recovery by extraction (Purex) process. After dissolution, neptunium is separated from the spent fuel by solvent extraction and ion exchange by careful adjustments of acid concentrations, oxidations states, and volume percent of tributyl phosphate (TBP). The separated neptunium is precipitated as neptunium oxalate, calcined to neptunium oxide, and fabricated into targets. Targets of the separated isotope are irradiated in a high neutron flux. After irradiation, the targets are cooled for a specific amount of time to allow for fission product decay and then dissolved. ^{238}Pu is then separated from ^{237}Np by taking advantage of the differences in the characteristic oxidation states of the resulting fission products, neptunium, and plutonium.

To date, the reprocessing of irradiated nuclear fuel has focused on the separation of plutonium and uranium from fission products and other actinides. Proposed transmutation and advanced nuclear fuel cycles will require the development of separations that include the actinides and are safe, efficient, and environmentally acceptable. The need for these new technologies will create significant opportunities for research and development activities in the field of actinide chemistry.

6.4 NEPTUNIUM IN NATURE

^{237}Np ($t_{1/2} = 2.144 \times 10^6$ years) has the longest half-life of neptunium isotopes. Because this half-life is considerably shorter than the age of the Earth, which is about 4.5×10^9 years, primordial ^{237}Np no longer exists on Earth.

Neptunium isotopes can be formed by nuclear reactions continuously taking place in the Earth's crust, resulting in a dynamic equilibrium between the rate of formation and the rate of decay. Neutron capture by ^{238}U produces ^{239}Np (see reaction (6.6)), and an (n,2n) reaction on ^{238}U forms ^{237}Np (see reaction (6.2)). The neutrons originate from the spontaneous fission of ^{238}U, the neutron-induced fission of ^{235}U, (α,n) reactions on elements of low atomic number, and/or fission or spallation reactions induced by cosmic rays. Small amounts of ^{239}Np are expected to occur in uranium minerals by continuous formation from ^{238}U, but its half-life of 2.36 days is too short to permit any significant equilibrium concentration to be reached (Garner *et al.*, 1948; Seaborg and Perlman, 1948; Levine and Seaborg, 1951). The isolation of microgram amounts of ^{239}Pu by Peppard *et al.* (1951) from Belgian Congo (now Democratic Republic of the Congo) uranium undoubtedly establishes the existence of ^{239}Np in nature. The isotope ^{237}Np itself has been identified in and isolated from a uranium ore concentrate from Belgian Congo and in other minerals (Peppard *et al.*, 1952). The maximum ratio of ^{237}Np to uranium in such minerals is about 10^{-12}.

The primary sources of neptunium in the biosphere, as with the other transuranium elements, are atmospheric nuclear explosions. On the basis of the analyzed results on global fallout, it was calculated that 2500 kg of ^{237}Np had been generated, which is comparable in mass with the quantity of plutonium (4200 kg of ^{239}Pu and 700 kg of ^{240}Pu) (Efurd *et al.*, 1984). There is little information about the man-made neptunium content of various natural materials, because of the low specific radioactivity of the long-lived ^{237}Np and the systematic difficulties in its determination (Novikov *et al.*, 1989). For global fallout, the ^{237}Np/^{239,240}Pu ratio lies within one order of magnitude $(1\text{–}10) \times 10^{-3}$. When 5×10^{-3} is taken as an average value of the ratio, the concentration of ^{239,240}Pu in seawater is 13×10^{-3} mBq L^{-1}, and the ^{237}Np concentration comprises 6.5×10^{-5} mBq L^{-1} (Holm *et al.*, 1987).

6.5 SEPARATION AND PURIFICATION

Reprocessing of spent nuclear fuels to recover reusable uranium and plutonium and the partitioning of high-level radioactive liquid wastes (HLW) constitute the main processes of the nuclear fuel cycle. ^{237}Np, α emitter with a 2.144×10^6 years half-life, is one of the major nuclides to be separated from Purex process solutions and HLW. Several separation methods satisfying requirements for process-scale operation have been developed. At the same time, separation methods suitable for relatively small-scale operations are necessary to prepare pure neptunium as a source material in the synthesis of neptunium metal or its compounds, and to isolate or preconcentrate neptunium in analytical samples before determination.

Solvent extraction, ion-exchange chromatography, extraction chromatography, coprecipitation, and electrolytic deposition methods are used for the separation of neptunium ions. Most of the wet-chemical methods involve the control of neptunium ion oxidation states which varies between 3+ and 6+ or even 7+ and utilization of specific chemical behavior of the ion in each oxidation state. Well-established separation methods are reviewed by Burney and Harbour (1974). Choppin and Nash (1995) and Nash and Choppin (1997) recently evaluated separation methods. A report published by OECD/NEA (1997) reviewed separation chemistry of actinides in nuclear waste streams and materials.

6.5.1 Solvent extraction

Many extractants have been employed for the solvent extraction of neptunium ion (cf. reviews by Laskorin *et al.* (1985) and Rozen and Nikolotova (1988)). Multi-dentate β-diketone derivatives, organophosphorus compounds, and amine compounds are commonly used. Mathur *et al.* (2001) reviewed solvent extraction technology from the viewpoints of engineering the management of nuclear spent fuels and radioactive wastes.

Typical β-diketone, 2-thenoyltrifluoroacetone (HTTA, $\mathrm{p}K_\mathrm{a} = 6.23$), is most widely used for the extraction of neptunium ions. The separation scheme as shown in Fig. 6.1, which is for the analysis of ^{237}Np in sediments and soils by alpha-counting, inductively coupled plasma-mass spectrometry (ICP-MS), or neutron activation analysis, was proposed by Hursthouse *et al.* (1992) and is based on HTTA extraction and anion-exchange chromatography. In this procedure, Np(VI) and Np(V) in the sample solution are reduced to Np(IV), which is extracted from 1 M HNO_3 to 0.5 M HTTA (toluene) phase ($D_{\mathrm{Np(IV)}} \geq 10^3$). Here, *D* denotes the distribution ratio of a metal ion, which is a ratio of the concentration of the metal in the organic phase to that in the aqueous phase under the extraction equilibrium condition. Coexisting U(VI) and Pu(III) are not extracted ($D_{\mathrm{U(VI)}} \leq 5 \times 10^{-5}$ and $D_{\mathrm{Pu(III)}} \leq 10^{-5}$), which enables the separation of neptunium from plutonium and uranium. Np(IV) in the toluene phase is back-extracted into 8 M HNO_3 solution. Alternatively, Np(IV) in toluene is reduced to Np(V) and back-extracted to 1 M HNO_3 ($D_{\mathrm{Np(V)}} \leq 5 \times 10^{-4}$).

1-Phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HPMBP, cf. Fig. 6.2) and its derivatives are useful extractants for actinide ions. The $\mathrm{p}K_\mathrm{a}$ of HPMBP (4.11), which is smaller than the $\mathrm{p}K_\mathrm{a}$ of HTTA, extracts Np(IV) from highly acidic solution, e.g. 1–4 M HNO_3. The ability of HPMBP to extract Np(IV) from such an acidic solution avoids an interference by hydrolysis of Np(IV). Np(VI) and Np(V) are not extracted under this condition.

The synergistic extraction with HPMBP and tri-*n*-octylphosphine oxide (TOPO) was employed to separate Np(V) from Am(III), Cm(III), U(VI), Pu(IV), and lanthanide(III) ions (Pribylova *et al.*, 1987). Zantuti *et al.* (1990) developed a

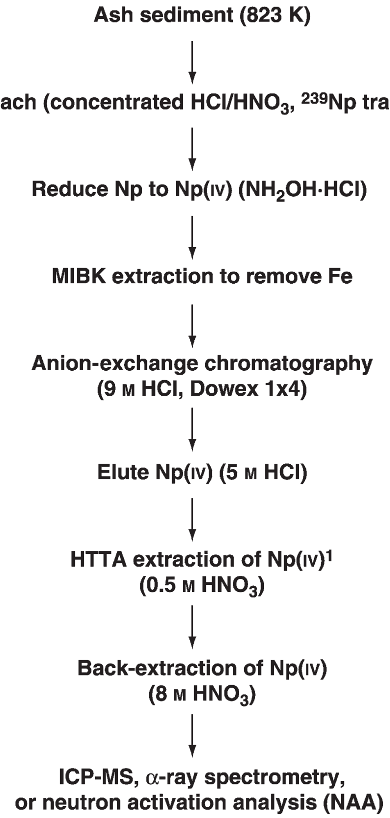
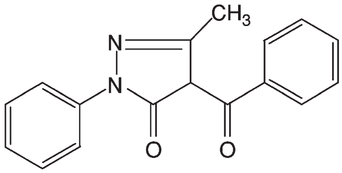


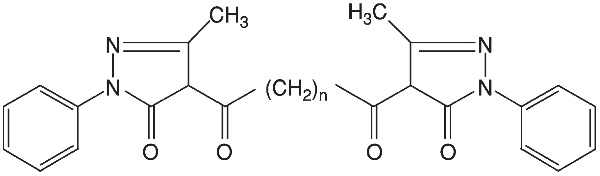
Fig. 6.1 *Procedure for the determination of* ^{237}*Np in sediment samples* (*Hursthouse* et al., 1992). [1]*HTTA extraction is repeated for* α*-ray spectrometry or NAA.*

method for the separation of a trace amount of neptunium from nitric acid solution containing a large quantity of uranium using the synergistic extraction with HPMBP and di-2-ethylhexylphosphoric acid. Tochiyama *et al.* (1989) showed that Np(v) was extracted efficiently with HPMBP in the presence of methyltrioctylammonium chloride. The 3-phenyl-4-bezoyl-5-isoxazolone was demonstrated to be powerful to extract Np(IV) and the procedure was developed for the separation of ^{237}Np from ^{236}Pu and ^{235}U in the irradiated sample of uranium target (Mohapatra and Manchanda, 1993).

Takeishi *et al.* (2001) studied the extraction behavior of actinide ions using bis (1-phenyl-3-methyl-4-acylpyrazol-5-one) derivatives H_2BPn, where n denotes the number of methylenes in a chain, having a structure as shown in Fig. 6.2. The log D vs $-\log[H^+]$ plots for the extraction of Np(IV) with various derivatives of HBPn (n = 3, 4, 5, 6, 7, 8, 10, 22) are shown in Fig. 6.3. The slopes of



1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP)



Bis(1-phenyl-3-methyl-4-acylpyrazol-5-one)
(H_2BPn; $n = 3, 4, 5, 6, 7, 8, 10, 22$, etc)

Fig. 6.2 *Structure of pyrazolone derivatives.*

log D vs $-\log[H^+]$ plot as well as slopes of log D vs $\log[H_2BPn]$ plot suggest $Np(BPn)_2$ as the extracted species. The H_2BPn derivatives are a stronger extractant than HPMBP, which is one of the remarkable characteristics of quadridentate H_2BPn compared with bidentate HPMBP. H_2BP7 and H_2BP8 exhibit higher extractability than the other H_2BPn derivatives examined. Based on their data a procedure for the separation of actinide ions of various oxidation states using H_2BP7 or H_2BP8 was developed.

TBP is the most useful extractant for the separation of actinide ions at the process scale. The early works with TBP are summarized in the reviews by Geary (1955) and Schneider and Harmon (1961), which provide a wide scope of TBP extraction chemistry and engineering. Np(VI) and Np(IV) are extracted as $NpO_2(NO_3)_2(TBP)_2$ and $Np(NO_3)_4(TBP)_2$, respectively, and the extraction efficiency increases with increasing concentrations of TBP and HNO_3 (1–10 M). The distribution ratios of Np(IV) and Np(VI) are 3.0 and 12.0, respectively, between 4 M HNO_3 and 30% TBP(dodecane) at 298 K. The procedure for the separation of neptunium from uranium and plutonium consists in the adjustment of the oxidation state to Np(VI), co-extraction with U(VI) and Pu(IV) and back-extraction of Np(V) by the reduction of Np(VI) to Np(V).

The *n*-octyl(phenyl)-*N*,*N*-diisobutyl-carbamoyl methylphosphine oxide (CMPO) is an effective extractant for the separation of actinide ions from acidic solutions (Kolarik and Horwitz, 1988). The mixed organic solvent of (0.1–0.2) M CMPO + (1.2–1.4) M TBP in dodecane is usually employed. Distribution ratios for Np(IV), Pu(IV), and Pu(III) between nitric acid solution and 0.1 M

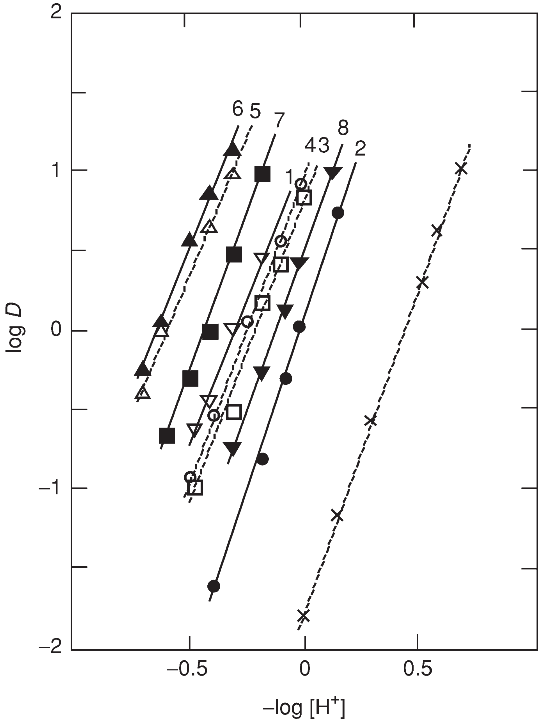


Fig. 6.3 *Log D vs −log* $[H^+]$ *plots for the extraction of* Np^{4+} *in* HNO_3 *solution with* 1×10^{-3} M H_2BPn *and HPMBP in chloroform solution.* (*From Takeishi* et al., 2001, *with permission from Elsevier*). (1) H_2BP_3, (2) H_2BP_4, (3) H_2BP_5, (4) H_2BP_6, (5) H_2BP_7, (6) H_2BP_8, (7) H_2BP_{10}, (8) H_2BP_{22}; *dotted line, HPMBP.*

CMPO + 1.4 M TBP + dodecane are shown in Table 6.2 (Mincher, 1989). For the separation of neptunium and plutonium, the oxidation states are adjusted to Np(IV) and Pu(III) with 0.1 M Fe(II) sulfamate and Np(IV) is then extracted into the CMPO/TBP phase. Pu(III) is removed by stripping with 0.01 M HNO_3 in the presence of 3% hydroxylamine nitrate. Neptunium is removed from the organic phase by an aqueous solution containing complexing agents such as $(COOH)_2$, CO_3^{2-}, or ethylenediaminetetraacetic acid (EDTA). Mathur *et al.* (1996c) compared the extraction behavior of Np(IV), Np(VI), Pu(IV), and U(VI) from nitric acid solutions with CMPO, dibutyldecanamide (DBDA), dihexyldecanamide (DHDA), and bis-2-ethylhexylsulfoxide (BEHSO) in dodecane. The extraction ability is in the order of CMPO > BEHSO > DHDA > DBDA.

Bis(2-ethylhexyl)phosphoric acid (HDEHP), which shows distinguished capability for the extraction of trivalent actinides and lanthanides ions, is also utilized for the separation of neptunium from uranium, plutonium, and

Table 6.2 *Distribution ratios of neptunium and plutonium ions between HNO_3 solution and* 0.1 M *CMPO* + 1.4 M *TBP* (*dodecane*) *at* (278 ± 1) K (*data cited from Mincher,* 1989).

	Concentration of HNO_3 (M)					
Ions	0.5	1.0	2.0	3.0	4.0	5.0
NpO_2^{2+}	43	100	114	133	150	150
NpO_2^+	10^{-2}	2×10^{-2}	4×10^{-2}	7×10^{-2}	0.12	0.18
Np^{4+}	0.55	6	113	670	1500	2200
Pu^{4+}	16	40	76	110	144	174
Pu^{3+}	1.6	3.0	5.2	7.1	10	14

americium. After the oxidation state of the actinide ions are adjusted to Np(V), U(VI), Pu(IV), and Am(III) in 1 M HNO_3 by adding $NaNO_2$, all actinide ions except Np(V) are extracted with HDEHP. Np(V) is then oxidized to Np(VI) and extracted with HDEHP. Np(VI) is reduced to Np(V) and back-extracted with 0.1 M HNO_3.

The extraction behavior of Np(IV) and Pu(IV) was investigated using eight kinds of multi-dentate organophosphorus compounds such as dioxides of diphosphine and carbamoyl phosphoryl compounds (Rozen *et al.*, 1988). The extraction behavior of Np(V) was studied systematically with TBP, TOPO, and phosphine oxide derivatives (Rozen *et al.*, 1992). The results of K_{ex} suggested that the stability of the complex between Np(V) and the bidentate extractant was remarkably enhanced in the organic solution.

Solvent extraction with tri-*n*-octylamine (TnOA) has been extensively employed for the separation of ^{237}Np from environmental analytical samples. The separation scheme for ^{237}Np in soils and sediments, which was recommended by Yamamoto *et al.* (1994), is shown in Fig. 6.6 (see Section 6.10). Np(IV) in 10 M HCl is extracted with 10% TnOA (xylene) ($D_{Np(IV)} = 300$). Np(IV) is then back-extracted with a solution of 1 M HCl + 0.1 M HF.

Heptavalent neptunium ion as a form of $NpO_4(OH)_2^{3-}$ produced in 0.1–2 M LiOH (KOH) solution is extracted with various extractants such as TBP, TOPO, crown ether derivatives, HDEHP, etc. (Rozen *et al.*, 1990). The most effective extractant is dicyclohexyl-18-crown-6 ether (in TBP) or HDEHP. Karalova *et al.* (1992a,b) studied the solvent extraction of Np(VII) from alkaline solutions with HPMBP, bis(2-oxy-4-alkyl-benzoyl)amine, bis(2-hydroxy-5-octylbenzyl) amine, and 2-hydroxy-5-*tert*-butylphenyl disulfide. The highest extraction efficiency is obtained when Np(VII) exists as $NpO_4(OH)_2^{3-}$, suggesting that the extraction process involves removal of OH^- from $NpO_4(OH)_2^{3-}$ and H^+ from the OH groups of the extractant molecules. During the extraction process the reduction of Np(VII) to Np(VI) or the oxidation of the extractant is possible, which must be taken into account for the practical use of the Np(VII) extraction procedure.

(a) Neptunium control in advanced Purex process

Currently operated commercial reprocessing plants are based on the Purex process consisting of the solvent extraction of uranium and plutonium with TBP. In principle, all neptunium is rejected into the HLW as a form of inextractable Np(v). The oxidation state of neptunium ion in the process solution, however, varies significantly depending on the chemical environment. Np(v) is oxidized to Np(vi) in the presence of HNO_2 which coexists in nitric acid solution of high concentration; the Np(v) slowly disproportionates generating Np(vi) and Np(iv) in highly acidic solution. Thus, the neptunium behavior is not fully controlled in the Purex process and neptunium distributes in different fractions of the process. Fig. 6.4 shows possible oxidation states of neptunium ions in the main stream of the Purex process. Experimental results at the THORP miniature pilot plant indicated that only 30% of the total neptunium was found in the

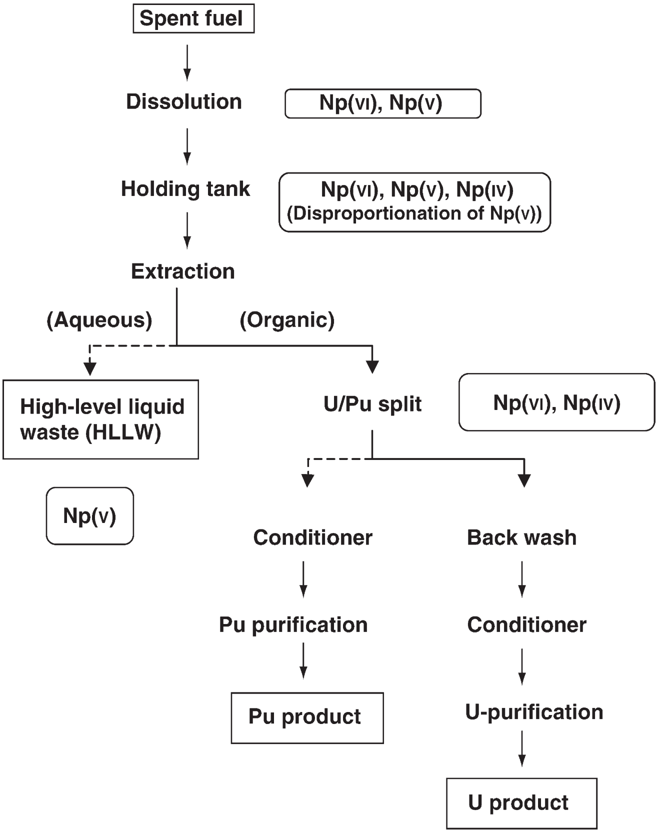


Fig. 6.4 *Flowsheet of the Purex process and the probable oxidation state of neptunium ion in the process solution.*

HLW (Taylor *et al.*, 1997). The remaining neptunium was extracted with uranium and plutonium in the solvent product.

Many attempts have been done to design an advanced Purex process. Taylor *et al.* (1997) summarized the chemical behavior of neptunium in the reprocessing plant. Recent R&D activities at BNFL (UK) attempt to control neptunium in the advanced Purex process. The advanced Purex process is required to satisfy criteria including cost and environmental impact. Reducing the size and complexity of the process and minimizing the secondary waste generation assist in fulfilling these requirements. Efficient control of neptunium within the flowsheet is an important goal assigned to the advanced Purex process. Several scenarios for the control of neptunium in the flowsheet are recommended, i.e. all neptunium is led to: (1) the HLW stream; (2) the Pu fraction; or (3) the U fraction followed by the isolation from uranium, or (4) the recovery in the Np fraction before the U/Pu split process. In all cases, the method to control neptunium behavior is based on precise control of the oxidation state of the ion. Such appropriate redox reagents must be chosen to fulfill all criteria including (1) kinetics of redox reaction, (2) decomposability after the use and (3) stability toward high acidity and radiation.

The back-extraction of Np(v) is an effective way to separate neptunium from Pu(iv) and U(vi) that remain in the organic phase. Many studies have been carried out to select suitable salt-free organic reagents to reduce Np(vi) to Np(v). Taylor *et al.* (1998a) confirmed the selectivity between the reduction of Np(vi) to Np(v) and Pu(iv) to Pu(iii) by comparing reduction rates with a wide range of potential reductants such as carboxylic acids, aldehydes, ketones, guanidines, and hydrazine derivatives. The hydrazine derivatives, i.e. *tert*-butyl hydrazine and 1,1-dimethyl hydrazine, are most promising from both viewpoints of the selectivity in the reduction of Np(vi) toward that of Pu(iv) and the reduction kinetics. The results of demonstration solvent extraction tests show that the reduction of Pu(iv) is accelerated by the presence of U(vi).

Uchiyama *et al.* (1998a) studied the reduction kinetics of Np(vi) and Pu(iv) with aldehyde derivatives and concluded that *n*-butyraldehyde was promising as a selective reductant of Np(vi). They proposed an advanced Purex process for the separation of neptunium, technetium, plutonium, and uranium, which consisted of five steps for (1) co-decontamination of these elements, (2) Np oxidation with V(v) and TBP extraction of Np(vi), (3) Np separation by the reduction of Np(vi) to Np(v) with *n*-butyraldehyde, (4) Tc separation using highly acidic scrubbing solution, and (5) U/Pu partitioning by the selective reduction of Pu (iv) to Pu(iii) with iso-butyraldehyde.

Taylor *et al.* (1998b) employed hydroxamic acids such as formohydroxamic acid and acetohydroxamic acid, and found that they selectively and rapidly reduced Np(vi) to Np(v). The investigators also reported that the reagent preferentially complexed Np(iv) and Pu(iv) in the aqueous solution. These characteristics may offer advantages in the control of neptunium in the advanced Purex process.

One way to control neptunium separation in the Purex process flowsheet is to extract all neptunium as Np(vi) together with U(vi) and Pu(iv) and then to separate neptunium from U(vi) as the reduced form, Np(v), along with Pu(iii). A suitable reductant to reduce Np(vi) to Np(v) and Pu(iv) to Pu(iii) efficiently and rapidly must be used. Hydroxylamine derivatives such as hydroxylamine and methyl-, dimethyl-, diethyl-, isopropyl-, and dibutyl-hydroxylamines, have been extensively examined for this purpose (Koltunov and Baranov, 1987). Koltunov *et al.* (1999) performed a kinetic study on the reduction of Np(vi) and Pu(iv) with the recently synthesized reductants *N*,*N*-ethyl(hydroxyethyl) hydroxylamine (EHEH). The reduction rates of Np(vi) and Pu(iv) with EHEH are among the highest of the salt-free reductants examined. This rapidity of the reduction makes EHEH particularly suitable for solvent extraction contactors such as centrifugal contactors of very short residence time in the advanced Purex process. A recent study by Koltunov *et al.* (2000) provides data on the rate of the reduction of Np(vi) and Pu(iv) with acetaldoxime in nitric acid solution, and suggests that Np(vi) and Pu(iv) are reductively stripped from 30% TBP (dodecane) phase in the presence of U(vi).

A photochemical procedure for the control of the oxidation state of the neptunium ion in the process solution is attractive due to its potential for minimization of secondary waste generation and simplicity of process design. Enokida and Suzuki (1989) used a KrF excimer laser to induce the reduction of Np(vi) to Np(v) in a 30% TBP (dodecane) phase, which was then stripped into the aqueous solution. Uchiyama *et al.* (1998b) studied the selective reduction of Np(vi) to Np(v) indirectly by nitrous acid produced photochemically with a low-pressure mercury lamp. Using a mixer-settler equipped with a photochemical reactor they demonstrated the applicability of this technique to the selective reduction and stripping of Np(v), leaving Pu(iv) and U(vi) in the 30% TBP (dodecane) phase. Photochemical processes were proposed (Wada *et al.*, 1996) for the selective extraction of Pu(vi) and Pu(iv) from Np(v), the oxidation states of which were controlled by 2 M HNO_3 + 10^{-2} M hydroxylamine nitrate + hydrazine under photoirradiation. A similar photochemical process was used for the coextraction of Pu(vi), Pu(iv), and Np(vi) prepared in 3 M HNO_3 + 10^{-2} M urea solution under irradiation.

(b) Partitioning of neptunium from high-level liquid wastes

The α emitters with a long half-life, such as ^{237}Np and other transplutonium nuclides contained in the HLW from the Purex process, are of great environmental concern. A considerable amount of work has been performed to develop methods for the partitioning of the actinides from the HLW. Several partitioning processes based on the solvent extraction technique using different extractants have been proposed as follows. Mathur *et al.* (1996a) proposed a method based on the TBP extraction for the removal of neptunium and plutonium together with U(vi). Quantitative extraction of Np(vi) and Pu(vi) from various kinds of simulated and real HLW was attained with 30% TBP (dodecane) after oxidizing neptunium and plutonium using 0.01 M $K_2Cr_2O_7$. More than 99% of neptunium and plutonium was stripped from the organic phase by reducing neptunium to Np(v) and plutonium to Pu(iii) with 0.01 M ascorbic acid + 0.1 M H_2O_2 + 2 M HNO_3 solution, leaving most of the uranium in the organic phase. Feasibility of this method was confirmed by counter-current experiments using mixer-settlers with simulated HLW (Chitnis *et al.*, 1998). Pentavalent vanadium ion, VO_2^+, is also effective to adjust the oxidation state at Np(vi) and Pu(vi).

CMPO has been evaluated to be one of the best reagents for the partitioning strategy because of its high ability to extract hexavalent, tetravalent, and trivalent actinide ions from an acidic solution of relatively wide range of acid concentrations. The well-known TRUEX process for the recovery of all actinides from various types of nuclear waste solutions is based on CMPO extraction. Kolarik and Horwitz (1988), Wisnubroto *et al.* (1991), and Mathur *et al.* (1996b) accumulated the extraction data of neptunium ion of various oxidation states using TRUEX solvent. Np(v) is inextractable and must be oxidized to Np(vi) with $K_2Cr_2O_7$ or HNO_2 or reduced to Np(iv) with Fe(ii) sulfamate or H_2O_2. Wisnubroto *et al.* (1991) showed that Np(v) readily disproportionated to Np(vi) and Np(iv) and the extraction efficiency of neptunium present initially as Np(v) in the sample solution increased, when the acid concentration of the aqueous solution was high enough, e.g. >4 M HNO_3. Np(iv) extracted in the TRUEX solvent was stripped quantitatively into the diluted HNO_3 solution containing complexing agents such as HF, $(COOH)_2$, carbonate, or EDTA. Np(vi) in the organic phase was easily stripped with diluted HNO_3 in the presence of H_2O_2 through the reduction of Np(vi) to Np(v).

The solvent extraction with diisodecylphosphoric acid (DIDPA) was applied to the partitioning of actinides in HLW (Morita *et al.*, 1996). The DIDPA extraction exhibits an advantage in that trivalent actinide ions, Am(iii) and Cm(iii), can be extracted from an aqueous solution of fairly low acidity, e.g. 0.5 M HNO_3, together with tetravalent and hexavalent ions. Even Np(v) in the sample solution is extracted by DIDPA. The addition of H_2O_2 enhances the rate of the extraction of Np(v) (Morita and Kubota, 1988). Rapid reduction of Np(v) to Np(iv) occurs during the DIDPA extraction in the presence of H_2O_2. The back-extraction of Np(iv) is achieved with 1 M $(COOH)_2$.

Trialkyl(C_6–C_8) phosphine oxides (TRPO) have been studied as an appropriate class of extractants for the recovery of Np, Pu, and Am from HLW (Zhu and Song, 1992). The optimum organic phase is 30 vol% TRPO (kerosene), and >99% of Np(iv) and Np(vi) with U(vi), Pu(vi), and Pu(iv) and >95% of trivalent actinide and lanthanide ions were extracted from 0.2 to 1 M HNO_3. The neptunium ion extracted is stripped with the plutonium ions into 0.5 M $(COOH)_2$ solution. In the recommended flowsheet, the oxidation state of neptunium is adjusted at 4+ by electrolytic reduction.

6.5.2 Chromatography using various resins

(a) Chromatography with ion-exchange resin

Various methods based on ion-exchange chromatography have been used for the separation of neptunium ions (Burney and Harbour, 1974). Cation-exchange chromatography of NpO_2^{2+}, NpO_2^{+}, and Np^{4+} with dilute acid solutions has been developed. The adsorption of ions of different oxidation states differ from each other so that the distribution ratio follows the order $Np^{4+} \gg NpO_2^{2+} \gg NpO_2^{+}$, which enables the mutual separation of neptunium ions of different oxidation states. Utilization of cation-exchange methods is limited because NpO_2^{2+} and NpO_2^{+} are often reduced to Np^{4+} when in contact with the resin; the adsorption behavior of Np^{4+} is not so selective from other coexisting cations.

Np(vi) and Np(iv) form anionic chloride or nitrate complexes in aqueous solutions containing high concentration of chloride or nitrate ions, and the anionic complexes formed are strongly adsorbed on anion-exchange resins. Well-established anion-exchange chromatographic methods are available and have been utilized for the isolation of neptunium from other actinides and fission product elements. From the viewpoint of the selectivity among neptunium ions and the other ions, nitrate media are preferable to chloride media. One such example is the procedure shown in Fig. 6.1 for the separation of ^{237}Np from environmental analytical samples, which consists of anion-exchange chromatography after solvent extraction with HTTA. The common procedure consists of the adjustment of neptunium ion at Np(iv) and the adsorption of Np(iv) nitrate complex, i.e. $Np(NO_3)_6^{2-}$, on the anion-exchange resin from 7 to 8 M HNO_3 solution. The anionic nitrate complexes of Pu(iv) and Th(iv) are also adsorbed on the resin. Pu(iv) is eluted as Pu(iii) with a mixture of 6 M HNO_3 + 0.05 M Fe(ii) sulfamate + 0.05 M hydrazine. Th(iv) is eluted with 8 M HCl. Np(iv) is then recovered by elution with 0.3 M HNO_3. Maiti *et al.* (1992) developed another method for the sequential separation of actinides by anion-exchange chromatography. Np(iv), Pu(iv), and U(vi) in 9 M HCl–0.05 M HNO_3 solution are adsorbed on the anion-exchange resin and Am(iii) is not adsorbed under these conditions. Pu(iv), Np(iv), and U(vi) are eluted successively using 9 M HCl–0.05 M NH_4I, 4 M HCl–0.1 M HF, and 0.5 M HCl–1 M HF, respectively. The Pu(iv) is eluted by the reduction of Pu(iv) to Pu(iii).

(b) Chromatography using chelate resins

Extraction chromatography using porous chelate resin loaded with an extractant is useful for the separation of actinides. A large number of theoretical plates of solvent extraction process is achieved during the column operation, which leads to an improvement of the selectivity in the separation. Maxwell (1997) developed a rapid method for the separation of neptunium using a resin loaded with Aliquat™ 336, which is called TEVA resin. Flowsheet is shown in Fig. 6.5. The oxidation states of neptunium and plutonium are adjusted to Np(IV) and Pu(III) by reducing them in a solution of Fe(II) sulfamate and ascorbic acid. Np(IV) is retained on the resin while >99.9% Pu(III) is eluted and removed. This method can be applied to such samples as nuclear materials process samples, waste solutions, and environmental samples.

TnOA-loaded Teflon resin was used for the rapid and simple separation of ^{237}Np from environmental samples (Ji *et al.*, 2001). Np(IV) in 2 M HNO_3 solution was adsorbed on the resin and eluted with 0.02 M $(COOH)_2$ + 0.16 M HNO_3 at 368 K. The decontamination factor for U(VI) was $>10^5$, allowing direct determination of ^{237}Np by ICP-MS.

Kimura (1990b) and Seranno and Kimura (1993) developed an extraction chromatographic method with TBP-loaded Amberlite XAD-4 resin for the

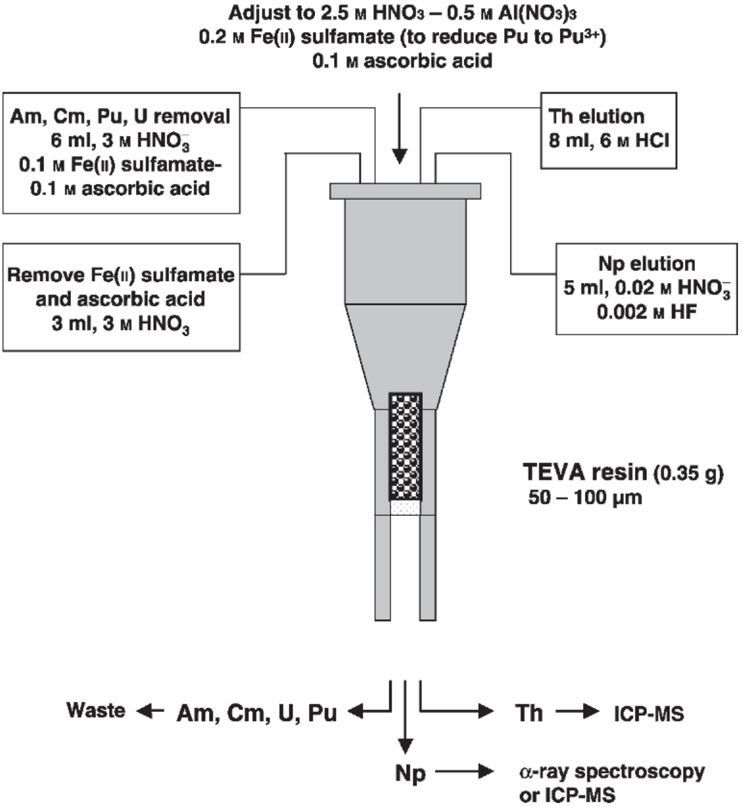


Fig. 6.5 *Procedure for the separation of neptunium ion from other actinide ions using TEVA resin.*

sequential separation of uranium, neptunium, plutonium, and americium. Np(vi) prepared by oxidizing neptunium ion in 3 M HNO_3 with 0.001 M $KBrO_3$ adsorbs on the resin and is eluted as Np(v) with the reductive effluent of 3 M HNO_3 + 0.05 M $NaNO_2$.

Heinrich and Klaus (1999) developed an automatic separation system, that is based on the extraction chromatography with silica gel particles loaded by TOPO, for the pretreatment of samples for nuclear material safeguards analysis. Np(iv), U(vi), and Pu(iv) in 3 M HNO_3 solution adsorb on the resin and are separated from Am(iii), Cm(iii), and fission products. Neptunium is eluted from the column as Np(v) with 0.1 M HNO_3 + 0.3 M H_2O_2 solution, plutonium is then eluted as Pu(iii) with formic acid + ascorbic acid, and finally U(vi) is eluted with $(NH_4)_2CO_3$ solution.

Diphonix resin combines methylenediphosphonate, carboxylate, and sulfonate functional groups in a cross-linked polystyrene resin. This resin has strong affinity toward actinide and lanthanide ions of various oxidation states (Chiarizia *et al.*, 1994). Horwitz *et al.* (1994) obtained data of the adsorption of Np(iv), U(vi), and Am(iii). One of the most distinguished features of this resin is its high adsorption ability of actinide ions from aqueous solutions even of high acidity.

6.5.3 Coprecipitation

Coprecipitation methods are traditional, well-established, and widely used for the separation of trace amounts of radioactive elements and the recovery of actinides such as neptunium. A typical example is the coprecipitation method for the preconcentration of ^{237}Np from a large volume of seawater for analytical purposes. Simplicity, rapidness, and applicability to treat large volumes of sample solution are the main advantages of this method. On the other hand, poor selectivity of coprecipitation often requires additional separation processes by solvent extraction or ion-exchange chromatography for the isolation of neptunium ions.

Several kinds of precipitates such as LaF_3, $BiPO_4$, $BaSO_4$, $Fe(OH)_3$, and MnO_2 have been used as a matrix. Np(iv) coprecipitates quantitatively with LaF_3 together with Pu(iii), Pu(iv), Th(iv), and lanthanide (iii). Because Np(vi) as well as Np(v) do not coprecipitate on LaF_3, neptunium can be separated from these metal ions by adjusting the oxidation state at Np(vi) or Np(v) before the coprecipitation procedure. U(vi) does not coprecipitate on LaF_3 from sulfate medium; therefore, U(vi) can be removed from the coprecipitated ions. Np(iv), Ce(iii), Ba(ii), and lanthanides (iii) coprecipitate on $BiPO_4$ very efficiently. Kimura *et al.* (1986) developed a sequential separation procedure utilizing the coprecipitation of neptunium, plutonium, and americium ions with $BiPO_4$. Hoelgye (1998) employed the $BiPO_4$ coprecipitation method for the separation of neptunium from urine samples.

6.5.4 Electrodeposition methods

The electrodeposition reaction of a metallic actinide at a cathode in a eutectic mixture of LiCl + KCl (ca. 700–900 K) was applied as the separation method for the actinide. This method has been expected to be a novel technology for pyrometallurgical reprocessing of nuclear spent fuels or partitioning of the HLW. Electrolytic reaction reduces an actinide (III) to actinide (0) in LiCl + KCl melt and deposits the metallic actinide at the surface of the solid cathode such as tungsten or dissolves the actinide in the liquid cathode such as bismuth or cadmium melt. There have been fundamental studies on the electrode process between Np(III) and Np(0) to obtain thermodynamic data including the equilibrium redox potential of Np(III)/Np(0), the activity coefficient and the diffusion coefficient of Np(III) in LiCl + KCl (Roy *et al.*, 1996; Sakamura *et al.*, 1998, 2000; Shirai *et al.*, 2001). Martinot (1991) developed a method for the preparation of metallic neptunium of high purity by electrodeposition in LiCl + KCl (723 K). The metal product contained a total of 500 ppm impurities.

6.5.5 Biotechnology

Biotechnological methods exhibit the potential of removal of neptunium from the solution. Lloyd *et al.* (2000) proposed a procedure utilizing a combination of two microbial activities that reduce Np(V) in the sample solution to Np(IV) using the reductive capability of *Shewanella putrefaciens* followed by the formation of Np(IV) precipitate with a phosphate ligand enzymatically liberated by *Citrobacter species*. Immobilized cells of a *Citrobacter species* were prepared and employed for the removal of neptunium and plutonium ions from the sample solution (Macaskie and Basnakova, 1998).

6.6 THE METALLIC STATE

6.6.1 Neptunium metal

Although tracer quantities of neptunium were first produced by McMillan and Abelson (1940), it was not until 1945 that microgram quantities of metallic neptunium were synthesized by Magnusson and LaChapelle (1948). Their method reacted NpF_3 with barium at 1473 K. Several methods are currently used to produce gram-sized quantities of metallic neptunium. The first of these reacts NpF_4 with a stoichiometric excess of calcium and 0.15 mol of iodine 'booster' per mole of neptunium (Haire, 1986). A second method uses NpO_2 as a starting material, although other compounds such as $Cs_2NpO_2Cl_4$ and $Cs_3NpO_2Cl_4$ can be used as starting materials, and applies molten salt electrochemistry (Reavis *et al.*, 1985). A salt of LiCl/KCl is used as the electrolyte maintained at 723 K and the material is subjected to stream of HCl and H_2 gas

(Martinot, 1984). The neptunium produced can be collected either as a solid cathodic deposit on a tungsten mandrel or through use of a vitreous magnesia crucible suspended in the salt and positioned around the tungsten cathode to harvest the drops of neptunium from the cathode. The second method of collection is more challenging due to a higher operating temperature of 1023 K but can yield gram-sized quantities. A third method for producing neptunium is the reduction of NpC using tantalum followed by distillation of the neptunium metal (Spirlet and Vogt, 1984). The purity of the neptunium produced from the methods mentioned above is high, typically 99.95%, although the method involving calcium may require further electrorefining to obtain such an elevated level of purity. Recently, Hasegawa *et al.* (1998) developed a new method for the preparation of metallic neptunium based on the electrodeposition from aqueous solution. Neptunium is amalgamated by electrolysis at a mercury cathode with electrolyte solution of 1 M CH_3COOH + 0.3 M CH_3COONa (pH = 3.5) containing 0.05 M neptunium and then separated from mercury by evaporation at 1523 K.

Metallic neptunium is silvery in appearance and forms a thin oxide layer when exposed to air at ordinary temperatures. The reaction to form oxide is more pronounced at higher temperatures. The metallic form is similar to uranium in physical workability. The accepted values for melting point and density are (912 ± 3) K and 19.38 $cm^3\ g^{-1}$ (Lemire *et al.*, 2001, pp 85–87), respectively. Boiling point has not been determined experimentally; however, a value of 4447 K has been obtained via extrapolation of vapor pressure results (Eick and Mulford, 1964).

The thermodynamic properties of neptunium have been compiled by Oetting *et al.* (1976). Metallic neptunium exists in three crystalline forms (allotropes): α-form (orthorhombic), β-form (tetragonal), and γ-form (body-centered cubic (bcc)). The accepted transition temperatures, obtained by several independent groups (Zachariasen, 1952; Lee *et al.*, 1959; Wittenberg *et al.*, 1970), for the transitions are: $\alpha \rightarrow \beta$ (553 ± 5 K) and $\beta \rightarrow \gamma$ (849 ± 5 K). The enthalpies and entropies of transition for the three allotropes are: (1) for the $\alpha \rightarrow \beta$ transition, 5607 J mol^{-1} ($\Delta H°$) and 10.1 J $K^{-1}mol^{-1}$ ($\Delta S°$) and (2) for $\beta \rightarrow \gamma$ transition, 5272 J mol^{-1} ($\Delta H°$) and 6.23 J $K^{-1}mol^{-1}$ ($\Delta S°$). A later determination of these temperatures and enthalpies of transition using differential thermal analysis has yielded slightly different values: (1) for the $\alpha \rightarrow \beta$ transition (555 K), 4730 J mol^{-1} ($\Delta H°$) and (2) for $\beta \rightarrow \gamma$ transition (856 K), 2990 J mol^{-1} ($\Delta H°$) (Foltyn, 1990). The largest difference between the latter values and earlier set are in the enthalpies of transition. It is reasonable to state that improvement in methods and instrumental techniques could account for this 'refinement' of the values of $\Delta H°$. Some mention of a possible fourth allotrope has been advanced in the literature but without conclusive proof at this time (Foltyn, 1990).

The pertinent thermodynamic values at 298 K for metallic neptunium are: entropy, 50.5 J K^{-1} mol^{-1}, heat capacity, 29.6 J $K^{-1}mol^{-1}$, and the enthalpy component, $\{H°(298) - H°(0)\}$ 6.60 kJ mol^{-1}. The enthalpy and entropy of

Table 6.3 *Lattice parameters and space groups for allotropes of neptunium.* (*Lemire* et al., 2001)

Allotrope	*Symmetry*	*Space group*	a_0 (Å)	b_0 (Å)	c_0 (Å)
α-Np	orthorhombic	*Pnma*	6.663	4.723	4.887
β-Np[a]	tetragonal	*P*42	4.897	–	3.388
γ-Np[b]	Body-centered cubic	*Im*3*m*	3.518	–	–

[a] at 586 K.
[b] at 873 K.

fusion for neptunium are 5.19 kJ mol^{-1} and 5.69 J $K^{-1}mol^{-1}$, respectively (Wittenberg, 1970).

The fundamental studies of the crystallography of metallic neptunium were performed by Zachariasen (1952). This work was repeated, to a certain extent and with a different emphasis, by Mardon and Pearce (1959) as a portion of their study of the neptunium–uranium equilibrium diagram. The complete phase diagram for the allotropes of neptunium was first published by Stephens (1966). The lattice parameters for the allotropes are listed in Table 6.3.

The α allotrope of Np is orthorhombic and resembles a highly deformed bcc cell (Zachariasen, 1952). The coordination in this configuration has been reduced from 8 to 4 with a bond length of approximately 2.60 Å. The β allotrope of neptunium is a distorted tetragonal close-packed cell with 4 atoms per unit cell and a bond length of 2.76 Å. The bond length in the γ allotrope of neptunium is 2.97 Å. The phase diagram, fully developed by Stephens (1966), allows for several observations. The region of γ allotrope stability diminishes as the pressure is increased. The melting point of neptunium increases as the pressure is increased. The triple point of β-phase/γ-phase/liquid occurs at 998 K and 3200 MPa.

6.6.2 Neptunium alloys and intermetallic compounds

The past two decades have seen a resurgence of interest in the basic chemistry of neptunium in the area of alloys and intermetallic compounds (Hill, 1971; Aldred *et al.*, 1975; Elliot and Giessen, 1982; Potzel *et al.*, 1983, 1993; Gal *et al.*, 1987; Spitsyn and Ionova, 1987; Schafer *et al.*, 1989; Foltyn, 1990; Kalvius *et al.*, 1992, 1994; Yaar *et al.*, 1992; Gibson and Haire, 1993; Kitazawa *et al.*, 1993; Ogawa, 1993; Sanchez *et al.*, 1993, 1995; Wastin *et al.*, 1993; Zwirner *et al.*, 1993; Gibson *et al.*, 1994, 1996, 1999; Oddou *et al.*, 1994; Rodriguez *et al.*, 1994; Stewart *et al.*, 1994; Seret *et al.*, 1995; Jeandey *et al.*, 1996; Akabori *et al.*, 1997; Keiser *et al.*, 2000; Meresse *et al.*, 2000). The interest in intermetallic compounds in particular has been keen with the focus being the interesting and complex behavior observed due to the presence of f-shell electrons. The actinides and their intermetallic compounds exhibit magnetic behavior ranging from itinerant, band-like character, similar to transition metals, to local moment behavior, similar to the rare earths. The variety of behavior stems from either the overlap of the 5f wave functions or the hybridization of f electrons with the ligand orbitals. For contrasting example, $NpAl_3$ is a ferromagnet, no ordering was found in $NpGe_3$, and $NpSn_3$ was thought to exhibit heavy fermion behavior (Sanchez *et al.*, 1993). The observation of heavy fermion behavior for compounds of several actinides (U, Np, Pu) has been reported by several groups (Potzel *et al.*, 1983, 1993; Gal *et al.*, 1987; Spitsyn and Ionova, 1987; Schafer *et al.*, 1989; Kalvius *et al.*, 1992, 1994; Yaar *et al.*, 1992; Sanchez *et al.*, 1993, 1995; Wastin *et al.*, 1993; Zwirner *et al.*, 1993; Gibson *et al.*, 1994; Oddou *et al.*, 1994; Rodirguez *et al.*, 1994; Seret *et al.*, 1995; Jeandey *et al.*, 1996; Meresse *et al.*, 2000). To restate this unusual behavior in other (more chemical) terms, the 5f electrons of neptunium are relatively unshielded from the crystalline electric field interaction, unlike the rare earths where the 4f electrons are very well shielded thus quenching the angular momentum term leading J to be a good quantum number. In metallic neptunium and other actinides, the spin–orbit coupling is on the same order as the crystalline electric field interaction, leading to possible mixing of the J multiplet and a metallic solid that does not strictly adhere to Hund's rule (Potzel, 1983).

The primary instrumental methods for investigating the various neptunium intermetallics have been: specific heat measurements (Stewart *et al.*, 1994), Mössbauer spectroscopy (Gal *et al.*, 1987; Yaar *et al.*, 1992; Potzel *et al.*, 1993; Sanchez *et al.*, 1993, 1995; Kalvius *et al.*, 1994; Oddou *et al.*, 1994; Jeandey *et al.*, 1996), electrical conductivity (Seret *et al.*, 1995), X-ray diffraction (Wastin *et al.*, 1993; Meresse *et al.*, 2000), magnetization measurements (Yaar *et al.*, 1992; Kitazawa *et al.*, 1993; Sanchez *et al.*, 1993), and neutron diffraction (Oddou *et al.*, 1994).

The investigations of magnetic properties of the intermetallic compounds of neptunium has primarily focused on crystalline compounds, however, some early work was also performed on metallic glasses by Elliott and Giessen (1982). They conducted a study of some 13 metallic glasses containing Np, U, and Pu using X-ray diffraction to determine the interatomic distances. The primary experimental focus has been in the area of crystalline compounds of several types: (1) ternary compounds of composition RMt_2X_2 (R is either Th, Np or Pu, Mt is a 3d, 4d, or 5d transition metal, and X is Si or Ge) (Potzel *et al.*, 1993; Wastin *et al.*, 1993; Jeandey *et al.*, 1996); (2) ternary compounds such as AnT_2Al_3 (where An is either Np or Pu and T is Ni or Pd) or Np_2T_2Sn (where T is Ni, Pd, or Pt) (Zwirner *et al.*, 1993; Sanchez *et al.*, 1995; Seret *et al.*, 1995); (3) binary compounds of composition NpX_3 (where X is Al, Ga, Ge, In, or Sn) (Sanchez *et al.*, 1993; Kalvius *et al.*, 1994; Oddou *et al.*, 1994; Meresse *et al.*, 2000); (4) binary compounds of composition $NpCd_{11}$ (Stewart *et al.*, 1994); (5) binary compounds such as $NpBe_{13}$, $NpRu_2$, $NpOs_2$, and $NpIr_2$ (Gal *et al.*, 1987); (6) ternary compounds of the composition $AnFe_4Al_8$ (where An is Th, U, or Np) (Schafer *et al.*, 1989); and (7) binary compounds of the composition NpM_2 (where M is Al, Cr, Mn, Fe, Co, Ni, Cu, Os, Ir, Ru, or Zn) (Spitsyn and Ionova, 1987).

The effort in the nuclear industry to minimize the amount of the long-lived heavy isotopes of Np, Am, and Pu present in spent fuel so as to make the disposal of the spent fuel more environmentally and economically palatable has led to the efforts in the field of alloying Np with Zr, U, Am, and Pu (Gibson and Haire, 1993; Rodriguez *et al.*, 1994). Modeling efforts have also been employed to better understand the alloying behavior of neptunium with U, Am, Pu, Zr, and Fe (Ogawa, 1993; Gibson *et al.*, 1999). The intent of these efforts is to take long-lived actinides that have been separated from light water reactor spent fuel and recast them into fuel for irradiation in either an accelerator or a breeder reactor and thus transform the long-lived heavy isotopes into shorter-lived isotopes. This work is still underway and the success or failure of these efforts may play a pivotal role in the needed capacity of future geologic repositories for spent fuel in the world.

The formation of binary compounds with stainless steel components such as Fe, Ni, Mn, and Co has been studied from two distinct vantage points. There has been some interest in their magnetic properties (Aldred *et al.*, 1975). More recently intermetallic neptunium compounds (with Fe, Cr, Ni, and Zr) have been formed in a HLW produced from cladding hulls of spent breeder reactor fuel (Keiser *et al.*, 2000). Some neptunium is left in the cladding hulls after electrometallurgical processing for recovery of the uranium. The neptunium that is left forms Laves-type intermetallics with iron, from the stainless steel cladding, and the zirconium, from the metallic alloy fuel, U/10 wt% Zr. More extensive investigations in the general behavior of neptunium with a variety of transition metals have been undertaken by Gibson *et al.* (1994) and Akabori *et al.* (1997).

With the continued interest in making the most economic and environmentally conscious use of the geologic repository for spent fuel and the focus on materials that exhibit possible superconducting properties this area of neptunium chemistry promises to be a lively one for years to come.

6.7 IMPORTANT CLASSES OF COMPOUNDS

Since the discovery of neptunium in 1940 several important activities have directed the synthesis and characterization of neptunium compounds. These activities include the importance of neptunium compounds to fundamental research, as source material for producing Pu-238, and recently neptunium's role as an environmental concern in waste disposal or as a 'burnable' component in future nuclear reactor fuels. As a result of these activities numerous publications are found in the open literature. Synthetic methods, crystal structure, chemical behavior, and thermodynamic properties have been reviewed in a number of books and publications as follows: *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim, Keller (1971); *Gemlin Handbuck der Anorganischen Chemie*, Suppl. Work 8th edn, Transuranium, Verlag Chemie, Weinheim, vol. 4 part C, Compounds (1972); *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 4, Part 6, Part 8, Part 9 (ed. F. L. Oetting), International Atomic Energy Agency, Vienna, *Comprehensive Inorganic Chemistry* (ed. A. F. Trotman-Dichinson), Pergamon Press, Oxford, vol. 10, pp. 141–429 (1975); *Handbook on the Physics and Chemistry of the Actinides*, vol. 3 (eds. A. J. Freeman and C. Keller), Elsevier Science Publishers B.V., Amsterdam; (1985); *Handbook on the Physics and Chemistry of the Actinides*, vol. 6 (eds. A. J. Freeman and C. Keller), Elsevier Science Publishers B.V., Amsterdam; (1991); *Synthesis of Lanthanide and Actinide Compounds* (eds G. Meyer and L. R. Morss), Kluwer Academic Publishers, Dordrecht, The Netherlands (1991); and *Chemical Thermodynamics of Neptunium and Plutonium* (Lemire, R. J. *et al.*), Elsevier, Amsterdam (2001).

6.7.1 Hydrides

The reaction of neptunium with hydrogen results in the formation of hydrides similar to those produced by the reaction of hydrogen with plutonium (Fried and Davidson, 1948). Two hydrides, NpH_{2+x} and NpH_3, were synthesized and characterized by Mulford and Wiewandt (1965). Mintz *et al.* (1976) and recently Ward *et al.* (1987) confirmed the existence of these phases. A phase diagram proposed by Ward *et al.* (1987) for the neptunium–hydrogen system is shown in Fig. 6.6.

Mulford and Wiewandt (1965) found NpH_{2+x} to be face-centered cubic (fcc) and isostructural with PuH_{2+x} but with increasing lattice constants as hydrogen content increases. This trend is opposite of that expected when compared to the lattice constants for the plutonium–hydrogen system (Mulford and Wiewandt, 1965). Ward *et al.* (1987) confirmed this trend in neptunium–hydrogen lattice constants. A comparison of the lattice constants from the two investigations is given in Table 6.4. Both studies show the NpH_3 phase is hexagonal and isostructural with PuH_3. The lattice parameters found by Ward *et al.* (1987) are $a_0 = 6.5338$ Å and $c_0 = 6.7204$ Å.

Pressure–composition isotherms generated by Mulford and Wiewandt (1965) and later by Mintz *et al.* (1976) show flat plateaus to a [H]/[Np] value of approximately 2.16 in contrast to other actinides and lanthanides that show a phase boundary at 1.90. Another anomalous behavior found by Mulford and Wiewandt (1965) is increasing hydrogen content with increasing temperature as opposed to decreasing hydrogen with increasing temperature in the plutonium–hydrogen system. In addition to the anomalous behaviors described above, a comparison of the two reports show contrasting and conflicting thermodynamic values calculated from the pressure–composition isotherms. Ward *et al.* (1987) gives a detailed review of the two studies.

Thermodynamic data taken from Ward *et al.* (1987) are presented here. These data are selected for reporting because Ward re-examined the neptunium–hydrogen system using ultrapure, double-refined neptunium metal, and a

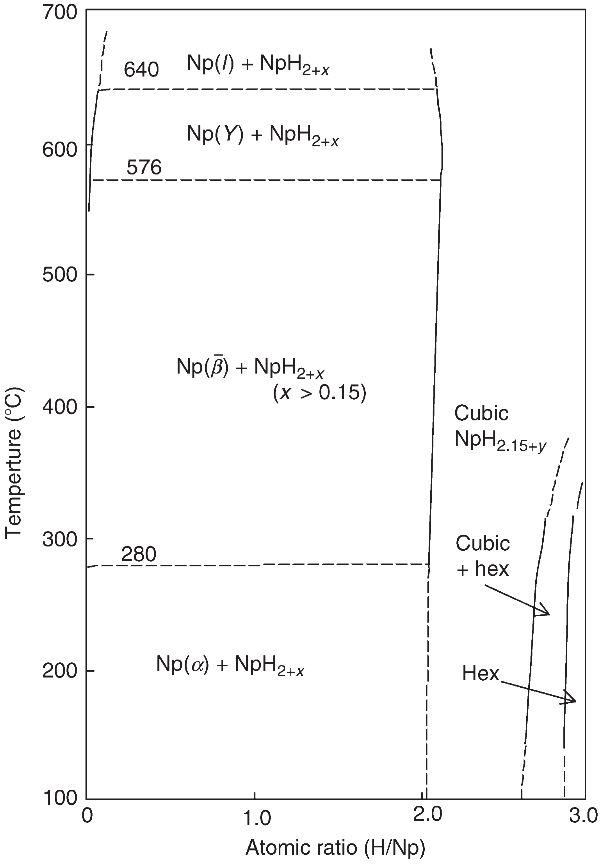


Fig. 6.6 *Partial phase diagram for the neptunium–hydrogen system. Reprinted from Ward* et al. (1987) *with permission from Elsevier Science.*

sophisticated Sievert's type apparatus. The pressure for hydrogen above $NpH_{2.13}$ below 849 K is given by:

$$\ln p\,(\text{pascals}) = 25.043 - 13421T^{-1} \tag{6.10}$$

From this equation enthalpies and entropies of formation for the reaction 0.94 $Np + H_2 = 0.94\ NpH_{2.13}$ are -118.8 kJ mol^{-1} (-28.38 kcal mol^{-1}) and -119.7 J K^{-1} mol^{-1} (-28.6 cal K^{-1} mol^{-1}), respectively. Ward calculated the enthalpy and entropy of formation for NpH_3 to be -153.9 kJ mol^{-1} (-36.78 kcal mol^{-1}) and -174.0 J $K^{-1}mol^{-1}$ (-41.63 cal K^{-1} mol^{-1}), respectively. Ward tabulated calculated partial and integral enthalpies and entropies and compared the data vs the data of Mulford and Wiewandt (1965) and Mintz *et al.* (1976).

There are no known heat capacity data for neptunium hydrides. Flotow *et al.* (1984) estimated the heat capacity of NpH_2(s) from the data of Mulford and

Table 6.4 *Comparison of lattice parameters for cubic neptunium hydride.*

[*H*]/[*Np*]	*Mulford* et al. a_0 (Å)	*Space group*	*Ward* et al.
0.5	5.343	*Fm*3*m*	
1.5		*Fm*3*m*	5.3565
1.78	5.3428	*Fm*3*m*	
2		*Fm*3*m*	5.3475
2.15		*Fm*3*m*	5.3481
2.18	5.3431	*Fm*3*m*	
2.3		*Fm*3*m*	5.349
2.36	5.3463	*Fm*3*m*	
2.42	5.3478	*Fm*3*m*	
2.5	5.36	*Fm*3*m*	5.3516
2.8	5.355	*Fm*3*m*	5.3578

Wiewandt (1965) and Mintz *et al.* (1976). The estimated C_p° at 298 K is 47.279 J K^{-1} mol^{-1}. Flotow *et al.* (1984) lists estimated heat capacities from 298 to 900 K in tabular form.

There are few published data describing chemical behavior of neptunium hydrides. Haschke (1991) reviews the practical aspects of actinide hydrides focusing on safety, compound purity, reaction rates, and preparatory procedures. Recognizing the well-known pyrophoricity of both plutonium and uranium and the fact that neptunium hydride decomposes above 573 K in vacuum, yielding finely divided pyrophoric elemental neptunium, one must take great care in handling neptunium hydrides.

6.7.2 Oxides, hydrated oxides, and hydroxides

Given that neptunium has five oxidation states, it is surprising that there are only two known anhydrous oxides, NpO_2 and Np_2O_5. Attempts to synthesize higher oxides have not been successful (Katz and Gruen, 1949) and the early reported existence of Np_3O_8 has been shown to be the neptunium pentoxide (Sudakov *et al.*, 1972; Fahey *et al.*, 1976a,b). Richter and Sari (1987) on the basis of their work and recent new information on the two-phase boundaries between Np and NpO_{2-x} experimentally determined by Bartscher and Sari (1986) proposed modifications to the partial phase diagram constructed by Belyaev (1983). Their phase diagram, shown in Fig. 6.7, shows the effects of the three metal phases and the substoichiometric range, NpO_{2-x}, first noted by Ackerman *et al.* (1966). However much important work remains to be done to fully understand the neptunium–oxygen system. Recently, Beauvy *et al.* (1998) did not find neptunium metal in their investigation of the preparation of actinide compounds for actinide transmutation, contrary to the data shown in the neptunium–oxygen phase diagram.

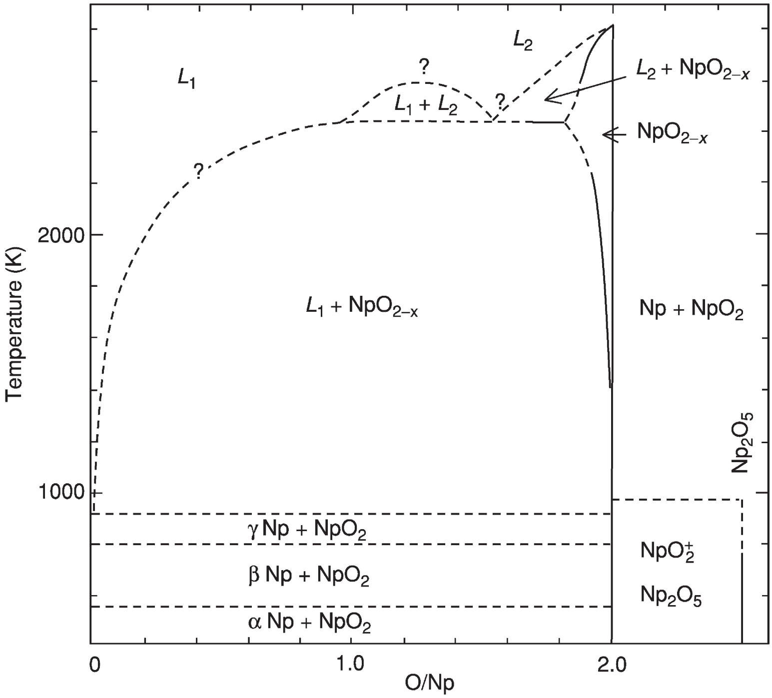


Fig. 6.7 *Phase relation of the neptunium–oxygen system. Reprinted from Richer and Sari* (1987), *with permission from Elsevier Science.*

NpO_2 is synthesized by the thermal decomposition of many neptunium compounds of any oxidation state. The oxide has a fluorite structure with a lattice parameter of (5.4334 ± 0.0003) Å and is isostructural with other actinide oxides (Fahey *et al.*, 1974). Martinot *et al.* (1970) grew single crystals of NpO_2 electrochemically. Spirlet *et al.* (1980) prepared single crystals of NpO_2 by means of a chemical transport reaction using tellurium tetrachloride as a transporting agent in a quartz ampoule at 1233 to 1323 K. X-ray diffraction characterization of the single crystals showed a fluorite lattice parameter of (5.433 ± 0.001) and (5.434 ± 0.001) Å, respectively, in relatively good agreement with literature data of Fahey *et al.* (1974, 1976a,b). Recently, Finch (2002) reported the crystallization of NpO_2 during corrosion experiments in which neptunium-doped U_3O_8 is reacted with humid air at 423 K for several weeks.

NpO_2 is extremely stable over a wide range of temperatures and pressures. The compound does not show a phase transition at low temperatures (Marples, 1975). Benedict *et al.* (1986) studied NpO_2 at pressures up to 50 GPa. Their study shows a phase transition from the fluorite fcc structure to orthorhombic between 33 and 37 GPa. The phase returned to the fcc structure on releasing pressure. The compound is stable at oxygen pressures and temperatures to 2.84 MPa and 673 K (Fahey, 1986). Non-destructive assay standards require materials of known purity for calibration and certification of instruments. Starting with impure NpO_2 and metal, Yarbro *et al.* (1991) synthesized rather pure NpO_2 and metal using two different procedures. Following dissolution, double peroxide precipitations, ion exchange, and an oxalate precipitation of the impurities in the resulting oxides were below 100 ppm each.

The identification of Np_2O_5 and its position in the neptunium–oxygen system result from several investigations of earlier contradictory information (Fahey *et al.*, 1976a,b; Richter and Sari, 1987). Cohen (1963) and Cohen and Walter (1964) obtained Np_2O_5 by precipitation of the compound by bubbling ozone through molten $LiClO_4$ containing NpO_2^+. Bagnall and Laidler (1964) prepared the compound by the thermal decomposition of $NpO_3 \cdot H_2O$ and Sudakov *et al.* (1972) prepared the compound by the decomposition of NpO_2OH(am). Investigations by Fahey *et al.* (1976a,b) and Sudakov *et al.* (1972) provided clarification of early reported contradictory information. Bessonov *et al.* (1989a) reported the synthesis of Np_2O_5 from neptunium(IV) peroxide, double nitrate, and oxalate, apparently contradicting previously published reports. Neptunium peroxide was quantitatively converted to the pentoxide by heating at 573 to 623 K for 2 to 3 h or by heating in an ampoule at 453 to 473 K under a layer of water. The preparation of Np_2O_5 from the double nitrate and oxalate was complex involving several steps for the double nitrate. Attempts to prepare Np_2O_5 by oxidation of NpO_2 at temperatures between 700 and 970 K and oxygen pressures at 0.3 MPa were not successful (Richter and Sari, 1987). Brown Np_2O_5 is monoclinic with the following lattice parameters: $a_0 = (4.183 \pm 0.003)$ Å, $b_0 = (6.584 \pm 0.005)$ Å, and $c_0 = (4.086 \pm 0.003)$ Å, and $\beta = (90.32 \pm 0.03)^\circ$ (Fahey *et al.*, 1976a,b). Np_2O_5 is not very stable decomposing to NpO_2 and O_2 at 693 to 970 K (Bagnall and Laidler, 1964; Richter and Sari, 1987).

Neptunium hydrated oxides and hydroxides are very important in the context of the disposition of nuclear waste. Considerable interest has been devoted to Np(V) since it is the most stable valence of neptunium in the environment. Recent publications reporting the results of studies particularly on chemical thermodynamics have been exhaustively reviewed and summarized by Lemire *et al.* (2001), pp 105–29.

Heptavalent neptunium hydroxide has been precipitated from acidic solutions containing Np(VII) by addition of NaOH or LiOH to a pH at approximately 10 (Krot *et al.*, 1968a; Chaikhorskii and Leikina, 1972). Both studies reported a formula of $NpO_2(OH)_3$. Later, Musikas *et al.* (1974) reported the formula to be $NpO_3(OH)$ based on a titration study showing one hydroxyl ion per Np(VII) ion. Chaikhorskii *et al.* (1972) obtained Np(VII) hydroxide by passing ozone through a suspension of Np(V) hydroxide. The reaction was carried on at 363 K for 5 h or by passing ozone over dried Np(V) hydroxide at 368 to 373 K for 5 h. Nikonov *et al.* (1994) investigated the oxidation of Np(V) hydroxide to form a compound containing Np(vii). The investigators reported the preparation of $(NpO_2OH)(NpO_4) \cdot 4H_2O$.

Several preparations for the synthesis of neptunium(vi) hydrates and hydroxides have been developed. LaChapelle *et al.* (1947) reported the precipitation of neptunium(vi) hydroxide by the addition of ammonia and sodium hydroxide to sulfuric acid solutions containing Np(vi). Cohen (1963) reported the preparation of $NpO_3 \cdot 2H_2O$ by oxidation of Np(v) in a molten $LiNO_3/KNO_3$ eutectic at 423 K with ozone. Bagnall and Laidler (1964), Chaikhorskii *et al.* (1974), and Belyaev *et al.* (1975) precipitated $NpO_3 \cdot H_2O$ and $NpO_3 \cdot 2H_2O$ by adding ozone to aqueous suspensions of neptunium(v) hydroxide. $NpO_2(OH)_2$ was prepared by bubbling ozone into an aqueous solution of NpO_2ClO_4 at pH = 5 and 363 K (Belyaev *et al.*, 1979). Kato *et al.* (1996) prepared $NpO_3 \cdot H_2O$ from an acidic solution. The X-ray diffraction pattern and infrared spectrum for their compound was different from that found by Bagnall and Laidler (1964). Recently, Saito *et al.* (1999), to prevent the formation of Np(vii), developed several methods to prepare neptunyl hydroxides. The authors prepared a starting solution containing $NpO_2(NO_3)_2 \cdot xH_2O$. Anhydrous $NpO_2(OH)_2$ and $NpO_2(OH) \cdot H_2O$ (orthorhombic) were precipitated by the addition of pyridine at 373 and 343 K, respectively. $NpO_2(OH) \cdot H_2O$ (hexagonal) and $NpO_2(OH)_2 \cdot xH_2O \cdot yNH_3$ $(x + y = 1)$ were prepared by the addition of LiOH and ammonia water, respectively. The formula reported for the monohydrate has been reported variously as $NpO_3 \cdot H_2O$ and $NpO_2(OH)_2$ (Bagnall and Laidler, 1964; Kato *et al.*, 1996; Saito *et al.*, 1999). The recent review by Lemire *et al.* (2001), p 118 assigns the formula, $NpO_2(OH)_2$, to the dried solid of Bagnall and Laidler (1964) and the formula, $NpO_3 \cdot H_2O$, to the solid of Kato *et al.* (1996). In summary, Lemire *et al.* (2001), p 118 and Saito *et al.* (1999) describe the chemistry of the hydrated oxides and hydroxides of hexavalent neptunium to be a complicated system.

Interest in the solubility and hydrolysis reactions of Np(v) results from the stability and mobility of this oxidation state in the natural environment, the relatively long half-life of ^{237}Np (2.144×10^6 years), and its abundance in nuclear waste (Lierse *et al.*, 1985). Investigators obtained neptunium(v) hydroxide by adding ammonia, NaOH, or LiOH to slightly acidic or basic solutions containing Np(v) (LaChapelle *et al.*, 1947; Chaikhorskii *et al.*, 1974; Neck, 1992; Merli and Fuger, 1994). Neck *et al.* (1992) reported that freshly prepared green NpO_2OH in 1 M $NaClO_4$ turned to a gray-white precipitate with a lower solubility upon aging. The aged precipitate has a lower solubility than that obtained by the addition of ammonia water to a slightly acidic nitrate and $NaClO_4$ solutions containing NpO_2^+. Their preparations did not show any diffraction lines.

Neptunium(iv) hydroxides are formed in the manner of LaChapelle *et al.* (1947). There are apparently very few data on the hydrates/hydroxides of Np(iv) and Np(iii) oxides. Keller (1975) reported that hydrous oxides, $MO_2(aq)$ have varying amounts of absorbed water rather than forming distinct compounds such as $M(OH)_4$. In contrast, Rai *et al.* (1987), studying the solubility of $NpO_2 \cdot xH_2O$(am), reported that hydrous oxides are thermodynamically reproducible material over a period of 2 days to several months when maintained at 298 K. Lemire *et al.* (2001), pp 114–5 however, suggests that the compound is not thermodynamically stable representing a reproducible compound formed under different experimental conditions. Further research is required to fully characterize neptunium oxide hydrates.

Available thermodynamic data for the oxides, hydrates, and hydroxides have been extensively reviewed (Lemire *et al.*, 2001, pp 105–29). Table 6.5 lists the entropies, enthalpies, and Gibbs energies selected from the review Lemire *et al.* (2001).

Ternary oxides are primarily obtained by the reaction of NpO_2 with oxides of many different elements or by precipitation from alkaline solutions. The syntheses and characterization of these oxides have been extensively reviewed (Keller, 1972; Morss, 1982; Tabuteau and Pagès, 1985). Recently Morss *et al.* (1994) reviewed the pioneering work of Keller and co-workers in the synthesis and characterization of alkali neptunates and the importance of these compounds because of their bonding and electronic properties.

The known alkali and alkaline earth Np(vii) ternary oxides include: Li_5NpO_6, $Ba_3(NpO_5)_2$, Ba_2LiNpO_6, Rb_3NpO_5, K_3NpO_5, Cs_3NpO_5, $RbNpO_4$, $KNpO_4$, and $CsNpO_4$ (Keller and Seiffert, 1969; Awasthi *et al.*, 1971; Pages *et al.*, 1971; Mefod'eva *et al.*, 1976). Keller and Seiffert (1969) prepared Li_5NpO_6 by reacting Li_2O with NpO_2 at 673 K for 16 h. Awathi *et al.* (1971) reacted Li_2O_2 with $NpO_3 \cdot H_2O$ at 673 K for 16 h in a quartz tube in flowing oxygen at ambient pressure to obtain the compound. The compound was reported to be Li_5ReO_6 hexagonal structure with lattice parameters: $a_0 = (5.21 \pm 0.03)$ Å and $c_0 = (14.61 \pm 0.05)$ Å, the results of Awasthi *et al.* (1971) differing only slightly from those of Keller and Sieffert (1969). Recently Morss *et al.* (1994) reinvestigated the compound using X-ray and neutron diffractions. The objective of their

Table 6.5 *Thermodynamic properties of neptunium oxides and hydrated oxides at* 298.15 K.

	$\Delta_f H^\circ_m$ (kJ mol^{-1})	S°_m (J K^{-1} mol^{-1})	$\Delta_f G^\circ_m$ (kJ mol^{-1})	C°_{pm} (J K^{-1} mol^{-1})
NpO_2	−1074.0 ± 2.5	80.3 ± 0.4	−1021.731 ± 2.514	66.24 ± 0.5
Np_2O_5	−02162.7 ± 9.5	174 ± 20	−2031.6 ± 11.2	128.6 ± 5
$NpO_3 \cdot H_2O$	−1377 ± 5	129 ± 27	−1239.0 ± 6.1	120 ± 20
$NpO_2 \cdot OH$ (am, fresh)	−1222.9 ± 5.5	60 ± 27	−1114.7 ± 5.7	86 ± 20
$NpO_2 \cdot OH$ (am, aged)		70 ± 28	−1118.1 ± 6.3	
$NpO_2 \cdot$ (hyd,am)			−957.3 ± 8.0	

investigation was the redetermination of the structure based on the earlier finding that Li_5ReO_6 was monoclinic and not in the *R*3*m* space group (Betz and Hoppe, 1984). The investigators found the X-ray diffraction patterns to be consistent with past data. However, they did not confirm the originally suggested space group, *R*3*m*, or any other structure using any plausible model.

$Ba_3(NpO_5)_2$, Ba_2NaNpO_6, and Ba_2LiNpO_6 were obtained by solid state reactions of alkali and alkaline peroxides with $NpO_3 \cdot H_2O$ at temperatures between 673 and 873 K for 15 to 30 h (Awasthi *et al.*, 1971). Interestingly, the reaction between Na_2O_2 and $NpO_3 \cdot H_2O$ was incomplete under the conditions of the experiment. The authors reported the presence of both Np(VI) and Np(VII) absorption spectra in dilute NaOH solution of the dissolved product. Furthermore, X-ray examination of the product showed evidence of unreacted Na_2O_2. Attempts to produce K_5NpO_6 and Ba_2KNpO_6 using the appropriate reactants under similar conditions were not successful. Pagès *et al.* (1971) obtained K_3NpO_5, Rb_3NpO_5, and Cs_3NpO_5 by the general reaction:

$$NpO_2 + 3MO_2 \rightarrow M_3NpO_5(M = K, Cs, Rb) \tag{6.11}$$

Mefod'eva *et al.* (1976) precipitated $KNpO_4$, $RbNpO_4$, and $CsNpO_4$ from alkaline solutions containing the appropriate alkali metal nitrate, ozone, and Np(VII). Alkali metal to neptunium ratios for these compounds ranged from 1.07 to 1.19. The overestimation of the alkali metal content was explained by an admixture of nitrates.

A large number of hexavalent neptunium ternary oxides are obtained by solid state reactions of NpO_2 and alkali or alkaline earth oxides in a stream of oxygen. These oxides, generally isostructural, with uranates of the same chemical formula include: rhombohedral $Na_2Np_2O_7$, orthorhombic α-Na_2NpO_4 and β-Na_2NpO_4, tetragonal Li_4NpO_5 and α-Na_4NpO_5, orthorhombic β-Na_4NpO_5, Li_6NpO_6, and Na_6NpO_6 (Keller *et al.*, 1965a). Heating a 2:1 mixture of NpO_2 and Na_2O at temperature >673 K results in the formation of $Na_2Np_2O_7$. The heating of $Na_2Np_2O_7$ at >773 K gives α-Na_2NpO_4, which if heated to 1073 K results in the formation of β-Na_2NpO_4. Heating a 1:2 mixture of NpO_2 and Na_2O in an oxygen atmosphere at 673 K produces cubic α-Na_4NpO_5. Heating to >773 K may result in the formation of β-Na_4NpO_5. Further heating to 1073 K β-Na_4NpO_5 decomposes to β-Na_2NpO_4. When a 1:3 mixture of NpO_2 to Na_2O is heated to 773 K Na_6NpO_6 results. Heating a 1:2 mixture of NpO_2 and Li_2O at 673 to 773 K results in Li_4NpO_5 and heating a 1:3 mixture to 673 to 773 K results in Li_6NpO_6. $NaNp_2O_7$ is precipitated from molten salts containing either Np(V) or Np(VI) by reaction with BrO_3^- (Carnall *et al.*, 1965). Keller (1963) synthesized and characterized the following hexavalent Np(VI) alkaline earth oxides: $MNpO_4$ and M_3NpO_6 (where M = Ba, Ca, Sr). Appel *et al.* (1990) using crystallographic and spectroscopic techniques as well as magnetic susceptibility measurement and Mössbauer spectroscopy investigated the structure of $BaNpO_4$. The authors reported that structure to be isostructural with $BaUO_4$ with the lattice contants $a_0 = 5.726$ Å, $b_0 = 8.072$ Å, and $c_0 = 8.165$ Å. Hoekstra and Gebert (1977) synthesized M_2NpO_4 and M_2NpO_7 (where M = K, Rb, and Cs), $Cs_4Np_5O_{17}$, $Cs_2Np_3O_{10}$, and Li_2NpO_4. The researchers obtained the compound by two methods: (1) thermal decomposition of coprecipitated alkali-actinide nitrates and (2) reaction of alkali hydroxides with Np_2O_5.

Compounds of the types $K_2Np_2O_7$, K_2NpO_4, and $BaNpO_4$ have crystal structures made up of linear NpO_2^{2+} groups arranged in layers. By contrast, no NpO_2^{2+} groups are found in the crystal lattice of Li_6NpO_6 (Morss, 1982). Coordination, crystal chemistry, and thermochemistry of these oxides have been reviewed by Morss (1982) and Mössbauer studies have been reported by Jovè *et al.* (1988a,b).

Ternary oxides containing pentavalent neptunium include: Li_3NpO_4, Na_3NpO_4, and Li_7NpO_6 (Keller *et al.*, 1965b). Li_3NpO_4 is obtained by heating Li_6NpO_6 at 1173 to 1273 K apparently in a stream of argon. Na_3NpO_4 results from the heating of a mixture of Na_6NpO_6 and NpO_2 in vacuum at 773 K for 8 h. Li_3NpO_4 is obtained by heating Li_6NpO_6 in vacuum at 1173 to 1273 K for 4 h.

Ternary oxides with Np(IV) compounds with the formula $BaNpO_3$ and $SrNpO_3$ are prepared by reacting NpO_2 with BaO and SrO in an inert and reducing atmosphere between 1373 and 1573 K (Keller, 1963). Mössbauer spectra and magnetic susceptibility of these compounds have been investigated by Kanellakopulos *et al.* (1980a,b), Konig *et al.* (1983), and Bickel and Kanellakopulos (1986).

Neptunium forms a number of ternary oxides with the oxides of group III through group VII elements. Synthesis conditions, structural properties, and phase diagrams have been reviewed by Tabuteau and Pagès (1985). Self-assembled uranyl peroxide nanosphere clusters of 24, 28, and 32 polyhedra (some containing neptunyl) that crystallize from alkaline solution have been characterized (Burns *et al.*, 2005).

6.7.3 Halides, halide complexes, and oxyhalides

The preparation and characterization of neptunium binary halides, oxyhalides, and complex halides have not been as extensively studied with respect to other actinides such as uranium and plutonium and more attention has been given to neptunium–fluorine compounds.

(a) Fluorides, fluoride complexes, and oxyfluorides

There are four known neptunium binary fluorides: NpF_3, NpF_4, NpF_5, and NpF_6. The lower valent neptunium fluorides can be prepared by the following reactions as initially reported by Fried and Davidson (1947):

$$NpO_2 + 1/2H_2 + 3HF \rightarrow NpF_3 + 2H_2O\,(773\,K) \qquad (6.12)$$

$$NpF_3 + 1/4O_2 + HF \rightarrow NpF_4 + 1/2H_2O\,(773\,K) \qquad (6.13)$$

The tetravalent fluoride can also be prepared by the reaction of HF directly with the oxide by the following reaction:

$$NpO_2 + 4HF \rightarrow NpF_4 + 2H_2O \qquad (6.14)$$

Trevorrow *et al.* (1968) prepared NpF_4 by treating NpO_2 with a gaseous mixture of HF(75 v/o) and oxygen (25 v/o) at 773 K at approximatetly 101.3 kPa pressure. More recently, Kleinschmidt *et al.* (1992a) prepared NpF_4 by heating NpO_2 between 553 and 603 K in flowing fluorine. Neptunium is apparently transported downstream as NpF_6 and collected as NpF_4. An amorphous NpF_4 can be precipitated from a solution of Np(IV). Fried and Davidson (1947) did report that NpF_4 was not attacked by concentrated HNO_3. The crystal structures for NpF_3 and NpF_4 are shown in Table 6.6.

The preparation of NpF_5 has proved to be difficult. A number of preparations of NpF_5 are reported in the earlier literature (Cohen *et al.*, 1970; Drobyshevskii *et al.*, 1975, 1978; Baluka *et al.*, 1980). These preparations depend on the reaction of I_2 in IF_5 and KrF_2 or PF_3 in anhydrous HF with NpF_6, NpF_4, and NpF_6, respectively. Recently there have been two investigations searching for simpler alternatives to obtain NpF_5 in a pure form. Brown *et al.* (1982) reinvestigated the use of I_2 in IF_5 medium to reduce Np(VI) as shown in the following equation:

$$10NpF_6 + I_2 \rightarrow 10NpF_5 + 2IF_5 \qquad (6.15)$$

The authors reported the precipitation of a cream-white precipitate which was determined to be 70.25 wt% Np. NpF_5 is 71.35 wt% Np. There was no evidence of Np(IV) in contrast to the reported contaminant by a similar method employed by Cohen *et al.* (1970). Malm *et al.* (1993) investigated several preparations for NpF_5. NpF_5 is prepared from the reaction of $NONpF_6$ with LiF

Table 6.6 *Crystal structures of neptunium halides.*

			Lattice constants			
Halide	*Symmetry*	*Color*	a_0 (Å)	b_0 (Å)	c_0 (Å)	*Angle* (*deg*)
NpF_3	trigonal	purple	7.129		7.288	
NpF_4	monoclinic	green	12.68	10.66	8.34	126.3
NpF_5	tetragonal	bluish-white	6.53		4.45	
NpF_6	orthorhombic	orange	9.909	8.997	5.202	
$NpOF_3$	rhombohedral	green	4.185		15.799	
NpO_2F_2	rhombohedral	pink	4.185		15.790	
$NpOF_4$	hexagonal	brown	13.17		5.70	
$NpCl_3$	hexagonal	green	7.413		4.282	
$NpCl_4$	tetragonal	red-orange	8.266		7.475	
$NpOCl_2$	orthorhombic	orange	15.209	17.670	3.948	
$NpBr_3$	hexagonal	green	7.919		4.392	
$NpBr_3$	orthorhombic	green	4.109	12.618	9.153	
$NpBr_4$	monoclinic	dark red	10.89	8.74	7.05	94.19
NpI_3	orthorhombic	brown	4.30	14.03	9.95	
NpOI	tetragonal	?	4.051		9.193	

and BF_3. NpF_6 reacts with CO and light to produce a fine white powder presumed to be a mixture of NpF_5 and unidentified material. NpF_5 did not result from the reaction of NpF_6 with PF_3 in anhydrous HF in contrast to an earlier report (Baluka *et al.*, 1980). Both investigators studied some of the chemical behavior of NpF_5. In summary, NpF_5 does not react with BCl_3 in contrast to UF_5, NpF_5 hydrolyzes in $HClO_4$, NpF_5 reacts with LiF in anhydrous hydrogen fluoride to produce $LiNpF_6$, and NpF_5 thermally decomposes at 591 K to produce NpF_4 and NpF_6. Interestingly, UF_5 decomposes at 423 K into UF_6 and then in a orderly fashion to U_2F_9, U_4F_{17}, and UF_4. The product of both investigations were examined by X-ray diffraction and the patterns were similar to those in the literature (Baluku *et al.*, 1980) and similar to α-UF_5. From the study by Malm *et al.* (1993) the lattice parameters for the tetragonal compound are $a_0 = 6.5358$ Å and $c_0 = 4.4562$ Å (see Table 6.6). Significant differences in the IR data reported by Brown *et al.* (1982) and IR data reported by Drobyshevskii *et al.* (1975, 1978) have apparently not been resolved.

The volatility of NpF_6, presenting possible separation schemes to recover Np from spent nuclear fuel, led to early interest in preparations and characterization of NpF_6 (Malm *et al.*, 1958; Seaborg and Brown, 1961; Trevorrow *et al.*, 1968). The volatility of NpF_6 is similar to that of UF_6 and PuF_6. Florin (1943) first prepared NpF_6 by reacting NpF_3 with fluorine at high temperatures. Malm *et al.* (1958) achieved the preparation of gram quantities of NpF_6 in specially designed fluorination reactors which dripped liquid fluorine onto heated NpF_4. Convection currents moved NpF_6 to a condenser. Trevorrow *et al.* (1968) studied the fluorination of NpF_4 and NpO_2 with fluorine, BrF_3, and BrF_5. The reaction of both BrF_3 and BrF_5 with NpF_4 produced NpF_6 and bromine. The reaction of fluorine with NpF_4 confirmed the production of NpF_6. The researchers identified an intermediate solid, NpF_4, in the preparations of NpF_6 from NpO_2. Similar reactions with UO_2 show an intermediate as UO_2F_2. Later, Henrion and Leurs (1971) reported NpO_2F_2 as an intermediate in the fluorination of NpO_2 with fluorine. The investigators suggest that the NpF_4 identified by Trevorrow *et al.* (1968) was the result of a secondary reaction.

The use of KrF_2 as a fluorinating agent to prepare NpF_6 at low temperatures has been reported by several investigators (Drobyshevskii *et al.*, 1975, 1978; Peacock and Edelstein, 1976; Asprey *et al.*, 1986). Low-temperature fluorinations avoid the safety and material concerns intrinsic to high-temperature fluorinations with F_2. Peacock and Edelstein (1976) reported that NpF_6 resulted when $NpOF_4$ was contacted with KrF_2 at 213 K. Asprey *et al.* (1986) showed that NpF_6 is prepared by the reaction of gaseous KrF_2 and as well KrF_2 dissolved in anhydrous hydrogen fluoride with neptunium substrates.

Eller *et al.* (1998a) investigated the reaction of O_2F_2 with neptunium oxides and fluorides. NpF_6 is prepared by gas–solid reactions as shown below:

$$NpF_4(s) + xO_2F_2(g) \rightarrow NpF_6(g) + xO_2 + (x-1)F_2(g) \tag{6.16}$$

$$NpO_2(s) + xO_2F_2 \rightarrow NpF_6(g) + (x+1)O_2(g) + (x-3)F_2(g) \tag{6.17}$$

Both reactions proceed almost quantitatively at ambient temperatures. Reaction (6.16) is >95% complete after 45 min and reaction (6.17) is >95% complete after 30 min. Neptunium hexafluoride is produced by reaction with excess O_2F_2 in anhydrous hydrogen fluoride at 195 K with both NpO_2 and NpF_4, but the reactions are much slower. Reaction with NpF_4 was >95% complete after 2 h and reaction with NpO_2 was >95% complete after 3 h. Under both conditions, NpO_2 is converted to NpF_6 with NpO_2F_2 as one of the intermediates. The investigators attempted to study the reaction of the two substrates by condensing O_2F_2 directly on the solid and allowing the mixture to warm to 195 K. Using this procedure, the reaction became uncontrollable with total decomposition of the O_2F_2 and no detectable NpF_6 was produced.

Neptunium hexafluoride is an orange solid melting at 327.8 K to a liquid. Both solid and liquid evaporate to reddish-brown gas. The crystal structure of NpF_6(s) is orthorhombic and the lattice parameters are given in Table 6.6. The vapor pressure is given by the following:

$$\log p(\text{torr}) = A - B(T(\text{K})) + \text{C}\ \log(T(\text{K})) \tag{6.18}$$

For the temperature range 273–328.1 K, $A = 18.48130$, $B= 2892.0$, and $C = -2.6990$. For the temperature range 328.1–349.82 K, $A = 0.01023$, $B = 1191.1$, and $C = 2.5825$ (Keller, 1982). Keller (1982) pointed out that NpF_6 has a higher vapor pressure than either UF_6 or PuF_6. As with other volatile radionuclides and radionuclide-containing compounds, $^{237}NpF_6$ is a radiological as well as a chemical hazard and engineered safety precautions are required.

NpF_6 like UF_6 and PuF_6 is a very reactive compound. The chemical behavior has been studied by a number of investigators (Malm *et al.*, 1958; Trevorrow *et al.*, 1968; Peacock and Edelstein, 1976; Eller *et al.*, 1998b). Malm *et al.* (1958) studied the reaction of NpF_6 with both BrF_3 and water. The reaction of NpF_6 with BrF_3 was very slow resulting in a non-volatile product presumed to be NpF_4 in contrast to PuF_6 which reacts very rapidly with BrF_3. Similar to UF_6 and PuF_6, the authors report that NpF_6 reacts vigorously with water to form NpO_2^{2+}. Trevorrow *et al.* (1968) studied the reaction of NpF_6 with sodium fluoride. In this reaction, NpF_6 reacts reversibly with sodium fluoride at 523 to 673 K according to the following reaction:

$$Na_3NpF_8(s) + 1/2F_2(g) \leftrightarrow 3NaF(s) + NpF_6(g) \tag{6.19}$$

This investigaton shows that hexavalent Np is reduced to pentavalent Np; in contrast hexavalent U reacted with NaF under the same conditions results in a hexavalent compound Na_2UF_8. Peacock and Edelstein (1976) investigated the hydrolysis of NpF_6 in anhydrous hydrogen fluoride to form $NpOF_4$. Attempts to oxidize $NpOF_4$ to Np(vii) with KrF_2 were not successful. In the same study, the investigators attempted to produce higher chlorides by an exchange reaction with BCl_3 similar to exchange reactions with uranium and tungsten. In their study, Np(vi) was reduced to Np(iv) by the following reaction:

$$3NpF_6 + 2BCl_3 \rightarrow 3NpF_4 + 3Cl_2 + 2BF_3 \tag{6.20}$$

The investigators reported that NpF_6 reacts with CsF at 298 K to produce $CsNpF_6$. Recently Eller *et al.* (1998b) studied the reactions of neptunium hexafluorides with nitrogen oxides and oxyfluorides. NpF_6 reacts with excess NO. X-ray powder diffraction pattern of a resulting green product indicated NpF_4. NpF_6 reacts with FNO under a UV lamp to produce $(NO)[NpF_6]$ confirming the earlier work of Malm *et al.* (1993). The authors did not observe any reaction between NpF_6 and FNO_2 and F_3NO even when the reaction was carried out under irradiation by UV lamp.

Np(IV), (V), (VI), and (VII) form a number of fluoro complexes. Tetravalent fluoro complexes with Li, Na, K, Rb, NH_3, Ca, Sr, and Ba have all been prepared and are well-characterized. Brown (1972) reviewed and summarized a number of preparatory methods. Examples of these compounds are shown in Table 6.7. Known pentavalent fluoro hexavalent complexes include $CsNpF_6$, Rb_2NpF_7, Na_3NpF_8, and $K_3NpO_2F_5$. Reduction of NpF_6 in contact with alkali metal fluorides or fluorination of tetravalent compounds mixed with the appropriate univalent fluoride leads to the pentavalent compounds. A selection of typical compounds of this class taken in part from a table by Brown (1972) is shown in Table 6.8. Additional information on these complexes is given by Keller (1971) and Penneman *et al.* (1973).

The known or inferred neptunium oxyfluorides are NpO_2F, $NpOF_3$, NpO_2F_2, and $NpOF_4$ (Bagnall *et al.*, 1968a; Henrion and Leurs, 1971; Drobyshevskii *et al.*, 1975, 1978; Peacock and Edelstein, 1976; Holloway and Laycock, 1984; Asprey *et al.*, 1986; Kleinschmidt *et al.*, 1992b; Eller *et al.*, 1998a). These compounds have not been extensively studied and characterized. Fried (1954) first reported the preparation of NpO_2F_2 by reacting $NaNpO_2Ac_3$ with anhydrous hydrogen fluoride at 573 to 625 K. Bagnall *et al.* (1968a) reported the preparation of the compound by reacting $NpO_3 \cdot H_2O$ and Np_2F_5 with anhydrous hydrogen fluoride at 523 to 548 K and fluorine at 603 K, respectively. The authors also reported the preparation of NpO_2F_2 by the reaction of $NpO_3 \cdot H_2O$ with fluorine at 603 K and BrF_3 at 298 K. Henrion and Leurs (1971) reported that NpO_2F_2 was an intermediate compound in the fluorination of NpO_2 with fluorine to produce NpF_6. Kleinschmidt *et al.* (1992b) prepared NpO_2F_2 by reacting NpO_2 with fluorine at 603 K and by the controlled hydrolysis of NpF_6 with trace H_2O in anhydrous hydrogen fluoride. Recently, Eller *et al.* (1998a) inferred that NpO_2F_2 was a dominant intermediate species in the preparation of NpF_6 by the reaction of O_2F_2 with NpO_2 at ambient temperature. NpO_2F_2 is a pink solid that is soluble in water and mineral acid. The crystal structure is rhombohedral and the lattice constants are shown in Table 6.6.

Peacock and Edelstein (1976) investigated the preparation of $NpOF_4$ by hydrolysis of NpF_6 with water in anhydrous hydrogen fluoride. Drobyshevskii *et al.* (1975) prepared $NpOF_4$ by reacting NpO_2 with KrF_2 in anhydrous hydrogen fluoride at ambient temperatures. Malm *et al.* (1993) reported that $NpOF_4$ was an impurity in all reported preparations of Np_2O_5.

Table 6.7 *Crystal structure and lattice constants of selected neptunium halide complexes.*

Compound	*Symmetry*	*Lattice constants*			*References*
		a_0 (Å)	b_0 (Å)	c_0 (Å)	
Cs_2NpCl_6	trigonal	7.46		6.03	Bagnall and Laidler (1966)
Li_4NpF_8	orthorhombic	9.91 ± 0.01	9.83 ± 0.01	5.98 ± 0.01	Jove and Cousson (1977)
Cs_2NpBr_6	cubic	11.082 ± 0.01			Magette and Fuger (1977)
$(NH_4)Np_3F_{13}$	orthorhombic	7.298 ± 0.005	7.942 ± 0.005	8.392 ± 0.005	Abazli *et al.* (1979)
$CsNpO_2Cl_2(H_2O)$	monoclinic	11.71 ± 0.02	6.99 ± 0.02	8.76 ± 0.02	Tomilin *et al.* (1986)
$Cs_2NaNpCl_6$	cubic	10.9065			Schoebrechts *et al.* (1989)

Table 6.8 *Thermodynamic Properties of Solid Neptunium Halides, Oxyhalides, and Halide Complexes at* 298.15 K.

	$\Delta_f H^\circ_m$ (kJ mol^{-1})	S°_m (J K^{-1} mol^{-1})	$\Delta_f G^\circ_m$ (kJ mol^{-1})	$C^\circ_{p,m}$ (J K^{-1} mol^{-1})
NpF_3	−1529.0 ± 8.3	130.6 ± 3.0	−1460.5 ± 8.3	94.2 ± 3.0
NpF_4	−1874.0 ± 16	148 ± 3	−1783.8 ± 16.0	116.1 ± 4.0
NpF_5	−1941.0 ± 25.0	200.0 ± 15.0	−1834.4 ± 25.4	132.8 ± 8.0
NpF_6	−1970.0 ± 20.0	229.1 ± 0.5	−1841.9 ± 20.0	167.4 ± 0.4
NpO_2F_2				103.2
Na_3NpF_8	−3514.0 ± 21.0	369.0 ± 12.0	−3521.2 ± 21.3	272.3 ± 12.0
$NpCl_3$	−896.8 ± 3.0	165.2 ± 6.0	−829.8 ± 3.0	101.9 ± 4.0
$NpCl_4$	−984.0 ± 1.8	196 ± 5	−895.6 ± 3.0	122.0 ± 6.0
$NpOCl_2$	−1030.0 ± 8.0	143.5 ± 5.0	−960.6 ± 8.1	95.0 ± 4.0
Cs_2NpCl_6	−1976.2 ± 1.9	410.0 ± 15.0	−1833.0 ± 4.9	
$Cs_3NpO_2Cl_4$	−2449.1 ± 4.8			
$Cs_2NpO_2Cl_4$	−2056.1 ± 5.4			
$Cs_2NaNpCl_6$	−2217.2 ± 3.1			
$NpBr_3$	−730.2 ± 2.9	200 ± 6	−705.5 ± 3.8	103.8 ± 6.0
$NpBr_4$	−771.2 ± 1.8	233 ± 5	−737.8 ± 3.5	128.0 ± 4.0
$NpOBr_2$	−950.0 ± 11.0	160.8 ± 4.0	−906.9 ± 11.1	98.2 ± 4.0
Cs_2NpBr_6	−1682.3 ± 2.0	469.0 ± 10.0	−1620.1 ± 3.6	
Npl_3	−512.4 ± 2.2	218 ± 5	−512.5 ± 3.7	110.0 ± 8.0

$NpOF_3$ has been prepared by reacting Np_2O_5 with anhydrous hydrogen fluoride at 313 to 333 K and dehydrating the resulting $NpOF_3$ hydrate at 373 to 423 K or by treating NpO_2 with KrF_2 in anhydrous HF (Bagnall *et al.*, 1968a; Drobyshevskii *et al.*, 1978). Compounds similar to NpO_2F have been obtained by reduction of NpO_2F_2 in hydrogen or the existence of the compound has been inferred as an intermediate in the reaction of NpO_2 with KrF_2 in anhydrous HF, respectively (Bagnall *et al.*, 1968a; Drobyshevskii *et al.*, 1975).

Neptunium tetrachloride has been prepared by at least two methods. One method is to react either neptunium oxalate or neptunium dioxide with CCl_4 at approximately 773 K (Fried and Davidson, 1951). Under these conditions, $NpCl_4$ forms and sublimes and is collected by condensation. Using a modification of this method Choporov and Chudinov (1968) reacted NpO_2 with a stream of CCl_4 vapor at lower temperatures, 553 to 673 K, to obtain $NpCl_4$. Apparently sublimation is minimal at these temperatures. Sublimation under vacuum at 633 to 653 K was used to purify their product. In the second method Bagnall and Laidler (1966) reacted $NpO_2 \cdot OH$ with hexachloropropene to obtain $NpCl_4$. They purified their product by sublimation at 923 K. $NpCl_4(g)$ condenses as a dark red or orange red deposit.

There is still uncertainty in the melting point of $NpCl_4$. Several melting points for $NpCl_4$ have been reported. Fried and Davidson (1951) reported that $NpCl_4$

melts sharply at 811 K. Later, Choporov and Chudinov (1968) using both air and salt baths reported the melting point to be (790.5 ± 2.5) K. More recently, Gruen *et al.* (1976) reinvestigated the melting point of $NpCl_4$. Using data obtained from the spectroscopically measured vapor pressures, the investigators determined that 802.9 K is the best value.

As with most of the early man-made element investigations, $NpCl_4$ was initially identified by X-ray powder diffraction. Fried and Davidson (1951) reported that the crystal structure was tetragonal with lattice parameters $a_0 = (8.25 \pm 0.01)$ Å and $c_0 = (7.46 \pm 0.01)$ Å. Recently, Spirlet *et al.* (1994) performed a complete X-ray examination of single crystals of $NpCl_4$. They confirmed that the crystal structure is tetragonal and the lattice parameters are $a_0 = 8.229$ Å and $c_0 = 7.437$ Å in reasonably close agreement with the earliest work and the crystal structure data shown in Table 6.6.

Neptunium trichloride is prepared by several methods. Fried and Davidson (1951) obtained $NpCl_3$ by reduction of NpO_2 with a mixture of hydrogen and CCl_4 at 623 to 673 K. Brown and Edwards (1972) reported the quantitative synthesis of $NpCl_3$ by reducing $NpCl_4$ with an excess of zinc. In this method, $NpCl_4$ and zinc are sealed under vacuum in a quartz tube. The reactants are heated at 823 to 873 K for 12 to 24 h. After conversion, excess zinc and $ZnCl_2$ are purified by sublimation under high vacuum away from the $NpCl_3$. $NpCl_3$ is sublimed into a clean quartz tube at 1223 to 1273 K. Attempts by Brown and Edwards (1972) to reduce $NpCl_4$ with aluminum were not successful; conversions ranged from 15 to 60%. Recently, Foropoulus *et al.* (1992) prepared anhydrous $NpCl_3$ from aqueous solutions. In their patented method, neptunium is reduced to Np(III) in a chloride solution. The solution is evaporated and the resulting residue, $NpCl_3$ hydrate, is dehydrated by contacting with thionyl chloride. The authors report that an essentially pure $NpCl_3$, ca. 98%, is obtained by their method.

Efforts to prepare higher neptunium chlorides have been unsuccessful. Heating $NpCl_4$ in chlorine at 101.3 kPa does not result in the formation of $NpCl_5$. Efforts were also made to observe the possible formation of $NpCl_5$ spectroscopically in the vapor phase by heating $NpCl_4$ in a chlorine atmosphere. At temperatures up to 1273 K no new features in the absorption spectrum were found (Fried and Davidson, 1951).

Fried and Davidson (1948) reported the preparation of neptunium tetrabromide by reaction of NpO_2 with aluminum bromide at 623 K:

$$3NpO_2 + 4AlBr_3 \rightarrow 3NpBr_4 + 2Al_2O_3 \tag{6.21}$$

Brown and Edwards (1972) in a method identical to the method described above for the synthesis of $NpCl_3$ reported the quantitative synthesis of $NpBr_3$ by reacting $NpBr_4$ with excess zinc. Brown *et al.* (1970) prepared $NpBr_4$ by direct action of metallic neptunium and bromine. Neptunium metal and bromine were vacuum-sealed in a quartz tube. One end of the tube containing neptunium metal was heated between 673 and 698 K. $NpBr_4$ sublimed and condensed in a cooler section of the tube.

Brown *et al.* (1968) investigated the preparation of $NpBr_3$ by dehydration of $NpBr_3$ hydrates. The authors prepared the hydrates by exposing the anhydrous tribromide to oxygen-free water vapor resulting in $NpBr_3$ hexahydrate. By controlling the temperature and vacuum, the hydrate was easily converted to the anhydrous form. Previously unknown $NpBr_3$ hexahydrate was characterized using X-ray powder diffraction, radioanalytical, and gravimetric methods.

Neptunium triiodide was prepared by Fried and Davidson (1951) with aluminum iodide. Another, perhaps more convenient, method for the preparation of these halides is the direct action of hydrogen bromide/hydrogen iodide on NpO_2 at 773 K. Because the anhydrous gases (HBr and HI) are available in small, easily handled cylinders, this reaction is advantageous for laboratory preparations. The reaction products can be readily purified from unreacted NpO_2 by sublimation at the appropriate temperature. Brown and Edwards (1972) prepared the triiodide by reacting neptunium metal with excess iodine. The reactants were sealed in a tube under vacuum. The reactants were then heated at 773 K. Excess iodine was sublimed from the product, which was identified as NpI_3. Neptunium tetraiodide is predicted to be unstable (Brewer *et al.*, 1949). NpI_3 has been studied by X-ray powder diffraction and the crystal structure and lattice paramters are shown in Table 6.6.

For the synthesis of $NpBr_3$ and NpI_3 described above using aluminum halide, the aluminum halide required for these syntheses is conveniently prepared *in situ* from the elements. This method has the convenience that on the laboratory scale it is unnecessary to handle small amounts of the extremely hygroscopic aluminum halides. In this method, however, if excess aluminum is present, $NpBr_3$ is formed rather than $NpBr_4$. The reaction between NpO_2 and aluminum halide is best carried out in a sealed vessel at 623 to 673 K. Any excess aluminum halide is easily sublimed away at about 523 K. The crystal structures and lattice parameters of neptunium bromides are shown in Table 6.6.

Neptunium oxyhalides have been prepared and characterized. Fried and Davidson (1951) reported $NpOCl_2$ results when $NpCl_4$ was heated in sealed and evacuated capillary. They hypothesized that the compound was the product of the reactions of the tetrachloride with either oxygen or water impurities. The compound was investigated by X-ray powder diffraction and reported to be isostructural with $UOCl_2$. The crystal structure is shown in Table 6.6. Bagnall *et al.* (1968b) reported the synthesis of $NpOCl_2$ by reacting $NpCl_4$ and antimony sesquioxide at 673 K in a vacuum. $NpOCl_2$ can be sublimed at 823 K in vacuum. The synthesis of NpOCl has been observed during efforts to prepare $NpCl_3$ (Brown and Edwards, 1972). Pentavalent neptunium oxychlorides, $NpOCl_2$ and NpO_2Cl, are prepared by the dehydration of a solution containing chloride ions and Np(v) (LaChapelle, 1964). Brown *et al.* (1977) prepared and characterized NpOI. The oxyhalide was prepared by reacting Sb_2O_3 and NpI_3 stoichiometrically in a sealed and evacuated tube at 573 to 773 K. Product SbI_3 was sublimed away from NpOI. The crystal structure is shown in Table 6.6.

Np(III), (IV), (V), and (VI) halide complexes with both alkali metal and alkaline earth elements and ammonia are known and have been characterized (Bagnall and Laidler, 1966; Fuger and Brown, 1971; Jove and Cousson, 1977; Magette and Fuger, 1977; Abazli *et al.*, 1979; Fuger, 1979; Tomilin *et al.*, 1986; Schoebrechts *et al.*, 1989). A selection of compounds collected from the above references is shown in Table 6.7. More recently, Lemire *et al.* (2001, pp 148–53) reviewed the available chemical and thermodynamic data of the following neptunium halide complexes: Na_3NpF_8, Cs_2NpCl_6, $Cs_3NpO_2Cl_4$, $Cs_2NpO_2Cl_4$, $Cs_2NaNpCl_4$, and Cs_2NpBr_6. The information and references therein should be consulted for additional information.

Measured thermodynamic data for the halides is limited. Recently the Nuclear Energy Agency (NEA) published the exhaustive review of the published thermodynamic data (Lemire *et al.* (2001), pp 131–53) and Table 6.8 gives some of the data. In summary much of the thermodynamic data are interpolated from those of the corresponding thorium, uranium, and plutonium compounds. The thermodynamic data are collected from the recommended values in Lemire *et al.* (2001) and those adopted in Chapter 19.

6.7.4 Chalcogenides, pnictides, and carbides

Neptunium pnictides and chalcogenides have been extensively investigated primarily to understand their electronic and magnetic properties. These properties have been studied by magnetic susceptibility, Mössbauer spectroscopy, electrical resistivity, neutron and low-temperature X-ray diffraction experiments (Aldred *et al.*, 1974; Rossat-Mignod *et al.*, 1984, 1989; Burlet *et al.*, 1989; Vogt and Mattenberger, 1994; Lander and Burlet, 1995). The rock salt-type monopnictides and monochalcogenides form ideal models for studying the magnetic properties of the 5f electrons.

(a) Chalcogenides

The known sulfides and oxysulfides are NpS, NpS_3, Np_2S_5, Np_3S_5, Np_2S_3 (α-, β-, and γ-) Np_3S_4, NpOS, Np_4O_4S, and Np_2O_2S (Marcon, 1967, 1969).

NpS has been synthesized by several methods. The compound can be prepared by heating Np_2S_3 and neptunium metal at 1873 K (Marcon, 1967, 1969; Charvillat *et al.*, 1976). Bihan *et al.* (1997) prepared NpS by reacting stoichiometric amounts of the pure elements by vapor reaction in a sealed tube. Details of this method are described by Spirlet and Vogt (1984). A more facile method for preparing the compound was patented by Van Der Sluys *et al.* (1992). In their method NpS was synthesized by heating an admixture of an organometallic precursor, a suitable solvent, and a protic Lewis acid at temperature and for sufficient time to form an intermediate neptunium complex. The complex is then heated at a specific temperature and time to form the monosulfide. NpS is isostructural with PuS and US, exhibiting the NaCl-type structure with lattice parameter $a_0 = (5.532 \pm 0.001)$ Å. Bihan *et al.* (1997)

investigated the compressibility of NpS up to 60 GPa. The authors reported no phase transformation from NaCl to CsCl over the pressure range investigated.

Np_2S_3 was first prepared by treating NpO_2 with a mixture of hydrogen sulfide and carbon disulfide at 1278 K (Fried and Davidson, 1948, 1951). This compound was reported to be isostructural with U_2S_3 with lattice parameters $a_0 = (10.3 \pm 0.1)$ Å, $b_0 = (10.6 \pm 0.1)$ Å, $c_0 = (3.86 \pm 0.5)$ Å (Zachariasen, 1949a, b). Marcon (1967) obtained α-Np_2S_3 by thermal dissociation of Np_3S_5 at 1200 K. The compound is orthorhombic and isotypic with α-Pu_2S_3 and α-Ce_2S_3 with lattice parameters $a_0 = (3.98 \pm 0.01)$ Å, $b_0 = (7.39 \pm 0.02)$ Å, $c_0 = (15.50 \pm 0.03)$ Å. At about 1500 K, α-Np_2S_3 transforms into tetragonal β-Np_2S_3, isotypic with β-Pu_2S_3 and Ce_5S_7, $a_0 = (14.94 \pm 0.02)$ Å, $c_0 = (19.84 \pm 0.02)$ Å. Finally, around 1800 K, change to the cubic Np_2S_3 (γ) with the structure of the Th_3P_4-type occurred ($a_0 = 8.440 \pm 0.001$ Å) (Marcon, 1967). The γ-form can also have the composition of Np_3S_4 (Damien and Berger, 1976). Np_3S_4 was obtained after the heat treatment described above by Charvillat *et al.* (1976). Np_3S_4 is cubic with a lattice parameter of $a_0 = 8.440$ Å.

Np_3S_5 was obtained by thermal decomposition of NpS_3 at 773 K (Marcon, 1967, 1969; Marcon and Pascard, 1968). Blaise *et al.* (1982) reported the preparation of Np_3S_5 by reaction of the appropriate chalcogen and neptunium hydride at 923 K. Np_3S_5 is isostructural with U_3S_5 with lattice parameters $a_0 = (7.42 \pm 0.01)$ Å, $b_0 = (8.07 \pm 0.01)$ Å, $c_0 = (11.71 \pm 0.02)$ Å.

Np_2S_5 is prepared by heating mixtures of Np_3S_5 and sulfur at 773 K (Marcon, 1967, 1969). The crystal structure is tetragonal ($a_0 = (10.48 \pm 0.01)$ Å, $c_0 = (9.84 \pm 0.1)$ Å), and isotypic with Th_2S_5, Th_2Se_5, and U_2S_5.

NpS_3 was prepared from the elements at 773 K by Marcon (1967, 1969). NpS_3 is monoclinic with lattice parameters $a_0 = (5.36 \pm 0.01)$ Å, $b_0 = (3.87 \pm 0.01)$ Å, $c_0 = (18.10 \pm 0.05)$ Å, $\beta = 99.5°$ and isostructural with US_3, USe_3, UTe_3, $NpSe_3$, and $NpTe_3$.

The three oxysulfides NpOS, Np_2O_2S, and $Np_4O_4S_3$ have been reported (Zachariasen, 1949b; Marcon, 1969). Only NpOS has been extensively studied (Thevenin *et al.*, 1985; Collard *et al.*, 1986). Thevenin *et al.* (1985) prepared NpOS by vacuum sealing and heating NpO_2, Np_3S_5, and sulfur in a quartz tube to 1073 K for 1 week. NpOS is tetragonal with lattice parameters $a_0 = b_0 = 3.808$ Å and $c_0 = 6.627$ Å. $Np_4O_4S_3$ and Np_2O_2S were prepared and characterized by Marcon (1969) and Zachariasen (1949b). Hexagonal Np_2O_2S is isostructural with the actinide and lanthanide oxysulfides of the same composition (Zachariasen, 1949b; Haire and Fahey, 1977). Hoffman and Kleykamp (1972) have presented an extensive review of the preparation and properties of these sulfides and oxysulfides.

Known neptunium selenides and oxyselenides are NpSe, Np_3Se_4, γ-Np_2Se_3, Np_2Se_5, Np_3Se_5, $NpSe_3$, NpOSe, and Np_2O_2Se. These compounds have been prepared and characterized by Mitchell and Lam (1971), Damien and Wojakowski (1975), Damien *et al.* (1973), Charvillat *et al.* (1976), and Thevenin and Pagès (1982).

Damien and Wojakowski (1975) and Charvillat *et al.* (1976) obtained NpSe by reacting neptunium hydride with a stoichiometric amount of selenium metal. The reactants, sealed in a quartz tube under vacuum, were heated at 800 K for 24 h. The investigators reported that NpSe crystallizes in the NaCl-type structure with lattice constant $a_0 = (5.804 \pm 0.002)$ Å for samples heated between 1593 and 1783 K. Gensini *et al.* (1993) reported that the selenide transforms from the NaCl to CsCl structure at 23 GPa.

Mitchell and Lam (1971) investigated the alloying behavior of neptunium and selenium and obtained Np_3Se_4. Neptunium and selenium were sealed, in vacuum, in a quartz ampoule. The reactants were heated to the melting point of selenium, 494 K, then heated to and maintained at 1273 K for 5 to 24 h. The final steps in the procedure held the ampoule at 773 K for 15 to 22 days followed by furnace cooling and X-ray diffraction analysis. Damien *et al.* (1973) obtained this phase by decomposition of Np_3Se_5 at 1123 K at high vacuum. After heating at 1323 K and apparently cooling, the lattice parameter decreased from $a_0 = (8.8242 \pm 0.0002)$ to (8.8223 ± 0.0003) Å similar to the cubic structure lattice constant $a_0 = (8.8261 \pm 0.00\,02)$ Å reported by Mitchell and Lam (1971). Damien *et al.* (1973) could not determine if the composition of their product was γ-Np_2Se_3 or Np_3Se_4.

Damien *et al.* (1973) obtained Np_3Se_5 by thermal dissociation of $NpSe_3$ at 693 K in vacuum. Blaise *et al.* (1982) prepared Np_3Se_5 by heating the appropriate amounts of chalcogen with neptunium hydride at 923 K. The crystal structure is orthorhombic and the lattice parameters are $a_0 = (7.75 \pm 0.01)$ Å, $b_0 = (8.43 \pm 0.01)$ Å, and $c_0 = (12.24 \pm 0.02)$ Å. The compound is isostructural with U_3S_5, U_3Se_5, and Np_3S_5.

Np_2Se_5 is prepared either by thermal decomposition of $NpSe_3$ at 823 K for 2 weeks or by reaction of neptunium hydride and selenium metal at 753 K. Both preparations are performed in sealed and evacuated quartz tubes (Thevenin and Pagaès, 1982). The compound has an orthorhombic (pseudotetragonal) crystal structure with lattice parameters $a_0 = b_0 = 7.725$ Å and $c_0 = 10.6225$ Å.

$NpSe_3$ was synthesized by Damien *et al.* (1973) by reaction of neptunium hydride with excess selenium sealed in a quartz tube under vacuum and heating at 620 K for 1 week. Blaise *et al.* (1982) prepared $NpSe_3$ by reacting chalcogen with neptunium hydride at 1273 K. The investigators identified $NpSe_3$ by X-ray powder diffraction pattern to be analogous to that of USe_3. The triselenide crystal structure is monoclinic with lattice constants: $a_0 = (5.64 \pm 0.02)$ Å, $b_0 = (4.01 \pm 0.01)$ Å, $c_0 = (19.06 \pm 0.07)$ Å, $\beta = (79.60 \pm 20)°$.

The known oxyselenides are NpOSe and Np_2O_2Se (Marcon, 1969). Only NpOSe has been investigated (Thevenin *et al.*, 1985). Thevenin *et al.* (1985) prepared NpOSe by vacuum sealing and heating NpO_2 and Np_2Se_5 to 1073 K for 1 week. NpOSe is tetragonal with lattice parameters $a_0 = b_0 = 3.869$ Å and $c_0 = 6.911$ Å. The known neptunium tellurides and oxytellurides are NpTe, Np_3Te_4, $NpTe_3$, $NpTe_{2-x}$, $\eta\gamma$-Np_2Te_3, and Np_2O_2Te.

Damien and Wojakowski (1975) and Charvillat *et al.* (1976) obtained a two-phase NpTe product by reacting neptunium hydride with a stoichiometric amount of tellurium metal sealed in a quartz tube under vacuum at 800 K for 24 h. The product formed was made into a pellet, heated at 1563 K for 4 h in a sealed quartz tube under vacuum, cooled, and examined by X-ray diffraction. Under these circumstances the investigators determined that NpTe crystallizes in the NaCl-type structure with lattice constant $a_0 = (6.197 \pm 0.0001)$ Å. Dabos-Seignon *et al.* (1990) investigated X-ray diffraction patterns of NpTe at pressures up to 51 GPa. The investigators reported that NpTe maintains the NaCl structure to 12 GPa where CsCl-type structure began to appear. Only the CsCl-type structure exists above 20 GPa.

Mitchell and Lam (1971), investigating the alloying behavior of neptunium and tellurium, obtained Np_3Te_4. Neptunium and tellurium were vacuum-sealed in a quartz ampoule. The reactants were heated to the melting point of tellurium, 494 K, then heated to and maintained at 1273 K for 5 to 24 h. The final step in the procedure held the ampoule at 772 K for 15 to 22 days. The lattice constant for the cubic structure was reported to be $a_0 = (8.8261 \pm 0.0002)$ Å (Mitchell and Lam, 1971).

Blaise *et al.* (1976), investigating magnetic properties of some neptunium chalcogenides, prepared $NpTe_3$ by reacting tellurium with neptunium hydride at 628 K. $NpTe_3$ is isostructural with rare earth tritellurides with the lattice parameters $a_0 = b_0 = 4.355$ Å and $c_0 = 25.40$ Å in agreement with literature values (Damien and Berger, 1976).

Thevenin *et al.* (1985) investigated the preparation and crystal structure of Np_2O_2Te. The investigators obtained Np_2O_2Te by reacting Np_2Te_3 and NpO_2 in a vacuum-sealed quartz tube at 1273 K for 1 week. The black compound is tetragonal with lattice constants $a_0 = b_0 = 4.003$ Å, $c_0 = 12.73$ Å and is isostructural with U_2O_2 Te and Pu_2O_2Te.

(b) Pnictides

Neptunium pnictides have been studied because of their solid state properties and relationship to advanced reactor fuels. Neptunium nitride, NpN, was prepared by Sheft and Fried (1953) who reacted ammonia gas and neptunium hydride at 1023 to 1048 K in a quartz X-ray capillary tube. Later preparations by Olson and Mulford (1966), De Novion and Lorenzelli (1968), and Aldred *et al.* (1974) reacted neptunium metal with a mixture of nitrogen and hydrogen at temperatures to 1773 K, NpH_{2+x} with nitrogen at temperatures to 1873 K, and NpH_3 with nitrogen at temperatures between 573 and 623 K, respectively.

In the method of Olson and Mulford (1966) neptunium filings were heated in a tungsten vee with nitrogen 0.5% in hydrogen as a catalyst. The reaction started at 873 K and upon apparent completion the temperature was brought to 1783 K. Gaseous neptunium hydride and neptunium were removed by pumping. De Novion and Lorezelli (1968) directly reacted nitrogen with NpH_{2+x} at 673 K, while Aldred *et al.* (1974) reacted NpH_3 with nitrogen at 573 to 623 K for 5 h. The powder product was formed into pellets and heated at 1273 K for 2.5 h. More recently, Suzuki *et al.* (1994) synthesized NpN by a high temperature, 1823 K, carbothermic reduction of NpO_2 in a stream of N_2 gas. The crystal structure is NaCl-type (fcc) and the lattice parameter is $a = (4.8968 \pm 0.005)$ Å which agrees well with values reported in the literature (Olson and Mulford, 1966; De Novion and Lorenzelli, 1968). NpN is isomorphous with UN and PuN, reacts slowly with dilute hydrochloric and nitric acids, and appears to be relatively inert toward water (Sheft and Fried, 1953). The melting point of NpN has been determined to be 3103 K under a nitrogen pressure of ca. 1 MPa (Olson and Mulford, 1966). There is very little thermodynamic data reported for NpN. Arai *et al.* (1994) derived the following equation for the heat capacity of NpN: $C_p\,(\mathrm{J\,mol^{-1}\,K}) = 52.85 + 2.55 \times 10^{-3}T - 8.37 \times 10^{5}T^{-2}$. Suzuki and Arai (1998) reviewed and investigated some thermal and thermodynamic properties of NpN. They reported the free energy of formation to be $\Delta G_f\,(\mathrm{J\,mol^{-1}}) = 427\,000 - 98.88T(1700\text{–}2100\,\mathrm{K})$.

Lander *et al.* (1973) prepared neptunium monophosphide by a hydriding, dehydriding, and nitriding technique. First the metal is converted to powder by hydriding and dehydriding. Then the powder reacted with phosphine gas at 623 K. NpP is single-phase fcc. The lattice parameter is (5.614 ± 0.001) Å. A compound with the formula, Np_3P_4, is formed by reacting an excess of red phosphorus with neptunium metal at 1013 K in an evacuated and sealed quartz tube (Sheft and Fried, 1953). Excess phosphorus is removed by sublimation in vacuo at 1073 K. The compound does not react with water but does react with 6 M HNO_3 to yield dark-green Np(IV) solution.

$NpAs_2$ and NpAs are prepared by reacting stoichiometrically arsenic and neptunium hydride in a vacuum-sealed tube for 1 week (Charvillat and Damien, 1973; Blaise *et al.*, 1981). In this method NpAs was synthesized at 923 K and $NpAs_2$ synthesized at 723 K. Dabos *et al.* (1986) synthesized NpAs by reacting arsenic vapor and neptunium metal turnings in a vacuum-sealed quartz tube. In this method, the reactants are separated by a quartz membrane and heated to just below the melting point of neptunium metal: arsenic sublimes at 886 K and the melting point of neptunium is 903 K. X-ray studies show that NpAs has the cubic NaCl structure with the lattice parameter $a_0 = (5.8338 \pm 0.0002)$ Å (Charvillat and Damien, 1973). $NpAs_2$ is tetragonal, anti-Fe_2As type with lattice parameter $a_0 = (3.962 \pm 0.001)$ Å, $b_0 = (8.115 \pm 0.002)$ Å (Charvillat and Damien, 1973; Blaise *et al.*, 1981). Wojakowski and Damien (1982) reported the preparation of single crystals of both $NpAs_2$ and Np_3As_4 using iodine as a transporting agent in a transport reaction process in sealed quartz tubes. The investigators reported that $NpAs_2$ single crystals are more stable in air than powder material. $NpAs_2$ crystals are brown to gold and Np_3A_4 are black in color. The reported lattice parameters are in agreement with literature values.

NpSb was prepared by an isothermal annealing technique (Mitchell and Lam, 1971). In this technique, equal atomic percentages of neptunium and 99.999%

pure antimony were sealed in a quartz tube under vacuum, and the mixture was heated at the melting temperature of antimony. The temperature was then raised to 1000°C, held at this temperature for 16 days, and then cooled. In all samples, traces of Np_3Sb_4 were present (Aldred *et al.*, 1974).

There are limited reports for the preparation and characterization of NpBi. Aldred *et al.* (1974) attempted to prepare the compound by reaction of the elements at 1273 K for 16 days and was not successful. Attempts to prepare single crystals of NpBi by Burlet *et al.* (1992) using the mineralization method described by Spirlet and Vogt (1984) were successful.

(c) Carbides

The neptunium compounds NpC, Np_2C_3 and NpC_2 have been reported in the literature with limited characterization. This is unfortunate because of the importance of carbides as advanced reactor fuels. Holley *et al.* (1984) reviewed the earlier literature and determined that two phases had been identified and that the identification of NpC_2 was tentative. Nevitt (1963) reported that the monocarbide exists in the range of $NpC_{0.82}$ to $NpC_{0.96}$. De Novion and Lorenzelli (1968) prepared $NpC_{0.95}$ by heating a mixture of neptunium hydride and graphite to 1673 K. Sandenaw *et al.* (1973) prepared $NpC_{0.91}$ by arc melting the elements using a tungsten electrode. Sheft and Fried (1953) reported the syntheses of NpC_2 by heating NpO_2 at various temperatures between 2933 and 3073 K in a graphite crucible. When an attempt is made to prepare neptunium metal by reaction of lithium vapor on NpF_3 in a graphite crucible at 1373 K, the reaction yields a mixture of NpC and Np_2C_3. When NpC reacts with excess carbon it forms a pure phase with the composition of Np_2C_3 (Lorenzelli, 1968). Sandenaw *et al.* (1973) measured the heat capacity of $NpC_{0.91}$. Holley *et al.* (1984) and Lemire *et al.* (2001), pp 201–2 reviewed the very limited thermodynamic properties of neptunium carbides.

6.7.5 Other inorganic compounds

Many other inorganic neptunium compounds have been synthesized and characterized. Interest has been shown in the preparation and characterization of phosphates, sulfates, and carbonates. The stability of phosphates makes them a candidate for immobilizing radioactive waste (Bamberger *et al.*, 1984; Volkov *et al.*, 1994). Bamberger *et al.* (1984) reported the preparation of green neptunium pyrophosphate, α-NpP_2O_7, by reacting NpO_2 and BPO_4 at 1373 K. The lattice parameter for the cubic compound was (8.593 ± 0.002) Å. Attempts to prepare $Np_3(PO_4)_4$ by a similar reaction were unsuccessful. Volkov *et al.* (1994) studied a series of double phosphate of neptunium with the formula $NpA_2(PO_4)_3$ where A = Li, Na, K, Rb, Cs. The compounds were synthesized by heating the appropriate mixtures of NpO_2, LiOH, $N(K)H_2PO_4$, $Rb(Cs)NO_3$, and H_3PO_4 at 373 to 573 K for 5 h followed by annealing in air from 773 to

1923 K. Monoclinic and trigonal crystalline structures were identified for the double phosphates containing the cations Li^+, Na^+, and K^+. Transitions from the monoclinic to trigonal phases for $NaLi_2(PO_4)_3$, $NaNa_2(PO_4)_3$, and $NaK_2(PO_4)_3$ occurred at 1723, 1623, and 1423 K, respectively. Only the trigonal phase was reported for both $NpRb_2(PO_4)_3$ and $NpCs_2(PO_4)_3$ and the latter compound formed an unidentified high-temperature phase.

A number of neptunium sulfates have been synthesized and characterized. The most recent studies of solid neptunium sulfates are by Weigel and Hellmann (1986) and Budantseva *et al.* (1988). Neptunium hydroxysulfate was synthesized and characterized by Wester *et al.* (1982).

Preparation and characterization of neptunium carbonates is essential to research conducted to understand neptunium behavior in geologic repositories and the environment. Radionuclides placed in repository, particularly the long-lived radiotoxic actinides, may contact carbonate and bicarbonate containing water, forming soluble complexes. Recognizing this concern and the need for research, Clark *et al.* (1995) and Lemire *et al.* (2001, pp 203–83) have exhaustively reviewed the available literature on neptunium carbonates.

6.7.6 Coordination compounds

Interest in the coordination chemistry of neptunium compounds is enhanced by the unique properties of each of the five oxidation states of neptunium and by the changes in coordination chemistry caused by decreasing ionic size across the actinide series. Therefore a number of compounds of neptunium and various ligands have been prepared to characterize neptunium coordination chemistry. A selected listing of these compounds and some reported crystal structures and lattice parameters are given in Table 6.9.

There is little published information of Np(III) coordination compounds. According to Mefod'eva and Gel'man (1971) the reason is in the instability of Np(III) in aqueous solutions to atmospheric oxygen. These investigators, however, reported the reduction of Np(IV) to Np(III) by sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$. Apparently this compound stabilizes Np(III) and allows the formation of sparingly soluble compounds such as $Np_2(C_2O_4)_3 \cdot nH_2O(n = 11)$, $Np_2(C_6H_5AsO_3)_3 \cdot H_2O$ and $Np_2[C_6H_4(OH)COO]_3$. These compounds were formed by the addition of oxalic acid, phenylarsonic acid, or ammonium salicylate to solutions containing Np(III) reduced by $NaHSO_2 \cdot Ch_2O \cdot 2H_2O$. Atmospheric oxygen was removed from reagent solutions by argon purges and/or covering solutions with benzene. The precipitates were dried with ether and/or acetone and streams of argon.

A number of Np(IV) coordination compounds have been reported. Al-Kazzaz *et al.* (1972) prepared $(Et_4N)Np(NCS)_8$, where Et_4N = tetraethyl ammonium, which is isostructural with the uranium analog. Cousson *et al.* (1985) obtained $CoNp_2F_{10} \cdot 8H_2O$ and $CuNp_2F_{10} \cdot 6H_2O$. The investigators, using the method of Abazli *et al.* (1984), mixed and powdered transition metal cobalt or copper

Table 6.9 *Lattice parameters of selected neptunium coordination compounds.*

			Lattice constants				
Compound	*Symmetry*	*Space group*	a_0 (Å)	b_0 (Å)	c_0 (Å)	Angle (deg)	*References*
Np(III)							
$Np_2(C_2O_4)_3 \cdot nH_2O$							Mefod'eva and Gel'man (1971)
$Np_2(C_6H_5A_5O_3)_3 \cdot nH_2O$							Mefod'eva and Gel'man (1971)
$Np_2[C_6H_4(OH)COO]_3$							Mefod'eva and Gel'man (1971)
Np(IV)							
$(Net_4)Np(NCS)_8$			11.6		22.89		Al-Kazzaz *et al.* (1972)
$CoNp_2F_{10} \cdot 8H_2O$		$P2_1/a$	8.803	7.04	11.066	94.12	Cousson *et al.* (1985)
$CuNp_2F_{10} \cdot 6H_2O$		C_2/c	19.043	7.128	8.593	96.63	Cousson *et al.* (1985)
$NpCl_2 \cdot P(i\text{-}C_4H_9)_3O$							Bagnall *et al.* (1985)
$NpCl_4CH_3CON(i\text{-}C_3H_7)_2$							Bagnall *et al.* (1985)
$NpCl_4 \cdot 2.5HCON(CH_3)$							Bagnall *et al.* (1985)
$NpCl_4 \cdot 3.5P(CH_3)(C_6H_5)_2O$							Bagnall *et al.* (1985)
$Np(NO_3) \cdot C_{10}H_{10}N_2(NO_3) \cdot 2H_2O$		$P1/2$	8.445	9.013	11.87	102.56	Grigor'ev *et al.* (1986a)
$(C_{10}H_{10}N_2)[NP(NO_3)] \cdot 2H_2O$		$Pna2_1$	15.61	10.19	14.799		Grigor'ev *et al.* (1987)
Np(V)							
$Na_4(NpO_4)_2C_{12}O_{12} \cdot 8H_2O$		C_2/c	12.53	11.58	17.81	105.79	Cousson *et al.* (1984)
$(NpO_2)_2CH_2(CO_2)_2 \cdot 1H_2O$							
$(NpO_2)_2CH_2(CO_2)_2 \cdot 3H_2O$		$P2_1$	6.596	8.32	10.308	90.24	Grigor'ev *et al.* (1993b)

$(NpO_2)_2CH_2(CO_2)_2\cdot 4H_2O$	monoclinic	$P2_1/n$	8.84	15.475	9.07	114.51	Krot *et al.* (1993)
$NH_4NpO_2CH_2(CO_2)_2$		$P2_1/c$	7.703	13.02	7.704	111.08	Krot *et al.* (1993)
$CsNpO_2CH_2(CO_2)_2$		$P2_1/m$	9.184	13.636	7.45	101.97	Krot *et al.* (1993)
$NaNpO_2CH_2(CO_2)\cdot 2H_2O$	monoclinic	$P2_1/n$	12.935	7.645	7.968	97.09	Krot *et al.* (1993)
$NpO_2OOCH\cdot H_2O$							
$NpO_2OOCCH_3\cdot H_2O$							
$NpO_2SO_3NH_2\cdot H_2O$			9.067	5.439	12.184		Budantseva *et al.* (1989)
$Cs[NpO_2(SO_4)_2]\cdot 2H_2O$		$P1$	7.522	9.954	10.71	82.24	Grigor'ev *et al.* (1991c)
$[Co(NH_3)_6][NpO_2(SO_4)_2]\cdot 2H_2O$		$Pnma$	17.48	7.143	12.515		Grigor'ev *et al.* (1991b)
$[Co(NH_3)_6]H_8O_3[NpO_2(SO_4)_3]$		$Pbca$	19.437	14.595	12.744		Grigor'ev *et al.* (1991b)
$(NpO_2)_2SO_4\cdot H_2O$		$Pnma$	15.79	6.932	6.714		Grigor'ev *et al.* (1993c)
$Cs_4(NpO_2)_3Cl_6(NO_3)\cdot H_2O$		$Cmc2_1$	19.6	13.26	8.54		Tomilin *et al.* (1986)
Np(VI)							
$NpO_2C_2O_4$							Mefod'eva *et al.* (1969)
$(NH_4)NpO_2(CO_3)_3$							Marquart *et al.* (1983)
Np(VII)							
$LiCo(NH_3)_6Np_2O_8(OH)_2\cdot 2H_2O$	monoclinic	C_2/c	10.739	10.45	15.013	116.38	Burns *et al.* (1973)
$NaCo(NH_3)_6Np_2O_8(OH_2)\cdot 2H_2O$			10.865	10.597	14.867	115.13	Burns *et al.* (1973)
$Co(NH_3)_6NpO_4(OH)_2\cdot 2H_2O$		$P2_1/c$	6.778	8.449	12.448	119.3	Burns *et al.* (1973)
$CsNpO_2Cl_2(H_2O)$	monoclinic	$P2_1(P2_1/n)$	11.71	6.99	8.76	93.1	Tomilin *et al.* (1986)

difluorides and NpF_4. The mixtures were placed into gold tubes with a few drops of 40% HF. The tubes were sealed, placed in an autoclave, the pressure was adjusted to 152 MPa, and temperature increased to the desired reaction temperatures. The cobalt- and copper-containing compounds are reportedly formed at 400 and 600 K, respectively. Bagnall *et al.* (1985) reported the preparation of $NpCl_2 \cdot P(i\text{-}C_4H_9)_3O$, $NpCl_4 \cdot CH_3CON(i\text{-}C_3H_7)_2$, $NpCl_4 \cdot 2.5HCON(CH_3)$, and $NpCl_4 \cdot 3.5P(CH_3)(C_6H_5)_2O$. These compounds were obtained by mixing suspensions of Cs_2NpCl_6 in dichloromethane with the appropriate phosphine oxides and amides by stirring for 7 days and evaporating the solution to dryness. Complex nitrate compounds have been formed. Grigor'ev *et al.* (1986a) prepared $Np(NO_3)_4 \cdot 2C_{10}H_{10}N_2(NO_3)_2 \cdot 2H_2O$ with the intent of investigating the separation of Np(iv) as a more complicated compound. Grigor'ev *et al.* (1987) also prepared the Np(iv) coordination compound $(C_{10}H_{10}N_2)[Np(NO_3)_6] \cdot 2H_2O$. In both nitrate complex studies, the investigators formed single crystals by slow ambient temperature evaporation of solutions of Np(iv) in concentrated HNO_3 and excess 2,2′-pyridine.

The coordination chemistry of Np(v) compounds was stimulated by the discovery of the so-called cation–cation interaction in the solid state by Cousson *et al.* (1984). Interestingly, cation–cation interactions with actinyl ions in solution have been known since 1961 (Sullivan *et al.*, 1961). Cousson *et al.* (1984) obtained the neptunyl dimer, $Na_4(NpO_4)_2C_{12}O_{12} \cdot 8H_2O$, by dissolving neptunyl hydroxide in an aqueous solution of benzenehexacarboxylic acid (mellitic acid). The resulting solution was adjusted with NaOH to a pH of approximately 6.5 and was slowly evaporated, producing green crystals. The investigators reported, based on diffraction studies, the distance between the two neptunium atoms to be 3.4824 Å. Krot *et al.* (1993) and Grigor'ev *et al.* (1993a,b) synthesized and characterized Np(v) malonates and neptunyl malonate hydrates; $(NpO_2)_2CH_2(CO_2)_2 \cdot xH_2O$ where $x = 1, 3, 4$ and $MNpO_2CH_2(CO_2)_2$ where $M = NH_4$ or Cs and $NaNpO_2CH_2(CO_2) \cdot 2H_2O$. Grigor'ev *et al.* (1989) and Logvis' *et al.* (1994) prepared neptunyl formate, $NpO_2OOCH \cdot H_2O$, by reacting NH_4OOCH and HCOOH with a neptunyl(v) nitrate solution. Charushnikova *et al.* (1995) and Grigor'ev *et al.* (1995) prepared neptunyl glycolate by dissolving freshly prepared neptunyl hydroxide into excess glycolic acid and evaporation of the resulting solution until green crystals formed. In the same study Charushnikova *et al.* (1995) precipitated neptunyl trichloroacetate by dissolving the freshly prepared neptunyl hydroxide in equimolar amounts of trichloroacetic acid. The acetate, $NpO_2OOCCH_3 \cdot H_2O$, was obtained either by dissolving freshly prepared neptunyl(v) hydroxide in excess glacial acetic acid and collection of a resulting green precipitate by filtration or by the addition of $NaOOCH_3$ to a solution of Np(v) which had been adjusted to a pH of 4 to 5 with ammonia and collection of the resulting precipitate by filtration (Bessonov *et al.*, 1989b). Charushnikova *et al.* (1992) obtained neptunyl benzoate in a similar manner to the acetate. Ammonium benzoate was added to a solution of Np(v) which had been adjusted to a pH of 4 to 5 with ammonia water. Several oxalate compounds have been prepared and characterized (Jones and Stone, 1972; Tomilin *et al.*, 1984). Grigor'ev *et al.* (1991a) reported the results of their study on two complex neptunium(v) oxalates; $[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot nH_2O$ where $n = 3$ and 4. Single crystals of each compound formed were a function of the concentrations of $C_2O_4^{2-}$ and Np(v). Budantseva *et al.* (1989) synthesized and studied some of the properties of neptunyl sulfamate monohydrate. The air-stable compound, $NpO_2SO_3NH_2 \cdot H_2O$, was obtained by eluting Np(v) from a cation-exchange resin in the neptunyl form with sodium sulfamate. The eluent was evaporated in a stream of air at 298 K. Attempts to prepare single crystals were not successful. Simple and complex neptunyl sulfate complexes have been prepared and characterized (Grigor'ev *et al.*, 1991b,c, 1993c). The lattice parameter for these compounds are given in Table 6.9. Saeki *et al.* (1999) studied the correlation between isomer shifts of ^{237}Np Mössbauer spectra and coordination numbers of neptunium atoms in some Np(v) compounds.

Np(vi) coordination compounds include simple compounds such as $NpO_2C_2O_4$ (Mefod'eva *et al.*, 1969) and complex compounds such as $(NH_4)_4NpO_2(CO_3)_3$ (Marquart *et al.*, 1983). The oxalate was obtained by adding oxalic acid to a nitric acid solution of Np(vi) containing $KBrO_3$. The resulting compound is not stable, Np(vi) is reduced to Np(iv) after storage even at cold temperatures. Green $(NH_4)_4NpO_2(CO_3)_3$ was prepared by adding an excess of $(NH_4)_2CO_3$ to a nitric acid solution containing Np(vi). Hexavalent actinide complexes of the formula $M_4AnO_2(CO_3)_3$ (An=U, Np, Pu; M = single valent cation) have been extensively studied (Clark *et al.*, 1995).

Since the discovery of Np(vii) (Krot and Gel'man, 1967) several Np(vii) coordination compounds have been prepared and studied. Krot *et al.* (1968b,c) reported the preparation of a compound with the formulation $Co(NH_3)_6NpO_5 \cdot nH_2O$. Later, Burns *et al.* (1973) suggested the formulation should be $[Co(NH_3)_6][NpO_4(OH)_2] \cdot 2H_2O$ following their efforts to experimentally demonstrate the existence of $[NpO_4(OH)_2]^{3-}$ as the form of Np(vii) in alkaline solution. The investigators, using the method proposed by Krot *et al.* (1968a), precipitated $[Co(NH_3)_6][NpO_4(OH)_2] \cdot 2H_2O$ by the simultaneous dropwise addition of solutions of $Co(NH_3)_6Cl_3$ and Np(vii) in LiOH to a stirred solution of LiOH. In the same study Burns *et al.* (1973) reported the preparation of $LiCo(NH_3)_6Np_2O_8(OH)_2 \cdot 2H_2O$ by slowly diffusing a LiOH solution of Np (vii) into a solution of $Co(NH_3)_6Cl_3$. The investigators also prepared an analog containing sodium from NaOH solution of Np(vii) but attempts to prepare a potassium analog from Np(vii) in KOH was unsuccessful. Apparently, the formation of $[Co(NH_3)_6][NpO_4(OH)_2] \cdot 2H_2O$ or $LiCo(NH_3)_6Np_2O_8(OH)_2 \cdot 2H_2O$ is dependent on rapid precipitation vs slow diffusion, respectively. Grigor'ev *et al.* (1986b) obtained large single crystals of $Co(NH_3)_6NpO_4(OH)_2 \cdot 2H_2O$ by mixing a LiOH solution of Np(vii) with a LiOH solution containing small excess of $Co(NH_3)_6Cl_3$ and placing the mixture into a cooler for several hours. The resulting prismatic crystals were dark green and a maximum length of the edge 0.15–0.4 mm. The crystal structure and lattice parameters are given in Table 6.9. Nakamoto *et al.* (1999) reported the ^{237}Np Mössbauer spectroscopic study of $Co(NH_3)_6NpO_4(OH)_2 \cdot 2H_2O$. The preparation and some properties of $[Pt(NH_3)_5Cl]NpO_5 \cdot nH_2O$ (where $n =$ ca. 1) were reported by Krot *et al.* (1968b). Blackish-green $[Pt(NH_3)_5Cl]NpO_5 \cdot nH_2O$ was obtained by adding a saturated solution of $[Pt(NH_3)_5Cl]Cl_3$ to a basic solution of Np(vii). Mefod'eva *et al.* (1970a,b) synthesized $[CoEn_3]NpO_5 \cdot 3H_2O$ (where En = ethylenediamine) using a method similar to the preparation described above for the preparation of $[Co(NH_3)_6][NpO_4(OH)_2] \cdot 2H_2O$ modified to use more concentration solutions because of the solubility of $[CoEn_3]NpO_5 \cdot 3H_2O$. The precipitates formed are thin green plate-like crystals, which decompose to a brown-colored material after stored for 5 to 6 days in a dry desiccator.

6.7.7 Important organometallic compounds

Neptunium organometallic compounds have been prepared and characterized, but not nearly to the extent of uranium organometallics. A survey of the literature produced a limited number of well-characterized neptunium organometallics. The radioactive hazard associated with neptunium and its scarcity are two reasons for the scarcity of published information. Most investigations reported to date deal with the preparation of neptunium cyclopentadienyl and cyclooctatetraenyl compounds and derivatives of these compounds. These compounds have been extensively reviewed (Gysling and Tsutsui, 1970; Hayes and Thomas, 1971; Legin, 1979; Marks and Ernest, 1982; Mishin *et al.*, 1986). The synthesis, characterization, and catalytic processes of organometallic actinides are discussed in Chapters 25 and 26.

(a) Cyclopentadienyl compounds

A trivalent neptunium cyclopentadienyl complex was synthesized and characterized by Karraker and Stone (1972). The complex is formed by the reduction of $Np(C_5H_5)_3Cl$ with sodium:

$$Np(C_5H_5)_3Cl + Na \rightarrow Np(C_5H_5) \cdot 3THF + NaCl \qquad (6.22)$$

Attempts to obtain $Np(C_5H_5)$ by heating and vacuum to remove tetrahydrofuran (THF) were unsuccessful.

Tetravalent neptunium tetracyclopentadienyl was prepared and characterized by Baumgartner *et al.* (1968). The complex was prepared by reacting $NpCl_4$ with KC_5H_5 in benzene under reflux for 160 h:

$$NpCl_4 + 4KC_5H_5 \rightarrow Np(C_5H_5)_4 + 4KCl \qquad (6.23)$$

The reddish-brown complex dissolved in benzene and THF. The authors reported that the compound is less sensitive to oxygen and water than $Pu(C_5H_5)_3$ and $Am(C_5H_5)_3$.

Other Np(IV) cyclopentadienyl compounds have been prepared and characterized. Two reactions have been reported for the preparation of tricyclopentadienyl chloride, $(C_5H_5)_3NpCl$. Fischer *et al.* (1966) prepared the compound by reacting NpX_4 (X = Cl, F) with potassium cyclopentadienyl, $3K(C_5H_5)$, in THF. Later Karraker and Stone (1972) prepared the compound by reacting $NpCl_4$ with beryllium cyclopentadienyl. Equations describing the two reactions are:

$$NpX_4 + 3K(C_5H_5)_4 \rightarrow Np(C_5H_5)_3X + 3KX \qquad (6.24)$$

$$2NpCl_4 + 3BeC_5H_5 \rightarrow 2Np(C_5H_5)_3Cl + 3BeCl_2 \qquad (6.25)$$

A number of derivatives can be prepared starting with tetrakiscyclopentadienyl Np(IV), $Np(C_5H_5)_4$, and tris(cyclopentadienyl)Np(IV) chloride, $(C_5H_5)_3NpCl$. These compounds have the general formula $(C_5H_5)_3NpL$ with either inorganic ionic ($L = Br^-$, I^-, $1/2SO_4^{2-}$, NCS^-, $ALCl_4$) or organic ligands ($L = NC_4H_4^-$, $N_2C_3H_3^-$, $C = CH^-$, $1/2C = C_2^-$, $C_2H_5^-$, $C_6H_5^-$) (Bohlander, 1986). An interesting and unusual synthetic method was reported by Baumgartner *et al.* (1965). These authors obtained $Np(C_5H_5)_3Cl$ by (γ,n) reaction with U-238 in $U(C_5H_5)_3Cl$.

(b) Cyclooctatetraene compounds

Karraker *et al.* (1970) prepared bis(cyclooctatetraenyl) Np(IV) by reacting $NpCl_4$ with a THF solution of $K_2(C_8H_8)$:

$$NpCl_4 + 2K_2(C_8H_8) \rightarrow Np(C_8H_8)_2 + 4KCl \qquad (6.26)$$

After 16 h of stirring, the compound was precipitated by the addition of deaerated water and recovered by evaporation. The authors report that X-ray diffraction patterns indicate that $Np(C_8H_8)_2$ is isomorphous with $U(C_8H_8)_2$ and $Pu(C_8H_8)_2$. The chemical behavior of the three compounds are identical: the compounds are not sensitive to water or dilute base, they are air-sensitive, reacting quickly to form oxides, and they are very slightly soluble in organic solvents such as benzene and toluene.

Karraker (1973) synthesized both neptunium bis(ethylcyclotetraene) and bis (*n*-butylcyclotetraene) complexes by reacting the alkyl substitued potassium complex in THF with $NpCl_4$ as shown below:

$$2K_2RC_8H_7 + NpCl_4 \rightarrow Np(RC_8H_7)_2 + 4KCl \qquad (6.27)$$

where R = ethanol, butanol.

A trivalent neptunium cyclotetraene complex was prepared and characterized by Karraker and Stone (1974) by reacting stoichiometric amounts of NpX_3 (X = Cl, Br, I) and $K_2(C_8H_8)$ in THF:

$$NpXr_3 + 2K_2(C_8H_8) \rightarrow KNp(C_8H_8) \cdot 2THF + 3KX \qquad (6.28)$$

The compound is isostructural with $KPu(C_8H_8)_2 \cdot 2THF$ with an orthorhombic unit cell. Both compounds are reported to be air- and water-sensitive, converting to $Np(C_8H_8)_2$ by air oxidation and other trace amounts of oxidizing agents. The compound is soluble in THF but slightly soluble in benzene and toluene.

(c) Other organometallic compounds

Hydrocarbyl compounds of neptunium have been reported. Karraker and Stone (1976) reported the preparation of $Np(C_5H_5)_3R$ where $R = n$-butyl by reacting $Np(C_5H_5)_3Cl$ with RLi.

Recent investigations of suitable precursors for organometallic and inorganometallic compounds suggested the usefulness of solvated triiodide complexes for this purpose (Karraker, 1987; Zwick *et al.*, 1992). Karraker (1987) investigated the reaction of neptunium with diiodoethane. The reaction in THF is:

$$Np + 3/2C_2H_4I_2 \rightarrow NpI_3 \cdot x\mathrm{THF} + 3/2C_2H_4 \qquad (6.29)$$

The reaction was carried out in a dry argon. The mixture of reactants were stirred at ambient temperature at times up to 1 week. A yellow precipitate was mixed with thallous methylcyclopentadienide in THF. The reaction is complete in 5 to 10 min. Two pure products, $NpI_2(MeC_5H_5) \cdot 3THF$ and $NpI(MeC_5H_5)$ 2.3THF can be obtained by evaporation or precipitation with ether. Using $NpI_3(THF)_4$ Zwick *et al.* (1992) reported the preparation of $Np[N(SiMe)_2]_3$, $Np[O\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_3]_3$, and $Np[CH(SiMe_3)_2]_3$, demonstrating that $NpI_3(THF)_4$ is a precursor to new and existing compounds.

6.8 NEPTUNIUM IN AQUEOUS SOLUTION

6.8.1 Oxidation states of neptunium ions

Neptunium exists in an aqueous solution as ions of oxidation states from 3+ to 7+. These oxidation states are liable to change through reduction and oxidation reactions and disproportionation reaction of Np(v). The stability of the oxidation state is strongly affected by factors such as oxidants or reductants, acidity of the solution, presence of a complex forming ligand, and the concentration of neptunium itself in the solution. The stability of each ion can be simply predicted from the redox potentials as described below.

Trivalent and tetravalent neptunium exist as hydrated Np^{3+} and Np^{4+} in acidic solutions without ligand, Np^{3+} is quickly oxidized to Np^{4+} by air. Even in moderately acidic solutions, Np^{4+} is significantly hydrolyzed. Np(iii) and Np(iv) form insoluble hydroxides in aqueous solutions of low acidity and the hydroxide of Np(iii) is readily oxidized to the hydroxide of Np(iv) by air. The pentavalent neptunium ion, which is the most stable oxidation state in solution, and hexavalent neptunium ion behave as strong Lewis acids and these ions form dioxo species, NpO_2^+ and NpO_2^{2+}, in acidic solution. NpO_2^{2+} is stable in acidic solution but is relatively easily reduced to NpO_2^+. Np(V) and Np(VI) form hydroxides in neutral and basic solutions. The solubilities of these hydroxides in the aqueous solution are higher than that of Np(IV) hydroxide. Np(VII) was first prepared by Krot and Gelman (1967) in basic solution. The chemical forms of Np(VII) in acidic and basic media are described in Section 6.8.2. NpO_3^+ is quickly reduced to NpO_2^{2+} by water (Spitsyn *et al.*, 1969).

(a) Redox potentials of neptunium ions

(*i*) *Acidic media*

Np(III), Np(IV), Np(V), and Np(VI) ions exist in solutions of sufficiently high acidity or solutions containing ligands. Standard redox potentials are estimated from experimentally determined formal redox potentials by precise correction for activity coefficients. Alternatively, the standard redox potentials are calculated from standard enthalpies of formation and entropies of the ions. Chapter 19 of this work provides recommended values of the standard potentials of actinide ions as the following potential diagram:

$$\underbrace{NpO_2^{2+} \xrightarrow{+1.159} NpO_2^{+} \xrightarrow{+0.604}}_{+0.882} \underbrace{Np^{4+} \xrightarrow{+0.219} Np^{3+} \xrightarrow{-1.772} Np}_{-1.274}$$

Recently, Kihara *et al.* (1999) critically evaluated the redox potentials of uranium, neptunium, and plutonium ions in acidic solutions by extrapolating the formal potentials to the state of zero ionic strength, referring mainly to the works by Riglet *et al.* (1987, 1989) and based on the Bronsted–Guggenheim–Scatchard specific ion-interaction theory (SIT) (Pitzer, 1979).

The E° for such reversible redox couples as NpO_2^{2+}/NpO_2^+ and Np^{4+}/Np^{3+} proposed by Riglet *et al.* (1987, 1989) are reliable and most of the experimental data are in good agreement with these E° if the activity coefficient is properly corrected in the conversion of the formal potential to E°. The formal potential for the redox couple between NpO_2^+ and Np^{4+} is difficult to determine by conventional voltammetry or polarography, because the electrode reaction between NpO_2^+ and Np^{4+} is slow or irreversible because Np–O bonds must be made or broken. The E° for NpO_2^+/Np^{4+} couple in the diagram was evaluated from data of Gibbs energy of formation (Martinot and Fuger, 1985). Kihara *et al.* (1999) re-estimated the electromotive force (EMF) data (Cohen and Hindman, 1952) by the activity coefficient correction based on the SIT and obtained +0.596 for NpO_2^+/NP^{4+} couple. The E° for NpO_3^+/NpO_2^{2+} estimated by Musikas *et al.* (1974) given in the diagram is recommended at the present time.

(*ii*) *Basic media*

Standard potentials or formal potentials for neptunium ions in basic media are less precise and less reliable than those in acidic media. For some redox reactions even chemical forms of hydrolytic species participating in the processes have not yet been fully understood. The potential diagram for neptunium ions in basic media by Martinot and Fuger (1985) is recommended:

$$\mathrm{NpO_5^{3-}} \xrightarrow{+0.58} \mathrm{NpO_2(OH)_2} \xrightarrow{+0.6} \mathrm{NpO_2OH} \xrightarrow{+0.3} \mathrm{NpO_2} \xrightarrow{-2.1} \mathrm{Np(OH)_3} \xrightarrow{-2.2} \mathrm{Np}$$

Recently a new method for the determination of formal potentials by the use of *in situ* X-ray absorption near-edge structure (XANES) spectroscopy was applied to the redox couples of neptunium ions in 1 M $HClO_4$ (Soderholm *et al.*, 1999). The relative concentrations of Np(VI)/Np(V) or Np(IV)/Np(III) after the controlled potential electrolysis were determined from XANES spectra using the principal component analysis technique. XANES spectra specific for the hydrated neptunium ions of different oxidation states are shown in Fig. 6.8.

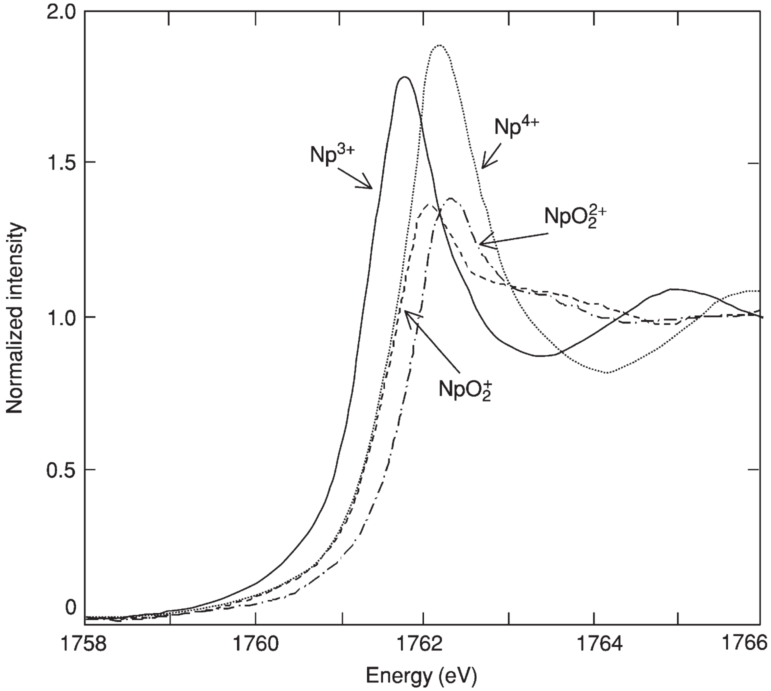


Fig. 6.8 *XANES spectra from the pure Np(*III*), Np(*IV*), Np(*V*), and Np(*VI*) ions in* $HClO_4$*; reprinted from Soderholm* et al. (1999) *with permission from American Chemical Society.*

The Nernstian plots between log([Np(vi)]/[Np(v)]) or log([Np(iv)]/[Np(iii)]) and the applied potential lead to the precise determination of the formal potential, at which [Np(vi)]/[Np(v)] or [Np(iv)]/[Np(iii)] equals unity. The formal potentials determined by this method are in good agreement with those determined by traditional voltammetry or polarography. An advantage of this method is that XANES is highly selective to the ion of interest that can interrogate a given redox couple in a complicated mixture such as the test solution containing multiple redox-active species.

(b) Electrolytic behavior of neptunium ions

(*i*) *Voltammetric behavior*

The measurements of current–potential relations by voltammetry, polarography, or related methods are important not only to elucidate the reaction mechanism and estimate the reaction rate but also to determine the formal potential for the evaluation of the standard redox potential. The voltammetric studies of the redox of neptunium ions, however, have not been conducted extensively enough.

Voltammetric data for the redox of neptunium ions in acidic media were provided by Niese and Vecernik (1981). The current–potential curves were recorded by cyclic voltammetry at a glassy carbon electrode with $HClO_4$, HNO_3, H_2SO_4, and acetate buffer solutions containing neptunium ion of a given oxidation state. Clear peaks due to one-electron redox reactions of NpO_2^{2+}/NpO_2^{+} and Np^{4+}/Np^{3+} were observed. The peak potentials $E_{p,a}$ and $E_{p,c}$, at which the anodic and cathodic current peaks were observed, for the redox couples of NpO_2^{2+}/NpO_2^{+} and Np^{4+}/Np^{3+} are summarized in Table 6.10. A difference between $E_{p,a}$ and $E_{p,c}$, ΔE_p, indicates that the redox processes of NpO_2^{2+}/NpO_2^{+} and Np^{4+}/Np^{3+} in the 0.5 M $HClO_4$ or 1 M HNO_3 solutions are practically reversible and those in the H_2SO_4 or acetate buffer solutions are not reversible. The peak potential for NpO_2^{2+}/NpO_2^{+} shifts more negatively with acetate buffer solution and the peak potential for Np^{4+}/Np^{3+} in HNO_3, H_2SO_4, and acetate buffer solution are more negative than that in $HClO_4$, which is due to stabilization of NpO_2^{2+} and Np^{4+} by the complex formation of NpO_2^{2+} with acetate ion and Np^{4+} with NO_3^-, SO_4^{2-}, and acetate ion.

The cathodic wave corresponding to further reduction of NpO_2^{+} to Np^{4+} or Np^{3+} was not observed in the experiments by Niese and Vecernik (1981). The rate of the redox between Np^{4+} and NpO_2^{+} as equation (6.30) is very slow, because the redox process involves formation or rupture of a Np–O bond which requires a large overpotential.

$$NpO_2^{+} + 4H^{+} + e^{-} \rightleftarrows Np^{4+} + 2H_2O \qquad (6.30)$$

The potential for the reduction of NpO_2^{+} to Np^{4+} is, therefore, more negative than that for the reduction of Np^{4+} to Np^{3+}, and the potential for the oxidation

Table 6.10 *Characteristics of voltammograms for redox of neptunium ions in $HClO_4$, HNO_3, H_2SO_4, or acetate buffer solutions.*

		Peak potentials (V vs SSE)		
Redox reactions	*Electrolyte*	*Anodic peak, $E_{p,a}$*	*Cathodic peak, $E_{p,c}$*	E_p
$NpO_2^{2+} + e^- = NpO_2^+$	0.5 M $HClO_4$	+1.01	+0.95	0.060
	1 M HNO_3	+1.04	+0.98	0.060
	0.5 M H_2SO_4	+1.02	+0.91	0.110
	0.5 M acetate buffer (pH = 4.2)	+0.84	+0.72	0.120
$Np^{4+} + e^- = Np^{3+}$	0.5 M $HClO_4$	+0.05	–0.02	0.070
	1 M HNO_3	–0.02	–0.08	0.070
	0.5 M H_2SO_4	–0.095	–0.23	0.135
	0.5 M acetate buffer (pH = 4.2)	–0.27	–1.06	0.790

of Np^{4+} to NpO_2^+ is more positive than that for the oxidation of NpO_2^+ to NpO_2^{2+} in $HClO_4$ and HNO_3 media.

Riglet *et al.* (1989) recorded voltammograms for the redox of Np(VI) and Np(V) in perchlorate media of various ionic strengths ($0.5 < I < 3$) for the precise determination of the formal redox potentials and re-evaluation of the standard redox potential at $I = 0$. The current–potential curves shown in Fig. 6.9 were recorded at rotating platinum disk electrode (2 mm in disk diameter) with rotation rate of 1500 rpm by scanning the potential at a rate of 0.002 V s^{-1}. The oxidation state of the neptunium ion in the test solution was controlled by the electrolysis so that NpO_2^+ initially present in the solution was partly oxidized to NpO_2^{2+} step by step (curves 2 to 5). The anodic wave developing at more positive potential and the cathodic wave at more negative potential than ca. +0.77 to +0.78 V correspond to the oxidation of NpO_2^+ and the reduction of NpO_2^{2+}, respectively. The redox reaction between NpO_2^+ and NpO_2^{2+} is not fully reversible at the platinum electrode because the slopes of the logarithmic analysis of the diffusion controlled waves are ca. 0.080 V per log unit, which are larger than the theoretical value.

Voltammetry using a rotating platinum electrode was applied to study the redox behavior of neptunium ions in 0.5– 4 M NaOH solution (Peretrukhin and Alekseeva, 1974). The successive reduction and oxidation among Np(VII), Np (VI), Np(V), and Np(IV) were investigated. The redox behavior of the neptunium ions strongly depends on the concentration of NaOH, which is interpreted as a change of the chemical form of Np(VI) during the electrolytic reduction and oxidation depending on the NaOH concentration.

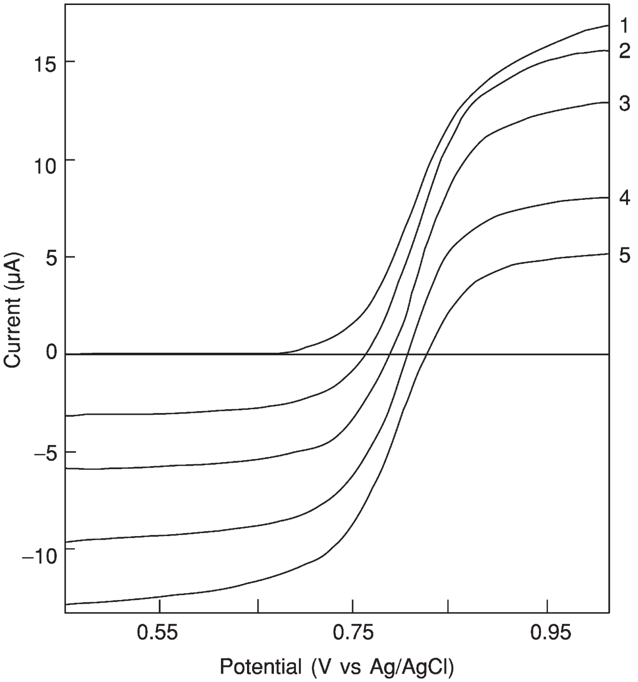


Fig. 6.9 *Current–potential curves for the redox couple of* NpO_2^{2+}/NpO_2^+ *in* 1 M $HClO_4$ + 1 M $NaClO_4$ *at rotating platinum disk electrode* (1500 rpm). *Concentration of Np*; 10^{-3} M, *Potential;* V *vs Ag/AgCl electrode* ($E^\circ = 0.3329$ V *vs NHE*).

Electrochemical and spectroscopic studies of neptunium ions in concentrated aqueous carbonate and carbonate–hydroxide solutions were carried out by Varlashkin *et al.* (1984). The formal potential of the Np(VI)/Np(V) couple was determined as a function of pH of the solution. The redox reaction between Np(VI) and Np(V) was found to be quasi-reversible at a platinum electrode and the formal potential was estimated to be (+0.23 ± 0.01) V vs saturated calomel electrode (SCE).

(*ii*) *Coulometric behavior*

Flow coulometry using multi-step column electrodes is a powerful technique to investigate a redox reaction even if the reaction is irreversible, because the surface area of the working electrode of the column electrode is very large comparing with a volume of the solution in the column and a quantitative electrolysis can be achieved very rapidly. The electrolysis method using column electrode is also useful for the preparation of ions of a desired oxidation state as well as for the rapid determination or collection of various metals (Fujinaga and Kihara, 1977; Yoshida *et al.*, 1991).

Flow coulometry has been applied to the studies of overall redox behavior of the neptunium ions in acidic aqueous solution. Coulopotentiograms, which are current–potential curves observed by flow coulometry, were measured by using the multi-step column electrodes connected in series. Coulopotentiograms for the redox of neptunium ions of various oxidation states are shown in Fig. 6.10 after correction for the residual current. In the figure, the number of electrons involved in the redox reaction, *n*, converted from the current is plotted on the ordinate instead of the current.

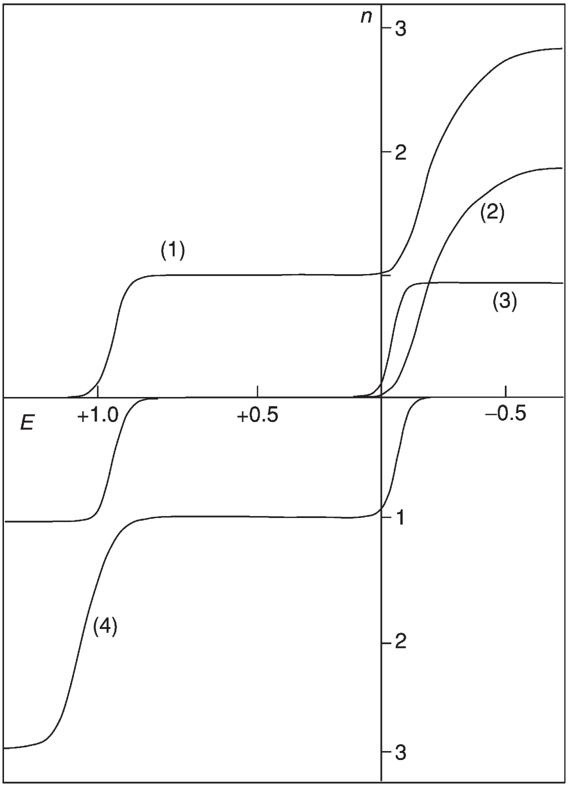


Fig. 6.10 *Coulopotentiograms for the redox of neptunium ions in* 1 M $HClO_4$ *solution.* n, *number of electrons involved in redox reaction;* E, *working electrode potential* (V *vs* Ag–AgCl *reference electrode*). (1) *Reduction of* NpO_2^{2+}, (2) *reduction and oxidation of* NpO_2^{+}, (3) *reduction of* Np^{4+}, (4) *oxidation of* Np^{3+}. *Sample solution;* 10^{-3} M *Np ion, flow rate,* 1.5 ml min^{-1}; *potential scan rate,* 0.002 V s^{-1}.

Coulopotentiogram 1 in Fig. 6.10 was recorded at a single column electrode with flowing 1 M $HClO_4$ solution containing 10^{-3} M NpO_2^{2+} and scanning the potential. The coulopotentiogram shows the reduction of NpO_2^{2+} to NpO_2^{+} at more negative potential than +0.85 V vs Ag–AgCl reference electrode (SSE) and further to Np^{3+} at more negative potential than −0.6 V. Coulopotentiogram 2 was recorded with a two-step column electrode system with the first column electrode kept at +0.5 V and the second column at the scanned potential. Here, NpO_2^{2+} in the test solution is converted to NpO_2^{+} quantitatively at the first column, and therefore, the redox behavior of NpO_2^{+} can be examined at the second column electrode. Coulopotentiogram 2 shows one-electron oxidation of NpO_2^{+} to NpO_2^{2+} at more positive potential than +1.1 V and two-electron reduction to Np^{3+} at more negative potential than −0.6 V. Coulopotentiograms 3 and 4 are recorded identically using two-step or three-step column electrode systems and show the reduction of Np^{4+} to Np^{3+} and the oxidation of Np^{3+} to Np^{4+} and further to NpO_2^{2+}.

(c) Disproportionation of NpO_2^{+}

NpO_2^{+} disproportionates to Np^{4+} and NpO_2^{2+} through the following reaction. The extent of the disproportionation is promoted when the acidity of the solution and the concentration of NpO_2^{+} are high:

$$2NpO_2^{+} + 4H^{+} \rightleftarrows Np^{4+} + NpO_2^{2+} + 2H_2O$$

$$K_{\mathrm{dispro}} = [Np^{4+}][NpO_2^{2+}]/[NpO_2^{+}]^2[H^{+}]^4 \qquad (6.31)$$

The equilibrium constant is increased by the addition of reagents that form complexes with Np^{4+} and $NpO_2^{2}+$ in the solution. For example, it was shown that $K_{\mathrm{dispro}} = 4 \times 10^{-7}$ for Np(V) in 1 M $HClO_4$ and $K_{\mathrm{dispro}} = 2.4 \times 10^{-2}$ for Np(V) 1 M H_2SO_4 solution (Keller, 1971). Hindman *et al.* (1954) suggested that the rate of the disproportionation reaction of equation (6.31) is expressed by equation (6.32).

$$-\mathrm{d}[NpO_2^{+}]/\mathrm{d}t = k[NpO_2^{+}][H^{+}]^2 \qquad (6.32)$$

(d) Methods for the control of oxidation state of neptunium ions

(*i*) *Redox reagents*

The oxidation state of neptunium ions can be adjusted using various redox agents. The agent and chemical procedure feasible for the promotion of the redox between reversible couples such as NpO_2^{2+}/NpO_2^{+} or Np^{4+}/Np^{3+} are chosen properly by referring to the redox potentials for neptunium ions and those for the agent as well as a ligand coexisting in the solution. Typical procedures for the control of the oxidation state of neptunium ions are shown

Table 6.11 *Procedures for adjusting the oxidation state of neptunium ion in aqueous solutions using redox agents.*

Oxidation states of neptunium ion		*Procedures*	
Before treatment	*After treatment*	*Agents*	*Conditions*
Oxidative treatment			
Np(III), Np(IV), Np(V)	Np(VI)	Ce(IV)	HNO_3, H_2SO_4
		MnO_4^-	HNO_3, H_2SO_4
		Ag(II)	1 M $HClO_4$
		BrO_3^-	
		$HClO_4$	fuming
		Cl_2	1 M HCl (348 K)
Np(III)	Np(IV)	O_2 (air)	
Reductive treatment			
Np(V), Np(VI)	Np(IV)	Fe^{2+}	H_2SO_4
		I^-	5 M HCl (373 K)
Np(VI)	Np(V)	NH_2NH_2	1 M H^+
		NH_2OH	1 M H^+
		NO_2^-	1 M HNO_3
		H_2O_2	0.5 M HNO_3
		Sn^{2+}	HCl
		SO_2	H_2SO_4
Np(IV), Np(V), Np(VI)	Np(III)	Zn(Hg)	
		H_2 (Pt black)	

in Table 6.11. The kinetic factors are required to be evaluated to complete slow processes between NpO_2^{2+} and Np^{4+} or between NpO_2^+ and Np^{4+} involved in the procedure for the oxidation state control. The kinetics of the redox reactions for Np(VI)–H_2O_2, Np(V)–V(III), Np(V)–Cr(II), and Np(VII)–Hg(I) systems were summarized by Newton (1975). Nakamura *et al.* (1992) proposed a method for the rapid reduction of Np(V) to Np(IV) by hydroxylamine nitrate in the presence of platinum black catalyst.

Recently much attention has been paid to the kinetics of the redox of neptunium ions by various organic agents for the development of an advanced Purex process. These studies aim at screening of the most suitable ‘salt-free’ redox agent, which enables precise control of the oxidation state of the neptunium ion in the process flowsheet. Taylor *et al.* (1997) reviewed the redox chemistry of neptunium ion in the proposed procedures.

Aldehyde derivatives such as *n*- and isobutyraldehydes are effective reductants for Np(VI) and Pu(IV) as reported by Kolarik and Dressler (1984) and Uchiyama *et al.* (1993). Hydroxylamine- and hydrazine derivatives have been suggested as effective reducing agents for Np(VI) and Pu(IV). Koltunov *et al.* (1993, 1999) investigated the reduction kinetics of Np(VI) by *N*,*N*-ethyl (hydroethyl)hydroxylamine ($HOC_2H_4(C_2H_5)NHOH^+$, EHEH) and *N*,*N*-diethyl hydroxylamine ($(C_2H_5)_2NHOH^+$, DEH) in nitric acid solution. The reduction reactions are expressed as follows.

$$4NpO_2^{2+} + HOC_2H_4(C_2H_5)NHOH^+ + 3H_2O \rightarrow 4NpO_2^+ + 2C_2H_5OH + HNO_3 + 9H^+ \tag{6.33}$$

$$8NpO_2^{2+} + (C_2H_5)_2NHOH^+ + 4H_2O \rightarrow 8NpO_2^+ + CH_3CHO + C_2H_5OH + HNO_3 + 5H^+ \tag{6.34}$$

The different characteristics of reactions by EHEH and DEH are explained by their different structures providing an availability of a hydroxyl group in the EHEH molecule. The kinetics of reactions (6.33) and (6.34) were studied in 0.3 – 2.0 M HNO_3 at ionic strength of 2.0. It was concluded that the reaction is first order relative to Np(VI) with excess reductants. The rate equations of reaction (6.33) and (6.34) are

$$-\mathrm{d}[\mathrm{Np(vi)}/\mathrm{d}t = k[\mathrm{Np(VI)}][\mathrm{EHEH}][\mathrm{H}^+]^{-0.8} \tag{6.35}$$

where $k = (334 \pm 12)\ \mathrm{L}^{0.2}\ \mathrm{mol}^{-0.2}\ \mathrm{min}^{-1}$ (298.6 K), and activation energy (E_A) = (42.3 ± 2.7) kJ mol^{-1}, and

$$-\mathrm{d}[\mathrm{Np(vi)}/\mathrm{d}t = k[\mathrm{Np(vi)}][\mathrm{DEH}][\mathrm{H}^+]^{-0.84} \tag{6.36}$$

where $k = (22.6 \pm 0.8)\ \mathrm{L}^{0.16}\ \mathrm{mol}^{-0.16}\ \mathrm{min}^{-1}$ (298 K), and $E_A = (68.5 \pm 0.9)$ kJ mol^{-1}. Np(VI) and Pu(IV) are reduced faster by EHEH than by DEH, which suggests that the introduction of the hydroxyl group into the reductant molecule enhances the kinetics.

A comprehensive study on the reduction kinetics of Np(VI) and Pu(IV) by Taylor *et al.* (1998a) suggests that 1,1-dimethylhydrazine (DMHz) and *tert*-butylhydrazine (*tert*-BHz) are the most promising agents for the rapid reduction of Np(VI) with high selectivity over Pu(IV) reduction. For example, 99% of Np(VI) (initial concentration (1–2) × 10^{-4} M) in 1 M HNO_3 solution was reduced to Np(V) at 298 K by the addition of 0.1 M DMHz or *tert*-BHz within 1 or 8.7 min, respectively, and only 0.23 or 0.11% of Pu(IV) (initial concentration (2–10) × 10^{-3} M) was reduced to Pu(III) during 99% reduction of Np(VI) under the equivalent condition. It was found that formohydroxamic acid (Taylor *et al.*, 1998b) and acetaldoxime (Koltunov *et al.*, 2000) were also effective reductants for the rapid reduction of Np(VI) to Np(V) in acid solution.

(*ii*) *Electrochemical methods*

Controlled potential electrolysis is available to control the oxidation state of neptunium ions. For example, Np(V) in acidic solutions such as 1 M $HClO_4$ solution is oxidized to Np(VI) completely at +1.20 V vs Ag–AgCl (saturated KCl) reference electrode, Np(v) is quantitatively reduced to Np(iii) at −0.20 V, and Np(iii) is oxidized to Np(iv) at +0.40 V by controlled potential electrolysis using carbon or platinum working electrodes. Controlled potential electrolysis was applied to the preparation of carbonate complexes of neptunium ion of a given oxidation state in neutral or basic solutions (Li *et al.*, 1993).

The electrolytic technique using multi-step column electrodes of glassy carbon fiber working electrode as described in Section 6.8.1b is also useful to adjust the oxidation state of the neptunium ion in the flowing sample solution. The applied potential and the other electrolytic conditions can be chosen consulting with the current–potential relationship as shown in Fig. 6.10.

(*iii*) *Miscellaneous*

A sonochemical technique was applied to oxidize Np(v) efficiently (Nikitenko *et al.*, 1999). Np(v) in HNO_3 solution was found to be oxidized to Np(vi) in the presence of argon under the effect of power ultrasound (20 kHz, 1 W cm^{-2}). The addition of urea which exerts a buffering effect related to nitrous acid concentration helps to stabilize Np(vi) formed under sonification. The oxidation mechanism is related to the formation of HNO_2 by sonolysis of HNO_3, followed by the oxidation of Np(v) with HNO_3 catalyzed by HNO_2.

Photochemical reaction is feasible to oxidize and reduce Np(v) and Np(vi) in nitric acid solution (Fukasawa *et al.*, 1991). Np(vi) is reduced to Np(v) by HNO_2 generated by the photolysis of HNO_3 and is shown in reactions (6.37) to (6.39).

$$HNO_3(\text{photo irradiation}) \rightarrow OH + NO_2 \tag{6.37}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{6.38}$$

$$NpO_2^{2+} + HNO_2 + H_2O \rightarrow 2NpO_2^{+} + 3H^{+} + NO_3^{-} \tag{6.39}$$

Addition of a scavenger for HNO_2, such as urea, allows the oxidation of Np(v) to Np(vi) by the action of OH radical as given by reactions (6.40) and (6.41).

$$2HNO_2 + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + 3H_2O \tag{6.40}$$

$$NpO_2^{+} + OH + H^{+} \rightarrow NpO_2^{2+} + H_2O \tag{6.41}$$

The kinetics of the photochemical reduction of Np(vi) to Np(v) in HNO_3 solution were investigated (Wada *et al.*, 1995) as a function of irradiation wavelength, the acidity of nitric acid, and the nature of the coexisting agents. It was concluded that the higher the irradiation rate and the HNO_3 concentration, the easier the oxidation reaction of Np(v) progressed.

6.8.2 Optical spectroscopy of neptunium

Optical spectroscopy has been extensively applied to neptunium to better understand the electronic structure of the aquo ions Np(III) through Np(VII), and of coordination complexes that occur in solution (Gruen, 1952; Waggener, 1958; Dukes and Shuler, 1960; Krot *et al.*, 1968a; Stafsudd *et al.*, 1969; Varga *et al.*, 1970; Chaikhorskii, 1971; Chaikhorskii and Leikina, 1972; Rykov and Frolov, 1972; Tsivadze and Krot, 1972; Kharitonov and Moskvin, 1973; Rykov *et al.*, 1973; Hessler *et al.*, 1980; Kanellakopulos *et al.*, 1980a,b; Lahalle *et al.*, 1986; Carnall *et al.*, 1987; Tait *et al.*, 1995; Matsika and Pitzer, 2000; Neck *et al.*, 2001). An excellent review article has been published by Gruen (1992) describing the development of the knowledge base for the f-electron elements, especially neptunium. Fig. 6.11 shows the visible absorption spectra for the neptunium ions (III, IV, V, and VI) in 2 M perchloric acid. Optical spectroscopy has been applied in both the visible and infrared portions of the spectrum with a wealth of information being gathered.

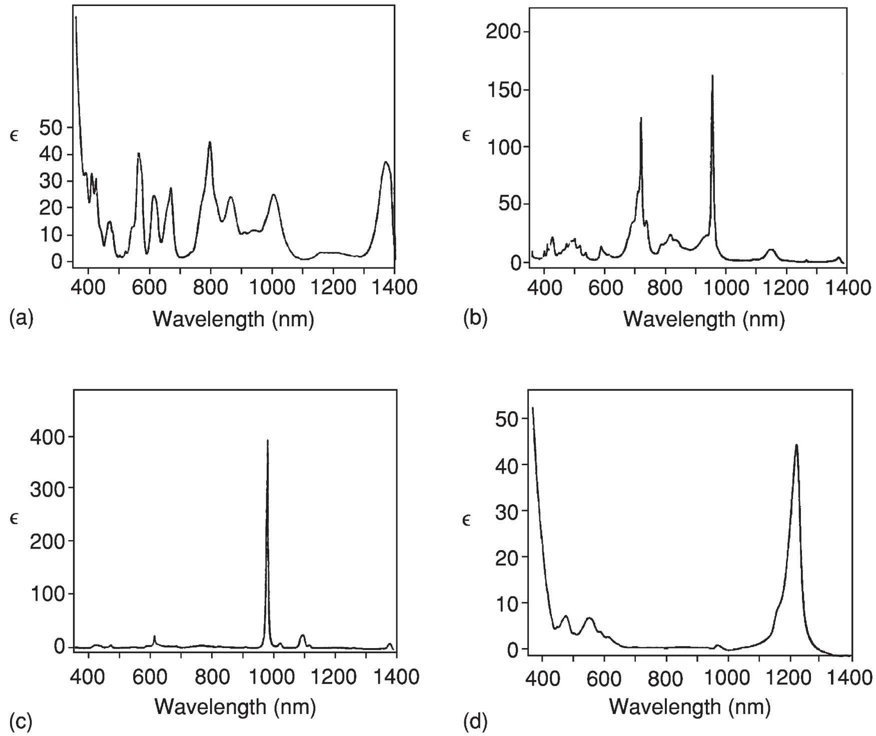


Fig. 6.11 *The absorption spectra of neptunium ions in* 2 M *$HClO_4$ solution:* (*a*)*Np*(*III*); (*b*) *Np*(*IV*); (*c*) *Np*(*V*); (*d*) *Np*(*VI*).

One of the earliest studies on the subject (Gruen, 1952) used optical means to obtain information on the spin–orbit coupling for NpO_2^{2+} species. A value of 950 cm^{-1} for the spin–orbit coupling energy provided the best agreement between calculated and experimentally observed results for the $5f^2$ configuration. This 'best fit' was obtained by using the intermediate case of mixing the pure spin–orbit coupling and the pure electrostatic case.

The absorption spectrum of neptunium has often been measured in nitric acid solution. This provides straightforward identification of what valence states are present as was shown by Dukes and Shuler (1960). Np(IV) displays a strong absorption band at 715 nm, while Np(V) displays a somewhat weaker band at 617 nm and Np(VI) displays a strong band in the region below 400 nm. The concentration of nitric acid was determined not to be a significant factor in the absorption spectrum from 1 to 6 M.

Absorption spectroscopy of the Np(VII) species is somewhat more difficult in that it can be observed only under basic conditions (Krot *et al.*, 1968a; Williams *et al.*, 2001) in a steady-state manner. The actual form of the Np(VII) in solution is as NpO_6^{5-} in basic solutions and NpO_2^{3+} in acidic solutions. The tetraoxo Np(VII) compound exhibits four 'short' bonded oxygen (~1.85 Å) and two 'long' bonded oxygen (~2.2 Å) in basic solutions. The acidic form can only be observed at room temperature for a matter of minutes before it is reduced to the Np(VI) state. The hydroxide, $NpO_2(OH)_3$ is assumed to have amphoteric properties in solution.

The absorption spectrum for Np(VII) in solution was investigated in more detail by Chaikhorskii (1971). They prepared Np(VII) species in the cationic form and then precipitated it for their study. It was determined that fine structure could be observed in the visible absorption bands (412 and 620 nm). This fine structure was attributed to two causes, electron transfer (oxygen $\pi \rightarrow 5f$) and vibrational states. Several vibrational states were identified with energies between 681 and 2338 cm^{-1}. The vibrational bands identified were consistent with the predicted symmetry of a compound involving the NpO_2^{3+} species.

The infrared spectroscopy study by Chaikhorskii (1971) was extended by Tsivadze and Krot (1972) to include several compounds of Np in the Np(VII) state. Their work validated the earlier work of Chaikhorskii (1971) and furthered the knowledge base in that they determined the neptunium in the solid compounds that contained no isolated NpO_2 groups but that there were chains of 'infinite' length which connected the NpO_6 octahedra.

Stafsudd *et al.* (1969) studied Np(VI) by doping NpO_2^{2+} into a matrix of $Cs_2UO_2Cl_4$ and applying infrared and visible spectroscopies. They identified several pure electronic levels at 6880, 13 277, 15 426, 17 478, and 19 358 cm^{-1}. The ground state and the 6880 cm^{-1} state belong to the $5f^1$ configuration, whereas the other energy levels were thought to likely belong to an excited configuration involving electrons in the non-bonding 5f shell.

A more recent theoretical effort sought to improve the assignments of the electronic states for both Np(VI) and Np(V) species (Matsika and Pitzer, 2000).

This work is more complete than the much earlier effort of Eisenstein and Pryce (1965, 1966). Their work resulted in the calculation of the energy levels of 15 excited states for NpO_2^{2+} and 19 for NpO_2^{+}, as well as their respective wave functions. Their methods used relativistic spin–orbit coupling configuration interactions based on effective core potentials.

Work on the Np(v) species with a focus on its interaction with polyvalent species in different solvents was reported by Rykov and Frolov (1972). Visible spectroscopy of solutions of NpO_2^{+} in several different mixed solvents (water–methanol, water–ethanol, water–acetone) were obtained at room temperature in the presence of Fe^{3+}. The interaction of Fe^{3+} with Np^{5+} ion in mixed solvents was studied and it was reported that the formation of a complex involving both ions mirrored that of the electron exchange for Fe^{2+} and Fe^{3+} for aqueous solutions kinetically. The degree of interaction between the two ions being inversely dependent on the effective dielectric constant of the solvent.

Varga *et al.* (1970) performed an extensive spectroscopic study of the Np(iv) species from 300 to 1800 nm using NpF_4 either dissolved in $CsF \cdot 2HF$ (300–1300 nm) and in a fluorocarbon mull (1300–1800 nm). This study allowed for the assignment of 17 excited-state transitions for Np^{4+}. The experimental values for these transitions were compared to calculated values with good agreement. Infrared spectroscopy was also applied to a Np(iv) species in the form of several oxalate compounds formed with neptunium in the 4+ state (Kharitonov and Moskvin, 1973). This work identified several vibrational bands and their respective force constants and bond lengths (Np–O). The bond length was reported as 1.78 Å, which agreed well with the literature value for this quantity based on the vibrational band of approximately 825 cm^{-1} (Kharitonov and Moskvin, 1973).

Rykov *et al.* (1973) investigated the complexation behavior of Np(iv) in nitrate solutions of varying concentrations. A total of three types (A–B–C) of complexes were observed depending on whether there was very little nitrate present (type 'A' spectra observed) or nitrate solutions with very little free water present (type 'C' spectra observed). Type 'B' spectra were considered as intermediate to 'A' and 'C'. The fundamental distinction between the three types of complexes was assigned to the structure of the first coordination sphere. The type 'A' were thought to be of the M_{aq}^{4+} formula whereas the type 'C' were assigned to be a neptunium ion coordinated with six nitrates. The type 'B' complex had been thought to be an intermediate nitrate complex (less than six coordination) but their results were shown to be consistent with change in the aqueous coordinated complex and did not involve complexation by nitrate at all.

A later study of Np(iv) utilized low temperature spectroscopy (4.2 K) and two different crystalline hosts, $ThSiO_4$ and ThO_2 (Lahalle *et al.*, 1986). The latter of the two crystalline hosts had been used in an earlier study by Gruber and Menzel (1969) and was used for comparison purposes. Their study identified 29 excited-state transitions in the $ThSiO_4$ host and 19 in the ThO_2 host for

Np(iv) using both absorption and fluorescence spectroscopies over the temperature range of 4.2–300 K. Work of a similar nature on alkali and alkaline earth neptunates involving Np(vi) was performed by Kanellakopulos *et al.* (1980a,b).

A spectroscopic investigation of Np(iii) was undertaken by Hessler *et al.* (1980) using low-temperature, high-resolution absorption, and fluorescence spectroscopies. A crystalline host of $LaCl_3$ was used. The temperature dependence of the homogeneous linewidth of D_1 to Z_1 (671.51 nm) and the D_1 to Z_2 (677.18 nm) transitions were obtained.

Carnall *et al.* (1987) investigated the interpretation of the spectra of neptunium obtained in silicate glasses with a focus on determining the valence state of the neptunium present. This work was undertaken to assist in the understanding of the local environment of neptunium in waste glasses bound for disposal in a geologic repository. Another spectroscopic investigation that has ramifications in the nuclear waste community is that of Neck *et al.* (2001) which utilized absorption spectroscopy, laser-induced photoacoustic spectroscopy (LIPAS), and laser-induced breakdown spectroscopy to study the colloids formed by neptunium in solution. An aqueous solution of $HClO_4$–$NaClO_4$ with Np(iv) present was used to obtain the solubility product constant of $Np(OH)_4$ at a wide range of pH. Kihara *et al.* (1996) also applied LIPAS to the study of neptunium species in Purex solutions.

A rather extensive study of Np(iv) and Np(v) in hydrolysis and carbonate reactions using optical and NMR spectroscopies was performed by Tait *et al.* (1995). Chaikhorskii and Leikina (1972) had earlier performed a similar study on Np(vii) during hydrolysis using optical spectroscopy.

With the relative importance of neptunium in the field of nuclear waste disposal, due to its long half-life, it is anticipated that the field of optical spectroscopy will continue to be an active one for many years with a particular emphasis on determining its local environment *in situ*.

6.8.3 Hydrolysis behavior

The hydrolysis reaction as a particular case of complex formation is the primary common property of all actinide ions in aqueous solution. The tendency for neptunium ions to undergo hydrolysis is in the order of $Np^{4+} > NpO_2^{2+} > Np^{3+} > NpO_2^+$, following the effective charge of the ions. The pentavalent NpO_2^+ ion is the most stable ion in solution and is not hydrolyzed appreciably at pH below 7. The trivalent Np^{3+} and hexavalent NpO_2^{2+} ions are the predominant species in solution at pH below 4–5 and 3–4, respectively, reflecting that the NpO_2^{2+} ion has an effective charge greater than the Np^{3+} ion. The tetravalent Np^{4+} ion shows a strong tendency towards hydrolysis and considerable hydrolysis is expected at pH 1 or above. Representative equilibrium constants for hydrolysis of neptunium ions, Np^{3+}, Np^{4+}, NpO_2^+, and NpO_2^{2+}, are listed in Table 6.12, together with some solubility products of the oxide or hydroxide.

Table 6.12 *Experimental equilibrium constants for hydrolysis of neptunium ion.*

Ion	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
Np^{3+}	pot	25	0.3 M $NaClO_4$	$\log{}^*K_{11} = -7.43 \pm 0.11$	Mefod'eva *et al.* (1974)
Np^{4+}	sp	25	1.0 M	$\log{}^*K_{11} = -1.90$	Paul (1970)
	sol	25	0.0	$\log{}^*K_{14} = -9.8 \pm 0.11$	Rai *et al.* (1987)
				$\log{}^*K_s = 1.5 \pm 1.0$; $NpO_2(s) + 4H^+ \rightleftarrows Np^{4+} + 2H_2O$	Lemire *et al.* (2001)
NpO_2^+	sol	25	0.1 M $NaClO_4$	$\log{}^*K_{11} = -11.36 \pm 0.16$	Neck *et al.* (1992)
				$\log{}^*K_{12} = -23.50 \pm 0.12$	
			1.0 M $NaClO_4$	$\log{}^*K_{11} = -11.13 \pm 0.20$	
				$\log{}^*K_{12} = -23.19 \pm 0.14$	
				$\log{}^*K_s = 4.50 \pm 0.06$; $NpO_2OH(s) + H^+ \rightleftarrows NpO_2^+ + H_2O$	
NpO_2^{2+}	pot	25	1.0 M $NaClO_4$	$\log{}^*K_{11} = -5.17 \pm 0.03$	Cassol *et al.* (1972a)
				$\log{}^*K_{22} = -6.68 \pm 0.02$	
				$\log{}^*K_{35} = -18.25 \pm 0.02$	
	sol	25	0.1 M $NaClO_4$	$\log{}^*K_s = 5.87 \pm 0.17$; $NpO_3H_2O(s) + 2H^+ \rightleftarrows NpO_2^{2+} + 2H_2O$	Kato *et al.* (1996)

* K_{mn} is the hydrolysis constant for the equilibrium: $mM^{a+} + nH_2O \rightleftarrows M_m(OH)_n^{am-n} + nH^+$.

(a) Neptunium(III)

The trivalent Np^{3+} ion is sufficiently stable in acidic solution to allow spectrophotometric studies, but it is rapidly oxidized by air to the tetravalent state. Therefore, Np^{3+} will be stable in the presence of strong reductants and/or in an oxygen-free atmosphere. The tendency of an ion to undergo hydrolysis increases with charge and with decreasing ionic radius. The order of the trivalent actinide ions for ease of hydrolysis should be as follows: $U^{3+} < Np^{3+} < Pu^{3+} < Am^{3+}$, because the stability of hydrolyzed ions increases as z/r_{ion} increases.

As only one experimental study for the equilibrium,

$$Np^{3+} + H_2O \leftrightarrows NpOH^{2+} + H^+ \tag{6.42}$$

Mefod'eva *et al.* (1974) determined $\log{}^*K_{11} = -7.43$ for 298 K and 0.3 M $NaClO_4$ from potentiometric measurements in the pH range 6–8. The Np^{3+} ion was produced by electrolysis of 0.022 M $Cs_2NpCl_6(aq)$ in 0.1 M HCl using a mercury cathode in an inert atmosphere. The titration curves of Np^{3+} were compared with those of Pr^{3+} and Nd^{3+} under the similar conditions to obtain the ratios of the hydrolysis constants.

There has been no systematic study to determine the solubility product for Np(III) and no usable experimental data for $Np(OH)_3(s)$ is available.

(b) Neptunium(IV)

From the same reasons as in the case of the trivalent state, the tendency of the tetravalent actinide ions to undergo hydrolysis follows the order: $Th^{4+} < U^{4+} < Np^{4+} < Pu^{4+}$. There are three reports of the first hydrolysis step of Np^{4+}.

$$Np^{4+} + H_2O \leftrightarrows NpOH^{3+} + H^+ \tag{6.43}$$

Sullivan and Hindman (1959) and Paul (1970) reported $\log{}^*K_{11} = -2.30$ ($I = 2.0$ M) and -1.90 ($I = 1.0$ M), respectively, in aqueous perchlorate solutions by spectrophotometry. From extraction experiments, Duplessis and Guillaumont (1977) reported $\log{}^*K_{11} = -0.50$ in 1.0 M $LiClO_4$. Two values $\log{}^*K_{12}$ for $Np(OH)_2^{2+}$ have been reported with a large discrepancy (three order of magnitude) (Duplessis and Guillaumont, 1977; Schmidt *et al.*, 1980), while there is no experimental evidence for the formation of $Np(OH)_3^+$.

Several groups (Ewart *et al.*, 1985; Rai and Ryan, 1985; Pratopo *et al.*, 1989; Eriksen *et al.*, 1993) measured the solubility of Np(IV) hydrated oxide or hydroxide in neutral to basic solutions at room temperature in the presence of reducing agents, e.g. $Na_2S_2O_4$, Fe, or Zn, and reported a limiting neptunium concentration of $10^{-8.5}$ to $10^{-8.1}$ M. The pH-independence of the solubility indicates that the main species in equilibrium with Np(IV) solids is uncharged $Np(OH)_4^0$ and that $Np(OH)_5^-$ is not an important species for Np(IV) hydrolysis. Rai *et al.* (1987) studied the solubility of $NpO_2 \cdot xH_2O$ in the presence of Cu(I)/Cu(II) buffer and in the pH range from 1.5 to 2.5. Based on the measured redox potentials, pH, and calculated activities of Np^{4+} and NpO_2^+, the thermodynamic equilibrium constants were determined. After recalculation of the results in the NEA/TDB neptunium and plutonium volume (Lemire *et al.*, 2001), $\log{}^*K_s = 1.5$ and $\log{}^*K_{14} = -9.8$ were reported for the following reactions, respectively:

$$NpO_2(s) + 4H^+ \leftrightarrows Np^{4+} + 2H_2O \tag{6.44}$$

$$Np^{4+} + 4H_2O \leftrightarrows Np(OH)_4^0 + 4H^+ \tag{6.45}$$

The experimental $\log{}^*K_s$ values of Th(IV) (Ryan and Rai, 1987), Np(IV) (Rai *et al.*, 1987), and Pu(IV) (Rai, 1984) hydrous oxides show a linear relationship with the inverse square of the M^{4+} ionic radii.

(c) Neptunium(V)

The pentavalent NpO_2^+ ion is stable and disproportionates only at rather high acidities. Many groups have reported the formation constants of the hydroxo species by using various experimental methods (see Lemire *et al.*, 2001). The recent hydrolysis studies by solubility measurements (Lierse *et al.*, 1985; Itagaki *et al.*, 1992; Neck *et al.*, 1992) show smaller constants than found in earlier studies (Kraus and Nelson, 1948; Moskvin, 1971; Sevost'yanova and Khalturin, 1976; Schmidt *et al.*, 1980; Maya, 1983; Bidoglio *et al.*, 1985), which is probably due to the effect of carbonate complexation.

Neck *et al.* (1992) studied the hydrolysis behavior of the NpO_2^+ ion at 298 K by solubility experiments in the pH range 7–14 in 0.1, 1.0, and 3.0 M $NaClO_4$ solutions under CO_2-free argon atmosphere. In 0.1 M $NaClO_4$ Np(V) hydroxide precipitate remained amorphous (green) over several months, while in 1.0 M $NaClO_4$ the precipitate changed from an amorphous to a more stable-aged state (white) within a relatively short time. In 3.0 M $NaClO_4$ the aged modification of $NpO_2OH(s)$ is formed from the beginning. As shown in Table 6.12, the hydrolysis constants and solubility product for aged $NpO_2OH(s)$ were reported for the following reactions:

$$NpO_2^+ + H_2O \leftrightarrows NpO_2OH^0 + H^+ \tag{6.46}$$

$$NpO_2^+ + 2H_2O \leftrightarrows NpO_2(OH)_2^- + 2H^+ \tag{6.47}$$

$$NpO_2OH(s) + H^+ \leftrightarrows NpO_2^+ + H_2O \tag{6.48}$$

The solids (fresh and aged NpO_2OH) were not analyzed for possible incorporation of sodium ions, however the parallel solubility curves obtained for the two solids in 1.0 M $NaClO_4$ strongly suggest that they have similar stoichiometries.

(d) Neptunium(VI)

The hexavalent NpO_2^{2+} ion is not as stable as the UO_2^{2+} and PuO_2^{2+} ions. Cassol *et al.* (1972a) studied the hydrolysis of the NpO_2^{2+} ion in 1 M $NaClO_4$ at 298 K by potentiometric titrations. The NpO_2^{2+} solution was prepared by electrolytic oxidation of a NpO_2^+ solution. The hydrolysis constants shown in Table 6.12 were reported for the following equilibria:

$$NpO_2^{2+} + H_2O \leftrightarrows NpO_2OH^+ + H^+ \tag{6.49}$$

$$2NpO_2^{2+} + 2H_2O \leftrightarrows (NpO_2)_2(OH)_2^{2+} + 2H^+ \tag{6.50}$$

$$3NpO_2^{2+} + 5H_2O \leftrightarrows (NpO_2)_3(OH)_5^+ + 5H^+ \tag{6.51}$$

The value $\log{}^*K_{11} = -5.17$ is consistent with the value ($\log{}^*K_{11} = -5.45$) reported by Schmidt *et al.* (1983), while the hydrolysis scheme proposed by Moskvin (1971) based on solubility measurements is rather different. Comparison of the results (Cassol *et al.*, 1972a) with some available data on the hydrolysis of U(VI) (Rush *et al.*, 1962; Rush and Johnson, 1963) and Pu(VI) (Cassol *et al.*, 1972b) indicates a close analogy in hydrolysis behavior for the three ions. The tendency in acidity with increasing atomic number is in the order of $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$.

Kato *et al.* (1996) have determined the solubility product of neptunium trioxide monohydrate at 298 K in acidic 0.1 M $NaClO_4$ solution prepared with ozone in air.

$$NpO_3H_2O(s) + 2H^+ \leftrightarrows NpO_2^{2+} + 2H_2O \tag{6.52}$$

The solid was characterized to be $NpO_3 \cdot H_2O$, not $NpO_2(OH)_2$, by X-ray diffraction and Fourier transform infrared spectroscopy (FTIR).

(e) Neptunium(VII)

A cationic Np(VII) species in acidic solutions (Shilov *et al.*, 1991) and an anionic species in strongly alkaline solutions (Chaikhorskii *et al.*, 1975) have been reported, but no thermodynamic data are available. Np(VII) hydroxide or hydrated oxide has been prepared by several groups (Chaikhorskii *et al.*, 1974; Nikonov *et al.*, 1994) using different methods. No thermodynamic data for Np(VII) hydroxide and oxide are available.

6.9 COORDINATION COMPLEXES IN SOLUTION

Representative equilibrium constants and the experimental conditions at which they were determined are collected in Tables 6.13 and 6.14 for neptunium complexes with inorganic and organic ligands, respectively. Data on complex formation of neptunium and of other actinides have been compiled in the literature, e.g. Gel'man *et al.* (1962), Degischer and Choppin (1975), Fuger *et al.* (1992), Lemire *et al.* (2001), Smith and Martell (2002), etc., and are reviewed in Chapters 19 and 23.

In Tables 6.13 and 6.14, the following abbreviations are used in experimental methods: cix, cation exchange; dis, distribution between two phases; em, electromigration; emf, electromotive force; ise, ion selective electrode; pot, potentiometry; red, emf with redox electrode; sol, solubility; sp, spectrophotometry. The stepwise stability constants K_i and overall constants β_i are defined for the reaction of a cation M with a ligand L as follows:

$$K_1 = \beta_1 = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}], K_2 = [\mathrm{ML_2}]/[\mathrm{ML}][\mathrm{L}], K_3 = [\mathrm{ML_3}]/[\mathrm{ML_2}][\mathrm{L}], \text{etc.}$$

$$\beta_2 = [\mathrm{ML_2}]/[\mathrm{M}][\mathrm{L}]^2, \beta_3 = [\mathrm{ML_3}]/[\mathrm{M}][\mathrm{L}]^3, \text{etc.}$$

Therefore

$$\beta_2 = \mathrm{K_1K_2}, \beta_3 = \mathrm{K_1K_2K_3}, \text{ etc.} \tag{6.53}$$

The other equilibrium constants are indicated in Tables 6.13 and 6.14.

6.9.1 Complexation with inorganic ligands

All of the equilibrium constants listed in Table 6.13 are for complexes of Np (IV), Np(V), and Np(VI). Only a few studies have been carried out on complexes of Np(III) and Np(VII). Shiloh and Marcus (1966) studied the $\mathrm{Np^{3+}}$–halide system quantitatively by measurement of the absorption spectra. The stability constants for $\mathrm{NpX^{2+}}$ and $\mathrm{NpX_2^+}$ ($\mathrm{X} = \mathrm{Cl^-}$, $\mathrm{Br^-}$) were obtained in concentrated LiCl and LiBr solutions, respectively. Mefod'eva *et al.* (1970a,b) reported the complex formation of Np(VII)($\mathrm{NpO_2^{3+}}$) with sulfate ion in acid solution. The stability constants obtained for $\mathrm{NpO_2SO_4^+}$ and $\mathrm{NpO_2(SO_4)_2^-}$ were greater than those of $\mathrm{NpO_2^{2+}}$.

The tendency of a neptunium ion for complex formation, as well as the hydrolysis reaction, depends on its ionic potential, i.e. its formal charge divided by its ionic radius. In analogy with neighboring uranium and plutonium, the order of decreasing ability for complex formation is

$$\mathrm{Np^{4+}} > \mathrm{NpO_2^{2+}} \geq \mathrm{Np^{3+}} > \mathrm{NpO_2^+}$$

The relative complex-forming ability of $\mathrm{Np^{3+}}$ and $\mathrm{NpO_2^{2+}}$ may depend on the ligand and/or the solvent with which these ions are associated. It is difficult to

Table 6.13 *Experimental equilibrium constants for neptunium complexes with inorganic ligands.*

Anion	*Ion*	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
Fluoride, F^-						
	Np^{4+}	dis	25	1.0 M $HClO_4$	$\log^*\beta_1 = 4.60 \pm 0.20$	Choppin and Unrein (1976)
		dis	25	2.0 M $HClO_4$	$\log^*\beta_1 = 4.70 \pm 0.15$	Bagawde *et al.* (1976)
		cix, red	20	4.0 M $HClO_4$	$\log^*\beta_1 = 4.82 \pm 0.02$	Ahrland and Brandt (1966)
					$\log^*\beta_2 = 7.57 \pm 0.15$	
					$\log^*\beta_3 = 9.85$	
					$\log^*\beta_4 = 11.15$	
					$\log^*\beta_n$; $Np^{4+} + n\text{HL} \rightleftarrows NpL_n^{4-n} + nH^+$	
	NpO_2^+	dis	23	1.0 M $NaClO_4$	$\log K_1 = 1.26 \pm 0.30$	Choppin and Rao (1984)
		dis	25	2.0 M $NaClO_4$	$\log K_1 = 0.99 \pm 0.10$	Rao *et al.* (1979)
	NpO_2^{2+}	ise	20	0.1 M $NaClO_4$	$\log K_1 = 4.18 \pm 0.15$	Sawant *et al.* (1985)
					$\log \beta_2 = 6.96 \pm 0.15$	
					$\log \beta_3 = 9.64$	
		emf	25	0.5 M $HClO_4$	$\log^*\beta_1 = 1.11 \pm 0.20$	Al-Niaimi *et al.* (1970a)
					$\log^*\beta_2 = 1.14 \pm 0.40$	
		dis	20	1.0 M $HClO_4$	$\log^*\beta_1 = 0.93 \pm 0.11$	Ahland and Brandt (1968a)
					$\log^*\beta_2 = 1.11 \pm 0.10$	
					$\log^*\beta_n$; $NpO_2^{2+} + n\text{HL} \rightleftarrows NpO_2L_n^{2-n} + nH^+$	
Chloride, Cl^-						
	Np^{4+}	dis	20	0.5 M $HClO_4$	$\log K_1 = 0.15 \pm 0.20$	Shilin and Nazarov (1966)
				1.0 M $HClO_4$	$\log K_1 = -0.04 \pm 0.20$	
				2.0 M $HClO_4$	$\log K_1 = 0.04 \pm 0.20$	
		dis	25	2.0 M $HClO_4$	$\log K_1 = -0.05 \pm 0.05$	Patil and Ramakrishna (1975)
	NpO_2^+	dis	25	2.0 M $NaClO_4$	$\log K_1 = -0.42 \pm 0.04$	Rao *et al.* (1979)
	NpO_2^{2+}	emf	25	0.5 M $HClO_4$	$\log K_1 = -0.35 \pm 0.40$	Al-Niaimi *et al.* (1970b)
Bromide, Br^-						
	Np^{4+}	dis	25	2.0 M $HClO_4$	$\log K_1 = -0.21 \pm 0.01$	Raghavan *et al.* (1975)

Iodide, I^-					
Np^{4+}	dis	25	2.0 м $HClO_4$	$\log K_1 = 0.04 \pm 0.30$	Patil *et al.* (1981)
Iodate, IO_3^-					
NpO_2^+	dis	25	2.0 м $HClO_4$	$\log K_1 = 0.32 \pm 0.30$	Rao *et al.* (1979)
NpO_2^{2+}	sp	25	0.3 м $HClO_4$	$\log K_1 = 0.61 \pm 0.02$	Blokhin *et al.* (1972)
Azide, N_3^-					
NpO_2^+	sp	25	5.0 м $NaClO_4$	$\log K_1 = 1.08$ $\log K_2 = 0.77$ $\log K_3 = 0.38$	Musikas and Marteau (1978)
Nitrite, NO_2^-					
NpO_2^+	dis	25	2.0 м $NaClO_4$	$\log K_1 = -0.05 \pm 0.05$	Rao *et al.* (1979)
Nitrate, NO_3^-					
Np^{4+}	dis	20	1.0 м $HClO_4$	$\log K_1 = 0.34 \pm 0.10$ $\log \beta_2 = 0.08$ $\log \beta_3 = -0.26$	Shilin and Nazarov (1966)
	dis	25	4.0 м $NaClO_4$	$\log K_1 = -0.15 \pm 0.12$ $\log \beta_2 = -0.74 \pm 0.15$	Danesi *et al.* (1971)
NpO_2^+	dis	20	2.0 м $NaClO_4$	$\log K_1 = -0.55 \pm 0.09$	Rao *et al.* (1979)
NpO_2^{2+}	pot	25	0.5 м $HClO_4$	$\log K_1 = -0.96 \pm 0.02$	Al-Niaimi *et al.* (1970b)
	dis	25	4.0 м $NaClO_4$	$\log K_1 = -0.68 \pm 0.06$	Danesi *et al.* (1971)
Thiocyanate, SCN^-					
Np^{4+}	dis	25	2.0 м $HClO_4$	$\log K_1 = 1.49 \pm 0.07$ $\log \beta_2 = 2.06 \pm 0.08$ $\log \beta_3 = 2.53 \pm 0.02$	Rao *et al.* (1978)
NpO_2^+	dis	25	2.0 м $NaClO_4$	$\log K_1 = 0.32 \pm 0.02$	Rao *et al.* (1979)
	sp	25	5.0 м $NaClO_4$	$\log K_1 = 0.86$ $\log \beta_2 = 1.05$	Cuillerdier *et al.* (1977)

Table 6.13 (*Contd.*)

Anion	*Ion*	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
Sulfate, SO_4^{2-}						
	Np^{4+}	dis	25	2.0 M $HClO_4$	$\log{}^*\beta_1 = 2.49 \pm 0.03$ $\log{}^*\beta_2 = 4.06 \pm 0.02$	Patil and Ramakrishna (1973)
		pol	25	3.0 M $NaClO_4$	$\log{}^*\beta_1 = 2.49 \pm 0.03$ $\log{}^*\beta_2 = 3.57 \pm 0.09$	Musikas (1963)
		cix	20	4.0 M $HClO_4$	$\log{}^*\beta_1 = 2.70 \pm 0.04$ $\log{}^*\beta_2 = 4.26 \pm 0.05$ $\log{}^*\beta_n$; $Np^{4+} + nHL^- \rightleftarrows NpL_n^{4-2n} + nH^+$	Ahrland and Brandt (1966)
	NpO_2^+	dis	25	1.0 M $NaClO_4$	$\log K_1 = 0.06 \pm 0.04$	Halperin and Oliver (1983)
		dis	25	2.0 M $NaClO_4$	$\log K_1 = 0.44 \pm 0.09$	Rao *et al.* (1979)
	NpO_2^{2+}	pot	25	0.1 M $HClO_4$	$\log{}^*\beta_1 = 0.88 \pm 0.01$	Al-Niaimi *et al.* (1970a)
				0.5 M $HClO_4$	$\log{}^*\beta_1 = 0.75 \pm 0.01$	
		dis	21	1.0 M $NaClO_4$	$\log{}^*\beta_1 = 0.79 \pm 0.13$ $\log{}^*\beta_2 = 0.55 \pm 0.31$	Ahrland and Brandt (1968b)
		dis	25	2.0 M $HClO_4$	$\log{}^*\beta_1 = 1.07 \pm 0.05$ $\log{}^*\beta_2 = 0.60 \pm 0.15$ $\log{}^*\beta_n$; $NpO_2^{2+} + nHL^- \rightleftarrows NpO_2L_n^{2-2n} + nH^+$	Patil and Ramakrishna (1976)
Carbonate, CO_3^{2-}						
	NpO_2^+	dis	25	0.1 M $NaClO_4$	$\log K_1 = 4.13 \pm 0.03$ $\log K_2 = 2.93$	Bidoglio *et al.* (1985)
		sol	25	1.0 M $NaClO_4$	$\log K_1 = 4.49 \pm 0.06$ $\log K_2 = 2.62 \pm 0.09$ $\log K_3 = 1.42 \pm 0.11$	Maya (1983)

NpO_2^{2+}	sol	25	0.1 M $NaClO_4$	log $K_{sp} = -10.14 \pm 0.04$; $NaNpO_2L(s) \rightleftarrows Na^+ + NpO_2^+ + L^{2-}$ log $K_1 = 9.02 \pm 0.10$ log $\beta_3 = 20.41 \pm 0.09$ log $K_{sp} = -14.04 \pm 0.07$; $NpO_2L(s) \rightleftarrows NpO_2^{2+} + L^{2-}$	Kato *et al*. (1998)
	pot	25	1.0 M $NaClO_4$	log $\beta_2 = 16.51 \pm 0.14$ log $\beta_3 = 21.15 \pm 0.12$ log $\beta_{213} = -1.49 \pm 0.14$; $2NpO_2^{2+} + L^{2-} + 3H_2O \rightleftarrows (NpO_2)_2L(OH_3^-) + 3H^+$	Maya (1984)
	sp	22	3.0 M $NaClO_4$	log $\beta_{36} = -10.1 \pm 0.1$; $3NpO_2L_3^{4-} \rightleftarrows (NpO_2)_3L_6^{6-} + 3L^{2-}$	Grenthe *et al*. (1986)
Chromate, CrO_4^{2-}					
Np^{4+}	sp	25	0.2 M $LiClO_4$	log $\beta = 1.81 \pm 0.17$; $Np^{4+} + HL^- \rightleftarrows NpL^{2+} + H^+$	Burkhart and Thompson (1972)
Phosphate, PO_4^{3-}					
NpO_2+	cix	20	0.2 M NH_4ClO_4	log $\beta = 2.85 \pm 0.15$; $NpO_2^+ + HL^{2-} \rightleftarrows NpO_2HL^-$	Moskvin and Peretrukhin (1964)
NpO_2^{2+}	dis	25	1.0 M $NaClO_4$	log $\beta = 2.52 \pm 0.50$; $NpO_2^{2+} + H_2L^- \rightleftarrows NpO_2H_2L^+$ log $\beta = 4.54 \pm 0.70$; $NpO_2^{2+} + HL^{2-} \rightleftarrows NpO_2HL$ log $\beta = 7.5 \pm 1.0$; $NpO_2^{2+} + 2HL^{2-} = NpO_2(HL)_2^{2-}$	Mathur and Choppin (1994)

Table 6.14 *Experimental equilibrium constants for neptunium complexes with organic ligands.*

Anion	*Ion*	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
Acetate, CH_3COO^-						
	NpO_2^+	em	25	0.3 м $NaClO_4$	$\log K_1 = 0.96$ $\log K_2 = 0.61$	Rösch *et al.* (1990)
		spec	25	2.0 м $NaClO_4$	$\log K_1 = 0.87 \pm 0.03$	Rizkalla *et al.* (1990a)
	NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 2.31 \pm 0.02$ $\log \beta_2 = 4.23 \pm 0.05$ $\log \beta_3 = 6.00 \pm 0.19$	Portanova *et al.* (1970)
Propionate, $C_2H_5COO^-$						
	NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 2.44 \pm 0.03$ $\log \beta_2 = 4.45 \pm 0.03$ $\log \beta_3 = 6.49 \pm 0.08$	Cassol *et al.* (1969)
Monochloroacetate, CH_2ClCOO^-						
	NpO_2^+	spec	25	2.0 м $NaClO_4$	$\log K_1 = 0.00 \pm 0.05$	Rizkalla *et al.* (1990a)
	NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 1.33 \pm 0.02$ $\log \beta_2 = 2.10 \pm 0.07$ $\log \beta_3 = 2.78 \pm 0.34$	Cassol *et al.* (1969)
β-Chloropropionate, $CH_2ClCH_2COO^-$						
	NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 1.88 \pm 0.03$ $\log \beta_2 = 3.30 \pm 0.04$ $\log \beta_3 = 3.60 \pm 0.32$	Cassol *et al.* (1969)
Glycolate, $CH_2(OH)COO^-$						
	NpO_2^+	spec	25	0.1 м $NaClO_4$	$\log K_1 = 1.51 \pm 0.03$	Eberle and Schaefer (1969)
		spec	25	2.0 м $NaClO_4$	$\log K_1 = 1.43 \pm 0.02$ $\log \beta_2 = 1.90 \pm 0.03$	Rizkalla *et al.* (1990a)
		dis	25	1.0 м $NaClO_4$	$\log K_1 = 1.31 \pm 0.04$ $\log \beta_2 = 2.06 \pm 0.03$	Tochiyama *et al.* (1992)
	NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 2.42 \pm 0.03$ $\log \beta_2 = 3.96 \pm 0.03$ $\log \beta_3 = 5.00 \pm 0.10$	Portanova *et al.* (1972)

Lactate, $CH_3CH(OH)COO^-$					
NpO_2^+	spec	25	0.1 M $NaClO_4$	$\log K_1 = 1.75 \pm 0.02$	Eberle and Schaefer (1969)
	dis	25	1.0 M $NaClO_4$	$\log K_1 = 1.40 \pm 0.02$ $\log \beta_2 = 2.01 \pm 0.02$	Tochiyama *et al.* (1992)
α-Hydroxybutyrate, $C_2H_5CH(OH)COO^-$					
NpO_2^+	spec	25	0.1 M $NaClO_4$	$\log K_1 = 1.62 \pm 0.02$	Eberle and Schaefer (1969)
	dis	25	1.0 M $NaClO_4$	$\log K_1 = 1.64 \pm 0.02$ $\log \beta_2 = 2.13 \pm 0.03$	Tochiyama *et al.* (1992)
α-Hydroxyvalerate, $C_3H_7CH(OH)COO^-$					
NpO_2^+	spec	25	0.1 M $NaClO_4$	$\log K_1 = 1.59 \pm 0.03$	Eberle and Schaefer (1969)
α-Hydroxycapronate, $C_4H_9CH(OH)COO^-$					
NpO_2^+	spec	25	0.1 M $NaClO_4$	$\log K_1 = 1.63 \pm 0.02$	Eberle and Schaefer (1969)
α-Hydroxyisobutyrate, $(CH_3)_2C(OH)COO^-$					
NpO_2^+	spec	25	2.0 M $NaClO_4$	$\log K_1 = 1.80 \pm 0.01$	Rizkalla *et al.* (1990a)
	dis	25	1.0 M $NaClO_4$	$\log K_1 = 1.73 \pm 0.02$ $\log \beta_2 = 2.46 \pm 0.02$	Tochiyama *et al.* (1992)
NpO_2^{2+}	pot	20	1.0 M $NaClO_4$	$\log K_1 = 3.15 \pm 0.04$ $\log K_2 = 2.10 \pm 0.10$	Magon *et al.* (1974)
Glycinate, $NH_2CH_2COO^-$					
NpO_2^+	spec	25	0.1 M $NaClO_4$	$\log K_1 = 3.31 \pm 0.02$ $\log \beta_2 = 5.44 \pm 0.07$	Eberle and Wede (1968)
α-Picolinate, $NC_5H_4COO^-$					
Np^{4+}	spec	25	1.0 M $NaClO_4$	$\log K_1 = 6.50 \pm 0.01$	Paul (1970)
NpO_2^+	dis	25	1.0 M $NaClO_4$	$\log K_1 = 3.53 \pm 0.03$ $\log \beta_2 = 6.01 \pm 0.03$	Tochiyama *et al.* (1992)
Salicylate, $C_6H_4(OH)COO^-$					
NpO_2^+	spec	25	2.0 M $NaClO_4$	$\log \beta_H = 0.20 \pm 0.01$	Rizkalla *et al.* (1990a)
Oxalate, $(COO^-)_2$ $(=L^{2-})$					
NpO_2^+	pot	20	1.0 M $NaClO_4$	$\log K_1 = 3.74 \pm 0.05$ $\log \beta_2 = 6.31 \pm 0.10$	Magon *et al.* (1972)
	dis	25	1.0 M $NaClO_4$	$\log K_1 = 3.71 \pm 0.02$	Tochiyama *et al.* (1992)

Table 6.14 (*Contd.*)

Anion	*Ion*	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
					log $\beta_2 = 6.15 \pm 0.02$	
Malonate, $^{-}OOCCH_2COO^{-}$ ($=L^{2-}$)						
	NpO_2^+	pot	20	1.0 M $NaClO_4$	log $K_1 = 2.75 \pm 0.02$	Magon *et al*. (1972)
		dis	25	1.0 M $NaClO_4$	log $K_1 = 2.62 \pm 0.02$ log $\beta_2 = 4.22 \pm 0.02$	Tochiyama *et al*. (1992)
Succinate, $^{-}OOC(CH_2)_2COO^{-}$ ($=L^{2-}$)						
	NpO_2^+	pot	20	1.0 M $NaClO_4$	log $K_1 = 1.72 \pm 0.03$	Magon *et al*. (1972)
		dis	25	1.0 M $NaClO_4$	log $K_1 = 1.45 \pm 0.06$ log $\beta_2 =2.43 \pm 0.05$	Tochiyama *et al*. (1992)
Maleate, $^{-}OOC(CH)_2COO^{-}$ ($=L^{2-}$)						
	NpO_2^+	pot	20	1.0 M $NaClO_4$	log $K_1 = 2.20 \pm 0.02$	Magon *et al*. (1972)
Phthalate, $C_6H_4(COO^{-})_2$ ($=L^{2-}$)						
	NpO_2^+	pot	20	1.0 M $NaClO_4$	log $K_1 = 2.22 \pm 0.02$	Magon *et al*. (1972)
		spec	25	1.0 M $NaClO_4$	log $K_1 = 1.62 \pm 0.02$	Choppin *et al*. (1998)
Trimellitate, $C_6H_3(COO^{-})_3$ ($=L^{3-}$)						
	NpO_2^+	spec	25	1.0 M $NaClO_4$	log $K_1 = 1.57 \pm 0.02$	Choppin *et al*. (1998)
Hemimellitate, $C_6H_3(COO^{-})_3$ ($=L^{3-}$)						
	NpO_2^+	spec	25	1.0 M $NaClO_4$	log $K_1 = 2.44 \pm 0.02$	Choppin *et al*. (1998)
Pyromellitate, $C_6H_2(COO^{-})_4$ ($=L^{4-}$)						
	NpO_2^+	spec	25	1.0 M $NaClO_4$	log $K_1 = 1.80 \pm 0.01$	Choppin *et al*. (1998)
Mellitate, $C_6(COO^{-})_6$ ($=L^{6-}$)						
	NpO_2^+	spec	25	1.0 M $NaClO_4$	log $K_1 = 2.34 \pm 0.01$	Choppin *et al*. (1998)
Oxydiacetate, $O(CH_2COO^{-})_2$ ($=L^{2-}$)						
	NpO_2^+	spec	25	0.5 M $NaClO_4$	log $K_1 = 3.72 \pm 0.01$	Rizkalla *et al*. (1990b)
	NpO_2^{2+}	pot	20	1.0 M $NaClO_4$	log $K_1 = 5.16 \pm 0.01$	Cassol *et al*. (1973)
Thiodiacetate, $S(CH_2COO^{-})_2$ ($=L^{2-}$)						
	NpO_2^+	spec	25	0.5 M $NaClO_4$	log $K_1 = 1.18 \pm 0.04$	Rizkalla *et al*. (1990b)

Citrate, $^{-}OOCCH_2C(OH)(COO^{-})CH_2COO^{-}$ (=L^{3-})					
NpO_2^+	spec	25	2.0 м $NaClO_4$	$\log K_1 = 2.49 \pm 0.01$	Rizkalla *et al.* (1990a)
	spec	25	0.5 м $NaClO_4$	$\log K_1 = 2.73 \pm 0.02$	Palade (1997)
			1.0 м $NaClO_4$	$\log K_1 = 2.74 \pm 0.02$	
			2.0 м $NaClO_4$	$\log K_1 = 2.81 \pm 0.02$	
Iminodiacetate, $^{-}OOCCH_2NHCH_2COO^{-}$ (=L^{2-})					
NpO_2^+	spec	25	0.1 м $NaClO_4$	$\log K_1 = 6.27 \pm 0.11$ $\log \beta_H = 1.35 \pm 0.52$; $NpO_2^+ + HL^- \rightleftarrows NpO_2HL$	Eberle and Wede (1970)
NpO_2^{2+}	pot	20	1.0 м $NaClO_4$	$\log K_1 = 8.72 \pm 0.02$	Cassol *et al.* (1973)
N-Methyliminodiacetate, $^{-}OOCCH_2N(CH_3)CH_2COO^{-}$ (=L^{2-})					
NpO_2^+	spec	25	0.1 м $NaClO_4$	$\log K_1 = 7.37 \pm 0.05$ $\log \beta_H = 1.28 \pm 0.48$; $NpO_2^+ + HL^- \rightleftarrows NpO_2HL$	Eberle and Wede (1970)
N-(2-Hydroxyethyl)iminodiacetate, $^{-}OOCCH_2N(C_2H_4OH)CH_2COO^{-}$ (=L^{2-})					
Np^{4+}	spec	25	1.0 м $NaClO_4$	$\log K_1 = 12.97 \pm 0.04$ $\log K_2 = 10.75 \pm 0.11$	Eberle and Paul (1971)
NpO_2^+	spec	25	0.1 м $NaClO_4$	$\log K_1 = 6.08 \pm 0.05$ $\log \beta_H = 1.45 \pm 0.25$; $NpO_2^+ + HL^- \rightleftarrows NpO_2HL$ $-\log \beta_{OH} = 11.42 \pm 0.03$; $NpO_2L^- + H_2O \rightleftarrows NpO_2(OH)L^{2-} + H^+$	Eberle and Wede (1970)
Nitrilotriacetate, $NH(CH_2COO^-)_3$ (=L^{3-})					
Np^{4+}	spec	25	1.0 м $NaClO_4$	$\log K_1 = 17.28 \pm 0.02$ $\log K_2 = 14.78 \pm 0.07$	Eberle and Paul (1971)
NpO_2^+	spec	25	0.1 м $NaClO_4$	$\log K_1 = 6.80 \pm 0.10$ $\log \beta_H = 1.77 \pm 0.37$; $NpO_2^+ + HL^{2-} \rightleftarrows NpO_2HL^-$ $-\log \beta_{OH} = 11.46 \pm 0.11$; $NpO_2L^{2-} + H_2O \rightleftarrows NpO_2(OH)L^{3-} + H^+$	Eberle and Wede (1970)

Table 6.14 (*Contd.*)

Anion	*Ion*	*Method*	*Temp.* (°C)	*Medium*	*Equilibrium constants*	*References*
Nitrilodiacetate mono-*n*-propionate, –OOC$(CH_2)_2N(CH_2COO^-)_2$ (=L^{3-})						
	NpO_2^+	spec	25	0.1 M $NaClO_4$	log $K_1 = 7.00 \pm 0.09$ log $\beta_H = 2.35 \pm 0.12$; $NpO_2^+ + HL^{2-} \rightleftarrows NpO_2HL^-$ $-\log \beta_{OH} = 11.57 \pm 0.09$; $NpO_2L^{2-} + H_2O \rightleftarrows NpO_2(OH)L^{3-} + H^+$	Eberle and Wede (1970)
N-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate, $(HOC_2H_4)(^-OOCCH_2)$ $N(CH_2)_2N(CH_2COO^-)_2$ (=L^{3-})						
	Np^{4+}	spec	25	1.0 M $NaClO_4$	log $K_1 = 20.82 \pm 0.13$ log $K_2 = 12.77 \pm 0.16$	Eberle and Paul (1971)
	NpO_2^+	spec	25	0.1 M $NaClO_4$	log $K_1 = 6.87 \pm 0.11$ log $\beta_H = 4.06 \pm 0.01$; $NpO_2^+ + HL^{2-} \rightleftarrows NpO_2HL^-$ $-\log \beta_{OH} = 11.37 \pm 0.10$; $NpO_2L^{2-} + H_2O \rightleftarrows NpO_2(OH)L^{3-} + H^+$	Eberle and Wede (1970)
Ethylenediamine-*N*,*N*,*N*′,*N*′,-tetraacetate, $(^-OOCCH_2)_2N(CH_2)_2N(CH_2COO^-)_2$ (=L^{4-})						
	Np^{4+}	spec	25	1.0 M $NaClO_4$	log $K_1 = 24.55 \pm 0.03$	Eberle and Paul (1971)
	NpO_2^+	spec	25	0.1 M $NaClO_4$	log $K_1 = 7.33 \pm 0.06$ log $\beta_H = 5.30 \pm 0.08$; $NpO_2^+ + HL^{3-} \rightleftarrows NpO_2HL^{2-}$ $-\log \beta_{OH} = 11.51 \pm 0.08$; $NpO_2L^{3-} + H_2O \rightleftarrows NpO_2(OH)L^{4-} + H^+$	Eberle and Wede (1970)
Diethylenetriamine-N,N,*N*′,*N*″,*N*″-pentaacetate, $^-OOCCH_2N[(CH_2)_2N(CH_2COO^-)_2]_2$ (=L^{5-})						
	Np^{4+}	spec	20	0.5 M $NaClO_4$	log $K_1 = 29.29 \pm 0.02$	Piskunov and Rykov (1972)
		spec	25	1.0 M $NaClO_4$	log $K_1 = 30.33 \pm 0.12$	Eberle and Paul (1971)

compare the data listed in Table 6.13 because of the wide range of experimental conditions used and the lack of data for a given oxidation state of the ions with some ligands. However, the stability sequence for complexes of Np(IV), Np(V), or Np(VI) with monovalent inorganic ligands is seen to be

$$F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^- > ClO_4^-$$

For divalent inorganic ligands, the sequence is

$$CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$$

as would be expected from the relative strengths of the corresponding acids. Divalent ligands are more strongly complexing than monovalent ligands.

In addition to the data in Table 6.13, Np(V) (NpO_2^+) is known to form 'cation–cation' complexes with some multiply charged cations. The dioxo cation NpO_2^+ in perchloric acid solution forms complex ions with trivalent cations of Al, Ga, Sc, In, Fe, Cr, and Rh (Sullivan, 1962, 1964). The relative strength of the interaction between NpO_2^+ and M^{3+} was found to follow the following order: Fe > In > Sc > Ga > Al. Some of these polynuclear complexes such as $[NpO_2^+Cr^{3+}]$ and $[NpO_2^+Rh^{3+}]$ have been isolated by using an ion-exchange method, while the others were detected by spectrophotometry. The $[NpO_2^+Cr^{3+}]$ complex is also formed by the reduction of NpO_2^{2+} with Cr^{2+}. The formation of the complex between NpO_2^+ and UO_2^{2+} has extensively been studied by the use of potentiometry, spectrophotometry, Raman spectroscopy, and large-angle X-ray scattering (Sullivan *et al.*, 1961; Guillaume *et al.*, 1982, 1983; Stout *et al.*, 1993).

6.9.2 Complexation with organic ligands

With some exceptions, most of the data in Table 6.14 are for complexes of Np(V) with organic ligands. The following presents the results on several selected systems.

Stability data for complexes of M(VI) ions MO_2^{2+} (M = U, Np, and Pu) with monocarboxylic ligands L (L = acetate, propionate, monochloroacetate, and β-chloropropionate) have been reported and discussed by Cassol *et al.* (1969) and Portanova *et al.* (1970). In the range of ligand concentrations examined, complexes are formed in which the highest average ligand number is three. The stability order of complexes of the various ligands examined is $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$. The stability of complexes of a given MO_2^{2+} ion increases with increasing ligand basicity (pK_a), which suggests a strong 'hard' ionic character of these oxycations.

The stability constants of Np(V) complexes with a series of α-hydroxycarboxylates (e.g. glycolate and lactate) have been obtained by spectrophotometry (Eberle and Schaefer, 1969; Rizkalla *et al.*, 1990a) and solvent extraction (Tochiyama *et al.*, 1992). The stability of the α-hydroxycarboxylate complexes appears to increase a little with pK_a of the ligand, although the stability of these complexes is not much different. The stability of Np(V) complexes with aliphatic dicarboxylates (e.g. oxalate and malonate) has also been studied by potentiometry (Magon *et al.*, 1972), spectrophotometry (Stout *et al.*, 1989), and solvent extraction (Tochiyama *et al.*, 1992). The stability of the complexes is controlled mainly by the size of the chelate ring. In spite of the increase in the basicity of the ligand, the stability of the complexes decreases with increasing the number of carbon atoms between two carboxylate groups in the ligand.

The complexation of Np(v) with aromatic polycarboxylates has been studied by spectrophotometry (Choppin *et al.*, 1998). The stability constants of the 1:1 complexes decreases in the order: hemimellitate > mellitate > pyromellitate > trimellitate≃phthalate. After correction for the number of chelating binding (bidentate) sites, the stability constants with all ligands except hemimellitate are approximately the same. The greater strength of hemimellitate complexation is attributed to an increase in electron density at the binding site through induction from the non-chelating carboxylate group.

With aliphatic aminopolycarboxylate ligands, the complexation of Np(iv) or Np(v) has been studied by spectrophotometry (Eberle and Paul, 1971; Eberle and Wede, 1970). The logarithms of the stability constants of the Np(iv) complexes increase linearly with the number of bound donor atoms of the ligands. On the other hand, the Np(v) ion forms protonated and normal chelates of 1:1 stoichiometry. In addition, at high pH chelate hydroxides with one ligand molecule and one hydroxyl group per NpO_2^+ are formed. The nature of the ligand has only slight or no influence on the stability constants of normal chelates or chelate hydroxides, respectively, suggesting that not more than two carboxylic groups and one amine-nitrogen are bound from one ligand to the central neptunium.

6.10 ANALYTICAL CHEMISTRY AND SPECTROSCOPIC TECHNIQUES

The concentration of ^{237}Np and the radioactivity arising from this nuclide in the environment is extremely low compared to most other α emitters. The background concentration of ^{237}Np in seawater due to global fallout was estimated to be at a level of 10^{-15} to 10^{-14} g L^{-1} (Novikov *et al.*, 1989; Jha and Bhat, 1994). However, with the increase in nuclear power generation, this nuclide has become one of the most important from the viewpoint of long-term disposal of the radioactive waste. In fact, the analytical results showing contamination of ^{237}Np in seawater from nuclear fuel reprocessing plants have been reported, e.g. the concentrations of ^{237}Np were $3 \times 10^{-12} - 5.5 \times 10^{-11}$ g kg^{-1} in some samples from Irish sea (Pentreath and Harvey, 1981), 3×10^{-12} g kg^{-1} from Goury near La Hague, France (Germain *et al.*, 1987), $(2.3 \pm 0.4) \times 10^{-11}$ g kg^{-1} from English disposal area (May *et al.*, 1987), and $2 \times 10^{-12} \sim 2 \times 10^{-11}$ g L^{-1} in a waste discharge point at Trombay, India (Jha and Bhat, 1994). More sensitive methods for measuring such low levels of ^{237}Np must be developed and applied. Novikov *et al.* (1989) reviewed the analytical methods to be applied to

^{237}Np in the environmental samples. Hursthouse *et al.* (1992) performed a comparative study to evaluate the practical advantages and disadvantages of the methods. Lee *et al.* (1995) reported the result of an intercomparison study by eight laboratories of low-level ^{237}Np determination in artificial urine samples in order to evaluate and establish the optimal method for a routine *in vivo* radioassay program. In addition, precise determination of the ^{237}Np in the nuclear spent fuel or HLW from the reprocessing process is still a major concern in the field of nuclear engineering as well as the related research and development works.

6.10.1 Radiometric methods

Radiometric methods that are based on counting of alpha particles from ^{237}Np and neutron activation of ^{237}Np have been widely employed for the quantitative analysis of trace amount of ^{237}Np in environmental samples. The alpha-particle counting method is useful for the rapid and low-cost determination of trace quantity of ^{237}Np (specific radioactivity $= 2.6 \times 10^7$ Bq g^{-1}). A recent report by Pavlotskaya (1997) reviewed critically the radiochemical analysis methods for the determination of a trace quantity of neptunium in environmental samples.

(a) Alpha- and gamma-ray spectrometry

Alpha spectroscopy with solid state detectors enables the determination of ^{237}Np in a thin sample of a mixture with other α emitters such as ^{239}Pu and ^{241}Am. A preparation of sufficiently thin counting source is a key in the measurement of a reproducible spectrum without a disturbance from the self-absorption of alpha particles in the source. A simple method adopting an evaporation of the sample solution on the source substrate such as a plate of stainless steel or platinum is typically employed. Methods based on the electrodeposition of neptunium directly on the source substrate are useful to prepare thinner sources. Coprecipitation methods are simple and feasible for the preparation of counting sources but may not yield a sufficiently thin source for energy discrimination. Kimura (1990a) utilized $BiPO_4$ precipitate for the quantitative recovery and the preparation of alpha-counting sources for the simultaneous determination of Np, Pu, Am, and Cm.

Holm *et al.* (1987) applied alpha spectroscopy to the determination of the fallout level of ^{237}Np in large volume samples of seawater. They employed a method for the isolation of ^{237}Np by a hydroxide coprecipitation, ion-exchange chromatography, a LaF_3 coprecipitation, and a solvent extraction with HTTA. Yamamoto *et al.* (1989) developed a method for determination of low levels of ^{237}Np in soil and sediment samples. The separation scheme they developed is shown in Fig. 6.12 and consists of leaching of neptunium by aqua regia, separation and purification by TnOA extraction, LaF_3 coprecipitation, and

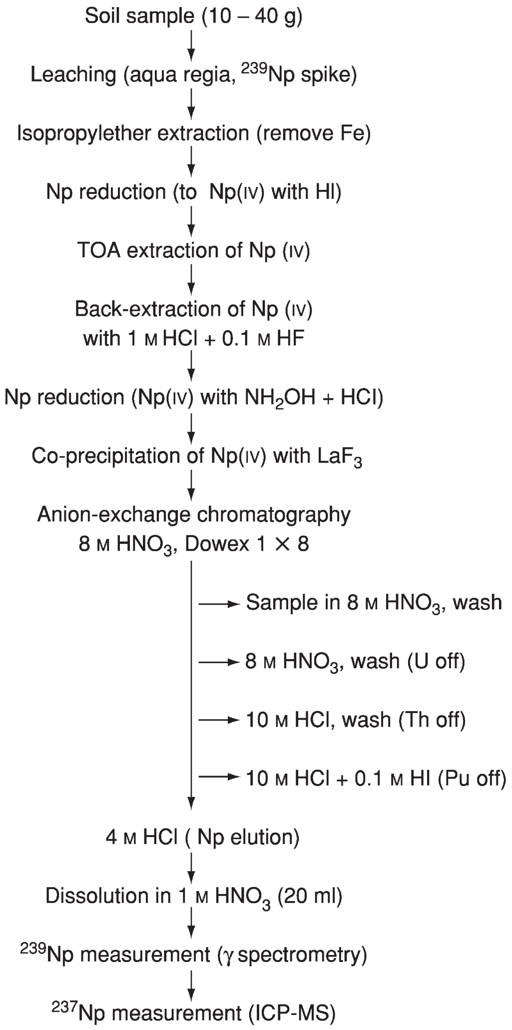


Fig. 6.12 *Chemical separation scheme for the determination of ^{237}Np by high-resolution ICP-MS.* (*Yamamoto* et al., 1994, *with permission from Elsevier Science*).

two steps of anion-exchange chromatography. ^{239}Np was used as a chemical yield monitor. The chemical yield of neptunium ranged from 50 to 84%. The detection limit for ^{237}Np was about 0.1 mBq per sample.

A method for the simultaneous determination of ^{237}Np and ^{239}Np in air, total deposition and sediment samples in ocean was developed (Rosner *et al.*, 1993). Alpha- and gamma-ray spectroscopies were used.

Alpha- and gamma-ray spectroscopies were applied to the determination of ^{237}Np in spent nuclear fuels (Shinohara *et al.*, 1989). After ion-exchange separation of the dissolved fuel solution, the content of ^{237}Np was determined from the activity of ^{237}Np or ^{233}Pa, which is in radioactive equilibrium with ^{237}Np. The chemical yield was determined using inherent ^{239}Np. The proposed method does not require quantitative separation of neptunium and can be applied to routine analyses of burnup for the nuclear spent fuel.

One of the few uses of gamma spectroscopy for Np radioanalysis was that of isotope dilution gamma-ray spectroscopy method using ^{239}Np as a spike for the determination of ^{237}Np in uranium, plutonium, and mixed oxide samples (Sus *et al.*, 1996). Extraction chromatography with trialaurylamine fixed on a SGX-C18 support was used for the isolation of neptunium. A pair of γ-rays of 86.53 keV (^{237}Np) and 106.13 keV (^{239}Np) was employed for the detection. The detection limit was evaluated to be 5×10^{-8} g ^{237}Np.

(b) Liquid scintillation counting method

Liquid scintillation counting method does not require extensive sample preparation and is very sensitive for alpha-decaying radionuclides such as ^{237}Np. The alpha liquid scintillation method with rejection of γ emitters (PERALS spectrometer) is useful because of its high sensitivity, selectivity, and rapid sample preparation. Aupiais *et al.* (1999) developed a method for the determination of ^{237}Np which consists of (1) oxidation of Np(v) to Np(vi) with Ag(ii), (2) extraction of Np(vi) from 0.5 to 0.75 M HNO_3 solution into the extractive scintillation cocktail of TOPO, and (3) gamma liquid scintillation counting with rejection of γ emitters. The method was applied to the biological samples.

The pulse shape discrimination (PSD) technique was introduced to liquid scintillation counting by Yang *et al.* (1994) for the determination of ^{237}Np coexisting with plutonium and americium. Np(iv) was separated from Pu(iii), Am(iii), and fission product elements by two steps of solvent extraction using TTA–xylene and triisooctylamine(TIOA)–xylene. The PDS technique enabled the alpha counting with an efficiency of higher than 99% and a beta discrimination factor of higher than 99.95%. The proposed method was applied to the determination of neptunium, plutonium, and americium in the HLW.

(c) Activation analysis

Neutron activation analysis based on ^{237}Np(n,γ)^{238}Np ($t_{1/2}$ of ^{238}Np $= 2.117$ days) reaction, for which the activation cross section is large and 170 barns, is one of the most sensitive methods for the determination of ^{237}Np. In general, neutron activation analysis is ca. 500 times more sensitive than the alpha-counting method. The procedure consists of (1) pretreatment of the sample, i.e. the leaching of ^{237}Np from the solid sample and the oxidation state adjustment at Np(iv), (2) the separation and preconcentration of Np(iv), (3) neutron irradiation, (4) separation of Np(iv) from the irradiated sample, and (5) the determination of ^{238}Np by gamma-ray spectroscopy. May *et al.* (1987) applied this method to irradiated nuclear fuels, radioactive waste solutions, and environmental samples such as seawater and submarine fauna and flora of disposal areas. Cation-exchange chromatography with Dowex 1 × 8 was employed to separate Np(IV) both before and after the irradiation. They determined the detection limit to be 5×10^{-13} g ^{237}Np. A similar procedure was applied to the sediment samples around Sellafield, Cumbria (Bryne, 1986) and the samples taken from the marine environment of coastal nuclear sites in India (Jha and Bhat, 1994). Depending on the nature of the sample, the removal of the bulk of the iron is required, and they employed solvent extraction with methylisobutylketone (MIBK) or isopropyl ether. After the irradiation, ^{238}Np purified by solvent extraction of Np(IV) with HTTA (cf. Fig. 6.12). If necessary, neptunium ions in a large volume of the sample solution such as seawater sample was preconcentrated by coprecipitation with iron(III) hydroxide precipitate, and Na^+ (^{24}Na) was removed from the irradiated sample using the flow-through column of the hydrated antimony pentoxide. The chemical yield was monitored, usually with ^{239}Np tracer. Bryne (1986) evaluated the detection limit by this method to be 0.1 to 0.5 mBq ^{237}Np.

Neutron activation analysis using epithermal neutron was applied to the determination of ^{237}Np for the purpose of an environmental monitoring of Yucca Mountain area (Riggle, 1992). The sensitivity obtained by the activation analysis using epithermal neutrons was found to be similar to that by using thermal neutrons. The neutron activation analysis method is also feasible for the determination of ^{235}Np and Zhao *et al.* (1991) applied this method to the determination of ^{235}Np in silicate samples.

Maslov *et al.* (1997) developed a highly sensitive method based on the (γ,f) reaction of ^{237}Np followed by the fission track counting. The proposed method was feasible for the determination of ultra-trace amount of ^{237}Np, e.g. in environmental water, and the detection limit was estimated to be 1×10^{-14} g ^{237}Np.

6.10.2 Spectrophotometric method

Several spectrophotometric methods are available: (1) absorption spectrophotometry of Np ions (direct absorption spectrophotometry); (2) absorption spectrometry of the colored complexes formed by Np ions and a chelating reagent; and (3) fluorescence spectrophotometry. A report by Burney and Harbour (1974) summarized and evaluated traditional spectrophotometric methods.

The direct absorption spectrophotometry is useful for the speciation of the Np ions in a solution by a simple procedure, though the sensitivity is not high. The most appropriate wavelengths for the determination of Np^{3+}, Np^{4+}, NpO_2^+, and NpO_2^{2+} in 2 M $HClO_4$ are 786 nm (molar extinction coefficient ε is approximately 45 $mol^{-1}\ dm^3\ cm^{-1}$), 960 nm ($\varepsilon = 160\ mol^{-1}\ dm^3\ cm^{-1}$), 980 nm

($\varepsilon = 395$ mol^{-1} dm^3 cm^{-1}), and 1223 nm ($\varepsilon = 45$ mol^{-1} dm^3 cm^{-1}), respectively (cf. Fig. 6.11). This method is useful for rapid and non-destructive speciation of the Np ions in acidic solution. The detection limits are approximately 5×10^{-4} M Np^{3+}, 1×10^{-4} M Np^{4+}, 5×10^{-5} M NpO_2^+, and 5×10^{-4} M NpO_2^{2+} simply assuming that the lowest detectable absorption is 0.02.

LIPAS enables the direct detection of the ions of relatively low concentration in the solution (Schrepp *et al.*, 1983; Klenze and Kim, 1988). An utilization of LIPAS leads to an enhancement of the sensitivity by a factor of ten or more compared with traditional absorption spectrophotometry. Pollard *et al.* (1988) realized the sensitivity in the measurement of Np(IV), Np(V), and Np(VI) of ca. 10^{-7} M in acidic solution using a dual beam LIPAS system equipped in Harwell. The LIPAS was applied to the monitoring of Np(V) in the nitric acid solution of the Purex process condition (Kihara *et al.*, 1996).

Colored complexes of neptunium with high absorption ability have been utilized for the sensitive determination of neptunium (Burney and Harbour, 1974). A method using the complex of Np(IV) and 1,8-dihydroxy–3,6-disulfonicnaphthalene–2,7diazo, commonly referred to as arsenazo-III, is one of the most sensitive with a molar extinction coefficient of 10^5 mol^{-1} dm^3 cm^{-1} at 665 nm, when the complex is formed in 4–6 M HNO_3. Uranium, thorium, plutonium, and other ions also form complexes with arsenazo-III, and therefore these ions should be removed from the sample solution before the color formation reaction. Solvent extraction with HDEHP acid or TIOA was used to separate neptunium from these interfering ions. The detection limit obtained by arsenazo-III method is approximately 4×10^{-8} g ml^{-1} of neptunium. Thorin, xylenol orange, and chlorophosphonazo III are other common color-forming reagents for use in the determination of neptunium.

6.10.3 Luminescence methods

Measurement of the luminescence intensity from a phosphor such as CaF_2- or $PbMpO_4$-based crystal that is doped with neptunium makes the sensitive determination of neptunium possible. Aleksandruk *et al.* (1990, 1991a) developed a method that consisted of the leaching of neptunium from solid samples such as soil, the isolation of the neptunium by solvent extraction and extraction chromatography, and counting the luminescence intensity at 651 or 663 nm from a CaF_2(Np) crystal at 77 K using a nitrogen pulsed laser (337 nm) as the excitation source. Neptunium was concentrated on the surface layer of a CaF_2 pellet, which resulted as a remarkable improvement of the sensitivity (Aleksandruk *et al.*, 1990). The detection limit of the absolute amount of neptunium was approximately 10^{-12} to 5×10^{-13} g. The proposed method was applied to the determination of Np in soil samples taken from the 30 km zone of the Chernobyl area.

Several attempts have been made to improve the reliability or the sensitivity of the luminescence method. Stepanov *et al.* (1997) proposed a method using uranium as an internal standard to enhance the reliability of determination of neptunium with CaF_2 phosphor. The procedure was applied to the neptunium analysis of nuclear materials. Ivanova *et al.* (1994) utilized a novel method for the preconcentration of neptunium with high concentrating efficiency by the use of a solid-supported liquid membrane containing trioctylmethylammonium nitrate, which was directly subjected to the preparation of the CaF_2 or $PbMoO_4$ phosphor. The detection limit was 1×10^{-13} g ml^{-1} in pure water and 5×10^{-13} g g^{-1} in soil sample. An alternative membrane technique, which is chemically compatible with the preparation of $PbMoO_4$ phosphor, was utilized by Novikov *et al.* (1997) for the preconcentration of neptunium and plutonium. The elaborate procedure for the determination of neptunium and plutonium consists of the HDEHP solvent extraction of Np(IV) and Pu(IV) from the soil leach and accumulation of these ions on the solid-supported aqueous membrane with $K_{10}P_2W_{17}O_{61}$.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) was applied for the analysis of Np in plutonium samples (Aleksandruk *et al.*, 1991b) to attain a detection limit of 2×10^{-12} g Np.

6.10.4 X-ray fluorescence spectroscopy (XRF)

The XRF technique, which is essentially a non-destructive method, does not require the removal of uranium, plutonium, and other elements, and can be applied to solid and liquid samples. This technique was utilized to monitor the neptunium content in the products of nuclear spent fuel reprocessing (Akopov *et al.*, 1988). It was found that neptunium of more than 4 mg L^{-1} could be determined by XRF using a high intensity X-ray source and Si:Li detector, when the Np/U and Np/Pu ratios were higher than 1/80 and 1/40, respectively. If the sample contained higher concentration of U or Pu, extraction chromatography was employed to remove these elements from neptunium and the detection limit was lowered to 0.1 mg L^{-1}.

A gamma-ray induced energy-dispersive K-line XRF was applied to the determination of heavy metals such as neptunium, uranium, and plutonium in the Purex process solution using a gamma-ray excitation source of ^{57}Co ($t_{1/2} =$ 27.1 days, 10 mCi), ^{133}Ba ($t_{1/2} = 10.7$ years, 10 mCi), or ^{192}Ir ($t_{1/2} = 74$ days, 10 Ci) (Pilz *et al.*, 1989). One of the most distinct advantages of this method is the wide dynamic concentration range from ppm level to 400 g L^{-1}.

6.10.5 Mass spectrometry

(a) Surface ionization mass spectrometry (SIMS)

Isotope dilution mass spectrometry using ^{235}Np or ^{239}Np as a spike is a useful method for the sensitive and precise determination of ^{237}Np. An ion source of surface ionization diffusion (SID)-type, which is prepared by electroplating neptunium and overplating the sample with rhenium or platinum metal film, was applied to the detection of neptunium (Efurd *et al.*, 1986). This technique was applicable to ^{237}Np amounts ranging from 10^{-17} to 10^{-8} g.

(b) ICP-MS

ICP-MS has become one of the most powerful methods for the determination of ultra-trace levels of ^{237}Np in many kinds of samples such as environmental and biological samples, uranium fuels, and Purex process solutions. Distinct advantages of this method are a capability of a simultaneous multi-element analysis providing information on the isotopic composition for a large number of elements with high precision and accuracy, as well as a rapid analysis compared with traditional alpha spectrometry and neutron activation analysis, which require tedious pretreatment and measurement procedures. Interfering elements such as uranium and other heavy elements must be removed from the sample solution using optimum chemical separation methods. The separation of uranium, in particular, is important to avoid the interference from the downmass tailing of ^{238}U.

Kim *et al.* (1989) recommended a separation scheme for the ICP-MS analysis of ^{237}Np in a soil:solvent extraction with isopropyl ether to remove iron, solvent extraction with TOA to recover neptunium, and three-step anion-exchange chromatography. They obtained a detection limit of 0.02 mBq ml^{-1} (ca. 8×10^{-13} g ml^{-1}) of ^{237}Np. Yamamoto *et al.* (1994) conducted ICP-MS analysis of ^{237}Np in paddy field soil samples in Japan using high-resolution ICP-MS equipped with a double-focusing mass spectrometer in order to elucidate the temporal feature of global fallout of ^{237}Np deposition.

Riglet *et al.* (1992) applied ICP-MS to the determination of ^{237}Np in enriched uranium solutions. After extracting neptunium as Np(IV) from 1 M HNO_3 solution into 0.5 M HTTA xylene solution and back-extracting in 10 M HNO_3, the ICP-MS signal of ^{237}Np was recorded. Concentrations of ^{237}Np of more than 5 ng in a 1 g uranium sample could be determined. Fig. 6.13 shows a typical ICP-MS spectrum for ^{237}Np in uranium samples.

Barrero Moreno *et al.* (1997) developed a method for the online separation of neptunium, plutonium, and uranium by ion chromatography using a high-capacity cation-exchange column followed by the direct injection of the effluent to the ICP-MS system to determine neptunium and plutonium in the presence of a high concentration of uranium. The method was applied to various kinds of irradiated UO_2 and MOX fuels.

(c) Other methods based on mass spectrometry

Resonance-ionization mass spectroscopy (RIMS) is expected to be powerful for the ultra-trace analysis of long-lived radioactive elements such as neptunium because of its extremely high sensitivity and selectivity. Riegel *et al.* (1993)

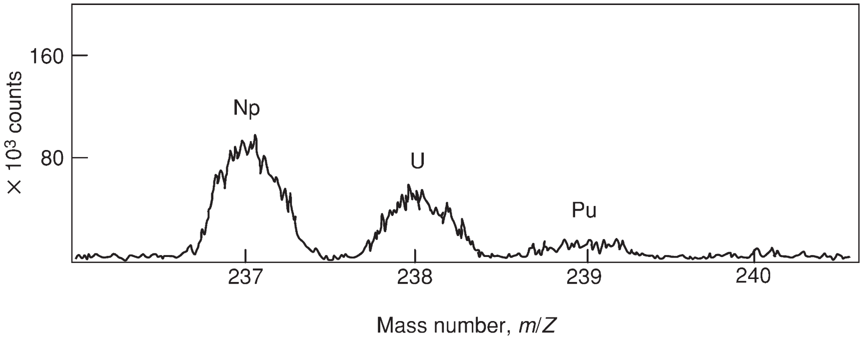


Fig. 6.13 *ICP mass spectrum for* ^{237}*Np in environmental samples. The mean value of the concentration of* ^{237}*Np was obtained to be* 6.2×0.1 Bq kg^{-1} *based on intercomparison analysis using spectrometry by seven laboratories. Reprinted from Kim* et al. (1989), *with permission from Elsevier Sequoia S. A.*

carried out the ^{237}Np detection by RIMS and estimated the detection limit as 4×10^8 atoms (1.6×10^{-13} g) which is almost two orders of magnitude more sensitive than that by alpha spectrometry.

Accelerator mass spectrometry (AMS) was applied to the detection of ^{237}Np in environmental samples such as mud, sediment, and pore water (Fifield *et al.*, 1997). It was estimated that sensitivity by AMS approached 10^5 atoms (4×10^{-17} g) of ^{237}Np. The results obtained by such a highly sensitive method make it possible to elucidate a distribution behavior of neptunium in natural environment and therefore to conclude that neptunium is more mobile than plutonium in the environment.

6.10.6 Electrochemical methods

Electrochemical methods are feasible for the determination of the total concentration and redox speciation of neptunium ions. The reduction–oxidation processes between Np(vi) and Np(v) and between Np(iv) and Np(iii) are practically reversible and of simple one-electron transfer characteristics, which enables various electroanalytical performance based on these electrode reactions. The electroanalytical data of neptunium mainly obtained by voltammetry and polarography were reviewed by Kihara *et al.* (1999).

(a) Potentiometric titration and coulometry

Titration methods based on the reduction–oxidation of neptunium ions have been widely used for the accurate and precise determination of 1–10 mg quantities of neptunium. A method proposed by Godbole and Patil (1979) consists of the oxidation of neptunium ions to Np(vi) with Ag(ii), destruction of excess

Ag(II) with sulfonic acid, reduction of Np(VI) to Np(IV) by a slight excess of Fe(II) in 2 M H_2SO_4, and potentiometric titration of the excess Fe(II) with standard Ce(IV) solution. The end point was detected potentiometrically using a platinum indicator electrode. Cao *et al.* (1994) proposed an alternative amperometric titration method by the use of Cr(VI) instead of Ce(IV) to titrate Fe(II). They attained less than 0.3% relative standard deviation in the determination of 2 mg of neptunium.

Controlled-potential coulometry is the standard method based on a primary theory, which enables an accurate and precise determination of neptunium. Stromatt (1959) recommended the procedure that consists of the oxidation of neptunium ion to Np(VI) with Ce(IV), the electrolytic reduction of Np(VI) and the excess Ce(IV) to Np(V) and Ce(III), and coulometric determination of Np(V) by the oxidation of Np(V) to Np(VI).

Kasar *et al.* (1991) determined 2–5 mg of neptunium with a relative standard deviation of ±0.25% by controlled-potential coulometry consisting of oxidation to Np(VI) with Ce(IV), decomposition of the excess Ce(IV) with $NaNO_2$, and titration based on the reduction of Np(VI) to Np(IV) with internally and electrolytically generated Fe(II). Karelin *et al.* (1991) developed constant current coulometry adopting amperometric end point detection, which enabled the determination of neptunium in the solution coexisting with uranium, plutonium, cerium, chromium, iron, and manganese. Chemists at the Savannah River Plant, USA, developed an automatically controlled apparatus for coulometry that was applied to the determination of neptunium. Measurement precision within 0.1% was achieved (Holland and Cordaro, 1988). Narrow span controlled-potential coulometry, which can minimize the interference from ions of formal redox potential close to that of the ion to be determined, was developed (Kalsi *et al.*, 1994) and applied to the determination of neptunium with enough high reproducibility, e.g. with relative standard deviation of 0.2%, even in the presence of five times the concentration of plutonium. Kihara *et al.* (1999) proposed a flow-coulometry method using multi-step column electrodes of glassy carbon fibers working electrode for the determination and speciation of neptunium ions in acidic solutions. (The redox behavior of neptunium ions observed by flow-coulometry is described in detail in Section 6.8.1b.)

(b) Voltammetry and polarography

Polarography was applied to the simultaneous determination of Np(V) and U(VI) in samples from the spent nuclear fuel reprocessing process based on the fluoride vaporization (Li *et al.*, 1988). The reduction currents of Np(V) and U(VI) were recorded with the electrolyte solution of a mixture of 2 M acetic acid and 2 M ammonium acetate. Kuperman *et al.* (1988) developed potentiostatic voltammetry for the determination of 2×10^{-8} to 1×10^{-5} M of neptunium and plutonium ions. Yakovlev and Kosyakov (1991) developed anodic stripping voltammetry method for the determination of neptunium using column electrode of carbon fibers as a working electrode whose surface was modified by bis(2-ethylhexyl) phosphate. The recommended procedure consists of the electrolytic preconcentration of Np(VI) at the electrode surface and the measurement of the current peak due to the oxidation of Np(V) to Np(VI). The detection limit was ca. 10^{-7} M.

6.10.7 Mössbauer spectroscopy of ^{237}Np materials

Neptunium–237 is one of the best Mössbauer nuclei in the periodic table. ^{237}Np has the following characteristics which allow the Mössbauer spectroscopic measurement successful: (1) the lifetime of the excited state for Mössbauer transition is long enough, 68 ns, to obtain a sharp resonance line; (2) the spread range of the isomer shift is large enough to differentiate nature of chemical bonds from the shift; and (3) the radiation from a ^{237}Np absorber is low enough to record a spectrum in a standard transmission geometry. The most useful Mössbauer measurement system is the 60 keV radiation from ^{237}Np excited in the alpha decay of ^{241}Am. Nakada *et al.* (1998) developed a source assembly with small sources of ^{241}Am metal and designed the sealed holders to encapsulate the sample without the seepage of liquid helium.

Kalvius (1989) summarized basics and the power of Mössbauer spectroscopy of ^{237}Np in his review article demonstrating examples of study on 5f-electron structure of antiferromagnetic NpAs compounds and various Np(VI) and (VII) compounds. Jovè *et al.* (1991) reviewed applications of Mössbauer spectroscopy to the study of insulating neptunium compounds and discussed correlations between isomer shift, electric field gradient, and bonding or crystallographic structure of neptunium in crystallized or amorphous compounds of Np(III–VII).

Each oxidation state has a characteristic isomer shift range that is correlated with the number of 5f electrons present, and thus the isomer shift is a good indicator of the coordination number as well as the oxidation state of Np in a compound. The isomer shift increases regularly with decreasing oxidation state. Systematic trend of the isomer shift of ^{237}Np in various metal coordination complexes was studied and a linear dependence was found between the isomer shift and the mean neptunium–ligand distance in a series of Np(VI) compounds, which were summarized by Jovè *et al.* (1988a,b, 1991). Ionova and Jovè (1989) proposed a model, which correlated the population of the 5f orbital of ^{237}Np with the isomer shift, for the estimation of covalent effect in neptunium compounds based on the isomer shift. Bickel *et al.* (1987) studied the Mössbauer spectra of such oxoneptunates as $Li_5Np^{(VII)}O_6$, $Li_6Np^{(VI)}O_6$, $BaNp^{(VI)}O_4$, $Np^{(IV)}GeO_4$, $SrNp^{(IV)}O_3$, and $BaNp^{(IV)}O_3$. The isomer shifts were more negative or positive for the bond of ionic or covalent characteristics, respectively.

Sanchez *et al.* (1988) studied the electronic and magnetic properties of a novel intermetallic $NpRh_2Si_2$ by ^{237}Np Mössbauer spectroscopy. The isomer shift ranging from 5.3 (at 4.2 K) to 4.8 mm s^{-1} (at 77 K) with respect to $NpAl_2$ suggested a Np^{4+} electronic configuration in conducting materials.

Nakamoto *et al.* (1998) and Saeki *et al.* (1999) measured Mössbauer spectra of Np(v) compounds such as formate, $NpO_2OOCH \cdot H_2O$, and $NH_4NpO_2(OOCH)_2$, glycolate, $NpO_2OOCCH_2OH \cdot H_2O$, malonate $(NpO_2)_2C_3H_2O_4 \cdot 4H_2O$, and phthalate $(NpO_2)_2(OOC)_2C_6H_4 \cdot 4H_2O$, and found a good correlation between coordination numbers of Np atoms and isomer shifts in the range from –18.6 to –19.1 mm s^{-1} for the compounds with Np atoms surrounded by seven oxygen atoms, i.e. coordination number = 7. The isomer shift for Np of coordination number 8 in the compound is larger than that of coordination number 7. Isomer shifts of Np(iv) to (vii) with different coordination numbers in the compounds are summarized in Fig. 6.14 (Saeki, 2003).

Heptavalent neptunium compounds have been studied by Mössbauer spectroscopy. The characteristic isomer shift of Np(vii) has been reported to be from –64 to –75 mm s^{-1} with respect to $NpAl_2$ (Stone *et al.* 1969; Fröhlich *et al.* 1972; Ilyatov *et al.* 1975; Grigor'ev *et al.* 1979; Ananyev *et al.* 1980). Recently Nakamoto *et al.* (1999) reinvestigated the Mössbauer spectra for Np(vii) in $[Co(NH_3)_6][NpO_4(OH)_2] \cdot 2H_2O$ at 4.2 K. They pointed out that the fitting by using two quadrupole-split peaks did not give a good agreement with the previous data by Stone *et al.* (1969), although the spectrum observed by Nakamoto *et al.* (1999) consisted of two quadrupole-split peaks.

Filin *et al.* (1989, 1990) studied ^{237}Np Mössbauer emission spectra resulting from the alpha decay of ^{241}Am in various solid solutions of actinide dioxides. The oxidation state of ^{237}Np in ^{241}Am(0.6 and 11 at%) + PuO_2 was determined from the isomer shifts of –5.8 and 18.5 mm s^{-1} relative to $NpAl_2$ to be Np^{4+} and Np^{5+}, respectively. They found that the oxidation state strongly depended on the matrix stoichiometry of PuO_2 as well as on the content of the impurity in the sample.

6.10.8 Miscellaneous methods

Speciation of neptunium in samples has been a strong analytical interest and requirement, because the ions of five oxidation states from (iii) to (vii) are stable under certain conditions and the ions form complexes differently with many kinds of ligands. The methods for the speciation were evaluated recently by OECD/NEA (2001).

The redox speciation of neptunium ion of relatively high concentration can be performed by direct absorption spectrophotometry (see Section 6.10.2) or electrochemical methods (see Section 6.10.6). For the redox speciation of neptunium ion at lower concentration, e.g. in environmental samples, a method utilizing chemical separation between ions of different oxidation states followed by the determination of the ions using sensitive methods such as radiometric methods and ICP-MS is employed. Coprecipitation with such precipitates as LaF_3, followed by solvent extraction with, e.g. HTTA, can be used for the separation. It is essential that the separation method does not disturb the

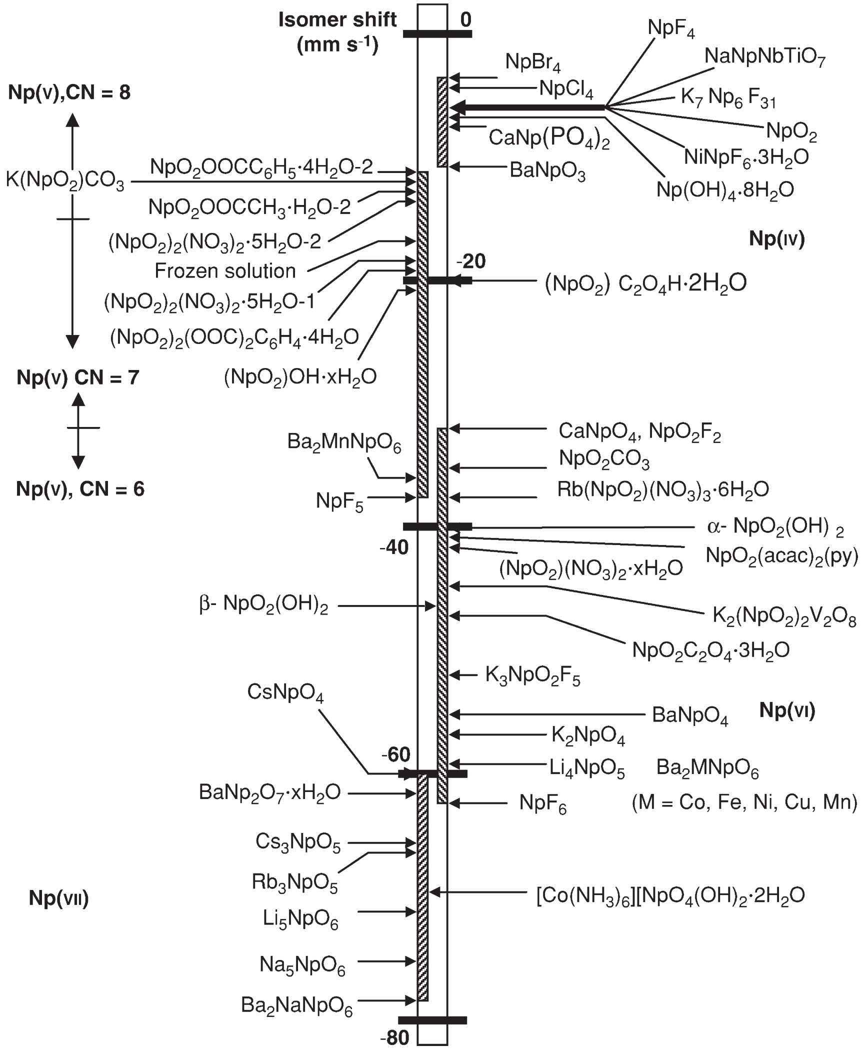


Fig. 6.14 *Isomer shifts of Np(iv), (v), (vi), and (vii) compounds.*

redox equilibrium during the treatment of the sample. Mang *et al.* (1993) investigated a continuous electrophoretic ion focusing method for the separation of Np(vi) from Np(v) at a trace concentration level, e.g. 10^{-14} M level using ^{239}Np tracer. Np(vi) was not stable enough under the recommended conditions. The Np(iv) and Np(v) species were well focused and separated with very reproducible peaks by continuous ion focusing with glycolic acid and tartaric acid.

Chen *et al.* (1992) employed traditional solvent extraction with HTTA and TOPO for the separation of Np(VI), Np(V), and Np(IV). Enokida and Suzuki (1987) employed extraction chromatography with TBP-impregnated resin for the separation of 10^{-5} M levels of neptunium ions of different oxidation states. Nagasaki *et al.* (1988) recommended a paper electrophoresis method for the redox speciation of neptunium ions.

X-ray absorption fine structure (XAFS) was applied to the speciation of Np(V) in an aqueous solution containing high concentration of chloride salt (Allen *et al.*, 1997), and adsorbed at the interface between alpha-Fe hydroxide solid and aqueous solution (Combes *et al.*, 1992).

High-resolution ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) were applied to characterize the surface of neptunium metal (Naegele *et al.*, 1987). An oxide layer of Np(III), i.e. Np_2O_3, was found in the near surface of about 10 Å in thickness of the sample.

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