Alkaline Chemistry of Transuranium Elements and Technetium and the Treatment of Alkaline Radioactive Wastes

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Alkaline Chemistry of Transuranium Elements and Technetium and the Treatment of Alkaline Radioactive Wastes

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<i>Atom. Energ.</i>	Atomnaya Energiya	Atomic Energy	<i>Sov. At. Energy (Engl. Transl.)</i>
<i>Dokl. Akad. Nauk SSSR</i>	Doklady Akademii Nauk SSSR	Proceedings of the Academy of Sciences of the USSR	<i>Dokl. Chem. (Engl. Transl.)</i> or <i>Dokl. Phys. Chem. (Engl. Transl.)</i>
<i>Izv. Sib. Otd. Akad. Nauk, Ser. Khim.</i>	Izvestiya Sibirskogo Otdeleniya Akademii Nauk, Seriya Khimicheskikh	Proceedings of the Siberian Department of the Academy of Sciences of the USSR, Series on Chemical Sciences	<i>Sib. Chem. J. (Engl. Transl.)</i>
<i>Izv. Akad. Nauk, Ser. Khim.</i>	Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya	Proceedings of the Academy of Sciences of the USSR, Chemical Series	<i>Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)</i>
<i>Khim. Vys. Energ.</i>	Khimiya Vysokikh Energii	High Energy Chemistry	<i>High Energy Chem. (Engl. Transl.)</i>
<i>Radiokhimiya</i>	Radiokhimiya	Radiochemistry	<i>Sov. Radiochem. (Engl. Transl.)</i> [through volume 34, 1992] <i>Radiochemistry (Engl. Transl.)</i> [since volume 35, 1993]
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<i>Zh. Anal. Khim.</i>	Zhurnal Analiticheskoi Khimii	Journal of Analytical Chemistry	<i>J. Anal. Chem. USSR (Engl. Transl.)</i>
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1.0 INTRODUCTION

The chemistry of transuranium (TRU) elements neptunium (Np), plutonium (Pu), americium (Am), and curium (Cm) in alkaline media is developed rather poorly when compared with knowledge in acid media. In addition, no literature survey exists devoted to the chemistry of TRU in alkaline media. However, some information is available in monographs (Seaborg et al. 1986; Krot et al. 1977; and Pikaev et al. 1983), a Los Alamos National Laboratory report (Marsh 1993) and numerous articles quoted in the present survey.

The main steps of spent fuel treatment take place in nitric acid media. Sodium hydroxide media are used for aluminum cladding dissolution and for high-level waste (HLW) storage in the form of sludge in tanks. Alkaline radioactive sludges exist in tanks in reprocessing plants worldwide. The sludges, accumulated during many years, must be transformed to safer forms (such as glass) for long-term storage. No technology currently is available to perform this transformation with alkaline sludges in any country. Additional information on the physical and chemical properties of TRU and fission products in alkaline media are required as a basis to undertake processing of this waste.

Initial information on the alkaline chemistry of TRU was obtained by the researchers of the Manhattan Project in the 1940s. They determined that TRU in oxidation states (III) to (VI) form sparingly soluble precipitates in alkaline media (Kraus 1949a, Kraus 1949b, and Connick et al. 1949). This information was further augmented in the 1950s and the beginning of the 1960s.

The heptavalent state of Np, Pu, and Am was discovered in 1967 to 1969 at the Institute of Physical Chemistry of the USSR Academy of Sciences (Krot and Gel'man 1967). The heptavalent TRU element compounds were determined to be stable and somewhat soluble in strongly alkaline media. This discovery increased scientific interest in the alkaline chemistry of TRU and new information about the fundamental physical and chemical properties of Np, Pu, and Am in alkaline media has been obtained in the laboratories of various countries.

Important conclusions regarding the thermodynamical and real stability of Pu(V) in alkaline solution and waste made by French, Russian, and American investigators (Bourges 1972, Peretrukhin and Alekseeva 1974; and Delegard 1987) have practical importance. However, few published papers exist devoted to the development of methods for the isolation of the TRU elements from alkaline wastes (Marsh 1993).

The goal of this survey is to generalize the known data on the fundamental physical-chemical properties of TRU and technetium (Tc), on the methods of their isolation, and to provide recommendations that will be useful for partitioning them from alkaline HLW media. Unfortunately, several of the US national laboratories' reports on TRU alkaline chemistry are not available in Russia. In such cases, these papers are included, without evaluation, in the list of references. Note that the majority of the published research on the alkaline chemistry of TRU and Tc was conducted at the Institute of Physical Chemistry of the Russian Academy

of Sciences. Therefore, the authors working in the Institute appreciated the opportunity to write this survey, which was sponsored by the U.S. Department of Energy (DOE) and coordinated by Westinghouse Hanford Company (WHC).

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- Seaborg, G. and J. Katz, and L. Morss, Eds. 1986, *Chemistry of Actinide Elements*, Chapman and Hall Ltd., London, UK, New York, New York.

2.0 OXIDATION STATES OF TRANSURANIUM ELEMENTS AND TECHNETIUM AND THEIR THERMODYNAMIC STABILITY IN ALKALINE MEDIA

2.1 INTRODUCTION. RELEVANCE OF THERMODYNAMIC STABILITY OF THE ELEMENTS IN SOLUTION TO THEIR OXIDATION POTENTIALS

The thermodynamic stability of the oxidation state in aqueous solution is one of the important physical-chemical characteristics of an element. An element that is thermodynamically stable in a certain oxidation state does not undergo disproportionation reactions or redox reactions with water. Thus, values of the Gibbs free energy for such hypothetical (but, in practice, impossible) reactions should be positive ($\Delta G > 0$). The latter value is easily calculated using standard oxidation potentials in the solutions (E°), according to the equation:

$\Delta G^\circ = -nF\Delta E^\circ$, where n is the number of the electrons involved to the redox process and F is the Faraday number. The usual way to estimate the direction of a disproportionation reaction is to estimate the sign of ΔE° using the values of the neighbor couples' oxidation potentials. To determine the direction of redox reactions of the element of interest with water, the oxidation potential of the neighboring oxidation states are compared with the standard potentials of H_2 or O_2 evolution from water at a given pH value. Unfortunately, the values of the actinides' standard redox standard potentials in alkaline media are not currently reported. Only the values of formal redox potentials for actinides in different media have been determined. The formal potentials were used in all the papers quoted in the present review. Formal potentials differ from standard potentials by assuming that the unknown activity coefficients of the elements of interest are equal to 1. In general, this uncertainty of formal potentials' values does not affect the estimation of the redox reactions' directions.

2.2 OXIDATION POTENTIALS AND STABILITY OF TRANSURANIUM ELEMENTS AND TECHNETIUM IN ALKALINE MEDIA

The oxidation states (+2 to +7) have been reported for Np, Pu, Am, and Tc in aqueous solutions. The oxidation state (+2), reported for Np, Pu, and Am in acidic media, is unstable and has not been detected in alkaline solutions. The thermodynamic and experimental stability of each oxidation state can change sharply with an increase of solution pH. The general regularity, characteristic for actinide and technetium ions, means that the highest oxidation states (+7 to +5) are more stable in alkaline than in acidic media, while the reverse effect is noticed for lower oxidation states (+3 and +4) [excluding Am(IV)].

The data on the oxidation potentials of TRU elements in 1 M $HClO_4$ and alkaline media are summarized in Table 2-1. Clearly, in alkaline solution, more is known about higher actinide oxidation states (+7, +6, +5) than about lower states (+3, +4). This is because actinide hydroxides and salts in oxidation states VII, VI, and V have higher solubilities than analogous compounds in oxidation states IV and III. The low solubility of actinide(IV) and actinide(III) hydroxides in alkaline media makes the majority of conventional experimental

techniques inapplicable to direct oxidation potential measurements. Figure 2-1 presents the scheme of Np, Pu, and Am oxidation potentials in 1 M HClO₄ and in 1 M NaOH. The data for plotting this scheme have been taken from Table 2-1. The presented graph illustrates the trend of actinide oxidation potentials to shift towards lower values as the solution acidity decreases. When the acidity is decreased from 1 M HClO₄ to 1 M NaOH, about -1.9 V shift in Np, Pu, and Am (IV)/(III) oxidation potentials occurs. In accordance with the values of their oxidation potentials, Np(III) and Pu(III) hydroxides are able to reduce water molecules, with hydrogen evolution, in alkaline media. The data on the oxidation potentials of Np and Am (Table 2-1 and Figure 2-1) do not differ from those reported in Martinot and Fuger (1985) and Katz et al. (1986a). In case of plutonium, however, sharp contradictions between the Pu(V)/Pu(IV) oxidation potential values reported by different authors are found. Therefore the Pu(V)/Pu(IV) redox equilibrium in alkaline media needs more detailed examination.

Table 2-1. Formal Potentials for the Actinide Redox Couples, Measured vs. NHE.

Media	VII/VI	VI/V	VI/IV	V/IV	IV/III	III/II	III/I	II/I
Uranium								
1 M HClO ₄		0.063 [1,2]	0.321 [1]	0.58 [1]	-0.631 [1,2]	-4.7 [3]	-1.66	-0.1 [3]
0.05 M Na ₂ CO ₃		-0.671 [4]						
1 M K ₂ CO ₃		-0.6 [5]		0.0 [5]	-2.03 [5]			
1 M NaOH		-0.65 [6]	-0.3 [3]		-2.6 [3]		-2.10 [3]	
Neptunium								
1 M HClO ₄	2.04 [7]	1.137 [1,2]		0.739 [1,2]	0.155 [1,2]	-4.7 [2,3]	-1.79 [2,3]	-0.3 [2,3]
0.05 M Na ₂ CO ₃		0.445 [4]						
1 M K ₂ CO ₃		0.44 [8]		0.1 [5]	-1.32 [5]			
1 M NaOH	0.582 [9]	0.18 [11]						
1 M NaOH	0.587 [10]	0.11 [12]		-0.95 [13]	-1.8 [13]		-2.32 [2]	
10 M NaOH	0.25 [13]	0.05 [13]		-1.0 [13]	-2.0 [13]			
1 M LiOH	0.604 [14]	0.150 [14]						

Table 2-1. Formal Potentials for the Actinide Redox Couples, Measured vs. NHE.

Media	VII/VI	VI/V	VI/IV	V/IV	IV/III	III/II	III/I	II/I
Plutonium								
1 M HClO ₄	≈2.3 [15]	0.916 [16]	1.043 [16]	1.170 [16]	0.982 [16]	-3.5 [3]	-2.0 [3]	-1.2 [3]
0.05 M Na ₂ CO ₃	0.334 [4]							
1 M K ₂ CO ₃	0.32 [8]			0.6 [5]	-0.495 [5]			
1 M NaOH	0.849 [17]	0.23 [18]		0.76 [20]	-0.95 [19]		-2.46 [3]	
1 M NaOH		0.21 [19]		0.86 [21]	-1.4 [3]			
1 M NaOH	-			-0.75 [19]				
1 M NaOH				0.9 [3]				
4 M NaOH				0.44 [18]				
11 M NaOH	0.35 [19]	0.16 [19]		-1.03 [19]	-1.34 [19]			

Table 2-1. Formal Potentials for the Actinide Redox Couples, Measured vs. NHE.

Media	VII/VI	VI/V	VI/IV	V/IV	IV/III	III/II	III/0	II/0
Americium								
1 M HClO ₄		1.60 [1,3]		0.82 [3]	2.62 [3]	-2.3 [3]	-2.07 [3]	-1.95 [3]
1 M Na ₂ CO ₃		0.9 [22]						
2 M NaHCO ₃ Na ₂ CO ₃ pH=9.7					0.92 [23]			
2 M NaHCO ₃ Na ₂ CO ₃ pH=10.0		0.93 [24]			0.89 [24,25]			
2 M NaHCO ₃ Na ₂ CO ₃ pH=10.0		0.975 [26]						
1 M K ₂ CO ₃		0.9 [8]		0.5 [5]				
1 M K ₂ CO ₃		0.86 [22]						
2.82 M KHCO ₃ K ₂ CO ₃ pH=8.87					0.93 [27]			
2.82 M KHCO ₃ K ₂ CO ₃ pH=11.2					0.81 [27]			
1 M NaOH	1.05 [28]	0.65 [29]						-2.53 [3]
1 M NaOH		0.68 [30]		0.25 to 0.50 [30]	<0.25 [30]			
10 M NaOH		0.63 [30]		0.17 to 0.50 [30]	<0.18 [30]			

Table 2-1. Formal Potentials for the Actinide Redox Couples, Measured vs. NHE.

Media	VII/VI	VI/V	VI/IV	V/IV	IV/III	III/II	III/0	II/0
Curium								
1 M HClO ₄	2.7 [31,32]	1.5 [31,32]		1.7 [31,32]	3.1 [3]	-3.7 [3]	-2.06 [3]	-1.2 [3]
1 M K ₂ CO ₃				0.5 [5]	1.6 [5]			
1 M NaOH					0.7 [3]		-2.53 [3]	

References:

- [1] Martinot and Fuger 1985
- [2] Katz et al. 1986a
- [3] Katz et al. 1986b
- [4] Mulac et al. 1984
- [5] Fedoseev et al. 1979
- [6] Musicas and Rousset 1971
- [7] Musicas et al. 1974
- [8] Simakin et al. 1974
- [9] Zielen and Cohen 1970
- [10] Shilov et al. 1970
- [11] Simakin et al. 1973
- [12] Peretrukhin and Alekseeva 1974a
- [13] Peretrukhin and Spitsyn 1982
- [14] Ermakov et al. 1977b
- [15] Krot et al. 1977
- [16] Rabideau et al. 1958
- [17] Peretrukhin et al. 1972
- [18] Bourges 1972
- [19] Peretrukhin and Alekseeva 1974b
- [20] Kraus 1949
- [21] Connick 1955
- [22] Simakin 1977
- [23] Hobart et al. 1982
- [24] Frenkel et al. 1985a
- [25] Frenkel et al. 1985b
- [26] Bourges et al. 1983
- [27] Berger et al. 1988
- [28] Nikolayevsky et al. 1975a
- [29] Nikolayevsky et al. 1974
- [30] Peretrukhin et al. 1974
- [31] Spitsyn and Ionova 1978a
- [32] Spitsyn and Ionova 1978b

Figure 2-1. Oxidation Potentials Scheme of Actinides in 1 M HClO₄ and 1 M NaOH Media (in Volts vs. Standard Hydrogen Electrode).

1 M HClO ₄		U (VI)	$\frac{0.06}{-0.65}$	U (V)	$\frac{0.58}{-1.1}$	U (IV)	$\frac{-0.63}{-}$	U (III)	$\frac{-1.80}{-}$	U (0)	
1 M NaOH											
1 M HClO ₄	Np(VII)	$\frac{2.04}{0.59}$	Np (VI)	$\frac{1.14}{0.14}$	Np (V)	$\frac{0.74}{-0.95}$	Np (IV)	$\frac{0.15}{-1.8}$	Np (III)	$\frac{-1.82}{-}$	Np (0)
1 M NaOH											
1 M HClO ₄	Pu(VII)	$\frac{2.3}{0.85}$	Pu (VI)	$\frac{0.92}{0.12}$	Pu (V)	$\frac{1.17}{-0.67}$	Pu (IV)	$\frac{0.98}{-0.96}$	Pu (III)	$\frac{-2.02}{-}$	Pu (0)
1 M NaOH											
1 M HClO ₄	Am(VII)	$\frac{2.5}{1.05}$	Am (VI)	$\frac{1.6}{0.68}$	Am (V)	$\frac{0.82}{0.4}$	Am (IV)	$\frac{2.62}{0.27}$	Am (III)	$\frac{-2.3}{-}$	Am (0)
1 M NaOH											
1 M HClO ₄	Cm(VII)	—	Cm (VI)	$\frac{1.5}{0.7}$	Cm (V)	$\frac{1.7}{-}$	Cm (IV)	$\frac{3.1}{1.2}$	Cm (III)	$\frac{-2.69}{-}$	Cm (0)
1 M NaOH											

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2.3 Pu(V)/Pu(IV) OXIDATION POTENTIAL AND STABILITY OF Pu(V) AND Pu(IV) IN ALKALINE MEDIA

The Pu(V)/Pu(IV) oxidation potential in 1 M NaOH, calculated by Kraus (1949) as $E^\circ = 0.76$ V vs. the standard hydrogen electrode (SHE) (Simakin 1977) is widely cited (Martinot and Fuger [1985]; and Katz et al. [1986a]). In his calculations, Kraus (1949) has taken into account that the $\text{PuO}_2^+/\text{Pu}^{4+}$ potential in acidic solutions decreases with an increase of pH at the rate 236 mV/pH. He made the questionable assumption that the Pu(V)/Pu(IV) oxidation potential is pH-independent in the range $1.4 < \text{pH} < 10$. He based this assumption on the hydrolysis of the reduced form [Pu(IV)] and assumed that the oxidized form [Pu(V)] does not undergo hydrolytic reactions in these conditions. At pH values greater than 10, Kraus assumed the further decrease of the oxidation potential value with the rate of 59 mV/pH. Using this assumption and the value of Pu(IV) polymerization free energy, Kraus obtained his reported value of Pu(V)/Pu(IV) oxidation potential ($E^\circ = 0.76$ V). Since 1949, Kraus has published splendid and accurate data on plutonium chemistry, but he never reconsidered his data on the plutonium oxidation potentials in alkaline media. The redox potential value, reported by Kraus, compared with the value of Pu(VI)/Pu(V) potential ($E^\circ = 0.23$ V vs SHE in 1 M NaOH) shows the possibility of Pu(V) disproportionation in alkaline solutions, as occurs in acidic media. The instability of Pu(V) and its ability to disproportionate in alkaline solutions is emphasized in many modern books dealing with plutonium chemistry (Martinot and Fuger 1985; and Katz et al. 1986a).

In studies of Pu(VI) electrochemical reduction to Pu(V) in 1 to 4 M NaOH, Bourges (1972) proved Pu(V) hydroxide to be stable and soluble. Moreover, he found Pu(IV) hydroxide fresh precipitate dissolved in these solutions when Pu(VI) was added. Dissolved species of Pu(V) were proved to be the product of the latter reaction. These observations mean that the well known disproportionation reaction of Pu(V), occurring in acidic media, changes its direction in alkaline solutions.

Unfortunately, Bourges (1972) did not measure the value of the Pu(V)/Pu(IV) oxidation potential, but estimated it as $E^\circ = 0.35$ V vs. SHE for 1 M NaOH. The latter result seems to contradict his own data on the Pu(VI) - Pu(IV) reproporationation with formation of Pu(V).

The Pu(V)/Pu(IV) oxidation potential in 1 M NaOH was determined for the first time using electrochemical measurements (Peretrukhin and Alekseeva, 1974a). In spite of the low solubility of Pu(IV) in alkaline media, direct current polarograms of the irreversible Pu(V) reduction to Pu(IV) were recorded using a dropping mercury electrode. The value of the Pu(V)/Pu(IV) oxidation potential in 1 M NaOH was determined as:

$$E^\circ = E_{1/2} - E_{\text{dif.}} - E_{\text{over}}$$

where: $E_{1/2}$ is the half-wave potential of Pu(V)/Pu(IV) reduction, determined experimentally; $E_{\text{dif.}}$ is the diffusion potential in the liquid junction of the reference electrode, reliably estimated in the literature as 30 mV; and $E_{\text{over.}}$ is the overvoltage of Pu(V) reduction arising from the irreversibility of the electrochemical process. The $E_{\text{over.}}$ was estimated as 0.13 mV using the results of the study of Am(IV) electrochemical oxidation in 1 M NaOH. The application of such an approach for estimating the Pu(V)/Pu(IV) oxidation potential resulted in the value -0.67 V vs. SHE.

The difference of the value obtained by Peretrukhin et al. (1993) from that of Kraus (1949) (+0.76 V vs. SHE) (Figure 2-2) is large and indicates one of them is erroneous. All the data on the chemical behavior of Pu(V) in alkaline media [(for example, its high stability and formation as a result of reproporationation of Pu(VI) and Pu(IV)] appear to contradict the value 0.76 V vs. SHE and more likely confirm the value reported by Peretrukhin et al. (1993). Moreover, the value $E^\circ = -0.67$ V vs. SHE indicates that the oxidation of Pu(IV) to Pu(V) by several oxidizing agents, such as O_2 , CrO_4^{2-} , and Fe(III) as FeO_2^- ions, should be possible in alkaline media.

Noticeable dissolution of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in air-equilibrated 1 to 15 M NaOH solutions was reported by Delegard (1987). Later, the dissolution of Pu(IV) hydroxide in 2 to 8 M NaOH solutions, purged by air during a 1-month period, has been reported in a common Russian-French study (Peretrukhin et al. 1994). They have found that plutonium concentration (4.0×10^{-5} M) in air-equilibrated solutions after a 1-month exposure had appeared to be 100 times greater if compared with the same solutions purged with argon and used as a reference. The concentration of soluble plutonium(V) in 2 to 8 M NaOH in the presence of $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, K_2CrO_4 , and $\text{Co}(\text{OH})_3$ also was found to increase during a 1-month exposure. This chemical observation once more proves that the value of oxidation potential for Pu(V)/Pu(IV) (-0.67 V vs. SHE) accords better with reality.

Diagrams of $E^\circ - \text{pH}$ for Np, Pu, and Am, taken from Maslennikov et al. (1993) and shown in Figure 2-3, may be successfully used for predicting the directions of actinide redox reactions. Note that the value of Pu(V)/Pu(IV) potential in neutral media, shown in Figure 2-2, is lower than that reported in widely used books (Martinot and Fuger 1985; and Katz et al. 1986). The data in Figure 2-2 also indicate that Pu(V) should be stable toward disproportionation above pH 5. This fact is consistent with the observation of Pu(V) reported for some natural waters (Bondietti and Trabalka 1980; and Nitsche 1991).

2.4 OXIDATION POTENTIALS AND STABILITY OF Np, Pu AND Am IN HIGHER OXIDATION STATES

The values of oxidation potentials for the Np(VII)/Np(VI), Np(VI)/Np(V) (Zielen and Cohen 1970; Shilov et al. 1970; Simakin et al. 1973; Peretrukhin and Alekseeva 1974a; Ermakov et al. 1977b; and Peretrukhin et al. 1972) and Pu(VII)/Pu(VI) (Peretrukhin and Alekseeva 1974b) pairs have been determined potentiometrically. Voltammetric

Figure 2-2. Pu Oxidation Potentials in 1 M HClO₄ and in 1 M NaOH.

Data Taken from Table 2-1.

References:

- [1] Martinot and Fuger 1985
- [2] Kraus 1949
- [3] Bourges 1972
- [4] Peretrukhin et al. 1993

Figure 2-3. Redox Potentials of Actinides in Acidic and Alkaline Solutions.

The Dashed Line is the E-pH Curve for Pu(V)-Pu(IV) Oxidation Potentials.

measurements have been carried out to determine potentials for Pu(VII)/Pu(VI), Pu(VI)/Pu(V), Pu(V)/Pu(IV) and Pu(IV)/Pu(III) redox pairs (Peretrukhin and Alekseeva 1974b). The data on Np and Pu oxidation potentials in higher oxidation states are presented in Figure 2-4. Only small differences have been noticed between the potential values determined in NaOH and LiOH at the same OH⁻ concentrations (Ermakov et al. 1977a). Alkaline concentrations, expressed in the original studies in molarity, M, have been changed to the corresponding values of activities $a = m\gamma$, where m, molality, is the alkaline concentration in mol per 1000 grams H₂O and γ is the activity coefficient. The calculations were made using handbook data for the densities of NaOH solutions and corresponding data on the γ of NaOH and LiOH (Handbook 1964).

The dependence of neptunium $E_f^{VII/VI}$ oxidation potentials on the logarithm of the NaOH activity in solution plots as a convex curve. In the range $0.07 < a < 0.2$, the tangent, drawn with three experimental points, has a slope of -1.5×0.059 V per unit $\log(a_{NaOH})$. When the NaOH activity exceeds 0.2, the absolute value of the slope becomes greater. Oxidation potential values, determined in 0.33 M LiOH, also are located on this curve. Therefore the nature of alkali does not affect the potential value if the activity is used instead of the concentration.

Measurements, carried out at constant ionic strength ($\mu = 1$) in NaOH/NaClO₄ solutions (Zielen and Cohen 1970) and in NaOH/NaNO₃ solutions ($\mu = 1.0$ and $\mu = 1.5$) (Shilov 1970), have shown that Np(VI) oxidation to Np(VII) takes place with the participation of two OH⁻ ions. Other studies show that Np(VII) in alkaline media forms mainly $NpO_4(OH)_2^{3-}$ species (Krot et al. 1977). The rapid reversibility of the Np(VII)/Np(VI) pair indicates that the ion structures are similar and coordination numbers in both oxidation states are equal to 6. Therefore Np(VI) in alkaline solutions most probably exists as $NpO_4(H_2O)_2^{2-}$ or $NpO_2(OH)_4^{2-}$. The redox Np(VI) $\rightleftharpoons$ Np(VII) equilibrium may be written as:

The Nernst equation for this electrochemical process will look like

$$E_f^{VII/VI} = E^{\circ, VII/VI} + \frac{RT}{nF} \ln \frac{[Np(VII)]\gamma_3 \cdot a_{H_2O}^2}{[Np(VI)]\gamma_2 \cdot a_{OH^-}^2} \quad (2)$$

In concentrated NaOH solutions, the slope E_f vs. $\log(a_{NaOH})$ increases to -3.36×0.059 . The additional potential drop is accounted for by the decrease of the γ_3/γ_2 ratio and by the decrease of water activity. The slope of this curve in dilute alkaline solutions, equal to -1.5×0.059 , proves that the electrochemical process may occur by two parallel pathways (1) and (3):

Figure 2-4. Dependence of Actinide Formal Potentials on Alkali Concentration.

The dependence of $E^{o,VI/V}$ on $\log(a_{NaOH})$ looks like a concave curve; the slope at low NaOH concentration is -3×0.059 . When the a_{NaOH} becomes greater than 0.8, the absolute value of the slope decreases to -0.93×0.059 .

Compounds of Np(V) with alkali metals (Me) were precipitated from alkaline solutions of different concentrations. The ratios Me/Np in these compounds are presented in Table 2-2.

Table 2-2. Me/Np Ratios in Solid Np(V) Compounds, Precipitated From Alkaline Solutions of Different Concentrations.

NaOH conc., M	0.02	2.1	15.0
Me/Np in precipitate	$\cong 0.01$	1.01 ± 0.03	2.2 ± 0.03

Thus in NaOH solutions, Np(V) may exist as $NpO_2OH \cdot xH_2O$, $NpO_2(OH)_2(H_2O)_2^-$, $NpO_2(OH)_3(H_2O)^{2-}$ and $NpO_2(OH)_4^{3-}$. Coordination number 6 was found to be characteristic for Np(V) in alkaline solutions since the Np(V)/Np(VI) redox pair is reversible and redox transformations are rapid. The existence of practically all mentioned ionic states of neptunium(V) was proved spectrophotometrically (Tananaev 1990b). Electrochemical Np(V)/Np(VI) processes in dilute alkaline solutions take place according to the reactions:

In solutions with a_{NaOH} greater than 0.8, the reaction is:

The dependence of $E_f^{VI/V}$ on the solution composition should look like:

$$E_f^{VI/V} = E^{o,VI/V} + \frac{RT}{nF} \ln \frac{[Np(VI)]\gamma_{2-a_{H_2O}}}{[Np(V)]\gamma_{2-a_{OH^-}}} \quad (7)$$

Because the slope of this curve, determined experimentally, was found to be -0.93×0.059 instead of -1.0×0.059 , the reaction:

seems to play a certain role in the electrochemical process. In the latter case, the value of the γ_2/γ_3 ratio should be included in the equation for $E_f^{VII/V}$ determination. This ratio increases approximately 0.06 V per unit of $\log(a_{NaOH})$, opposite the trend noticed for the Np(VII)/Np(VI) redox equilibrium. This increase to some extent depresses the potential drop caused by reaction 8.

The dependence of $E_f^{VII/VI}$ on $\log(a_{NaOH})$ for plutonium is expressed by a convex curve. The tangent of the starting part of the curve has a slope -2×0.059 , indicating the participation of two hydroxide ions in the redox reaction. Pu(VII) exists in alkaline solutions as $PuO_4(OH)_2^{3-}$ (Krot et al. 1977). Because of the demonstrated reversibility of the Pu(VII)/Pu(VI) pair and the high rate of the corresponding redox reactions, Pu ions in both oxidation states are likely to possess similar structures and the same coordination number 6. Therefore the most probable forms for plutonium(VI) existence in alkaline media are $PuO_2(OH)_4^{2-}$ and $PuO_4(H_2O)_2^{2-}$. The equation of the redox reaction in alkaline media has the form:

and the Nernst equation may be written as

$$E_f^{VII/VI} = E^{\circ, VII/VI} + \frac{RT}{nF} \ln \frac{[Pu(VII)]\gamma_3 \cdot a_{H_2O}^2}{[Pu(VI)]\gamma_2 \cdot a_{OH^-}^2} \quad (10)$$

In concentrated NaOH solutions the downward slope of the curve $E_f^{VII/VI}$ vs. $\log(a_{NaOH})$ is found to increase, reaching -3.09×0.059 . The additional potential drop of 0.060 V per unit $\log(a_{NaOH})$ is caused by the reduction of the γ_2/γ_3 ratio and the simultaneous reduction of water activity.

The $E_f^{VI/V}$ potential for the Pu(VI)/Pu(V) pair was found to decrease by 20 mV/unit $\log(a_{NaOH})$. Pu(V) compounds, obtained by Pu(VI) reduction, were isolated from 4 M NaOH solution. They were found to be of the same structure as the corresponding Np(V) compounds: $MeNpO_2 \cdot xH_2O$ and $Me_2NpO_2(OH)_3 \cdot xH_2O$ (Tananaev 1992). Based on these data it may be assumed that Pu(V) exists in alkaline solutions as $PuO_2(OH)_2(H_2O)_2$ and $PuO_2(OH)_3(H_2O)^{2-}$ ions, containing a number of water molecules satisfying the coordination number 6. If Pu(V) participates in redox reactions as an anion with a double negative charge, the redox equilibrium may be written as:

and the dependence of $E_f^{VI/V}$ on the solution composition should have the form:

$$E_f^{VI/V} = E^{\circ, VI/V} + \frac{RT}{nF} \ln \frac{[Pu(VI)]\gamma_2 \cdot a_{H_2O}}{[Pu(V)]\gamma_2 \cdot a_{OH^-}} \quad (12)$$

It is difficult to imagine a significant difference between the activity coefficients of Pu(VI) and Pu(V). Therefore the mechanism of the electrochemical process including the two parallel reactions (11) and (13) may be assumed.

In the latter case, the γ_2/γ_3 ratio should be included in the Nernst equation. The latter ratio is known to increase 60 mV per unit $\log(a_{NaOH})$, opposite to the trend noticed in the Pu(VII)/Pu(VI) pair. This increase impedes to a significant degree the potential drop caused by reaction (11).

The dependence of $E_f^{VI/V}$ on $\log(a_{NaOH})$ may be satisfactorily explained by a semilogarithmic plot. The slope of the plot is -2×0.059 per unit $\log(a_{NaOH})$. Therefore the equation of the redox reaction Pu(IV)/Pu(V), taking into account the chemical state of the latter in the alkaline solution, is consistent with:

The Nernst equation for this equation may be written as:

$$E_f^{VI/V} = E^{\circ, VI/V} + \frac{RT}{nF} \ln \frac{[Pu(V)]\gamma_2 \cdot a_{H_2O}}{[Pu(IV)]\gamma_2 \cdot a_{OH^-}^2} \quad (15)$$

The possibility of the existence of the $Pu(OH)_5^-$ form in alkaline media is made after careful comparison of corresponding U(IV) hydroxide behavior. U(IV) is known to undergo hydrolysis according to the complex five-step mechanism.

Moreover, the compound $NH_4U(OH)_5$ was prepared under hydrothermal conditions and its structure has been investigated (Mefod'eva and Krot 1987).

The oxidation potential of the Pu(IV)/Pu(III) pair is linearly dependent on $\log(a_{\text{NaOH}})$; the slope is -0.15 V per unit $\log(a_{\text{NaOH}})$. Redox equilibrium in the Pu(IV)/Pu(III) system may be described by the equation:

Such a reaction should give the slope equal to 2×0.059 . The reason for the additional potential drop has not yet been found.

The form of existence of actinide ions in alkaline media deduced from considerations of redox equilibria do not exclude the possibility of the existence of other chemical states proved by different analytical techniques. This is particularly the case for Pu(IV) species, known to be present in alkaline solutions mainly as $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. Oxidation potentials of the actinides in neutral and alkaline solutions were calculated using the information about the different chemical forms of the actinides (Connick 1955; and Latimer 1954). To estimate the oxidation potential for the Am(VI)/Am(V) pair, the hydrolysis constants of PuO_2^{2+} and PuO_2^+ in solutions with pH greater than 7 were used. In the case of Np and Pu, the theoretical estimates were found to be in good compliance with experimental data (Simakin et al. 1973; Bourges 1972; and Peretrukhin and Alekseeva 1974b). At the same time, the experimentally determined oxidation potential values for Am appear to be approximately 400 mV lower than predicted by theoretical estimations (Nikolayevsky et al. 1974).

In the case of the Pu(V)/Pu(IV) pair, the calculations of oxidation potential have given 0.86 V, while experimental data have shown -0.75 V (Peretrukhin and Alekseeva 1974b). As previously discussed, such a significant discrepancy is caused by several effects. In particular, to calculate the concentration of plutonium(IV) in alkaline solutions, the value deduced from the $\text{Pu}(\text{OH})_4$ solubility product, determined in weakly acidic solution, has been used. Because the composition of Pu(IV) hydroxide in equilibrium with alkaline solutions should differ sharply from that in weakly acidic media, this value should be used very carefully.

Among another oxidation potential values obtained by theoretical estimations, the potential of Cm(IV)/Cm(III) in 1 M NaOH seems to be doubtful. If 0.7 V were the potential for the Cm(IV)/Cm(III) couple, Cm(III) should be oxidized by ozone and other strong oxidizers. No experimental proof for this effect has been found (Mefod'eva and Krot 1987). The value reported for the U(VI)/U(IV) oxidation potential in 1 M NaOH also requires re-examination.

The thermodynamic stability of any actinide ion or compound is determined by several factors:

1. Propensity to disproportionation reactions; i.e., ability to form ions (compounds) containing actinides in oxidation states higher and lower than the starting material. U(V), Np(V), Pu(IV), Pu(V), Am(IV), and Am(V) are found to be unstable towards disproportionation in acidic media. In alkaline solutions, the mentioned ions lose this

ability. At the same time, disproportionation reactions in alkaline media were reported for Np(VI) (Krot et al. 1970) and Am(VI) (Nikolayevsky et al. 1975b), and proved experimentally. Theoretically, in highly concentrated alkaline solutions, the disproportionation of Pu(VI) may be assumed, but until now, no experimental proof exists for this assumption.

2. Reactions between the ions of the same element present in the solution simultaneously in different oxidation states. For example in acidic media, U(III) reacts with U(V) and U(VI); Np(III) reacts with Np(V), Np(VI), and Np(VII); Np(V) reacts with Np(VII); and Pu(III) reacts with Pu(V), Pu(VI), and Pu(VII). In alkaline media, hydroxides of U, Np, and Pu in oxidation states (+3) and (+4) exhibit the ability to reduce the corresponding actinide ions in oxidation states (+6) and (+7). At the same time actinide ions in oxidation state (+7) are able to oxidize corresponding hydroxides in oxidation state (+5).
3. Stability toward reactions with water to evolve with hydrogen or oxygen. In acidic media, only U(III), in being oxidized to U(IV), can reduce water to form molecular hydrogen. In alkaline solutions, U(III), Np(III), Np(IV), and Pu(III) hydroxide exhibit this possibility. Np(VII) and Pu(VII) in alkaline solutions oxidize water to form molecular oxygen. They are reduced to Np(VI) and Pu(VI), correspondingly.

2.5 OXIDATION POTENTIALS AND STABILITY OF TECHNETIUM IONS IN ALKALINE MEDIA

Oxidation potentials for the redox couples of technetium ions are presented in Table 2-3. Precise values are not determined for most of the oxidation potentials because of technetium instability in all oxidation states except (+7). The potential values in acidic media are calculated indirectly using other thermodynamic functions of technetium. The values for Tc oxidation potentials in alkaline media, presented in Table 2-3, are the half-wave potentials of technetium obtained by polarographic reduction in alkaline media. Included in the potential values are the unknown values of the overvoltage of the electrochemical reductions (Founta et al. 1987). Nevertheless, the data presented in Table 2-3 are sufficiently reliable to predict instability of lower oxidation states of technetium in alkaline media.

The oxidation potential for the Tc(VII)/Tc(VI) couple ($E^\circ = -0.64$ V vs. SHE) seems to be the most reliably determined couple in alkaline solution because the polarographic reduction of Tc(VII) to Tc(VI) was found to be reversible in 1 M NaOH. In this case, the value of $E_{1/2}$ is known to be close to the value of the corresponding standard oxidation potential. The Tc(VI)/Tc(V) oxidation potential is more positive than that of Tc(VII)/Tc(VI). This means that Tc(VI) hydroxide compounds should possess low thermodynamic stability due to disproportionation.

Table 2-3. Formal Oxidation Potential for Technetium Redox Couples in Acidic (Spitsyn and Kuzina 1981) and Alkaline (Founta et al. 1987; and Deutsch et al. 1978) Media.

Medium	VII/VI	VI/V	VI/IV	V/IV	IV/0	-1/0
1 M HClO ₄	0.57		1.39	0.71	0.28	-0.5
1 M NaOH	-0.64	-0.1		-0.88	-1.35	

This disproportionation reaction has been shown to be extremely fast at pH greater than 13 (Founta et al. 1987). Therefore it is impossible to prepare Tc(VI) solutions in alkaline media. Tc(V) and Tc(IV) should be more stable than Tc(VI) in alkaline solutions, but Tc(IV) hydroxide may be easily oxidized by many oxidizing agents usually present in alkaline radwastes (O₂, CrO₄²⁻, and others) possessing oxidation potentials, E°, greater than -0.7 V in 1 M NaOH.

2.6 SOLUBILITY OF TRU HYDROXIDES AND SPECIATION IN ALKALINE MEDIA

Amorphous friable hydroxides of actinides in the oxidation states (+3) and (+4) form when the corresponding acidic actinide solutions are neutralized to higher pH values. The precipitation follows actinide ions hydrolysis with formation of intermediate oxo-forms. The cations AnOHⁿ⁺ or AnO₂OHⁿ⁺ are reported to be the primary products of the actinide hydrolysis in acidic solutions. Continued hydrolysis processes include the attachment of additional OH⁻ groups to these cations. Irreversible hydroxoform polymerization occurs simultaneously with the primary hydrolysis until solid hydroxides form. The affinity for hydrolysis reactions for the actinide ions in different oxidation states decreases in the series:

Actinide hydroxides in higher oxidation states possess marked amphoteric properties. The trend to formation of anionic species is found to increase in the row (Mefod'eva and Krot 1987):

The precipitation of actinide(III) hydroxides is known to be complete in solutions with pH greater than 10. Lower actinide(III) hydroxides are unstable toward oxidation at higher pH. Increase of the pH of U(III) and Np(III) solutions results in their oxidation to oxidation state (+4) even in the absence of oxygen (see Section 2.2). The precipitate of Pu(III) hydroxide was shown to be comparatively quickly oxidized by atmospheric oxygen with

formation of Pu(IV). Am(III) and Cm(III) hydroxide at first are precipitated in amorphous forms. After heating, their crystallization followed by dehydration was noticed. X-ray analyses of Am(III) and Cm(III) hydroxide crystals have shown that they possess a hexagonal cell with space symmetry group $P6_3/m$ (Mefod'eva and Krot 1987). The nuclear gamma resonance spectrum of $\text{Am}(\text{OH})_3$ was found to have a chemical shift, δ , of 4.6 cm/s (vs. AmO_2) (Mefod'eva and Krot 1987). This value shows $\text{Am}(\text{OH})_3$ has the highest covalent properties of all Am compounds studied by this method. The An(III) hydroxides appear to be practically insoluble in water (see Table 2-4), but in crystal state are found to be easily peptized. The concentration of pseudo-soluble Am and Cm hydroxide sols may exceed 100 g/L (Haire et al. 1977).

The solubility of Am(III) hydroxide was found to be constant in solution with pH ranging from 7 to 12 up to 3 to 5 M NaOH (Pazukhin and Kochergin 1989). Constant 1.6×10^{-6} M Am concentration in solution was attributed to the chemical speciation of americium as the neutral $\text{Am}(\text{OH})_3$ molecule.

Hydroxides of actinides in oxidation state (+4), possessing the general composition $\text{AnO}_2 \cdot x\text{H}_2\text{O}$, have been reported for U, Np, Pu and Am. U(IV), Np(IV), and Pu(IV) are prepared by neutralization of the corresponding acidic solutions. At the first step, $\text{An}(\text{OH})_4$ are formed. Then, polymerization takes place, especially in case of Pu(IV) hydroxide. The exposition of the system results in the aging of the solid phase, accompanied by partial dehydration. Aging of amorphous $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}$ does not result in complete crystallization (compared with Th(IV) hydroxide); instead, precipitates with an insignificant degree of crystallinity are formed (Rai and Ryan 1982). This is attributed to the suppressing effect of precipitate auto-radiolysis on the dehydration and crystallization processes. Aging of $^{238}\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in tridistilled water during a 1,300-day period was shown to result in formation of not only amorphous hydroxide, but also a highly disperse polymer phase (Rai and Ryan 1982). Along with pH reduction due to the radiolytic formation of nitric acid in the system, the presence of this polymer phase accounts for the high plutonium(IV) solubility observed in this study.

Taking into account the values of oxidation potentials reported in Section 2.2 for the Am(IV)/Am(III) and $\text{O}_2/\text{H}_2\text{O}$ pairs in alkaline media, $\text{Am}(\text{OH})_3$ should undergo molecular O_2 oxidation with Am(IV) formation. However, the rate of this heterogeneous process was found to be so small that it could hardly be noticed experimentally (Penneman et al. 1961). Hydrated americium oxide (most probably $\text{AmO}_2 \cdot x\text{H}_2\text{O}$) was found to be formed during oxidation of $\text{Am}(\text{OH})_3$ suspensions with NaClO in 0.2 M NaOH (Penneman et al. 1961; and Penneman and Asprey 1956), with $\text{K}_2\text{S}_2\text{O}_8$ in 7 M NaOH (Penneman et al. 1961; and Penneman and Asprey 1956), or with H_2O_2 in KOH solutions (Penneman and Asprey 1956; and Buijs and Louwrier 1966)).

An(IV) hydroxides are practically insoluble in water and in alkaline solutions (see Table 2-5). Nevertheless, in presence of CO_3^{2-} ions in alkaline solutions, soluble species of An(IV) may

be prepared (Mefod'eva and Krot 1987). Moreover the solubility of Np(IV) in a 0.8 M Na_2SO_4 /0.8 M NaOH solution was reported to be 8.5×10^{-6} M (Cunningham and Hindman 1955).

Table 2-4. Selected Properties of An(III) Hydroxides.

Compound	Color	Medium	$-\log K_{sp}$	References ^a
$\text{Pu}(\text{OH})_3$	blue	$\mu=0$	19.7	[1]
			26.2	[2]
$\text{Am}(\text{OH})_3$	light-pink	0.1 M NaClO_4	25.7	[3]
		0.003 M CaCl_2	24.2	[4]
		0.1 M NaClO_4	24.8	[5,6]
		0.1 M NaClO_4	27.49	[7]
		Calculated	24.5	[8]
		Calculated	23.5	[9]
		$\mu=3.0$	27.4	[10]
$\text{Cm}(\text{OH})_3$	white			[11]

^aReferences:

- [1] Katz and Seaborg 1957
- [2] Felmy et al. 1989
- [3] Stadler and Kim 1988
- [4] Rai et al. 1983
- [5] Silva 1982
- [6] Silva 1983
- [7] Bernkopf and Kim 1984
- [8] Phillips 1982
- [9] Allard 1982
- [10] Pazukhin and Kochergin 1989
- [11] Mefod'eva and Krot 1987

An(IV) hydroxides may exist as $\text{An}(\text{OH})_4$, $\text{AnO}_2 \cdot x\text{H}_2\text{O}$, $\text{AnO}_2(\text{cryst.})$, and $\text{An}(\text{OH})_5^-$ ions. The solubility of actinide hydroxides in alkaline media in the presence of such complex forming agents as α -oxycarbonic acids and aminocarboxylic acids has been reported (Myasoedov et al. 1980).

An(V) hydroxides are known to possess slightly amphoteric properties. Their existence is reported for uranium, neptunium, plutonium, and americium. Soluble U(V) hydroxide has been prepared by electrochemical reduction of U(VI) in NaOH solutions. The solubility product of uranium(V) hydroxide is presented in Table 2-6 and is also available in Musicas and Rousset (1971).

$\text{NpO}_2\text{OH} \cdot x\text{H}_2\text{O}$ may be precipitated as a pale-green amorphous solid phase from acidic Np(V) solutions after addition of a small excess of ammonia or alkali (Cunningham and Hindman 1955). If the excess of alkali added to the Np(V) solution is too large, violet compounds of $\text{NaNpO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ or $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ composition are formed (Visyascheva et al. 1984). The structures of these compounds are expected to consist of layers of $\text{NpO}_2(\text{OH})_2^-$ and $\text{NpO}_2(\text{OH})_3^{2-}$, correspondingly. NpO_2^+ ions in these layers are situated in the equatorial plane and are coordinated with 6 OH^- groups.

Reactions of NpO_2^+ ion with hydroxyl ions may be expressed by the equations:

Existence of these forms was proved potentiometrically (see Section 2.4) and spectrophotometrically (Tananaev 1990b). The solubility product of NpO_2OH and equilibrium constants for Np(V) anion formation in alkaline media are presented in Table 2-7.

Actinide solubility in aqueous alkaline solutions may be calculated according to the equation:

$$[\text{An(V)}] = K_{\text{sp}} \times [\text{OH}^-]^{-1} \times (1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2 + \dots + \beta_n[\text{OH}^-]^n)$$

For example, the solubility of Np(V) in 1 M NaOH was calculated as 1.3×10^{-5} M (Neck et al. 1992) or 1.2×10^{-4} M (Lierse et al. 1985). The solubilities of Np(V) hydroxide, determined experimentally, are presented in Table 2-7.

The addition of alkaline solutions to weakly acidic solutions of Np(V) may result in formation of alkaline Np(V) solutions with concentration up to $(6 \text{ to } 7) \times 10^{-4}$ M in 1 M NaOH (Simakin et al. 1973). Such systems seem to be metastable. If tetraalkylammonium hydroxide solutions were used in such experiments, Np(V) concentration in the final solution was found to achieve more than 10^{-3} M (Cohen and Fried 1969).

The precipitate of $\text{PuO}_2\text{OH}\cdot x\text{H}_2\text{O}$ has been obtained by the addition of alkali to a freshly prepared weakly acidic solution of Pu(V) (Gel'man and Zaitseva 1964). The solubility product of this compound is presented in Table 2-6. Pale green compounds are formed upon reduction of Pu(VI) in 4 M MeOH (Me = Li, K, Rb). The compounds are found to be isostructural with the corresponding Np(V) hydroxides with composition $\text{MeNpO}_2(\text{OH})_2\cdot x\text{H}_2\text{O}$. At alkali concentration was greater than 4 M, white compounds isostructural with $\text{Me}_2\text{NpO}_2(\text{OH})_3\cdot x\text{H}_2\text{O}$ were reported to be formed (Tananeav 1992).

Table 2-5. Values of Solubility of Actinide (IV) Hydroxides in Different Media and their Solubility Products.

Compound	Medium	Solubility M	$-\log K_{\text{sp}}$	References ^a
$\text{U}(\text{OH})_4$	$\mu=0.09-0.18$		51.96 ± 0.22	[1]
$\text{UO}_2\cdot x\text{H}_2\text{O}$	0.045-1.0 LiOH		59.16 ± 0.2	[2]
UO_2 (cr)	1M NaOH	10^{-8}		[3]
$\text{UO}_2\cdot x\text{H}_2\text{O}$	calculation	10^{-14}	52.6	[3]
$\text{UO}_2\cdot x\text{H}_2\text{O}$	$\mu=0$		52.0 ± 0.8	[4]
$\text{Np}(\text{OH})_4$	0.8 M Na_2SO_4	8.5×10^{-6}		[6]
$\text{Np}(\text{OH})_4$	0.8 M NaOH		55.22	[7]
$\text{Np}(\text{OH})_4$	Calculation		53 ± 2	[8]
$\text{Np}(\text{OH})_4$ (cr)			56	[9]
$\text{NpO}_2\cdot x\text{H}_2\text{O}$		5×10^{-9}		[10]
$\text{NpO}_2\cdot x\text{H}_2\text{O}$			54.5 ± 0.3	[4]
$\text{Pu}(\text{OH})_4\cdot x\text{H}_2\text{O}$	Calculation		55.15	[11]
$\text{Pu}(\text{OH})_4$			52.0	[12]
$\text{Pu}(\text{OH})_4$	$\mu=0.288$		58.19	[13]
$\text{Pu}(\text{OH})_4$	$\mu=0.0033$		51.06	[13]
$\text{Pu}(\text{OH})_4$	$\mu=0.0003$		47.97	[13]
$\text{Pu}(\text{OH})_4$			50.2	[14]
$\text{PuO}_2\cdot x\text{H}_2\text{O}$			56.85 ± 0.36	[15]
$\text{Pu}(\text{OH})_4$ (am)			57.82 ± 0.17	[16]
$\text{Pu}(\text{OH})_4$ (cr)			60.20 ± 0.17	[16]
$\text{Pu}(\text{OH})_4$	$\mu=3$		51.43	[17]
$\text{AmO}_2\cdot x\text{H}_2\text{O}$	Calculation		58.0	[4]
$\text{CmO}_2\cdot x\text{H}_2\text{O}$	Calculation		59.1	[4]

Table 2-5. Values of Solubility of Actinide (IV) Hydroxides in Different Media and their Solubility Products.

*References:

- [1] Stepanov and Galkin 1960
- [2] Nikolaeva and Pirozshkov 1978
- [3] Ryan and Rai 1983
- [4] Rai et al. 1987
- [5] Rai et al. 1990
- [6] Cunningham and Hindman 1955
- [7] Moskvina 1971
- [8] Allard et al. 1980
- [9] Lieser et al 1985
- [10] Rai and Ryan 1985
- [11] Connick 1955
- [12] Latimer 1954
- [13] Perez-Bustamante 1965
- [14] Rai et al. 1980
- [15] Rai 1984
- [16] Kim and Kanellakopulos 1989
- [17] Pazukhin and Kudryavtsev 1990

Table 2-6. Solubility Products and Hydrolysis Constants of An(V).

Actinide	$-\log K_{sp}$	$\log \beta_1$	$\log \beta_2$	μ	References ^a
U(V)	9				[1]
Np(V)	9.0	3.92		0.2	[2]
	9.73	5.1		0.02	[3]
		3.92			[4]
		4.68		1.0	[5]
	9.2			0.1	[6]
	8.81	2.33	4.89	1.0	[7]
		4.16		1.0	[8]
	9.85	3.18	5.15	3.0	[9]
	9.30	2.67	4.41	2.0	[9]
	8.56	2.44	4.10	0.1	[9]
	10.21	2.91	5.50	0.8	[10]
	8.94	2.67	5.74	0.1	[10]
	8.04		5.16	0.012	[10]
Pu(V)	8.8	4.6		0	[6]
	9.3				[11]
Am(V)	9.3	1.7		3.0	[12]

^aReferences

- [1] Allard et al. 1980
- [2] Moskvina 1971
- [3] Sevostyanova and Khalturin 1976
- [4] Vodovatov et al. 1976
- [5] Maya 1983
- [6] Kraus 1955
- [7] Lierse et al. 1985
- [8] Bidoglio et al. 1985
- [9] Neck et al. 1992
- [10] Itagaki et al. 1992
- [11] Gel'man and Zaitseva 1964
- [12] Stadler and Kim 1988

Table 2-7. Solubilities of Np(V) in Different Basic Solutions
(Cunningham and Hindman 1955).

Medium	Solubility, M
Diluted NH_4OH	7.6×10^{-4}
1 M NaOH	7.2×10^{-5}
2.2 M NaOH	5.9×10^{-5}

The equilibrium solubility of Pu(V) has not yet been determined. Taking into account that the hydrolytic behavior of Np(V) and Pu(V) are similar and both of them have similar values of solubility products, the value of about 1.0×10^{-4} M may be expected for Pu(V) solubility in 1 M NaOH. As in case of Np(V), the preparation of concentrated Pu(V) alkaline solutions has been reported. For example, the UV-Vis spectrum of 4×10^{-3} M Pu(V) solution in 4 M NaOH is presented (Bourges 1972).

The precipitation of $\text{AmO}_2\text{OH} \cdot x\text{H}_2\text{O}$ has been achieved by the addition of NH_4OH or KOH to weakly acidic solutions of Am(V) (Zubarev and Krot 1982). The solubility product of this compound is presented in Table 2-6. In 0.86 M NH_4OH solution, Am(V) concentration in equilibrium with solid $\text{AmO}_2\text{OH} \cdot x\text{H}_2\text{O}$ was found to be 0.22 g/L. Increase of the NH_4OH concentration to 7 M resulted in the corresponding increase of Am(V) concentration to 1.41 g/L (Zubarev and Krot 1982). In KOH solution the reverse effect of alkali concentration has been observed: in 0.46 M KOH, Am(V) concentration was found to be 0.029 g/L and in 5.3 M NaOH, less than 0.02 g/L (Zubarev and Krot 1982).

The compounds $\text{MeAmO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ (Me = Li, Na, K) were found to be formed in 0.1 to 0.5 M alkaline solutions. In NaOH or KOH solutions of less than 2 M OH^- , $\text{Me}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ formation has been reported (Tananaev 1990a). These data prove the existence of such chemical forms of Am(V) as $\text{AmO}_2(\text{OH})_2(\text{H}_2\text{O})_2$ and $\text{AmO}_2(\text{OH})_3(\text{H}_2\text{O})_2^-$ in alkaline media (Tananaev 1992a).

Actinide(VI) hydroxides are reported for uranium, neptunium, plutonium, and americium. Alkaline metals and ammonium mono- and polyuranates are obtained by adding ammonia or the corresponding alkali to the aqueous uranyl solutions. In the reactions of uranates (polyuranates) with H_2O_2 , peroxouranates are formed. Uranates are characterized by much lower solubility in aqueous solutions than corresponding peroxouranates (see Table 2-8 and [Weigel 1986]). The solubility of uranium(VI) hydroxide in 1 M NaOH equals 200 ppm or 4×10^{-4} M (Zantuti et al. 1991).

Table 2-8. Solubility Products of An(VI) Hydroxides.

Actinide	$-\log K_{SP}$	References ^c
U(VI)	22.7 ^a	[1]
	21.74 ^b	[2]
	22.4 $\pm$ 0.2 ^a	[3]
Np(VI)	22.7	[4]
	22.7 $\pm$ 1.2	[3]
Pu(VI)	24.5	[5]
	22.75	[6]
	22.8 $\pm$ 1	[3]

^acalculated value^bdetermined experimentally in solution with $\mu=2$.^cReferences:

[1] Latimer 1954

[2] Babko and Kodenskaya 1960

[3] Allard et al. 1980

[4] Moskvina 1971

[5] Gel'man et al. 1961

[6] Moskvina and Zaitseva 1962

Plutonium(VI) hydroxides possess noticeable solubility in alkaline media (see Table 2-9).

Table 2-9. The Solubility of Plutonium(VI) Hydroxides in Alkaline Solutions of Different Concentrations (Perez-Bustamante 1965).

[OH ⁻], M	0.11	1.00	2.00	5.00	10.0
10 ⁵ x [Pu(VI)], M	1.05	3.24	4.36	6.98	10.3

Addition of concentrated alkali to weakly acidic solution of Np(VI) or Pu(VI) yields solutions containing up to 0.01 M Np(VI) in 1 M LiOH and to 0.0075 M Pu(VI) in 1 to 3 M NaOH (Mefod'eva et al. 1977). When Np(VII) is reduced in alkaline media, metastable solutions of Np(VI) are formed. Electrochemical reduction of Np(VII) in NaOH results in the formation of Np(VI) solution with metal concentration 20 times higher than can be obtained by direct Np(VI) dissolution in alkali (Zielen and Cohen 1970).

Potentiometric measurements prove An(VI) to exist in alkaline media as $AnO_2(OH)_4^{2-}$ (see Section 2.4). The same form is expected after consideration of results of spectrophotometric investigations Np(VI) and Am(VI) in alkaline solutions (Tananaev 1989).

Hydroxides of actinides in oxidation state (+7) are prepared only in the cases of Np, Pu, and Am. $\text{AnO}_4(\text{OH})_2^{3-}$ is known to be the common chemical form of An(VII) existence in alkaline media. Solid actinide(VII) compounds, however, may contain other structures. The preparation of MeNpO_4 and $\text{MeNpO}_4 \cdot x\text{H}_2\text{O}$ ($\text{Me} = \text{Li, Na, NH}_4$) from solutions has been reported (Mefod'eva and Krot 1987). An(VII) compounds are soluble in water and aqueous alkaline solutions. It is possible to prepare 0.2 M Np(VII) solution in 2 to 3 M LiOH (Mefod'eva and Krot 1987).

The present review shows that actinide hydrous oxides in different oxidation states may exist in alkaline media as ions, neutral molecules, colloid and pseudocolloid particles, as well as solid phases. The solubility products of $\text{An}(\text{OH})_3$ and $\text{An}(\text{OH})_4$ are found to be so small that the concentration of An^{+3} and An^{+4} ions in alkaline solution, equilibrated with the solid hydroxide phase, should be rather small. Nevertheless, in the case of Am(III), Am(OH)₃ molecules were proved to exist in the supernatant after separation of solid phase and colloid particles.

Potentiometric measurements have proved An(IV) to exist in alkaline solutions not only as $\text{An}(\text{OH})_4$ and $\text{AnO}_2 \cdot x\text{H}_2\text{O}$, but also as $\text{An}(\text{OH})_5^-$ ions. An(V) exists as AnO_2OH , $\text{AnO}_2(\text{OH})_2^-$, $\text{AnO}_2(\text{OH})_3^{2-}$, and $\text{AnO}_2(\text{OH})_4^{3-}$; An(VI) as AnO_2OH^+ , $\text{AnO}_2(\text{OH})_2$, $\text{AnO}_2(\text{OH})_3^-$, $\text{AnO}_2(\text{OH})_4^{2-}$ or $\text{AnO}_4(\text{H}_2\text{O})_2^{2-}$; and An(VII) as $\text{AnO}_4(\text{OH})_2^{3-}$.

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3.0 REDOX REACTIONS OF ACTINIDES AND TECHNETIUM IN ALKALINE MEDIA AND PREPARATION OF ACTINIDES IN SELECTED OXIDATION STATES

Redox reactions of actinides in alkaline media were studied primarily in the preparation of heptavalent neptunium, plutonium, and americium and for the reduction of heptavalent actinides by different reagents. In addition, the oxidation reactions of Am(III) and Pu(IV) in alkaline media were investigated.

3.1 OXIDATION REACTIONS

Different oxidizing agents were used in the oxidation reactions of actinides. The principal oxidizing agent studied is ozone. Other oxidizing agents include persulfate, hypobromite, hypochlorite, ferricyanide, xenon compounds, silver oxides, and permanganate.

3.1.1 Oxidation by Ozone

Ozone is one of the strongest oxidizing agents in alkaline media, $E^\circ = 1.24 \text{ V (NHE)}$. Its potential is higher than the potentials of all the actinide pairs considered in Section 2.0.

3.1.1.1 Preparation of Neptunium(VII). The oxidation of suspensions of sodium or potassium neptunates in 0.5 to 5.0 M alkalis by ozone was the initial method of neptunium(VII) preparation (Krot and Gel'man 1967; Krot et al. 1968). After some improvements this method has become the most effective procedure for the preparation of high purity neptunium(VII) solutions used in research practice.

The interaction of ozone with Np(VI) in alkaline media is a complex heterogeneous process dependent on many factors. The solution purity plays an important role (Krot et al. 1968). For example, Np(VI) oxidation can begin only after the complete decomposition of reducing agent impurities by ozone.

The kinetics of the reaction between ozone and Np(VI) strongly depends on the state of neptunium in alkaline media. When suspensions of neptunates in NaOH or KOH solutions are ozonized, the physical-chemical properties of the solid phase (in addition to the regime of O_3 bubbling) have a considerable effect on the Np(VII) formation rate. Under otherwise similar conditions, the rate of Np(VI) oxidation increases with increasing surface area of the neptunate precipitate. The surface area depends on many diffusion-controlled factors. Because of the variability, data on the ozonation kinetics of neptunate suspensions are not reproducible, and only qualitative conclusions are possible.

Note that long standing of precipitates leads to a decrease in the rate of Np(VI) oxidation because of the aging effect. Because of the aging, accumulation of Np(VII) by use of ozonation decreases with time and the complete dissolution of neptunates usually can not be reached. In this connection, the use of the NpO_2OH suspension in NaOH solution instead of neptunates is interesting (Zielen and Cohen 1970). Upon ozonation, Np(V) is oxidized initially to Np(VI) and then to Np(VII).

The oxidation of Np(VI) in the form of the hydroxide precipitate in NaOH or KOH proceeds best in solutions with alkali concentration of 2 to 3 M. In solutions with other concentrations, the formation rate of Np(VII) is lower. This is due to the overlapping of two opposite effects: increase in the solubility of neptunates, and decrease in the solubility of O_3 in the solution phase, with increase in alkali concentration.

The maximal concentration of Np(VII) attainable by the oxidation of neptunate suspensions in NaOH or KOH solutions is about 6 to 8 g/L. More concentrated solutions of Np(VII) can be prepared when LiOH is used (Blokhin et al. 1970). Solutions with Np(VII) concentration of about 30 g/L may be produced by ozonation of neptunates in 2 to 3 M LiOH. The higher concentrations can be explained by the higher solubility of lithium neptunates (Cohen and Fried 1969).

The kinetics of Np(VII) formation in dilute alkaline solutions free of neptunate precipitates is determined primarily by the rate of ozone supply and the intensity of mixing the phases; (i.e. by diffusion parameters) (Krot et al. 1968, Shashukov and Kozlov 1970, Mefod'eva et al. 1977). The rate of reaction between ozone and Np(VI) is controlled by kinetic parameters only at low concentrations of reagents [0.1 to 0.5 vol. % O_3 in the gas mixture, $(2 \text{ to } 4) \times 10^{-5}$ M Np(VI) in KOH solution] (Shashukov and Kozlov 1970). Under such conditions, the accumulation of Np(VII) is described by the equation:

$$d\text{Np(VII)}/dt = k[\text{Np(VI)}][\text{O}_3^{\text{gas}}]^{1/2} \quad (1)$$

The constant k is equal to $0.59 \text{ mol}^{-1/2}\text{L}^{3/2}\text{s}^{-1}$ for 1 M KOH and 20°C . The k value increases with the decrease in alkali concentration. However, from these data it is impossible to determine the reaction order for hydroxide ions, because the solubility of O_3 in the solution phase changes with the change in alkali concentration. In the same way, the complex temperature dependence of the Np(VI) oxidation rate reflects a combination of the influence of temperature on the reaction of Np(VI) with the dissolved ozone and the distribution of ozone between the gas phase and the alkali solution.

At Np(VI) concentrations of about 10^{-2} M, the oxidation by ozone usually is in a kinetic regime controlled by diffusion parameters (Mefod'eva et al. 1977). Under these conditions, the rate of Np(VII) accumulation at constant rates of O_3 supply and stirring intensity is typical for reactions of zero order:

$$d[\text{Np(VII)}]/dt = v = \text{constant} \quad (2)$$

The rate of Np(VI) oxidation is constant during the entire period required to complete the reaction.

Under otherwise similar conditions, the rate, v , is proportional to $[O_3^{2-}]^{1/2}$. The dependence of the oxidation rate on LiOH concentration is described by a curve with a maximum. The rate of Np(VII) formation decreases with decrease in the alkali concentration, in spite of the increased solubility of O_3 in the liquid phase. On this basis, it is possible to conclude that Np(VI) is oxidized not only by O_3 but also by the products of its decomposition (e.g., by the ozonide ion, O_3^-). The decomposition of O_3 by reducing agents is accelerated by decreasing alkali concentrations.

In spite of the decrease in the reaction rate, Np(VI) is oxidized by ozone even at pH 9 to 10 (Shilov 1977). Moreover, neptunium is converted partially to the heptavalent state upon ozonation of a NpO_2OH suspension in water (Chaikhorsky 1974).

The completeness of Np(VI) oxidation depends upon the Np(VI) concentration. For instance, $(2 \text{ to } 4) \times 10^{-5}$ M Np(VI) is oxidized to 80% completion (Shashukov and Kozlov 1970), and 3×10^{-3} M Np(VI) to 98 to 100% completion (Mefod'eva et al. 1977).

3.1.1.2 Preparation of Plutonium(VII). Like Np(VII), heptavalent plutonium was originally prepared using ozone (Krot and Gel'man 1967; Komkov et al. 1968). Ozonation remains the principal method for the preparation of pure Pu(VII) solutions of different concentrations.

The interaction of Pu(VI) with ozone in alkaline media is similar to the oxidation of Np(VI) (Mefod'eva et al. 1977). The reaction rate in homogeneous solutions is determined by diffusion parameters. At sufficiently low concentrations of Pu(VI) and O_3 , it may be possible to find conditions at which the reaction rate will be within the kinetic region. However, no supporting experimental data exist.

The rate of Pu(VII) formation, when the O_3 supply to the solution is constant, is described by an equation of zero order (Mefod'eva et al. 1977):

$$d[Pu(VII)]dt = v = \text{constant} \quad (3)$$

In solutions of alkalies containing hydroxide precipitates, the Pu(VI) oxidation occurs considerably faster than the Np(VI) oxidation. This effect is explained by the higher solubility of plutonates in NaOH solutions in comparison with neptunates.

The completeness of Pu(VI) oxidation in solutions with OH^- concentrations less than 1 M depends to some extent on the instability of Pu(VII); the rate of its reduction by water increases with decreasing OH^- concentration (Krot et al. 1977a).

3.1.1.3 Preparation of Americium(VII). The oxidation of Am(VI) can be carried out successfully in solutions with high concentration of hydroxide (Krot et al. 1974). However, the solubility of O₃ decreases strongly at high concentration of OH⁻. Taking into account these opposite trends, it was determined that the optimal concentration of OH⁻ for Am(VI) oxidation is about 3 to 4 M. Temperature also is an important parameter. The rate of Am(VII) reduction by water is decelerated on cooling while O₃ solubility increases. Therefore, lower temperatures favor Am(VII) formation. Finally, it is important to use pure solutions, because even low concentrations of impurities sharply decrease the stability of strong oxidizing agents in alkaline media.

It was established that 30 to 60 minutes of bubbling of a gas mixture with O₃ concentrations of 20 to 50 mg/L through a cooled (to 0 °C) solution of Am(VI) in 3 to 4 M NaOH leads to a change of the color and optical absorption spectrum of the solution. If a freshly-ozonized alkaline solution of americium is added to a stoichiometric excess of Pu(VI) in 1 M NaOH solution, the color characteristic of Pu(VII) appears almost instantly.

It has been shown that Am(VI) does not oxidize Pu(VI) in solutions with less than 3 M NaOH (Nikolaevsky 1974). The observed formation of Pu(VII) proves that Am(VI) is converted to Am(VII) by ozonation in alkaline solution:

The yield of Am(VII), evaluated by measurements of the formed Pu(VII) concentration, was 40 to 60%. Similar results were obtained from study of the stoichiometry of the reaction:

3.1.1.4 Preparation of Americium(VI). Ozone oxidizes Am(OH)₃ to Am(VI) at all pHs from neutral medium to 1 M NaOH (Penneman et al. 1961). In 1 M NaOH, the oxidation occurs slowly; to increase the O₃ solubility, it is necessary to work at 0 °C. At 25 °C, Am(OH)₃ in 0.1 M NaOH is oxidized with moderate rate to Am(VI), a soluble yellow complex. In water, Am(OH)₃ can be oxidized at 90 °C by 1 to 2 hours bubbling of ozone. The pH upon ozonation should not be less than 5.

The spectrum of the yellow complex of Am(VI) is identical to the spectrum of the solution obtained upon the addition of alkali to an acid solution of AmO₂²⁺.

3.1.2 Disproportionation of Neptunium(VI) and Americium(VI)

Compared with the extensively-studied disproportionation reactions of tetra- and pentavalent actinides in acid solution, the disproportionations of hexavalent neptunium and americium in alkaline media are not well known.

By electrochemical arguments, the necessary condition for the occurrence of the disproportionation of an element in the hexavalent state is the proximity of the potentials E_f (VII/VI) and E_f (VI/V). In the case of neptunium and americium, the potentials of the mentioned pairs in 1 M NaOH differ by about 0.4 V. The value of E_f (VII/VI) decreases strongly with increasing alkali concentration, whereas the value of E_f (VI/V) changes slightly. Therefore, at greater than 10 M NaOH, penta-, hexa- and heptavalent states of neptunium or americium can coexist.

Experimental tests have shown that rapid 10 to 20-fold dilution of a colorless 5×10^{-3} M solution of Np(VI) with 17 M NaOH leads to the appearance of the green color characteristic of Np(VII) (Krot et al. 1970). The optical absorption spectrum of the solution in the visible region after the removal of air bubbles is close to the spectrum of Np(VII). A difference in the absorbance over the wavelength region occurs because of the presence of Np(VI).

The equilibrium:

is achieved at room temperature in less than one minute. The equilibrium position strongly depends on the NaOH concentration. Neptunium(VII) is practically not formed in solutions with less than 9 M NaOH. The yield of Np(VII) increases sharply with increasing alkali concentration to 17 M. The values of the equilibrium constant, $K_6 = [\text{Np(VII)}][\text{Np(V)}]/[\text{Np(VI)}]^2$, are shown in Table 3-1.

The disproportionation of Np(VI) was also studied in the case of hot solutions of NaOH (in which neptunates are more soluble than at room temperature) (Ermakov et al. 1977). Because the viscosity of the alkali solutions decreases with increasing temperature and, as a consequence, air bubbles are easily removed, well-reproducible values of the equilibrium constant could be obtained.

The K_6 values under the studied conditions are not temperature dependent. Hence, the activation energy for the disproportionation of Np(VI) and the reduction of Np(VII) by Np(V) are equal within experimental error.

Disproportionation was studied for KOH and CsOH aqueous solutions and also for water-ethanol solutions of KOH (Tananaev 1991). The nature of alkali plays a low role, whereas the decrease in the water content favors disproportionation. For example, in a solution containing 60 vol. % CH_3OH , disproportionation occurs to noticeable extent in 4 M KOH.

Table 3-1. Disproportionation of Np(VI) in NaOH Solutions (at 21 to 23 °C).

[NaOH], M	[Np(VI)] _o x 10 ⁴ , M	[Np(V)] _o x 10 ⁴ , M	[Np(VII)] x 10 ⁵ , M	K ₆ x 10 ²
8.7	9.52	-	1.2	1.7 x 10 ⁻²
10.7	9.52	-	3.5	0.16
11.8	2.38	-	1.4	0.44
12.4	5.00	-	3.8	0.8
13.6	2.38	-	2.8	2.4
14.8	4.55	-	7.8	6.8
15.3	2.38	-	4.3	8.0
17.2	2.38	-	5.1	13.2
13.6	2.38	0.33	1.8	2.2
13.6	2.38	0.84	1.5	3.4
13.6	2.38	2.50	0.45	2.5

Disproportionation of Am(VI) has been observed (Nikolaevsky 1975). In a quartz cell, 2.5 to 3.0 mL of cooled (to 0 °C) 18 M NaOH were mixed with 0.2 mL of cooled slightly-acid 3 x 10⁻² M Am(VI). The optical absorption spectrum of the resulting solution had a band with a peak at 740 to 750 nm characteristic of Am(VII). Because there were no other oxidizing agents in the solution, the formation of Am(VII) was possible only as a result of the disproportionation of Am(VI):

The approximate values of K₇ (= [Am(VII)][Am(V)]/[Am(VI)]²) are shown in Table 3-2.

Disproportionation of Am(VI) is slightly more extensive than that of Np(VI) at a given NaOH concentration. However, in both cases, features of influence of the NaOH concentration on the equilibrium are the same.

Table 3-2. Disproportionation of Am(VI) in NaOH Solutions (at 0 to 3 °C).

[NaOH], M	[Am(VI)] x 10 ³ , M	[Am(VII)] x 10 ⁴ , M	K ₇
8.5	1.74	Not detected	-
12.4	1.61	2.0	2.8 x 10 ⁻²
14.2	2.04	3.4	6.3 x 10 ⁻²
15.4	2.30	8.0	1.3
16.6	1.37	4.5	0.9
17.2	1.39	6.1	13.0

3.1.3 Oxidation by Persulfate

Persulfate, $S_2O_8^{2-}$, was used to oxidize transuranium elements to higher valent states.

3.1.3.1 Preparation of Neptunium(VII). The interaction of Np(VI) with $S_2O_8^{2-}$ in alkaline solutions is a complex process; under certain conditions, Np(VII) may be formed (Spitsyn et al. 1968; Shilov et al. 1971). The mechanism of the process has been studied in NaOH solutions having low concentrations (2.5×10^{-4} M) of Np(VI) (Shilov et al. 1971).

The experiments have shown that the oxidation of Np(VI) by persulfate should be carried out in solutions with low concentration of alkali. At 0.1 to 0.7 M NaOH and 0.1 M $K_2S_2O_8$, a moderate rate of reaction is ensured by heating the solution to more than 50 °C. Under these conditions, the oxidation proceeds to completion. Kinetic curves are linear almost to completion; i.e., the reaction is zero order with respect to Np(VI):

$$-d[Np(VI)]/dt = d[Np(VII)]/dt = \text{constant} \quad (8)$$

Toward the end of the reaction, Np(VI) interacts with the $S_2O_8^{2-}$ decomposition products. The rate of the decomposition products' formation does not depend on the Np(VI) concentration. Therefore, the rate of formation of the decomposition products is constant during the entire experiment, because during this period the $S_2O_8^{2-}$ concentration changes slightly.

The first step of the process at low concentration of NaOH (as in neutral solutions) is the decomposition of $S_2O_8^{2-}$ (Kolthoff and Miller 1951):

The further fast reactions in alkaline solutions give rise to the formation of O_3 radical ions; they convert Np(VI) to Np(VII) (Gogolev et al. 1989):

The SO_4^- radical ions also may react directly with Np(VI) :

However, the reaction described by equation 10 is more probable, because it occurs with a sufficiently high rate ($k_{10} = 4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [Hart and Anbar 1970]). It is unlikely that k_{14} is much higher; at the same time, the OH^- concentration exceeds the Np(VI) concentration by about 3 orders of magnitude.

The kinetics of the $\text{K}_2\text{S}_2\text{O}_8$ decomposition in dilute alkali solutions is described by an equation for a first-order reaction (Kolthoff and Miller 1951). The same order via persulfate should also apply to the oxidation of Np(VI) ; i.e.

$$v = d[\text{Np(VII)}]/dt = k[\text{S}_2\text{O}_8^{2-}] \quad (15)$$

The k values shown in Table 3-3, under otherwise similar conditions, are constant over a wide range of the $\text{K}_2\text{S}_2\text{O}_8$ concentrations.

The rate constant of the $\text{S}_2\text{O}_8^{2-}$ decomposition in 0.1 M NaOH at 60 °C is $3 \times 10^{-4} \text{ min}^{-1}$ (Kolthoff and Miller 1951). The rate of Np(VII) accumulation under these conditions is about $2.1 \times 10^{-5} \text{ M min}^{-1}$. Therefore, not all SO_4^- radical ions formed from the $\text{S}_2\text{O}_8^{2-}$ decomposition are consumed for the Np(VII) formation. Probably, as in the case of the oxidation by ozone, it is due to the decomposition of O_3 in the dilute alkali solution (Gogolev et al. 1989).

Table 3-3. Kinetic Parameters of Np(VI) Oxidation at Different Concentrations of $S_2O_8^{2-}$ ($[Np(VI)]_0 = 2.3 \times 10^{-4}$ M; $\mu = 2.0$ M; $[OH^-] = 0.2$ M, $60^\circ C$).

$[S_2O_8^{2-}] \times 10^2, M$	$v \times 10^6, M \text{ min}^{-1}$	$k \times 10^4, \text{ min}^{-1}$
2.5	5.0	2.0
5	10.0	2.0
10	21.1	2.1
20	42.2	2.1
30	59.5	2.0

The concentration of alkali considerably influences the rate of accumulation and the yield of Np(VII). At $60^\circ C$ and 2.0 M ionic strength (μ), the rates of Np(VI) oxidation in 0.1 and 0.2 M NaOH are practically identical. Increase in the alkali concentration to 0.9 M leads to a decrease in the reaction rate. In 1 M NaOH, the rate decreases further; Np(VII) concentration also decreases later in the reaction, and thus the kinetic curve for the Np(VII) formation has a maximum. A maximum reaction rate is also observed at higher concentrations of alkali only the maximum appears earlier and its height is less. In 1 M NaOH at 70 and $80^\circ C$, the yield of Np(VII) reaches the same value as in solutions with lower concentrations of alkali; however with time, the Np(VII) concentration begins to decrease.

All the above-mentioned features of the process are caused by the mechanism of $S_2O_8^{2-}$ decomposition. It is quite probable that the decomposition proceeds via two pathways; one of them is non-catalytic and the second is catalytic, with the participation of OH^- . The decay of persulfate upon the action of OH^- ions proceeds with the formation of reducing agents (for example, H_2O_2). Such a pathway becomes predominant at 3 to 4 M NaOH.

Increase in the alkali concentration to 5 to 6 M again gives rise to Np(VII) formation. Apparently, under such conditions there is a further change in the mechanism of $S_2O_8^{2-}$ decomposition.

The rate of Np(VI) oxidation in 0.2 M NaOH depends slightly upon ionic strength, μ , within the range of 0.5 to 2.0 molar. In 0.7 M NaOH, the rate constant decreases with increasing μ , and at a μ of 3.1, the kinetic curve has a maximum; i.e., the process has the same features as in the case of 1 M NaOH with $\mu = 2.0$.

The activation energy of the reaction between Np(VI) and $S_2O_8^{2-}$ in solutions with 0.7 M OH^- and 1 M ionic strength (μ) is 140 kJ mol^{-1} . This value coincides with the value of the activation energy for the non-catalytic decomposition of $S_2O_8^{2-}$ (Kolthoff and Miller 1951).

The influence of hydroxides of some transition metals on Np(VI) oxidation by persulfate was studied. It was found that in 4 M NaOH, the addition of salts of the following metals at the indicated concentrations:

Element	Fe(III)	Ag(I)	Cu(II)	Ni(II)	Co(II)
Concentration, M	5×10^{-5}	1×10^{-5}	5×10^{-6}	1×10^{-7}	2×10^{-8}

caused the oxidation of Np(VI) to Np(VII) even at room temperature. Products having oxidizing properties are clearly formed on the catalytic decomposition of persulfate.

It is noteworthy that Np(VII) solutions containing Ni and Co compounds discolor on standing for 15 to 20 hours. Apparently, during this time, the catalysts coagulate in 4 M NaOH and are precipitated. As a result, their catalytic action disappears, and Np(VII) is gradually reduced. The added Ag(I), however, retains its catalytic properties even through 24 hours.

The catalytic action of salts of transition metals changes somewhat in dilute alkali solutions. In 0.5 M NaOH, iron and copper at concentrations to 5×10^{-5} M have slight influence on the oxidation process. The action of nickel becomes noticeable at concentrations of 5×10^{-6} M. Silver and cobalt compounds have the same catalytic activity as nickel.

3.1.3.2 Preparation of Plutonium(VII). The interaction of Pu(VI) with $S_2O_8^{2-}$ has been studied in KOH solutions (Komkov et al. 1969). In many aspects, this process is similar to the oxidation of Np(VI) by persulfate in NaOH solutions.

The formation of Pu(VII) in 0.2 to 1.0 M KOH at 0.02 to 0.15 M $K_2S_2O_8$ proceeds at an appreciable rate at 70 to 95 °C. The reaction rate initially is independent of the Pu(VI) concentration, but it is proportional to the concentration of oxidizing agent. The accumulation of Pu(VII) is described by an equation of zero order with respect to actinide and first order with respect to $S_2O_8^{2-}$, as in the case of Np(VI) oxidation:

$$v = d[\text{Pu(VII)}]/dt = -d[\text{Pu(VI)}]/dt = k[S_2O_8^{2-}] \quad (16)$$

The reaction rate increases with increasing temperature. The activation energy in 1 M KOH is 143 kJ mol⁻¹; within the limits of experimental error it coincides with the respective value for the thermal decomposition of $S_2O_8^{2-}$ (Kolthoff and Miller 1951). Hence, it is possible to confirm that both the oxidation of Pu(VI) and the oxidation of Np(VI) proceed by way of a mechanism with the participation of O_3 and/or SO_4 which are formed upon $S_2O_8^{2-}$ decomposition. However, the formation of Pu(VII) is complicated by its instability in

aqueous solutions, especially at low OH^- concentrations and elevated temperatures. The reduction of Pu(VII), in addition to the oxidation of Pu(VI), occurs more rapidly in hot solutions of KOH.

Because of the competing reactions, the oxidation of Pu(VI) cannot be complete. A steady state, in which the rates of the oxidation of Pu(VI) and the reduction of Pu(VII) are equal, is achieved after some period of time. The position of this steady state, i.e. the yield of Pu(VII), depends on the temperature and concentrations of OH^- and $\text{S}_2\text{O}_8^{2-}$.

Increase in temperature leads to an increase in the formation rate and the completeness of the Pu(VI) oxidation. This is because the activation energy of the reaction between Pu(VI) and $\text{S}_2\text{O}_8^{2-}$ is considerably higher than the activation energy of the reduction of Pu(VII) by water (which is 60.6 kJ mol^{-1} [Komkov and Krot 1970]).

Increase in the KOH concentration from 0.2 to 0.5 M leads to some increase in the oxidation rate of Pu(VI); above 0.5 M KOH, the rate decreases. The yield of Pu(VII) increases linearly up to 1 M KOH concentration; above 1 M KOH, the yield decreases sharply. Obviously, at low concentration of KOH, the rate of the Pu(VII) reduction by water is high, and its yield is small. The stability of Pu(VII) increases with increasing OH^- concentration and its yield increases. As in the case of Np(VI), the cessation of the Pu(VI) oxidation at greater than 1 M KOH can be explained by the change in the mechanism of the $\text{S}_2\text{O}_8^{2-}$ decomposition.

Based on these observations, the optimal conditions for the preparation of Pu(VII) by means of persulfate are: 0.8 to 0.9 M OH^- , 0.1 to 0.2 M $\text{S}_2\text{O}_8^{2-}$, and 80 to 90 °C temperature. Under these conditions, the yield of Pu(VII) with the plutonium concentration of $1 \times 10^{-3} \text{ M}$ is close to 100% after about 20 minutes.

3.1.3.3 Preparation of Americium(IV). It was reported that in alkaline media, pink $\text{Am}(\text{OH})_3$ can be oxidized by $\text{S}_2\text{O}_8^{2-}$ to an insoluble precipitate of black or dark-brown color; [probably $\text{Am}(\text{IV})$] (Penneman and Asprey 1955).

The oxidation of $\text{Am}(\text{OH})_3$ by persulfate has been studied in some detail (Penneman et al. 1961). The treatment of 5 mg $\text{Am}(\text{OH})_3$ in 0.1 M NaOH by excess $\text{K}_2\text{S}_2\text{O}_8$ in a boiling water bath for about 2 hours gave an olive-brown precipitate. Dissolution of the precipitate by acid showed the mean oxidation number of americium was 4.53; i.e., in addition to $\text{Am}(\text{IV})$, the precipitate contained americium in higher oxidation states.

Americium(IV) has been prepared in a concentrated solution of alkali. For this purpose $\text{Am}(\text{III})$ was added to a hot 7 M solution of KOH, saturated with $\text{K}_2\text{S}_2\text{O}_8$, and the mixture held at 90 °C for one hour. The precipitate was washed by water to remove the excess oxidizing agent. The mean oxidation number of the hydroxide was 4.0 ± 0.1 .

3.1.4 Oxidation by Hypobromite

Hypobromite, BrO^- , is another oxidizing agent for transuranium elements in alkaline media. It has been used for preparation of Np(VII) and Pu(VII) .

3.1.4.1 Preparation of Neptunium(VII). Neptunium(VI) in alkaline solutions is oxidized by 0.1 M hypobromite at an appreciable rate only on heating to 70 °C (Spitsyn et al. 1968). Study of the kinetics of reaction was carried out for 1.74 to 6.5 M NaOH and 2×10^{-4} M Np(VI) (Shilov et al. 1970a). In the experiments and calculations, the instability of BrO^- , which is gradually decomposed with the formation of Br^- and BrO_3^- , was taken into account. Hexa- and heptavalent neptunium have no effect on the decomposition rate.

The kinetics of the Np(VI) oxidation are described by an equation for reaction of first order with respect to the metal:

$$-d[\text{Np(VI)}]/dt = d[\text{Np(VII)}]/dt = k[\text{Np(VI)}] \quad (17)$$

The k value depends upon concentrations of alkali and oxidizing agent and the temperature. The treatment of experimental data gave the following empirical equation:

$$k = k' [\text{OH}^-]^{1.6} [\text{BrO}^-]^{0.6} \quad (18)$$

Where:

$$k' = (6.65 \pm 0.35) \times 10^{-2} \text{ M}^{-2.2} \text{ min}^{-1} \text{ at } 70^\circ \text{C}.$$

The activation energy for the reaction in 6.5 M NaOH with 0.1 M BrO^- is 87.8 kJ mol^{-1} (at 50.7 to 70 °C).

The complicated dependence of the Np(VI) oxidation rate by hypobromite on the NaOH concentration reflects not only the participation of OH^- ions in the formation of the activated complex, but also the change in the salt composition and, respectively, the ionic strength of the solution. The fractional order via BrO^- can be explained by the fact that the process has several parallel pathways. Probably, in addition to the direct interaction of Np(VI) with BrO^- (in a reaction of first order relative to the oxidizing agent), the intermediate products of the BrO^- decomposition contribute considerably to the kinetics of the Np(VII) formation in a reaction of zero order.

The oxidation of Np(VI) by hypobromite is accelerated by salts of transition metals. For example, Np(VII) is practically not formed in 0.5 M NaOH at 0.1 M BrO^- and 30 °C. However, if 2.5×10^{-5} M of Cu(II) salt is added to this solution, Np(VI) is oxidized completely in about 40 minutes. A similar result is observed in the presence of $(1 \text{ to } 5) \times 10^{-6}$ M nickel or cobalt compounds.

The oxidation of Np(VI) by hypobromite in solutions containing microamounts of cobalt salts occurs in a reaction of first order relative to the metal:

$$-d[\text{Np(VI)}]/dt = k[\text{Np(VI)}] \quad (19)$$

The k value is independent of the NaOH concentration within the range of 0.5 to 2 M but depends strongly on temperature, concentrations of BrO^- , and catalyst (see Table 3-4). The order of reaction via hypobromite is close to 0.6 (as in the absence of catalyst). The activation energy for the reaction in the absence of catalyst decreases to 71 kJ mol^{-1} .

Iron and silver salts (at concentrations to $5 \times 10^{-5} \text{ M}$) have no effect on the oxidation of Np(VI) by hypobromite in 0.5 M NaOH at 30°C .

The above-mentioned data show that the optimal conditions of Np(VII) preparation by means of hypobromite are the following: 3 to 4 M OH^- , 0.05 to 0.1 M BrO^- and 60 to 80°C temperature. The oxidation can be carried out in 0.5 M NaOH at 30°C when $5 \times 10^{-6} \text{ M}$ of Co(II) salt is added to the solution. The Np(VII) solutions prepared with hypobromite are stable.

Hexavalent plutonium in 0.5 M alkali solution is not oxidized by hypobromite (Komkov et al. 1969). Hence, under these conditions, it is possible to oxidize Np(VI) selectively in the presence of Pu(VI).

Table 3-4. The Influence of Experimental Conditions on the Np(VI) Oxidation Rate by Hypobromite in the Presence of Co(II) Salt ($[\text{NaOH}] = 0.5 \text{ M}$).

Temperature, $^\circ \text{C}$	$[\text{BrO}^-] \times 10^2, \text{ M}$	$[\text{Co(II)}] \times 10^6, \text{ M}$	$k \times 10^2, \text{ min}^{-1}$
30.0	10	5	40
30.0	19	5	51
30.0	5	5	32
30.0	2.5	5	22
30.0	10	1.5	6.9
30.0	10	0.5	2.2
40.1	10	5	96
49.2	10	5	211

3.1.4.2 Preparation of Plutonium(VII). Pu(VI) can be oxidized by hypobromite only in concentrated alkaline solutions. Semiquantitative data on the kinetics of this reaction were obtained for solutions 10 M or greater in KOH concentrations (Komkov et al. 1969). The oxidation of Pu(VI) occurs completely and rapidly upon heating the solutions to 50 to 90 °C. The decomposition of BrO⁻ with the intense formation of oxygen bubbles proceeds as a side reaction. Because of this, precise kinetic curves of Pu(VII) formation were impossible to determine using spectrophotometry. The available data on Pu(VI) oxidation by hypobromite therefore are approximate, and only limited conclusions can be drawn on their basis.

The completeness and rate of the Pu(VI) oxidation increase with increasing concentrations of alkali and hypobromite. The yield of Pu(VII) is close to 100% in solutions with 0.1 M KBrO and greater than 12 M KOH. The oxidation rate increases with increasing temperature from 50 to 90 °C.

The additions of Fe(III), Ag(I), Cu(II), and Mn(II) up to 1×10^{-5} M have practically no effect on the interaction of Pu(VI) with BrO⁻. Compounds of Co(II) and Ni(II) at the same concentrations considerably increase the reaction rate; the increase in the rate of BrO⁻ decomposition takes place simultaneously. Obviously, both these processes [the Pu(VI) oxidation and the BrO⁻ decomposition] are related.

Both dilute and concentrated solutions of Pu(VII) of high stability can be prepared by means of hypobromite. The solutions are stable at room temperature over several days. However, the difficulties of handling concentrated alkaline solutions limit the use of this method for Pu(VII) preparation.

3.1.5 Oxidation by Hypochlorite

Hypochlorite was used for the oxidation of Am(OH)₃. It was reported that the action of alkali solution containing ClO⁻ on microgram amounts of Am(III) led to the formation of a dark precipitate (Cunningham 1949). The oxidation of Am(OH)₃ has been studied in some detail (Penneman et al. 1961). It was found that the oxidation of Am(III) to Am(IV) proceeds only in an alkaline medium.

3.1.6 Oxidation by Ferricyanide

Another oxidizing agent for transuranium elements in alkaline solutions is ferricyanide, Fe(CN)₆³⁻. It was used for the oxidation of Np(VI), Pu(VI), and Am(III).

3.1.6.1 Reaction of Np(VI) with Ferricyanide. The oxidation of Np(VI) by ferricyanide is a reversible reaction; the OH⁻ concentration has a considerable effect on the position of the equilibrium (Krot et al. 1970). Np(VI) is practically not oxidized by an equimolar amount of K₃Fe(CN)₆ at OH⁻ concentrations less than 0.5 M. On the contrary, under these conditions, Np(VII) is reduced to Np(VI) completely and rapidly by Fe(CN)₆⁴⁻ (ferrocyanide).

In solutions with greater than 6 M KOH, Np(VI) is oxidized by $\text{Fe}(\text{CN})_6^{3-}$ quantitatively. In the intermediate region, the yield of Np(VII) depends on the excess of the oxidizing agent and the experimental conditions. The equilibrium of the reaction is achieved rapidly.

The equilibrium constant, $K_{20} [= ([\text{Np(VII)}][\text{Fe}(\text{CN})_6^{4-})]/([\text{Np(VI)}][\text{Fe}(\text{CN})_6^{3-}])]$, for 3.2 M KOH at 23 °C is 2.0 ± 0.2 . With the ionic strength of the solution maintained constant and equal to 4.0 by means of KF, the logarithmic scale dependence of K_{20} on the KOH concentration is a straight line of slope 3. At a constant concentration of KOH, the K_{20} value is proportional to ionic strength, μ . The total influence of μ and OH^- concentration causes the K_{20} value to be proportional to $[\text{KOH}]^4$.

The sharp influence of OH^- concentration on the equilibrium of the reaction between Np(VI) and $\text{Fe}(\text{CN})_6^{3-}$ is due to the strong dependence of the oxidation potential of the pair Np(VII)/Np(VI) on the alkali concentration (see previous sections). The variation of the potential of the pair $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in solutions with different concentrations of alkali is insignificant. Under otherwise similar conditions, substituting NaOH for the KOH leads to a small decrease in the K_{20} value. Substituting LiOH results in a large decrease in the Np(VII) yield (see Table 3-5) (Krot et al. 1977a).

Table 3-5. The Equilibrium Constants K_{20} and the Rate Constants k for Np(VI) Oxidation by $\text{Fe}(\text{CN})_6^{3-}$ ($[\text{MeOH}] = 4 \text{ M}$, 10°C).

Alkali	K_{20}	$k \times 10^{-2}, \text{M}^{-1} \text{min}^{-1}$
KOH	3.1	5.7
NaOH	2.7	3.8
LiOH	0.7	2.9

At room temperature, the oxidation of Np(VI) by ferricyanide occurs rapidly. However, at 10°C and with concentrations of reagents of about 10^{-4} M , the reaction is decelerated and its rate is measured by simple methods. Study has shown that Np(VI) oxidation by $\text{Fe}(\text{CN})_6^{3-}$ ions is described by an equation for a bimolecular reaction (Krot et al. 1977b):

$$-d[\text{Np(VI)}]/dt = k_{20} [\text{Np(VI)}][\text{Fe}(\text{CN})_6^{3-}] \quad (21)$$

The rate constant k_{20} in KOH solutions changes slightly within the ionic strength range of 1.5 to 3.0 (using KNO_3) but depends considerably on OH^- concentration (see Table 3-6). It is possible to consider, as a first approximation, that the k_{20} value is proportional to OH^- concentration. From here it follows that the Np(VII) reduction rate by $\text{Fe}(\text{CN})_6^{4-}$ decreases in

proportion to $[\text{OH}]^2$, because K_{20} is a function of $[\text{OH}]^3$. At an ionic strength, μ , of 3.0 M and 10 °C, the values of K_{20} and k_{20} in 2.5 M KOH are equal to 0.55 and $3.15 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$, respectively. Under these conditions, the rate constant of reaction between Np(VII) and $\text{Fe}(\text{CN})_6^{3-}$ is $k_{20} = k_{20}/K_{20} = 5.7 \times 10^2 \text{ M}^{-1} \text{ min}^{-1}$.

Table 3-6. Rate Constants for Np(VI) Oxidation by $\text{Fe}(\text{CN})_6^{3-}$ in KOH Solutions ($[\text{Np(VI)}]_0 = 1.26 \times 10^{-4} \text{ M}$, 10 °C).

[KOH], M	μ , M	k_{20} , $\text{M}^{-1} \text{ min}^{-1}$
4.0	4.0	570
3.5	3.5	460
3.0	3.0	400
2.5	3.0	315
2.0	3.0	265
1.5	3.0	215
1.5	2.8	210
1.5	2.8	195
1.5	2.0	185

The rate of Np(VI) oxidation by $\text{Fe}(\text{CN})_6^{3-}$ ions is somewhat decelerated upon the transition from KOH to NaOH and LiOH (see Table 3-5).

The activation energy of the reaction in 3 M KOH is 40.1 kJ mol^{-1} . The low value of the activation energy of the Np(VI) reduction is because K_{20} depends only slightly on temperature change.

3.1.6.2 Preparation of Plutonium(VII). The interaction of Pu(VI) with $\text{Fe}(\text{CN})_6^{3-}$ becomes noticeable in solutions with greater than 8 M KOH (Krot et al. 1977a). The oxidation of $5 \times 10^{-4} \text{ M}$ Pu(VI) in 12 M KOH and $2 \times 10^{-3} \text{ M}$ $\text{Fe}(\text{CN})_6^{3-}$ proceeds virtually to completion. Under these conditions the reaction has a high rate even in the cold. However, prepared solutions of Pu(VII) are unstable upon standing; their characteristic color disappears in about 2 hours. Most likely, Pu(VII) is reduced gradually by cyanide ions formed from the decomposition of the iron cyanide complex.

3.1.6.3 Oxidation of Americium(III). Am(III) in alkaline solutions is oxidized by ferricyanide to AmO_2^+ . The soluble complex, $(\text{AmO}_2)_3\text{Fe}(\text{CN})_6$, is formed as a result of the reaction. The complex is decomposed gradually with the release of the precipitate $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$. Americium(IV) hydroxide appears if equal amounts of Am(III) and $\text{K}_3\text{Fe}(\text{CN})_6$ are combined (Kulyako et al. 1993).

3.1.7 Oxidation by Xenon Compounds

Some xenon compounds (for instance, Na_4XeO_6 , XeO_3 , and XeF_2) are oxidizing agents for transuranium elements. In this section the use of these compounds for actinide oxidation in alkaline media is described.

3.1.7.1 The Use of Na_4XeO_6 . Np(VI) in alkaline solutions is oxidized by XeO_6^{4-} (perxenate) upon heating. The half-time for the oxidation of 2×10^{-4} M Np(VI) in 1 M KOH, using 1×10^{-3} M Xe(VIII) and at 70 °C, is 15 min (Spitsyn et al. 1968). The reaction rate increases somewhat with decrease in the KOH concentration. The addition of perxenate to slightly-acid or neutral solutions of Np(VI) does not lead to the formation of Np(VII).

Pu(VI) in 0 to 12 M NaOH solution does not react with perxenate (Komkov et al. 1968). To some extent, the low rate is due to the low solubility of Na_4XeO_6 in concentrated NaOH solution. Pu(VI) is partially oxidized by Xe(VIII) in hot concentrated solutions of KOH, but the yield of Pu(VII) is small. Only 25% of the Pu(VI) was converted to Pu(VII) during 15 min in 11 M KOH, 0.02 M XeO_6^{4-} , and 95 °C. Further heating did not increase the Pu(VII) yield.

3.1.7.2 The Use of XeO_3 . Xenon trioxide (XeO_3) reacts with Np(VI) in alkaline solutions more rapidly than perxenate ion (Spitsyn et al. 1968). The addition of 5×10^{-3} M XeO_3 to Np(VI) solution in 1 M KOH gives rise to the gradual appearance of the characteristic green color of Np(VII) even in cold solutions. The duration of reaction is more than 3 hours. The oxidation rate increases sharply upon heating. At 1 M NaOH, 2.5×10^{-3} M XeO_3 , and 50 °C, the time for the oxidation of 2×10^{-4} M Np(VI) to 50% is about 3 min; at 70 °C it is 4.5 times faster. Decrease in the alkali concentration to 0.25 M leads to some deceleration of the reaction. Increase in the KOH concentration accelerates the Np(VI) oxidation. The reaction proceeds to completion in about 35 min at 10 to 11 M KOH, 2.1×10^{-3} M XeO_3 , 2.1×10^{-4} M Np(VI), and 20 °C (Klimov et al. 1971). If the concentrations of the reacting components are the same and equal to 2×10^{-3} M under the above-mentioned conditions, the half-time of the Np(VI) oxidation is about 30 minutes.

The interaction of Np(VI) with XeO_3 in alkaline solutions is accompanied by an oxidant decomposition side reaction, forming perxenate, which can also participate in the Np(VI) oxidation.

The Use of XeF_2 . Xenon (XeF_2) difluoride is suitable for Np(VI) oxidation only in solutions with moderate concentrations of alkali (Klimov et al. 1971, Gusev et al. 1972). Aqueous solutions of XeF_2 are somewhat more effective. They can be used for Np(VI) oxidation in alkali concentrations up to 5 M (Zielen and Cohen 1970). The reaction proceeds rapidly.

A 200-fold excess of XeF_2 is required for the quantitative oxidation of Np(VI) in 0.2 to 1.0 M NaOH or KOH (Gusev et al. 1972). Addition of 5 to 200 mg XeF_2 to 20 mL of 2 M NaOH with 2×10^{-4} M Np(VII) prepared by ozonation leads to a decrease in Np(VII) concentration by 3 to 12%; i.e. reduction occurs.

In the presence of 10^{-5} M Cu(II) salt, Np(VI) oxidation by XeF_2 in 0.5 M NaOH is not observed. Under the same conditions, microamounts of cobalt and nickel have no effect on Np(VI) oxidation.

Only a short-lived coloration characteristic of Pu(VII) solutions appears upon the action of 200-fold excess of XeF_2 on Pu(VI) in 0.2 to 1.2 M NaOH. The color disappears in about 10 minutes. The yield of Pu(VII) 3 minutes after the addition of XeF_2 is not more than 10%. The Pu(VI) oxidation is not observed at greater than 2 M OH^- . The rapid discoloration of Pu(VII) solutions prepared by ozonation in 0.5 to 3 M KOH or NaOH proceeds upon the addition of XeF_2 ; the optical absorption spectrum of the formed solution is identical with the spectrum of Pu(VI) solution.

3.1.8 Oxidation by Silver Oxides

Silver oxides, Ag_2O and AgO , are also suitable for some oxidation reactions of transuranium elements in alkaline solutions.

3.1.8.1 Preparation of Np(VII). Both Ag_2O and AgO are usable for the preparation of Np(VII) in alkaline solutions (Krot et al. 1970). Np(VI) oxidation by Ag_2O occurs to a noticeable extent only in solutions with greater than 8 M OH^- . The reaction rate at room temperature is low; it is necessary to perform the process at temperatures more than 50 °C. In solutions heated to 60 °C, the reaction is finished in 15 to 20 minutes.

The fraction of Np(VI) oxidized depends upon the concentrations of alkali and oxidizing agent. The Np(VII) yield in 5×10^{-4} M Np(VI) and 9 M NaOH at 60 °C using freshly-prepared Ag_2O (10 mg cm^{-3}) is 10 to 15%. If the concentration of alkali is 12 M and the other conditions are the same, the Np(VII) yield reaches 70 to 80%. Decrease in the concentration of oxidizing agent from 10 to 2 mg cm^{-3} (under otherwise similar conditions) leads to a two-fold decrease in the yield. The Np(VII) yield increases slightly by increasing temperature to 90 °C.

AgO oxidizes Np(VI) even in 0.1 M KOH. The reaction rate is high even at room temperature. In solutions heated to 59 °C, equilibrium is achieved in 3 to 5 minutes (with intense stirring). Data from Table 3-7 illustrate the influences of alkali and oxidizing agent concentrations.

From the data, it is seen that in 2 to 3 M KOH, AgO in excess can oxidize Np(VI) to Np(VII) almost quantitatively.

3.1.8.2 Preparation of Plutonium(VII). Extensive oxidation of Pu(VI) by AgO takes place only with greater than 8 M OH^- (Peretrushin et al. 1971). The Pu(VII) yield in 10 M NaOH is close to 100%. The reaction rate in cold solutions is small. The rate increases rapidly with increasing temperature. At 80 to 90 °C, the Pu(VI) oxidation is complete in less than 15 minutes.

Table 3-7. The Effect of KOH and AgO Concentrations on the Np(VII) Yield at $[\text{Np(VI)}]_0 = 1.3 \times 10^{-4} \text{ M}$ and 50°C .

[KOH], M	[AgO], mg cm ⁻³	Np(VII) yield, %
0.18	2.0	54.0
0.32	2.0	60.8
0.68	2.0	72.0
1.27	2.0	88.7
2.48	2.0	92.6
3.36	2.0	98.5
1.27	0.4	72.7
1.27	0.8	79.0
1.27	2.0	88.7
1.27	4.0	92.7

3.1.9 Oxidation by Permanganate

The interaction of Np(VI) and Pu(VI) with KMnO_4 alkaline solutions occurs via reversible reactions (Peretrukhin et al. 1971; Shilov et al. 1970b):

The equilibria are established rapidly at 20 to 25 °C and strongly depend on the alkali concentration. Np(VI) is oxidized in 3 to 4 M NaOH. However, under these conditions, besides the preparation of Np(VII), there is the gradual decomposition of the excess MnO_4^- and the additional formation of MnO_4^{2-} . The rate of the last process depends on the presence of microamounts of catalysts and impurities. It is difficult to exclude this process completely (even using highly-purified reagents) since the potential of the pair $\text{MnO}_4^-/\text{MnO}_4^{2-}$ is higher than the potential of O_2 production from alkaline aqueous solutions.

The potential of the pair Np(VII)/Np(VI) sharply increases with decreasing alkali concentration, whereas the potential of the pair Mn(VII)/Mn(VI) changes slightly. As a result, in solutions with pH 10 to 11, Np(VII) rapidly oxidizes MnO_4^{2-} to MnO_4^- .

Pu(VI) is oxidized by KMnO_4 only in solutions with 10 to 14 M NaOH (Peretrukhin et al. 1971). The process is accompanied by the reduction of the excess MnO_4^- by water to form MnO_4^{2-} . This side reaction complicates the observation of reaction between Pu(VI) and MnO_4^- . Upon the dilution of the solution to 2 to 4 M NaOH, the fast reverse oxidation of MnO_4^{2-} by Pu(VII) is observed and the red-violet MnO_4^- is formed.

It was shown that MnO_4^- oxidizes Am(III) to Am(IV) in alkaline media (Penneman et al. 1961).

3.1.10 Other Oxidation Processes

Other oxidizing agents for transuranium elements in alkaline media are the Cu(III) periodate complex, periodate, bismuthate, other oxidized transuranium elements, hydrogen peroxide, and oxygen.

3.1.10.1 Periodate Complex of Cu(III). Excess Cu(III) complexed with periodate rapidly oxidizes Np(VI) and Pu(VI) at NaOH concentrations higher than 1 and 11 M, respectively (Shatokhina et al. 1977).

3.1.10.2 Periodate and Bismuthate. Np(VI) is oxidized by periodate only in hot alkaline solutions (Spitsyn et al. 1968). The time of 50% oxidation of 2×10^{-4} M Np(VI) at NaOH and periodate concentrations of 1 and 0.1 M, respectively, at 85 °C is 20 minutes. Increase in the alkali concentration causes an increase in the reaction rate; in 5 M KOH (under otherwise similar conditions), oxidation is complete in about 10 minutes.

Pu(VI) is not oxidized by periodate either in dilute or concentrated alkali solutions (Komkov et al. 1968).

Np(VI) oxidation by sodium bismuthate in dilute alkaline solution is a heterogeneous reaction occurring rapidly only at boiling temperatures (Spitsyn et al. 1968). Green solutions with an optical absorption spectrum characteristic of Np(VII) are formed at completion and are observed upon removal of the excess oxidant by centrifugation.

3.1.10.3 Plutonium(VII) and Plutonium(VI). Plutonium(VII) is a stronger oxidant than Np(VII). Hence, the reaction

is possible. Experiments have shown that this reaction is fast at room temperature (Shilov et al. 1970b). It is irreversible at any alkali concentration because the dependencies of the oxidation potentials of the pairs Pu(VII)/Pu(VI) and Np(VII)/Np(VI) on OH^- concentration are symmetrical.

Np(VI) in alkaline solutions can be oxidized not only by Pu(VII) but also Pu(VI) (Shilov 1976). The reaction

is reversible and occurs with high rate. Because of the rapid equilibration, it is concluded that the hepta-, hexa- and pentavalent ions in concentrated alkali solution have similar structures; i.e., the charge transfer occurs without appreciable reconstruction. The equilibrium depends upon the concentration of alkali. The equilibrium constant, K_{25} , is $[\text{Np(VII)}][\text{Pu(V)}]/([\text{Np(VI)}][\text{Pu(VI)}])$; in 7.8 M NaOH at 24 °C, K_{25} is 1.8×10^{-2} . The K_{25} value becomes 0.14 by increasing the NaOH concentration to 10.1 M.

It has been shown (Bourges 1972) that Pu(V) is formed on the addition of an equimolar amount of Pu(VI) to Pu(IV) hydroxide in 4 M NaOH.

3.1.10.4 Americium(VI). The rapid formation of Np(VII) is observed upon the addition of a bicarbonate or slightly-acid solution of Am(VI) to Np(VI) solution in 1 M NaOH (Nikolaevsky et al. 1974):

Am(V) does not react with Np(VI) in alkaline solutions. The equilibrium of reaction (26) depends upon the OH^- concentration. The Np(VI) oxidation begins at 0.016 M OH^- . The yield of Np(VII) increases with increasing alkali concentration and reaches about 100% in 3 to 4 M NaOH.

The addition of Am(VI) to Pu(VI) solution in 1 M NaOH does not lead to the formation of Pu(VII). The equilibrium of the reaction:

is shifted to the right only at OH^- concentrations greater than 7.5 M (Nikolaevsky et al. 1974). The equilibrium is established instantaneously on mixing the reagents.

3.1.10.5 Hydrogen Peroxide. The oxidation of Am(OH)_3 to Am(IV) by H_2O_2 was noted (Penneman and Asprey 1955) and later studied in some detail (Buijs and Louwrier 1966). In the more recent study, an acid Am(III) solution, containing H_2O_2 , was neutralized by a concentrated ammonia solution. The formed precipitate (probably, Am(III) hydroperoxide) was treated with concentrated solutions of ammonia or KOH. Am(IV) hydroxide product was prepared. Formation of Am(IV) was accelerated by heating to 90 °C.

3.1.10.6 Oxygen. The behavior of Pu(IV) and Pu(VI) in 1 to 15 M NaOH over extended time periods was studied (Delegard 1987). It was found that Pu(V) accumulated in the solution over the precipitate. The question of possible oxidants was not considered (Delegard 1987). We believe that such oxidants may be oxygen, products of water α -radiolysis, and NO_2^- formed on radiolytic reduction of NO_3^- .

3.2 REDUCTION REACTIONS

The reduction reactions can be divided conditionally into two groups: the first group includes the fast reactions studied by pulse methods, the second group consists of the reactions occurring with moderate rate, especially in solutions with high alkali concentration. The kinetics of some fast reactions are discussed in Section 5.0.

Reagents which rapidly reduce hepta- and hexavalent actinides are the hydrated electron (e_{aq}^-), the hydrogen atom, HO_2 , O_2^- , H_2O_2 , ascorbic acid, hydrazine, hydroxylamine, Sn(II), Np(V), and Pu(V). Heptavalent actinides in diluted alkali solutions react rapidly with $\text{Fe}(\text{CN})_6^{4-}$. Np(VI) rapidly reduces Pu(VII), Am(VII) and Am(VI). Pu(VI) interacts rapidly with Am(VII).

The second group includes the reactions of heptavalent and some hexavalent actinides with reducing agents such as formaldehyde, methanol, ethanol, sulfite, iodide, oxalate, thiosulfate, formate, ethylenediaminetetraacetate (EDTA), and citrate as well as many other organic compounds used as extractants (for example, tertiary amines and quaternary ammonium bases). Pu(VII) reacts with moderate rate with iodate and water (Krot et al. 1977a; Shilov and Krot 1969; Komkov et al. 1970).

3.2.1 Reduction of Np(VII)

Table 3-8 shows some data on the rate of Np(VII) reactions with compounds often used as reducing agents (Shilov and Krot 1969). In cold Np(VII) does not react to a noticeable extent with ethanol, nitrite, oxalate, and acetate both in 0.1 and 2 M alkali solutions. Increase in temperature to 65 °C leads to a decrease in Np(VII) stability with respect to ethanol and oxalate, especially at low OH^- concentration.

Formaldehyde is a particularly effective reducing agent which reduces Np(VII) in cold 0.1 M alkali solution. Citrate, formate, thiosulfate, and EDTA are weaker reducing agents than formaldehyde.

3.2.2 Kinetics of Pu(VII) Reduction by Water

Plutonium(VII) in alkaline solutions is reduced by water to Pu(VI), especially in solutions with low OH^- concentration. The kinetics of this process depends primarily on the purity of

the solutions and the alkali concentration (Komkov and Krot 1970). It was shown that the reduction of Pu(VII) within the range of concentrations of $(1.6 \text{ to } 2.5) \times 10^4 \text{ M}$ in 0.044 to 0.1 M KOH solutions is proportional to the metal concentration to the 1.2 to 1.3 power. The time of reduction to 50% at 25 °C and 1 M ionic strength (μ) is 18.3, 21, 26.2, and 29.8 min for KOH solutions with concentrations of 44, 53, 60, and 67.5 mM, respectively.

Hence, the reduction rate decreases with increasing alkali concentration (i.e., the rate constant is inversely proportional to OH^- concentration). The activation energy of the reduction reaction at 25 to 45 °C is 60.5 kJ mol^{-1} ($\mu = 1.0$ and 0.1 M KOH). The authors suggest that the step controlling the rate is the abstraction of OH from the hydrolyzed Pu(VII) anion (Komkov and Krot 1970). The OH then is converted to O^- . The combination of O^- with OH gives HO_2^- which rapidly reduces two Pu(VII) ions.

Table 3-8. Time, in Minutes, for 50% Reduction of $2.5 \times 10^{-4} \text{ M}$ Np(VII) with Different Compounds.

Reducing agent	Concentration, M	0.1 M NaOH ^a		2 M NaOH ^b	
		25 °C	65 °C	25 °C	65 °C
NH_3	0.3	> 100	> 100	-	-
NO_2^-	0.07	> 100	> 100	> 100	> 100
CH_3COO^-	0.20	> 100	> 100	> 100	> 100
$\text{C}_2\text{O}_4^{2-}$	0.07	> 100	32	> 100	> 100
EDTA	0.01	75	1.1	> 100	45
$\text{C}_6\text{H}_5\text{O}_7^{3-}$	0.09	12	0.4	-	22
HCOO^-	0.09	50	2.5	> 100	20
$\text{S}_2\text{O}_3^{2-}$	0.05	65	-	> 100	65
$\text{C}_2\text{H}_5\text{OH}$	1.50	> 100	5	> 100	30
CH_2O	0.06	1.5	0.1	-	0.3

^aAt ionic strength 0.5

^bAt ionic strength of about 2

The reduction of $(1.0 \text{ to } 1.7) \times 10^{-3} \text{ M}$ Pu(VII) in 0.3 to 1.96 M NaOH was studied (Bhattacharyya et al. 1982). The reduction rate is described by the equation

$$-d[\text{Pu(VII)}]/dt = k[\text{Pu(VII)}] \quad (28)$$

up to 75 to 95% completion of the reaction. The apparent rate constant is proportional to $[\text{OH}^-]^n$; n equals 1 at OH^- concentrations of greater than 1 M and n equals 2 when OH^- concentrations lie between 0.3 and 0.62 M. In 0.3 M NaOH solution, the rate constant for reduction of 1×10^{-3} M Pu(VII) does not depend on ionic strength within the range of 0.5 to 2 M; at ionic strength 0.5, the rate constant decreases by 25% when the solution contains 2×10^{-3} or 5×10^{-2} M CO_3^{2-} .

Activation energies for 1.7×10^{-3} M Pu(VII) are 121 kJ mol^{-1} for 1 M NaOH and 1 M NaClO_4 solution at 28.4 to 38.2 °C; and 33.4 kJ mol^{-1} for 0.5 M NaOH and 1.5 M NaClO_4 solution at 26.5 to 35.2 °C.

To detect OH radicals in the reaction of Pu(VII) with water, Pu(VII) was added to 0.5 and 1.0 M solutions of NaOH saturated with benzene (Bhattacharyya et al. 1982). In both cases, the product of the reaction between OH and benzene (i.e. phenol) was not found. It was suggested that the hydrolyzed Pu(VII) ion releases $1/2 \text{ O}_2$ and is converted to Pu(V). The Pu(V) then rapidly reacts with Pu(VII). It was not explained how $1/2 \text{ O}_2$ is abstracted from the Pu(VII) ion. The mechanism of the Pu(VII) reduction by water requires more detailed investigation.

The stability of Pu(VII) in 0.15 M KOH is unchanged by the addition of 1×10^{-6} M of Cr(VI), Mn(VII), Ag(I), Cd(II), Mn(II), Hg(II), or Pt(IV). Microamounts of ClO_4^- , SO_4^{2-} , and Cl^- also have no effect on Pu(VII) stability (Komkov and Krot 1970).

Pu(VII) reduction is accelerated by salts of Fe(III), Cu(II), Ni(II), and Co(II) (Komkov and Krot 1970). The catalytic influence of Fe(III) becomes noticeable beginning from a concentration of 8×10^{-7} M. The rate of Pu(VII) reduction in the presence of Fe(III) is proportional to the concentration of the latter. Similar results were obtained for compounds of copper and nickel.

The catalytic effect of iron, copper, and nickel is explained by the fact that they are able to be oxidized to higher valent states which then react rapidly with water.

The influence of cobalt on Pu(VII) stability is peculiar (Komkov and Krot 1970). The acceleration of Pu(VII) reduction becomes noticeable in 0.15 M KOH at cobalt concentrations of about 10^{-9} M. The kinetic curves for the reduction have an S-form characteristic of autocatalytic reactions. The sensitivity of Pu(VII) to the presence of cobalt decreases sharply with increasing OH^- concentration. In concentrated alkali solutions, the kinetic curves for Pu(VII) reduction in the presence of cobalt have the same shape as in the case of the solutions with additions of iron, nickel, and copper. The shapes of these kinetic curves are characteristic of first-order reactions.

3.2.3 Reduction of Np(VII) by Sulfite

The kinetics of the interaction between Np(VII) and SO_3^{2-} (sulfite) was studied at 0.7 M ionic strength, 0.1 to 0.5 M NaOH, and 20 to 35 °C (Shilov and Krot 1969). Under these conditions, Np(VII) is reduced by excess SO_3^{2-} at a moderate rate. The initial parts of the kinetic curves are described satisfactorily by an equation for a first order reaction; it is confirmed by their linearity in semilogarithmic coordinates. However, the reduction rate at the end of the process increases. Special experiments have shown that this is because the product formed, Np(VI), is converted by sulfite to Np(V). The Np(V) then reacts rapidly with Np(VII). The rate of the Np(VI) reduction by SO_3^{2-} ions is relatively low. Because of it, the autocatalytic acceleration of the reaction between Np(VII) and SO_3^{2-} becomes noticeable only after the accumulation of some amount of Np(VI).

The rate constant of first order k' , was determined from the initial slope of the kinetic curves; the bimolecular rate constant, k , was calculated from the ratio $k'/[\text{SO}_3^{2-}]$. Values of k are presented in Table 3-9. It is seen that the k values are constant within a wide range of sulfite concentrations, i.e. the reaction is first order relative to sulfite. The rate of the Np(VII) reaction with SO_3^{2-} depends strongly on OH^- concentration. The k value can be expressed by the equation

$$k = \frac{k_1}{[\text{OH}^-]} + \frac{k_2}{[\text{OH}^-]^2} \quad (29)$$

The presentation of k in the form of two terms becomes reasonable if one suggests that not $\text{NpO}_4(\text{OH})_2^{3-}$, but products of its hydrolysis, react with sulfite:

Plotting the temperature dependence of the k values in Arrhenius coordinates permits calculation of the activation energy of the Np(VII) reaction with SO_3^{2-} . The activation energy is 94.1 kJ mol⁻¹ (at 0.5 M OH^-).

Impurities of Cu(II), Co(II), and Mn(VII) compounds have an effect on the Np(VII) reduction. The catalytic action of Cu(II) becomes noticeable at 2×10^{-7} M. The reaction rate constant depends linearly on Cu(II) concentration (CuCl_2 was used):

$$k = k_0 + k'/[\text{Cu(II)}] \quad (32)$$

Table 3-9. Influence of Experimental Conditions on Np(VII) Reduction Rate by Sulfite (Ionic Strength 0.7 M with NaOH and NaNO₃).

Temperature, °C	[OH ⁻], M	[SO ₃ ²⁻] x 10 ² , M	k, M ⁻¹ min ⁻¹
34.9	0.50	2.20	1.22
34.9	0.50	5.02	1.29
34.9	0.50	7.07	1.22
34.9	0.50	10.35	1.31 ^a
34.9	0.50	13.50	1.22 ^b
30.0	0.50	7.07	0.62
25.0	0.50	7.11	0.38
25.0	0.37	7.06	0.60
25.0	0.35	7.15	0.67
25.0	0.29	7.15	0.85
25.0	0.25	7.07	0.94
25.0	0.19	7.15	1.38
25.0	0.14	7.15	2.55
25.0	0.13	7.06	3.24
25.0	0.10	7.15	4.85
20.1	0.50	7.07	0.19

^aAt ionic strength 0.8^bAt ionic strength 0.9

where k_0 is the rate constant without the catalyst and k' is $1.4 \times 10^6 \text{ M}^{-2} \text{ min}^{-1}$ (at 25 °C and ionic strength 0.7 M).

The catalytic activity of cobalt(II) and manganese(VII) is close to that of copper(II).

Besides the mentioned compounds, iron(III) is a catalyst for Np(VII) reduction by SO₃²⁻. However, the catalytic effect is observed at concentrations of 10⁻⁵ M.

Compounds of Ag(I) have no effect on the rate of reaction between Np(VII) and SO₃²⁻.

3.2.4 Reduction of Np(VII) by Iodide

Np(VII) in solutions with alkali concentration of 1 to 3 M does not react with I⁻, iodide. The oxidation properties of Np(VII) increases with decreasing pH. As a result, Np(VII) is reduced by iodide at a moderate rate without heating at $(0.5 \text{ to } 3) \times 10^{-2} \text{ M OH}^-$ (Shilov and Krot 1969).

An induction period is observed in the reduction of Np(VII) by iodide. The induction period is because direct reduction of Np(VII) by I⁻ occurs slowly. The acceleration of the reaction is connected with the formation of I⁻ oxidation products. Np(VI) does not participate in autocatalysis, since its addition to the initial solution does not change the kinetic curves.

The primary product of I⁻ oxidation is I₂, which is converted to I₂, IO⁻ and I₃⁻. To elucidate which of these forms catalyses the reaction, the interaction of Np(VII) with I₂ in dilute alkaline solution in the absence and in the presence of KI was studied. It was found that the rate of Np(VII) reduction by a small excess of I₂ without KI is relatively low. The addition of iodide ions accelerates the reaction sharply. From this it follows that the autocatalysis of the reaction between Np(VII) and I⁻ is caused by the formation and accumulation of I₃⁻. The rate of Np(VII) reduction by I⁻ increases upon the addition of microamounts of cobalt(II), copper(II), and manganese(II) to the solution. The limiting concentration at which their catalytic effect becomes noticeable is about $(1 \text{ to } 2) \times 10^{-7} \text{ M}$.

3.2.5 Reduction of Pu(VII) by Iodide

Pu(VII) in KOH solutions is reduced by equimolar amounts of KI with a high rate at room temperature (Komkov et al. 1970). The reaction occurs completely even when the concentration of reducing agent is less than the Pu(VII) concentration by seven to eight-fold. Hence, all the intermediate products of I⁻ oxidation to IO₄⁻ (or H₃IO₆²⁻) are able to participate in the Pu(VII) reduction. This behavior is due to the high oxidation potential of the Pu(VII)/Pu(VI) pair. The possibility of Pu(VII) reduction by IO⁻ and IO₃⁻ was confirmed by the respective experiments.

Therefore, the interaction of Pu(VII) with I⁻ proceeds according to the stoichiometric equation:

If the solution contains an excess of reducing agent, the kinetics of the reaction depend considerably on the alkali concentration. At less than 2 M KOH, the kinetic curves of Pu(VII) reduction are described by the equation:

$$-d[\text{Pu(VII)}]/dt = k[\text{Pu(VII)}][\text{I}^-] \quad (34)$$

The k value for 1 M KOH at 25.0 °C is $6.5 \times 10^3 \text{ M}^{-1} \text{ min}^{-1}$. Increase in the alkali concentration from 1 to 3.3 M leads to a 50-fold decrease in the k value. The temperature dependence of the k values corresponds to an apparent activation energy of 25 kJ mol^{-1} .

The process of Pu(VII) reduction involves the reactions:

The kinetic curves of the Pu(VII) reduction by excess KI in solutions with KOH concentrations higher than 2 M are distorted and become more distorted at higher alkali concentration. The curves in 4 M solution have an S-shape. The distortion is due to increasing participation of intermediate products of I⁻ oxidation in the reduction of Pu(VII).

3.2.6 Reduction of Pu(VII) by Iodate

The kinetics of Pu(VII) reduction by IO_3^- (iodate) was studied in solutions of 0.5 to 3.5 M KOH at 15 to 35 °C (Komkov et al. 1970). Under these conditions, the reaction proceeds irreversibly, according to the stoichiometric equation:

The reaction rate is expressed by the equation:

$$-d[\text{Pu(VII)}]/dt = k[\text{Pu(VII)}][\text{IO}_3^-] \quad (40)$$

The k value for 1 M KOH at 25 °C is $1.1 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$. In the range of alkali concentration from about 0.17 to 1.7 M, the k value decreases inversely with OH^- concentration. The k value then remains constant up to about 3.5 M.

The rate of Pu(VII) reduction by IO_3^- increases relatively slowly with increasing temperature. The apparent activation energy for the reaction in 2.5 M KOH is 24 kJ mol^{-1} .

The mechanism of Pu(VII) reduction may be presented by the reactions:

3.2.7 Reduction of Np(VII) and Pu(VII) by Organic Compounds

The kinetics of the reactions of Np(VII) with aliphatic alcohols, formaldehyde, and formate in alkaline solutions was studied (Tananaev 1989; Tananaev 1990b; Tananaev 1990c; Tananaev 1990d; Tananaev 1990e; Tananaev 1990f); the kinetics of the reaction of Pu(VII) with methanol and ethanol also has been investigated (Tananaev 1992). The reaction rates for all studied systems are described by the equation:

$$-\text{dln}[\text{An(VII)}]/\text{dt} = k \quad (43)$$

or

$$-\text{dln}[\text{An(VII)}]/\text{dt} = k_0[\text{Red}]^n[\text{OH}^-]^m \quad (44)$$

where Red is the reducing agent, k_0 is the rate constant at 1 M Red, and OH^- concentration is expressed in M (at 25 °C).

All the reactions are decelerated with increasing alkali concentration and are accelerated by increasing concentrations of reducing agents and temperature. In Tables 3-10 and 3-11, the kinetic parameters of reactions of Np(VII) and Pu(VII), respectively, are shown.

From Table 3-10 it is seen that normal alcohols with an odd number of carbon atoms are oxidized faster than alcohols with an even number of these atoms. Secondary alcohols, except isopropanol, and the products of alcohol oxidation are more reactive than normal alcohols.

Pu(VII), like Np(VII), reacts slower with ethanol than with methanol. The rate constants of the Pu(VII) reduction by the respective alcohols are about 100 times higher than the analogous rate constants for the Np(VII) reduction.

Table 3-10. Kinetic Parameters for Np(VII) Reduction by Organic Compounds.

Reducing agent	[Red], M	[KOH], M	T, °C	$k \times 10^2$, min ⁻¹	n	m	E, kJ mol ⁻¹	$k_o \times 10^4$, min ⁻¹	Reference ^b
CH ₃ OH	16.4	1.0	28.2	3.84	0.74	-1.5	50.7	44.0	[1]
C ₂ H ₅ OH	3.4	1.0	38.9	0.69	1.5	-1.1	49.7	4.47	[1]
<i>n</i> -C ₃ H ₇ OH	0.28	1.0	60.4	0.80	0.9	-0.96	46.3	34.5	[2]
<i>n</i> -C ₄ H ₉ OH	0.22	1.0	60.4	0.28	0.6	-1.0	58.4	5.77	[3]
<i>n</i> -C ₅ H ₁₁ OH	0.10	1.0	60.4	0.14	0.8	-1.0	81.4	2.71	[3]
<i>i</i> -C ₃ H ₇ OH	0.26	1.0	55.6	0.37	0.8	-1.0	52	16.4	[4]
<i>i</i> -C ₄ H ₉ OH	0.22	1.0	55.6	0.23	0.8	-1.0	54	10.9	[4]
<i>i</i> -C ₅ H ₁₁ OH	0.11	0.5	60.4	0.40	1.0	-0.95	71	9.0	[2]
CH ₂ O	0.0075	1.0	29.6	1.23	1.0	-1.0	59	1.14×10^4	[5]
(CH ₃) ₂ CO	0.27	1.0 ^a	30.3	0.42	0.9	-1.0	49	96	[5]
HCOONa	0.01	0.2	65.0	1.45	0.6	-0.33	56	93	[6]

^aNaOH was used^bReferences:

[1] Tananaev 1989

[2] Tananaev 1990e

[3] Tananaev 1990c

[4] Tananaev 1990d

[5] Tananaev 1990f

[6] Tananaev 1990b

Table 3-11. Influence of the Nature of the Alcohol on the Kinetics of Pu(VII) Reduction (Tananaev 1992).

Alcohol	[ROH] x 10 ² , M	[NaOH], M	T, °C	$k \times 10^2$, min ⁻¹	n	m	E, kJ mol ⁻¹	$k_o \times 10^4$, min ⁻¹
CH ₃ OH	3.4	0.95	25.2	0.26	1.5	-0.3	50	4×10^3
C ₂ H ₅ OH	2.4	0.94	25.2	0.23	0.94	-0.8	44	6.3×10^2

3.2.8 List of Methods for the Preparation of Actinides in Selected Oxidation States

Several methods are available to prepare actinides in selected oxidation states in alkaline media:

1. By the addition of alkali solution to slightly-acid solutions of U(IV), U(VI), Np(IV), Np(VI), Pu(III), Pu(IV), Pu(VI), Am(III), Am(V), Am(VI).
2. By electrochemical oxidation or reduction in alkaline media.
3. By the oxidation of actinide(III), (IV), (V) by ozone, KBrO₃, or other strong oxidizing agents.
4. By the reduction of Np(VII), Np(VI), Pu(VII), Pu(VI), Am(VII), Am(VI) by hydrogen peroxide or the other suitable reagent.

Table 3-12 shows some examples of the preparation of actinide ions in selected oxidation states.

Table 3-12. Methods for the Preparation of Actinides in Selected Oxidation States in Alkaline Media.

Element	Oxidation state	Method of preparation
Uranium	U(IV)	1. $U^{4+} + OH^-$ in inert atmosphere
	U(VI)	1. $UO_2^{2+} + OH^-$ 2. Oxidation of $UO_2 \cdot xH_2O$ by atmospheric oxygen or other suitable oxidizing agent
Neptunium	Np(IV)	1. $Np^{4+} + OH^-$ in inert atmosphere 2. $Np(V) + e^-$ (Pt cathode)
	Np(V)	1. $NpO_2^+ + OH^-$ 2. $Np(VI) + e^-$ (Pt cathode) 3. $Np(VI) + H_2O_2$ 4. $Np(VI) + SO_3^{2-}$ 5. $Np(IV) + Np(VI)$
	Np(VI)	1. $NpO_2^{2+} + OH^-$ 2. $Np(V) + O_3$, CO_3 , or O^- 3. $Np(V) + BrO^-$ 4. $Np(V) + S_2O_8^{2-}$ and so on 5. $Np(VII) + H_2O_2$ 6. $Np(VII) + N_2H_4$, NH_2OH , SO_3^{2-} and so on 7. Radiolysis of aerated Np(VII) solutions 8. $Np(V) + Np(VII)$

Table 3-12. Methods for the Preparation of Actinides in Selected Oxidation States in Alkaline Media.

Element	Oxidation state	Method of preparation
Neptunium (cont'd)	Np(VII)	1. Dissolution of Li_5NpO_6 in alkaline solutions
		2. Anodic oxidation of Np(VI) in alkaline solutions
		3. $\text{Np(VI)} + \text{O}_3$
		4. $\text{Np(VI)} + \text{S}_2\text{O}_8^{2-}$
		5. $\text{Np(VI)} + \text{BrO}^-$
		6. $\text{Np(VI)} + \text{O}^-$
		7. $\text{Np(VI)} + \text{Pu(VII)}$
		8. $\text{Np(VI)} + \text{Pu(VI)}$
		9. $\text{Np(VI)} + \text{Am(VII)}$
		10. $\text{Np(VI)} + \text{Am(VI)}$
		11. $\text{Np(VI)} + \text{MnO}_4^-$
		12. $\text{Np(VI)} + \text{Fe(CN)}_6^{3-}$
		13. $\text{Np(VI)} + \text{AgO}$
		14. $\text{Np(VI)} + \text{Ag}_2\text{O}$ and so on
		15. $2 \text{Np(VI)} \rightleftharpoons \text{Np(VII)} + \text{Np(V)}$
Plutonium	Pu(III)	1. $\text{Pu}^{3+} + \text{OH}^-$ in inert atmosphere 2. $\text{Pu(IV)} + \text{e}^-$ (Pt cathode)
	Pu(IV)	1. $\text{Pu}^{4+} + \text{OH}^-$ 2. $\text{Pu(III)} + \text{oxidizing agent (O}_2 \text{ and so on)}$ 3. $\text{Pu(V)} + \text{e}^-$ (Pt cathode)
	Pu(V)	1. $\text{PuO}_2^+ + \text{OH}^-$ 2. $\text{Pu(IV)} + \text{Pu(VI)}$ 3. $\text{Pu(VI)} + \text{H}_2\text{O}_2$ 4. Radiolysis of aerated Pu(VI) solutions
	Pu(VI)	1. $\text{PuO}_2^{2+} + \text{OH}^-$ 2. $\text{Pu(V)} + \text{O}_3$ 3. $\text{Pu(V)} + \text{O}^-$ 4. $\text{Pu(V)} + \text{S}_2\text{O}_8^{2-}$, BrO^- and so on 5. $\text{Pu(VII)} + \text{H}_2\text{O}_2$ 6. Radiolysis of aerated Pu(VII) solutions 7. Anodic oxidation of Pu(V) 8. $\text{Pu(VII)} + \text{e}^-$ (Pt cathode) 9. $\text{Pu(V)} + \text{Pu(VII)}$

Table 3-12. Methods for the Preparation of Actinides in Selected Oxidation States in Alkaline Media.

Element	Oxidation state	Method of preparation
Plutonium (cont'd)	Pu(VII)	1. Dissolution of Cs_3PuO_5 in alkaline solutions
		2. Anodic oxidation of Pu(VI) in alkaline solutions
		3. $\text{Pu(VI)} + \text{O}_3$
		4. $\text{Pu(VI)} + \text{O}^-$
		5. $\text{Pu(VI)} + \text{S}_2\text{O}_8^{2-}$
		6. $\text{Pu(VI)} + \text{BrO}^-$
		7. $\text{Pu(VI)} + \text{AgO}$
		8. $\text{Pu(VI)} + \text{Am(VI)}$
		9. $\text{Pu(VI)} + \text{MnO}_4^-$ and so on
Americium	Am(III)	1. $\text{Am}^{3+} + \text{OH}^-$
	Am(IV)	1. $\text{Am(III)} + \text{Fe(CN)}_6^{3-}$ (in equimolar amounts)
		2. $\text{Am(III)} + \text{ClO}^-$
		3. $\text{Am(III)} + \text{H}_2\text{O}_2$
		4. $\text{Am(III)} + \text{MnO}_4^-$
	Am(V)	1. $\text{AmO}_2^+ + \text{OH}^-$
		2. $\text{Am(VI)} + \text{H}_2\text{O}_2$
		3. $\text{Am(VI)} + \text{H}_2\text{O}$
		4. Radiolysis of aerated Am(VI) solutions
		5. $\text{Am(VI)} + \text{e}^-$ (Pt cathode)
		6. $\text{Am(III)} + \text{Fe(CN)}_6^{3-}$ (in excess)
	Am(VI)	1. $\text{AmO}_2^{2+} + \text{OH}^-$
		2. $\text{Am(III)} + \text{O}_3$
		3. Anodic oxidation of Am(III)
		4. $\text{Am(V)} + \text{O}^-$
		5. $\text{Am(VII)} + \text{H}_2\text{O}$
		6. $\text{Am(V)} + \text{O}_3$
	Am(VII)	1. $\text{Am(VI)} + \text{O}_3$
		2. $\text{Am(VI)} + \text{O}^-$
		3. $2 \text{Am(VI)} \rightleftharpoons \text{Am(VII)} + \text{Am(V)}$

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4.0 ELECTROCHEMICAL REACTIONS OF ACTINIDES AND TECHNETIUM IN ALKALINE MEDIA

A large body of data exists in the literature on actinide electrochemistry in alkaline media. Different redox actinide reactions are investigated, using electrochemical techniques. The electrochemical preparation methods for solid actinide compounds and for actinide stabilization in selected oxidation states are developed. Electrochemical methods, developed for alkaline solutions, are reported to be widely used in radioanalytical chemistry (actinide hydroxides electrodeposition for alpha-spectrometric source preparation) and in non-nuclear analytical chemistry of actinides (voltametric techniques for quantitative determination). At the same time, literature data on technetium behavior in alkaline media are much more restricted.

4.1 MECHANISM OF ELECTROCHEMICAL REACTIONS OF ACTINIDES IN ALKALINE MEDIA

Voltammetry at platinum and dropping mercury electrodes has been used to investigate actinide electrochemical reactions in alkaline media. Using voltametric techniques and Pt microelectrodes, Np(VII), Pu(VII), and Am(VI) were found to be reduced in alkaline media according to a step-by-step mechanism with transfer of one electron at each step of the reaction:

Processes of An(VII)/An(VI) reduction in alkaline solutions are found to be either irreversible or quasi-reversible. An(VI)/An(V) reduction is characterized by reversibility, but the further reduction of Pu(V) and Am(V) is completely irreversible. The reduction mechanism of Np(V) in 1 to 10 M NaOH has not been determined yet, since this process was proved to occur at negative electrode potentials (less than -1.0 V SHE); impossible to study due to the intense hydrogen evolution.

Formation and adhesion of poorly soluble An(V) hydroxides on the electrode surface in 0.1 to 2.5 M NaOH and 0.1 to 1.0 M LiOH are observed in An(VI) electrochemical reduction in alkaline media. This effect diminishes the values of limiting currents for the processes under study. The adhesion was found to be strong. Nevertheless, the An(V) hydroxide layers may be removed from the electrode after polarization at a potential sufficiently positive to oxidize An(V) to An(VI).

The mechanism of technetium(VII) electrochemical reduction in weakly alkaline media ($8 < \text{pH} < 11$) also was found to be a chain of one electron transfers.

This sequential reduction is found to be complicated by disproportionation. As described in Section 2.0, Tc(VI) is thermodynamically unstable in alkaline media and tends to disproportionate according to the reaction

In solutions with pH greater than 12, the rate of Tc(VI) disproportionation becomes so high that the limiting current of the polarographic wave, corresponding to Tc(VII)/Tc(VI), is found to be 2 times greater than that for the further reduction step $\text{Tc(VI)} + e^- \rightarrow \text{Tc(V)}$. In these electrolytes, voltametric techniques may indicate only two steps of the reduction process (Zhdanov et al. 1970; Founta et al. 1987):

If the pH of the supporting electrolyte is increased from 12 to 14, the half-wave potential of Tc(VII)/Tc(V) reduction shifts from -0.56 V vs. SHE at the rate of 80 mV/pH. This shift indicates the participation of OH⁻ ions in the electrochemical reduction of TcO₄⁻ to TcO₂·xH₂O. The latter compound in 0.1 to 1.0 M NaOH solutions, containing up to 10⁻³ M Tc(VII), was found not to form an insoluble film on the dropping mercury electrode surface, when the drop rate was changed from 0.5 to 1 s⁻¹. This in turn indicates a significant solubility of precipitated Tc(IV) hydroxide deposited at the electrode as a product of Tc(V) electrolysis (Founta et al. 1987).

4.2 ELECTROCHEMICAL PREPARATION OF An(VII), An(VI) AND An(V) (An=Np, Pu, Am) ALKALINE SOLUTIONS

Alkaline sludge, containing NpO₂ (or PuO₂) calcined powders or freshly prepared actinide(IV) hydroxides, were used as starting materials. Electrochemical cells with compartments separated by porous glass or anion exchange membranes and a Pt gauze anode,

were specially designed for An(III) and An(IV) oxidation in alkaline media. The Pt anode occupied approximately 25% of the anode compartment volume and the surface to volume (S/V) ratios ranged from 0.5 to 0.6 cm²/mL.

When calcined actinide dioxide powders were used (Shvedov and Seregin 1972; and Peretrukhin 1980), the oxidation process was slow, requiring 6 to 40 hours. The rate of dissolution was unaffected by anodic current density in the range 1 to 10 mA/cm² for Np and in the range 5 to 20 mA/cm² for Pu. The accumulation of An(V) and An(VI) soluble species in the solution was noticed in the first hours of the process. About (1 to 2) x 10⁻³ M Np(VII) or Pu(VII) with (3 to 6) x 10⁻⁵ M Np(VI) or Pu(VI) in 1 to 4 M NaOH were found to be the final products of this electrochemical process. About 2 to 3% of the original dioxide was found unreacted and adhering to the walls of the cell.

When freshly prepared hydroxide precipitates in 1 to 5 M OH⁻ were used as starting material, the dissolution - oxidation electrolysis appeared to be accomplished in 2 to 4 hours; i.e., much more rapidly than in case of the calcined oxides. For instance, 6 x 10⁻⁴ M Am(VI) solution in 5 M NaOH has been obtained, using Am(III) hydroxide precipitate, by 2.3 hours' electrolysis at a Pt anode with current density 7 mA/cm² and S/V ratio 0.5 cm²/mL (Peretrukhin et al. 1974).

A 1.5 x 10⁻³ M Pu(VII) solution has been prepared using PuO₂·xH₂O precipitate, with 2.5 hours' electrolysis at the current density 15 mA/cm², at 15 °C and a S/V ratio of 0.5 cm²/mL (Peretrukhin 1980). The current efficiency of the developed process was found to be about 1%. Temperature increase to 60 °C was found to increase the rate insignificantly. The mechanism of anodic precipitate dissolution apparently includes the interaction of solid hydroxide particles with OH radicals and other oxidizing reagents generated at the anode. The reaction of solid hydroxide particles with An(VI) and An(VII) accumulated in the solution during electrolysis also seems to be possible.

When actinide(V),(VI) alkaline solutions or precipitates are used as starting material for electrochemical oxidation, the accumulation of An(VII) in the solution is further accelerated compared to oxidation of the An hydroxide precipitates in the (+3) and (+4) oxidation states. Methods of Np(VII) and Pu(VII) solution preparation with anodes fabricated of Pt, PbO₂, and other materials have been developed (See Table 4-1).

The values of current efficiency obtained for Np(VI) electrochemical oxidation appear to be much higher than those of Pu(VI). Completeness of the reaction in both cases was found to be the same (97 to 99%). These values are comparable with chemical methods commonly used for actinide(VII) alkaline solutions preparation. Complete (100%) oxidation of Np and especially Pu in alkaline solutions seems to be impossible because of their thermodynamic instability and ability to reduce water.

Table 4-1. Current Density (i) and Current Efficiency (k) for Np(VII) and Pu(VII) Alkaline Solution Preparation Using Different Anodes at 25 °C.

Np(VI) - Np(VII) oxidation										
Anode	Pt		PbO ₂		C (gr.)		Ni		St. steel	
KOH, M	1	4	1	4	1	4	1	4	1	4
i, mA/cm ²	6.0	5.5	7.0	6.8	9.5	9.0	7.1	6.5	13.6	43
K, %	94	95	92	90	65	68	85	82	11.7	36
Pu(VI) - Pu(VII) oxidation.										
Anode	Pt				PbO ₂					
KOH, M	1	4	6.1	12.1	1	4	6.1	12.2		
i, mA/cm ²	150	100	60	20	2000	320	120	50		
K, %	3.5	5.3	8.8	24.1	0.2	1.6	4.4	10.6		

The stability of Np(VII) (Shatokhina and Peretrushin 1977), Pu(VII) (Komkov et al. 1969), and Am(VI) prepared electrochemically in alkaline solutions as a function of time has been studied. Time of spontaneous half reduction is 10 to 30% shorter for the electrochemically prepared solution samples as compared to those prepared by ozonolysis. Accelerated self-reduction of Np(VII) and Pu(VII) in electrochemically prepared alkaline solutions is explained by their contamination with anode corrosion products, since these products catalyze the actinide reduction with water (Krot et al. 1977).

The stabilities of Np(VII) and Pu(VII) in alkaline media are significantly reduced in the presence of anode materials (Pt, PbO₂, graphite) without application of polarization current. The rate of Pu(VII) and Am(VI) spontaneous reduction was found to be proportional to the square of area of the electrode material sample introduced to the alkaline solution (Ananiev 1978). The observed electrode material catalytic effect seems to be of electrochemical nature. Pu(VII) and Am(VI) create sufficiently high oxidation potentials in the solutions such that oxygen evolution on the surface of the electrode material takes place in the same manner as at the electrode polarized with same potential from an external power source.

Electrochemical preparation of Np(V) (Simakin and Matyashchuk 1969; and Zielen and Cohen 1970), Pu(V) (Bourges 1972), and Am(V) (Peretrushin et al. 1974) from An(VII)/An(VI) alkaline solutions may be easily carried out by potentiostatic electrolysis at potentials 200 mV more negative than the value of the corresponding formal potential. Conversely, the back oxidation of An(V) in alkaline media can occur when applying a polarization potential 200 mV more positive than the corresponding formal potential values (see Section 2.0).

4.3 ELECTROCHEMICAL METHODS OF DETERMINATION OF ACTINIDES AND TECHNETIUM IN ALKALINE MEDIA

A traditional electrodeposition technique with Pt or stainless steel cathodes, followed by α -spectrometry, is commonly applied for trace TRU determination. Pu(VI) electrodeposition from 1.6 to 2 M NaOH solutions was found to occur with 100% yield at current densities more than 40 mA/cm². Complete electrodeposition is achieved in 2 hours (Muller and Brouns 1952). At a current density of 25 mA/cm², the layers of electrodeposited Pu(IV) hydroxide appear to be more uniform, but 90% Pu deposition is achieved only in 4 hours (Milyukova et al. 1969). At high (0.4 to 0.5 A/cm²) current densities, 98 to 99% electrodeposition of uranium, trace amounts of thorium-234, plutonium, and cerium-144 may be reached in 40 minutes (Zantuti et al. 1991). Thus, pure NaOH solutions appear to be convenient electrolytes for actinide electrodeposition.

However, in presence of weighable amounts of other metals susceptible to electrodeposition in these conditions (for instance CrO₄²⁻), further α -spectrometric actinide determination becomes impossible due to the self-absorption of α -particles in the layer.

Weighable amounts of U, Np, Pu, and Am (in oxidation states +7, +6 and +5) may be determined by a direct voltametric method, because their solubilities in alkaline solutions are sufficiently high. Spectrophotometric methods, widely used for actinide determination in acidic solutions, finds its application in alkaline media only for determination of actinides in the heptavalent (+7) oxidation state. Actinides in lower oxidation states (+6 and +5) possess very low molar extinction coefficients and cannot be determined directly.

Therefore, voltammetry remains the primary method for non-destructive measurement of U(VI), Np(VI,V), Pu(VI,V), and Am(VI,V) concentrations in alkaline solutions. Determination of these elements with a Pt rotating disc electrode in NaOH and LiOH solutions have been described. U(VI) and Pu(VI,V) were shown to be determined in 1 to 4 M NaOH solutions with a dropping mercury electrode, using direct current or differential pulse polarography. Np(VII,VI,V) (Peretrukhin and Alekseeva 1975), U(VI), Pu(VI,V) (Bourges 1972; and Abuzwida et al. 1991), Pu(VII) (Peretrukhin 1980), and Am(VI,V) (Peretrukhin et al. 1974) voltametric determination in alkaline solutions is described.

Neptunium determination, using the values of limiting currents of the wave Np(VII)/Np(VI), appears to be possible in a wide range (0.2 to 10 M) of NaOH concentrations. Np(VI) and Np(V) determination in 0.1 to 3.5 M NaOH is complicated due to changes in the Np ions' chemical states accompanying the electron transfer reaction. Formation of poorly soluble Np(V) hydroxide and its adsorption on the electrode surface disturbs the results of quantitative determination. In this range of alkali concentrations in supporting electrolyte and in 0.1 to 1.9 M LiOH, the limiting current of the wave Np(VI)/Np(V) is determined not only by the concentration of Np in the sample but also is affected by alkali concentration (Peretrukhin and Alekseeva 1975). In more concentrated alkaline solutions (with greater than 4 M NaOH or 2 M LiOH), all the chemical species of Np(V) present in the solution appear

to be electroactive. The limiting currents of An(VI)/An(V) (An=U, Np, Pu, Am) reactions in solution are not affected by moderate changes in alkali concentration (e.g., 4.0 ± 0.25 M NaOH).

Direct current voltametry may be applied not only to solutions containing the element of interest in a given oxidation state [(Np(VII), Np(VI) or Np(V))], but also allows determination of concentration ratios between several oxidation states. For neptunium in the concentration range of 5×10^{-5} to 4×10^{-3} M, the method results in 3 to 5% experimental error regardless of the neptunium oxidation state in solution. Nitrate, sulfate, and uranyl do not interfere. In the presence of Pu(VI) and Pu(V), the determination of Np in alkaline media becomes more complicated (Peretrukhin and Alekseeva 1975).

Simultaneous determination of U(VI), Pu(VI), and Pu(V) in alkaline media has been elaborated by means of direct current and differential pulse polarography (Abuzwida et al. 1991). In 1 to 4 M NaOH, U(VI) is reduced at a dropping mercury electrode to U(V) at a half-wave potential ($E_{1/2}$) of -0.89 V vs. Ag/AgCl (See Figure 4-1). The limiting current of this wave was found to be proportional to U(VI) concentration in 4 M NaOH in the range 1.3×10^{-7} to 3×10^{-4} M. At higher uranium concentrations, deviations from linearity are observed due to polymerization of uranates. Pu(VI) and Pu(V) may be determined with a Pt microelectrode at an $E_{1/2}$ of +0.02 V vs. Ag/AgCl and with a dropping mercury electrode at -1.1 V vs. Ag/AgCl. The limiting currents of both plutonium reduction waves are found to be proportional to Pu concentration in the range 4×10^{-6} to 1.2×10^{-3} M. The determination of U(VI), Pu(VI), and Pu(V) are not affected by the presence of 2 M NaNO₃, 2 M NaNO₂, 1.5 M NaAlO₂, 0.5 M NaF, and ions such as Mo(VI), W(VI), V(V), and Cu(II). The presence of CrO₄²⁻ and FeO₂ disturbs the determination of U(VI) and Pu(V). The contribution of the reaction Fe(III)/Fe(II) to the limiting current of uranium reduction may, however, be calculated from the height of the second iron reduction wave, Fe(II)/Fe⁰.

Voltammetric methods have also been elaborated for determining the ratio of actinide [Np(VI)+Np(V); Np(VII)+Np(VI); Pu(V)+Pu(VI); Pu(VII)+Pu(VI)] concentrations present in alkaline solutions in different oxidation states (Peretrukhin 1980).

Figure 4-1. Voltammetry of U(VI), Pu(VI) and Pu(V) in 1 M NaOH.

Curves: 1a - 1×10^{-4} M U(VI), DC polarogram at DME, process $\text{U(VI)} + e^- \rightarrow \text{U(V)}$,
 1b - difference pulse polarography at DME,
 2a - 1.2×10^{-4} M Pu(VI), DC voltammetry at Pt electrode, process $\text{Pu(VI)} + e^- \rightarrow \text{Pu(V)}$,
 2b - DC polarogram at DME,
 i_1 corresponds to process $\text{Pu(VI)} + e^- \rightarrow \text{Pu(V)}$,
 i_2 - $\text{Pu(V)} + e^- \rightarrow \text{Pu(IV)}$,
 i_3 - $\text{Pu(IV)} + e^- \rightarrow \text{Pu(III)}$,
 3a - 1.2×10^{-4} M Pu(V), DC voltammetry at Pt electrode, process $\text{Pu(V)} + e^- \rightarrow \text{Pu(VI)}$,
 3b - DC polarogram at DME, process $\text{Pu(V)} + 2e^- \rightarrow \text{Pu(III)}$.

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5.0 RADIATION CHEMISTRY OF ACTINIDES AND TECHNETIUM IN CARBONATE AND ALKALINE SOLUTIONS

Highly radioactive aqueous solutions, including carbonate and alkaline solutions, are produced upon reprocessing of spent nuclear fuel and upon the separation of practically important radionuclides. The products of water radiolysis appear in the solutions as a result of the action of α -, β - and γ -radiations of actinides, cesium, strontium, rare earths, and other elements. Radiolysis products include short lived (hydrated electron, H atom, OH, and HO_2 radicals) and long lived species (H_2 and H_2O_2). Table 5-1 shows the yields (G values) of primary products of water radiolysis measured as a number of ions, molecules, or atoms per 100 eV of absorbed energy of ionizing radiation.

Table 5-1. The Yields of Primary Products of Water Radiolysis in Bulk Solution for ^{60}Co γ -Rays and Fast Electrons with Energies of 1 MeV and Higher (Pikaev 1986).

pH	$G_{e_{aq}^-}$	G_{H}	G_{OH}	G_{O}	G_{H_2}	$G_{\text{H}_2\text{O}_2}$	$G_{\text{H}_2\text{O}_2^*}$	G_{OH^*}
0-2	3.05	0.6	2.95	0.0067	0.45	0.8	-	-
4-9	2.8-2.9	0.6	2.8-2.9	0.0067	0.45	0.75	3.3-3.4	0.5-0.6
12-13	2.8-2.9	0.55	2.9	0.012	0.4	0.75	-	-

α -Particles emitted by actinides have an energy of 5 to 6 MeV. The yields of water radiolysis products for such α -particles were not determined. However, the yields in 0.4 M H_2SO_4 were measured in the case of ^{210}Po α -particles (see Table 5-2) (Vladimirova 1968).

Table 5-2. The Yields of Primary Products of Water Radiolysis for α -Particles.

Energy, MeV	Medium	$G_{e_{aq}^-} + G_{\text{H}}$	G_{OH}	G_{H_2}	$G_{\text{H}_2\text{O}_2}$	G_{HO_2}	References ^a
5.3	0.4 M H_2SO_4	0.55	0.35	1.4	1.3	0.2	[1]
6.4	pH 7	-	0.4	-	0.95	0.085	[2]

^aReferences:

[1] Vladimirova 1968

[2] Burns and Sims 1981

Because their energy is 5.3 MeV, the results of these measurements can be used for the interpretation of experimental data on radiolytic conversions in aqueous solutions upon the action of α -radiation. Table 5-2 contains also the yields for α -particles (helions) with energy 6.4 MeV in neutral solution (Burns and Sims 1981).

The hydrated electron is a powerful reducing agent. The standard redox potential (E°) for reaction

or

is -2.87 V (Pikaev 1986). In the electromotive series, it is located between Na and La. The reactions of e_{aq}^- are divided into three groups: (1) addition to ions (reduction), (2) addition to neutral molecules, and (3) dissociative addition.

Reduced ions in lower and often unusual oxidation states are formed in reactions of the first group. The process

is an example of reactions of the second group. The product radical ion is the alkaline form of the HO_2 radical. The third group involves reactions leading to the formation of radicals:

In the radiation chemistry of aqueous systems, reaction (6) may be used to produce the radical ion O^- (in alkaline medium) or the radical OH (in neutral and acid media) from e_{aq}^- .

Other reactions in which e_{aq}^- can be converted to the hydroxyl radical are:

The H atom is a weaker reducing agent than e_{aq}^- . The E° value for H is -2.3 V (Pikaev 1986). This species plays an important role in an acid medium. In alkaline media, it is converted to e_{aq}^- :

Reaction (10) is reversible: pK_{10} equals 9.6 (Pikaev 1986).

As a rule, the H atom reacts with inorganic compounds more slowly than does e_{aq}^- . Molecular oxygen and the OH radical are the exceptions; the rates of their reactions with e_{aq}^- and H are approximately the same.

The radical OH is a strong oxidizing agent. The E° value is 1.9 V (Pikaev 1986). Its reactions with inorganic compounds can be divided into two main groups: (1) simple oxidation and (2) abstraction of H from hydrogen-containing compounds.

In alkaline media, the OH radical dissociates:

The pK_{11} value is 11.9 (Pikaev 1986).

The radical ion O^- reacts with inorganic compounds generally more slowly than does OH. However, in contrast to OH, this radical ion reacts rapidly with oxygen:

The product ozonide ion O_3^- is an oxidizing agent.

The radical HO_2 and its alkaline form O_2^- play important roles upon radiolysis of aqueous solutions containing oxygen. The potentials of the pairs O_2/HO_2 and O_2/O_2^- are -0.3 and -0.56 V, respectively (Pikaev 1986).

Hydrogen peroxide, H_2O_2 , depending on the nature of the solute and the pH value of the solution, can act as both an oxidizing and a reducing agent. In alkaline media, hydrogen peroxide exists in an ionic form:

The pK_{13} value is 11.9 (Pikaev 1986).

As a rule, molecular hydrogen does not take part in reactions with solutes.

5.1 REACTIVITY OF ACTINIDE IONS TOWARDS WATER RADIOLYSIS PRODUCTS AND OTHER FREE RADICALS

Much is known on the reactivity of actinide ions towards water radiolysis products and other free radicals in aqueous solutions. The respective data for carbonate and alkaline media are considered in this section.

5.1.1 Carbonate Medium

The main radical products of the radiolysis of carbonate solutions are e_{aq}^- and the radical ion, CO_3^- (Zhestkova and Pikaev 1976). The reactions of these species with ions of actinides in higher oxidation states were studied thoroughly (Pikaev et al. 1974; Mulac et al. 1984; Gogolev 1990). The rate constants of e_{aq}^- reactions with ions of uranium, neptunium, and plutonium, measured by the pulse radiolysis methods, are listed in Table 5-3.

From the table it follows that the rate constants for Np(VI) depend slightly on CO_3^{2-} concentration. A conclusion was made that the limiting step of the reactions is the diffusion of reacting species (Pikaev et al. 1974). It was also suggested that the structure of $\text{NpO}_2(\text{CO}_3)_3^{4-}$ is not changed within the range of CO_3^{2-} concentrations studied; because of it, the change in K_2CO_3 or Na_2CO_3 concentration has an effect owing to the change in the viscosity of the medium.

Table 5-3. Rate Constants (k) of e_{aq}^- Reactions with Actinide Ions in Carbonate Solutions.

Ion	[Ion] x 10 ⁵ , M	[K ₂ CO ₃], M	E _r , V (NHE) ^c	k x 10 ⁻⁹ , M ⁻¹ s ⁻¹	Reference ^d
U(VI)	-	0.05 ^a	-0.671	11.8	[1]
Np(VI)	-	0.05 ^a	0.445	23.4	[1]
	2.7	^b	-	19	[2]
	5.4	^b	-	17	[2]
	5.4	0.1	-	19	[2]
	2.7	1.0	-	13	[2]
	5.4	1.0	-	11	[2]
	5.4	5.0	-	6.2	[2]
Np(V)	20	0.1	-	2.5	[2]
	20	1.0	-	2.0	[2]
	20	5.0	-	1.9	[2]
Np(IV)	5.0	0.1	-	5.0	[2]
	5.0	1.0	-	4.0	[2]
	6.7	1.0	-	4.0	[2]
	6.7	4.3	-	4.0	[2]
	5.0	4.5	-	3.7	[2]
	-	6.0	-	3.0	[3]
Pu(VI)	-	0.05 ^a	0.334	22.8	[1]
	-	0.1	-	23	[2]
	-	1.0	-	14	[2]
	-	5.0	-	6	[2]

^aNa₂CO₃^b0.5 M NaHCO₃ + 0.5 M Na₂CO₃^cNHE; normal hydrogen electrode^dReferences:

[1] Mulac et al. 1984

[2] Pikaev et al. 1974

[3] Gogolev et al. 1990

The reaction rate constant decreases by approximately one order of magnitude upon the transition from Np(VI) to Np(V). In the opinion of the authors of paper (Pikaev et al. 1974), this feature is connected with the fact that the transition from Np(V) to Np(IV) is accompanied by a considerable change in the structure. The influence of CO_3^{2-} concentration on the reaction rate in the case of Np(V) is also not strong. The limiting factor again is diffusion (Pikaev et al. 1974). The form of the Np(V) [it seems to be $\text{NpO}_2(\text{CO}_3)_2^{3-}$] is unchanged within the studied range of CO_3^{2-} concentration.

Reaction

occurs faster than the reaction between Np(V) and e_{aq}^- but slightly slower than the reaction of e_{aq}^- with Np(VI). It is explained by the fact that the transition of Np(IV) to Np(III) has a monoelectron mechanism without the change in the structure of ions as in the case of Np(VI) (Pikaev et al. 1974).

The calculation of k_{dif} for reactions of e_{aq}^- with Np(VI), Np(V), and Np(IV) in carbonate media was described (Pikaev et al. 1975). Although the radii of carbonate complexes are unknown, the authors of the paper evaluated them on the basis of the known crystallographic radii of Np^{4+} and NpO_2^{2+} and the bond lengths in similar complexes. The respective values of radii (r_x) are shown in Table 5-4.

Table 5-4. The Evaluation of k_o and k_{dif} for Reactions of Carbonate Complexes of Neptunium with e_{aq}^- (Pikaev et al. 1975).

Ion	$k_o, \text{M}^{-1} \text{s}^{-1}$	$r_x, \text{\AA}$	$D_x \times 10^5, \text{cm}^2 \text{s}^{-1}$	$k_{\text{dif}}, \text{M}^{-1} \text{s}^{-1}$
$\text{NpO}_2(\text{CO}_3)_3^{4-}$	2.1×10^9	3.5	0.8	1.1×10^9
$\text{NpO}_2(\text{CO}_3)_2^{3-}$	4.5×10^8	3.5	0.9	2.7×10^9
$\text{Np}(\text{CO}_3)_5^{6-}$	1.3×10^8	3.0	0.9	8.3×10^7

Because the rate constants were measured at comparatively high carbonate concentrations, the values of the constants should be specified because of the salt effect. It was taken into account by the Brönsted-Bjerrum equation:

$$\log(k/k_o) = -1.02 Z_x \mu^{1/2} / (1 + a\mu^{1/2}) \quad (15)$$

where k is the rate constant at the selected ionic strength μ , k_0 is the rate constant at $\mu = 0$, Z_X is the charge of ion X reacting with e_{aq}^- , and $a = r/3$ (r is the sum of the e_{aq}^- and X radii, in Å).

The constants for bimolecular reactions with a diffusion-controlled rate, k_{dif} , were calculated by means of the Debye equation:

$$k_{dif} = 4\pi N(r_e + r_X)(D_e + D_X)Q/[1000(e^Q - 1)] \quad (16)$$

where N is the Avogadro constant, r_e (2.5 Å) and r_X are the e_{aq}^- and ion X radii, D_e and D_X are the diffusion coefficients of e_{aq}^- ($4.96 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and X, $Q = -Z_X e^2 / [\epsilon kT(r_e + r_X)]$, Z_X and e are the charges of X and the electron, k is the Boltzmann constant, ϵ is the dielectric constant of the medium, and T is temperature, in K.

The constants k_0 and k_{dif} are shown in Table 5-4. On the basis of the data of Table 5-4, it is possible to conclude that the rate of reaction between e_{aq}^- and $\text{NpO}_2(\text{CO}_3)_3^{4-}$ is limited by diffusion. The value of k_0 for $\text{NpO}_2(\text{CO}_3)_2^{3-}$ is less than k_{dif} because of the change in the structure as a result of the reaction.

Note that the ions under consideration can form ionic pairs with counterions. Because of this, the ions' charges can be less negative than shown in Table 5-4. However, this effect does not influence the conclusions made. For example, if the charge of the Np(VI) ion is -3 or -2, the k_0 and k_{dif} values are 3.6×10^9 or $6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and 2.6×10^9 or $6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

The evaluation of rate constants for reactions of e_{aq}^- with Pu(III) and Am(III) was carried out (Gogolev et al. 1990). Their possible values are less than $10^6 \text{ M}^{-1} \text{ s}^{-1}$.

The rate constants of reactions of CO_3 with uranium, neptunium, and plutonium ions are listed in Table 5-5. The rate constants of reactions of Ce(III) with CO_3 are shown for comparison.

The rate constants depend strongly on the free energy of the reaction (difference of redox potentials) of the reacting species. The linear dependence between $\log k$ and $E_f(\text{VI/V})$ was established for uranium, neptunium, and plutonium. The values of constants are discussed on the basis of the Marcus theory for electron transfer. The linear dependence proposes that the inner sphere interaction, i.e. the oxidation of M(V) by CO_3 , occurs via electron transfer.

The dependence of $\log k$ on E_f is approximately linear for complex ions of Am(III), Pu(III), and Ce(III) (Gogolev et al. 1990). However, in the case of Np(III), the k value does not have this dependence. Obviously, the rate of the reaction of Np(III) with CO_3 is controlled by diffusion. The literature data allow evaluation of the diffusion limit (using the Debye equation) for the rate of the reaction of Np(III) with CO_3 . The calculation gives $k_{dif} = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 0$.

In 1 M solution, the constant can decrease owing to increasing viscosity; however, this decrease is offset by the ionic strength effect.

Table 5-5. The Rate Constants of Reactions of CO_3^{2-} with Actinide Ions

Ion	Medium	$[\text{CO}_3^{2-}]$, M	Pair	E_f , V (NCE)	$k \times 10^{-7}$ $\text{M}^{-1} \text{s}^{-1}$	Reference ^a
U(V)	Na_2CO_3	0.05	VI/V	-0.671 [1]	48.8	[1]
U(IV)	KHCO_3	~3	V/IV	0.0 [2]	1.4	[3]
Np(V)	Na_2CO_3	0.05	VI/V	0.445 [1]	1.52	[1]
Np(III)	K_2CO_3	1.0	IV/III	-1.32 [2]	330	[3]
Np(III)	K_2CO_3	3.0	IV/III	-	140	[3]
Pu(V)	Na_2CO_3	0.05	VI/V	0.334 [1]	2.73	[1]
Pu(III)	K_2CO_3	1.0	IV/III	-0.495 [2]	70	[3]
Pu(III)	K_2CO_3	1.1	IV/III	-	56	[3]
Pu(III)	K_2CO_3	4.3	IV/III	-	67	[3]
Am(III)	K_2CO_3	3.0	IV/III	0.86 [2]	2.5	[3]
Am(III)	K_2CO_3	4.6	IV/III	-	2.7	[3]
Am(III)	K_2CO_3	6.0	IV/III	-	1.5	[3]
Ce(III)	K_2CO_3	0.75	IV/III	-	4.3	[3]
Ce(III)	K_2CO_3	1.5	IV/III	-	6.7	[3]
Ce(III)	K_2CO_3	3.0	IV/III	-	9.0	[3]

^aReferences:

[1] Mulac et al. 1984

[2] Fedoseev et al. 1979

[3] Gogolev 1990

5.1.2 Alkaline Medium

If one compares the potentials of the pairs of neptunium, plutonium, and americium in alkaline solutions with the water radiolysis product potentials, it is possible to conclude that e_{aq}^- is able to reduce the compounds of these elements in any high oxidation state, and the radical ion O^- is able to oxidize the compounds of these elements in any low valent state.

The radical ion O_2^- is a reducing agent for Np(VII), Np(VI), Pu(VII), Pu(VI), Am(VII), and Am(VI); however, it is an oxidizing agent for Np(III), Np(IV), Pu(III), and Pu(IV). Hydrogen peroxide should reduce Np(VII), Np(VI), Pu(VII), Pu(VI), Am(VII), and Am(VI) and oxidize Np(III), Np(IV), Pu(III), Pu(IV), and Am(III). The radical ions O_3^- and CO_3^- should oxidize the compounds of low valency. Experimental results confirm these conclusions.

Thermodynamic values allow evaluation of the possible reaction pathways but do not allow calculation of the rate of one or another reaction. Kinetic restrictions connected with the changes in the structure [e. g. on the transition from Np(IV) to Np(V) and vice versa] can vary the reaction rate.

Pulse radiolysis with spectrophotometric registration of short-lived species was used for the determination of rate constants for the reactions of Np(VII), Np(VI), Np(V), Pu(VII), and Pu(VI) with e_{aq}^- , Np(VI) with O^- , Np(VI) and Np(V) with O_3^- and CO_3^- , and Np(VII) with Np(V). The solutions of neptunium or plutonium ions saturated with argon or N_2O were irradiated with electron pulses. The initial solutions of Np(VI) and Pu(VI) were prepared from specially purified samples by evaporation with perchloric acid to the appearance of white vapors. Neptunium(V) was prepared by the reduction of Np(VI) and the precipitation of NpO_2OH by ammonia; then NpO_2OH was dissolved in $HClO_4$. Valence determination was performed spectrophotometrically. The solutions of Np(VII) and Pu(VII) were prepared by the oxidation of Np(VI) and Pu(VI) in alkaline solutions with ozone.

5.1.2.1 Rate constants of e_{aq}^- reactions with neptunium and plutonium ions.

The reactions

occur in deaerated alkaline solutions as a result of the action of the electron pulse. In this system, in the absence of solutes, e_{aq}^- disappears predominantly by the following reactions:

Here X are unidentified impurities.

Obviously, reactions (21 to 24) should be taken into account upon the determination of rate constants of reactions between e_{aq}^- and neptunium and plutonium ions. The less these reactions contribute to the total decay of e_{aq}^- , the more accurate the measurement of the rate constant of the respective reaction becomes. The lifetime of e_{aq}^- increases with increasing alkali concentration. At greater than 5 M OH^- , the e_{aq}^- lifetime is sufficiently long for the accurate determination of the constants (Pikaev et al. 1973). To provide the increase in the e_{aq}^- lifetime at less than 5 M OH^- , 5×10^{-3} M CH_3OH were added to the solution. Methanol scavenging of O^- radical ions suppresses reaction (21) and, as a consequence, decreases the e_{aq}^- decay rate.

The rate constants of e_{aq}^- reactions with neptunium and plutonium ions were determined from curves of e_{aq}^- optical absorption decay at 650 nm (at greater than 7.5 M OH^-) or 700 nm (at less than 7.5 M OH^-) in the presence of different concentrations of actinide ions. The correction taking into account the participation of e_{aq}^- in reactions (21 to 24) or (22, 24) (in the presence or in the absence of CH_3OH , respectively) was introduced to the calculation of the constants. The measured rate constants of reactions:

are shown in Tables 5-6 and 5-7.

Table 5-6. Rate Constants of Reactions of e_{aq}^- with Neptunium Ions
(Pikaev et al. 1973; Pikaev et al. 1976).

Ion	[Ion] x 10 ⁵ , M	[OH ⁻], M	k x 10 ⁻¹⁰ , M ⁻¹ s ⁻¹
Np(VII)	2	0.1	2.9 ± 0.3
	2	0.5	3.2 ± 0.6
	4	1.0	2.0 ± 0.4
	3	2.0	2.1 ± 0.4
	4	5.0	1.7 ± 0.2
	4	7.5	1.3 ± 0.2
	4	10.0	0.88 ± 0.06
	4	12.5	0.6 ± 0.1
	8	12.5	0.8 ± 0.1
Np(VI)	1.5	0.5	2.3 ± 0.6
	5.3	1.0	1.3 ± 0.6
	2.0	2.0	1.3 ± 0.2
	5.3	2.0	1.1 ± 0.2
	5.3	5.0	2.0 ± 0.6
	5.3	7.5	1.1 ± 0.2
	5.3	10.0	0.83 ± 0.08
	5.3	12.5	0.68 ± 0.07
Np(V)	4.4	1.0	0.50 ± 0.06
	4.4	2.0	0.61 ± 0.08
	4.4	5.0	0.66 ± 0.07
	5.3	5.0	0.52 ± 0.07
	4.4	7.5	0.32 ± 0.04
	7.5	7.5	0.30 ± 0.03

The reaction rates for all the studied ions decrease noticeably at OH^- concentrations greater than 7.5 M. Several reasons for the decreasing rate of e_{aq}^- reactions in high-concentrated solutions of alkalis were postulated (Pikaev 1973). They are the viscosity of such solutions, the capture of electrons into deeper traps (the λ_{max} of the e_{aq}^- optical absorption band is shifted to shorter wavelengths [Pikaev 1976]), the formation of ionic pairs $\text{M}^+ \cdots e_{\text{aq}}^-$ (Gopithathan et al. 1970; Kabakchi 1971, Kabakchi and Shubin 1972) which can be less reactive, the change in the activity coefficients at high ionic strengths and so on.

It was suggested that the rate of reactions between Np(VI) and e_{aq}^- is controlled by diffusion; the tunnel electron transfer plays an important role in the reaction of Np(VII) (Pikaev et al. 1973). The calculation of diffusion rate constants, k_{dif} , for reactions of e_{aq}^- with actinide ions is considered (Pikaev et al. 1975). In alkaline solutions, Np(VII) and Pu(VII) exist as complex ions $\text{MO}_4(\text{OH})_2^{3-}$ (Krot et al. 1977). Because of it, the correction due to the salt effect by means of the Brönsted-Bjerrum equation was introduced into the rate constant of reaction between e_{aq}^- and Np(VII) in 0.1 M KOH solution. At $a = 1.8 \text{ \AA}$ [see equation (15)], $k_o = 7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($Z_X = -3$) or $k_o = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ($Z_X = -2$, if an ionic pair with K^+ is formed in 0.1 M KOH solution).

The constant of the diffusion-controlled reaction rate for charged species is calculated by the Debye equation [equation (16)]. The r_X and D_X values for $\text{NpO}_4(\text{OH})_2^{3-}$ are unknown. However, for other ions of similar structure, it was proposed that r_X lies in the range 2.5 to 3.5 $\text{\AA}$ and D_X is approximately $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Then for Np(VII) , k_{dif} lies in the range 1.4×10^9 to $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($Z_X = -3$) or 3.8×10^9 to $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($Z_X = -2$). As seen, k_{dif} is considerably less than k_o . Thus, it is possible to believe that the tunnel electron transfer plays an important role in the reactions of e_{aq}^- with Np(VII) .

In Section 2.0 it was shown, based on analyses of electrochemical and chemical data, that Np(VI) and Np(V) in alkaline solutions exist as $\text{NpO}_4(\text{H}_2\text{O})_2^{2-}$ or $\text{NpO}_2(\text{OH})_4^{2-}$ and $\text{NpO}_2(\text{OH})_3\text{H}_2\text{O}^{2-}$, respectively. These ions have the coordination number 6 and similar structures. The diffusion limits of the rate constants of e_{aq}^- reactions with Np(VI) and Np(V) may be evaluated by means of the Debye equation. The radius of $\text{NpO}_4(\text{H}_2\text{O})_2^{2-}$ is equal to the sum of the covalent radius of Np(VI) (0.141 nm [Zachariasen 1954]) and the two covalent radii of oxygen (0.066 nm [Handbook of Chemist 1971]). The radius of $\text{NpO}_2(\text{OH})_3\text{H}_2\text{O}^{2-}$ is also equal to the sum of the covalent radius of Np(V) (0.149 nm [Zachariasen 1954]) and two covalent radii of oxygen. The diffusion coefficients evaluated via the Stokes-Einstein equation [$D = kT/(6\pi\eta r)$, where η is the viscosity of the solution] are $0.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The k_{dif} values calculated are about $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for both ions. The correction due to the salt effect was difficult to perform reliably, because the Brönsted-Bjerrum equation can be used only at concentrations less than 0.1 M. The rate constants of e_{aq}^- reactions with Np(VI) and Np(V) were measured in the case of 0.5 and 1.0 M OH^- solutions. Despite the uncertainties, it is possible to conclude that e_{aq}^- reacts with Np(VI) with a rate close to the diffusion limit. In the case of Np(V) , the rate constant is somewhat lower, probably because of the shift of the potential for Np(V)/(IV) pair to the negative range (approximately by 1 V in comparison with the potential for Np(VI)/(V) pair).

Table 5-7. Influence of the Medium on the Rate Constants of Reactions Between e_{aq}^- and Plutonium Ions (Pikaev et al. 1973).

Ion	[OH ⁻], M	$k \times 10^{-10}, M^{-1} s^{-1}$
Pu(VII)	1.0	3.5 ± 0.6
	2.0	4.2 ± 0.8
	5.0	2.3 ± 0.4
	7.5	2.0 ± 0.4
Pu(VI)	2.0	1.9 ± 0.3
	5.0	2.0 ± 0.3
	7.5	0.66 ± 0.08

From Table 5-7, it is seen that ions of Pu(VI) and especially Pu(VII) in alkaline media are characterized by a high reactivity toward e_{aq}^- . The rate constants for Pu(VII) are somewhat higher than for the analogous valent state of neptunium. The rate of the Pu(VI) reaction is believed to be controlled by diffusion (Pikaev et al. 1975; Pikaev et al. 1973). The tunnel mechanism was proposed for the reactions of e_{aq}^- with both Pu(VII) and Np(VII) (Pikaev et al. 1975; Pikaev et al. 1973).

The fact that the values of the rate constants for Np(VI) and Pu(VI) are similar testifies that the form of the existence of these ions in alkaline media is the same. The ionic forms of Np(VII) and Pu(VII) are also the same, and the difference in the rate constants ($k[e_{aq}^- + \text{Pu(VII)}]$ is greater than $k[e_{aq}^- + \text{Np(VII)}]$) may be caused by the difference in the oxidizing properties of these ions [the oxidation potential of Pu(VII) is higher than the respective potential of Np(VII) by 0.26 V].

5.1.2.2 Rate Constants of O^- with Np(VI) and Np(V). It has been shown that the Np(VI) ion in alkaline solution saturated with N_2O is oxidized to the heptavalent state by a radiation-chemical mechanism (Pikaev et al. 1969; Pikaev et al. 1970). Nitrous oxide converts e_{aq}^- to the radical ion O^-

which oxidizes the Np(VI) ion

The value of k_{31} was measured by pulse radiolysis with spectrophotometric registration of Np(VII) ions (Pikaev and Shilov 1978). The optical absorption spectrum of Np(VII) ions in alkaline media has bands with peaks at 412 and 620 nm. The radical ions O_3^- and CO_3^- can be formed upon radiolysis of alkaline water as a result of the reactions of O^- and OH^- with oxygen and carbonate impurities (O_3^- can also be a product of radiolysis). Both O_3^- and CO_3^- have optical absorption in the region useful in the identification of Np(VII). Because of the overlapping absorption, initial studies used solutions not containing Np(VII) ions (Pikaev and Shilov 1978).

As a result of irradiation, a short-lived optical absorption at 412 nm appears in 1 M LiOH solution saturated with N_2O . After one pulse (dose 100-150 Gy), the absorption is negligibly small but becomes noticeable after 2 to 3 pulses. This absorption is due to the formation of ozonide [reaction (32)]. Molecular oxygen is accumulated because of the oxidation of hydrogen peroxide formed in spurs and in the bulk of the solution:

The absorption at 620 nm was small after both one and 20 pulses.

Intense absorption at 620 nm appears after one pulse (dose 100-150 Gy) in 0.03 M LiOH solution saturated with N_2O due to the radical ion CO_3^- . The peak of the respective band is at 600 nm (Weeks and Rabani 1966). After second and third pulses, the absorption at 620 nm decreases but the absorption at 412 nm increases. This is because the oxygen reaction, (32), begins to compete with reaction (33). The CO_3^- absorption does not appear in more concentrated LiOH solutions; the reason is the low rate constant of the reaction

Analogous results were obtained for NaOH solutions.

Increase in optical absorption in the region of 412 and 620 nm, i.e. the occurrence of reaction (31), was observed upon irradiation of solutions saturated with N_2O containing 0.03 to 2 M LiOH and $(4 \text{ to } 9) \times 10^{-3}$ M Np(VI). The maximal value of optical absorption was observed 10 to 35 μs after the pulse, depending on the Np(VI) concentration.

The Np(VII) yield was 3.2 to 4.0 ion/100 eV. It is necessary to take into account the reactions (17), (18), (26), (30), (31), and (36)

for the theoretical calculation of the yield. Because of it

$$G[\text{Np(VII)}] = G_{\text{OH}} + B(G_{\text{e}_{\text{aq}}} + AG_{\text{H}}) \quad (37)$$

where

$$A = k_{18} [\text{OH}^-] / (k_{18} [\text{OH}^-] + k_{36} [\text{Np(VI)}])$$

$$B = k_{30} [\text{N}_2\text{O}] / (k_{30} [\text{N}_2\text{O}] + k_{26} [\text{Np(VI)}]).$$

Because $k_{36} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for acid solution (Shilov and Pikaev 1982) (but it should be lower for alkaline solutions), $k_{18} = 2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982), and $[\text{Np(VI)}] \ll [\text{OH}^-]$, then $A \approx 1$.

If the G values of water radiolysis products in alkaline media (Table 5-1) are inserted into equation (37), the N_2O concentration is 0.02 M, and $k_{30} = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, then for $9 \times 10^{-3} \text{ M}$ Np(VI) in 1 M LiOH, B is about 6 and the yield should be 5.0 ion/100 eV. The comparison of experimental and calculated yields shows that not all the radical ions O^- are consumed in reaction (31); partial combination of the O^- is probable.

However, the main part of radical ions O^- oxidize Np(VI), and it is possible to believe that the accumulation of Np(VII) follows first-order reaction kinetics via Np(VI) and O^- :

$$d[\text{Np(VII)}]/dt = k_{31}[\text{Np(VI)}][\text{O}^-] \quad (38)$$

Assuming that $[\text{O}^-] = [\text{Np(VII)}]_{\text{max}} - [\text{Np(VII)}]$,

$$\ln\{[\text{Np(VII)}]_{\text{max}} - [\text{Np(VII)}]\} = -k't + \text{const},$$

where $k' = k_{31}[\text{Np(VI)}]$. Substituting the Np(VII) concentration by the optical density, D, which is proportional to Np(VII) concentration, we have

$$2.3 \log(D_{\text{max}} - D) = -k't + \text{const} \quad (39)$$

The mean obtained values of k' and k_{31} for solutions with various concentrations of LiOH are shown in Table 5-8.

As seen from Table 5-8, the rate constants within the range of LiOH concentrations from 0.72 to 2.0 M are virtually the same. The increase in 0.033 M solution can be explained by the fact that under these conditions, part of the OH radicals exists in the undissociated (OH) form. The reaction rate for OH should be higher than for O[•].

Increase in optical absorption both at 620 and 412 nm was observed after the electron pulse in NaOH solutions saturated in N₂O containing Np(VI). These observations give evidence for the appearance of Np(VII) in the solution. The Np(VII) yield was 3.2 to 4.1 ion/100 eV. The rate constants of reactions between Np(VI) and O[•] in 0.5 to 1.7 M NaOH solutions are given in Table 5-9. Comparison of the data from Tables 5-8 and 5-9 shows that the constants for LiOH and NaOH solutions are close.

Table 5-8. Rate Constants of Reactions Between Np(VI) and O[•] at Different Concentrations of LiOH (Pikaev and Shilov 1978).

[LiOH], M	[Np(VII)] x 10 ³ , M	k' x 10 ⁻⁵ , s ⁻¹	k ₃₁ x 10 ⁻⁷ , M ⁻¹ s ⁻¹
2	9.4	4.8	5.1
1.72	10.0	4.2	4.2
1.03	9.4	4.0	4.2
0.51	8.1	3.4	4.2
0.072	5.4	2.9	5.4
0.033	4.1	3.3	8.0

Table 5-9. Rate Constants of Reaction Between Np(VI) and O[•] at Different NaOH Concentrations (Pikaev and Shilov 1978).

[NaOH], M	[Np(VI)], x 10 ³ , M	k' x 10 ⁻⁵ , s ⁻¹	k ₃₁ x 10 ⁻⁷ , M ⁻¹ s ⁻¹
1.7	2.7	1.7	6.3
1.0	2.7	1.4	5.2
1.0	2.7	1.9	7.0
0.8	4.1	1.8	4.4
0.5	2.2	1.8	8.2

To elucidate the mechanism of charge transfer in reaction (31), the value of k_{31} was compared to the diffusion limit of k_{31} calculated by means of the Debye equation. The radius of $\text{NpO}_4(\text{H}_2\text{O})_2^{2-}$ is 0.273 nm (see above consideration); the radius of $\text{O}^\cdot$ is the arithmetic mean between the covalent radius of oxygen and the radius of O^{2-} (0.136 nm [Handbook of Chemist 1971]). The diffusion coefficient of $\text{O}^\cdot$ was evaluated via the Stokes-Einstein equation (see above consideration). The calculated value of k_{dif} is approximately $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, the interaction of Np(VI) with $\text{O}^\cdot$ is not controlled by diffusion. It is possible to suggest that the rate of reaction (31) is determined by the abstraction of a H atom from a water molecule in the $\text{NpO}_4(\text{H}_2\text{O})_2^{2-}$ ion by the radical ion $\text{O}^\cdot$. Such a reaction occurs, for example, in the case of Am(III) oxidation by the OH radical in acid media (Pikaev et al. 1977a). The value of $k[\text{Np(VI)} + \text{O}^\cdot]$ is less than $k[\text{Am(III)} + \text{OH}^\cdot]$. The difference is explained by the lower reactivity of $\text{O}^\cdot$ in comparison with OH in reactions of H atom abstraction (Neta and Schuler 1975).

As mentioned in the discussion of the calculation of the Np(VII) yield immediately after the pulse, part of the e_{aq}^- is consumed for the reduction of Np(VI) according to reaction (26). At given concentrations of Np(VI) and N_2O , the Np(V) yield is 1.44 ion/100 eV. If we take into account the absorbed dose, the initial concentration of Np(V) is $(1.5 \text{ to } 2.2) \times 10^{-5} \text{ M}$. The formed Np(V) reacts, initially, with $\text{O}^\cdot$:

The kinetics of reaction (40) was studied using solution containing 1 M LiOH, $(1 \text{ to } 2) \times 10^{-4} \text{ M}$ Np(V) , and saturated with N_2O , by the increase in optical density at 300 nm where Np(VI) absorbs (Gogolev et al. 1989a). The calculation was carried out by means of equation (39). It was found that k_{40} is $4.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

With this data, the contribution of reactions (31) and (34) to the consumption of $\text{O}^\cdot$ radical ions can be evaluated. The fraction due to reaction (40) is

$$k_{40}[\text{Np(V)}]/(k_{40}[\text{Np(VI)}] + 2 k_{34}[\text{O}^\cdot]_0) \approx 0.01.$$

The fraction due to reaction (31) is about 0.6.

5.1.2.3 Rate Constants of O_3 Reaction with Np(VI) and Np(V) . The kinetics of reaction of O_3 with Np(VI) and Np(V) was studied by pulse radiolysis with spectrophotometric registration of short-lived species (Gogolev et al. 1989b). To exclude the formation of colloid forms of Np(VI) or Np(V) in 0.2 to 0.5 M solution of LiOH, 1 to 2 mL of 3 M LiOH were initially added to slightly-acid 0.02 to 0.03 M solutions of Np(VI) or to 10^{-3} M solutions of Np(V) . To the LiOH and Np solutions, $\text{K}_2\text{S}_2\text{O}_8$ solution was added. Because $\text{S}_2\text{O}_8^{2-}$ in alkaline solutions forms products which reduce Np(VII) (Shilov et al. 1971), only freshly prepared solutions were used.

In aerated solutions of LiOH containing 0.02 M $K_2S_2O_8$, an optical absorption band with maximum at 430 nm belonging to O_3^- appears as a result of irradiation with the electron pulse (Pikaev 1986). The absorption after the first and second pulses decays following a rate law that is the mean between first and second orders. Further irradiation leads to the decay of optical absorption according to a first-order law.

The appearance of the short-lived absorption at 430 nm in alkaline solution of $K_2S_2O_8$ is caused by reactions (17) to (19), (41) to (43), and (32):

The decay of O_3^- is due to the shift of reaction (32) to the left and to reactions:

In solutions containing Np(VI), the optical absorption at 430 nm decays faster but not to 0. The residual absorption, which belongs to Np(VII), is observed for several seconds. The appearance of Np(VII) is caused by reaction (31) competing with reaction (32) and by the following reaction

In the presence of Np(VI), the optical absorption of O_3^- decays by a first-order rate law. Because of it

$$d[O_3^-]/dt = k_{49}[Np(VI)][O_3^-] + k'_o[O_3^-] \quad (50)$$

where k'_o is the apparent rate constant of the first-order decay of O_3^- in the absence of Np(VI). Since $[Np(VI)] \gg [O_3^-]$, then $d \ln[O_3^-] = -k dt$, where $k = k_{49}[Np(VI)] + k'_o$. If we substitute $[O_3^-]$ with the optical density difference $D - D_\infty$ which is proportional to $[O_3^-]$, (and where D and D_∞ are the optical densities at a given time and after finishing the decay of O_3^- respectively) then

$$2.3 \log (D - D_\infty) = -kt + \text{const} \quad (51)$$

In addition, the reactions (26), (40) and (52) occur in the system:

The rate constants of reactions (31) and (40) are 4.6×10^7 (Pikaev and Shilov 1978) and $4.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Gogolev et al. 1989a).

The precision of k_{49} evaluation depends on Np(VI) concentration and on the fraction A for the reaction (32) in the total balance of the O^- consumption where

$$A = k_{32} [O_2] / (k_{32}[O_2] + k_{31}[Np(VI)] + k_{40}[Np(V)]).$$

Preliminary experiments showed that these contradictory claims may be satisfied in aerated solutions with about $2 \times 10^{-3} \text{ M}$ Np(VI) and greater than 0.02 M $S_2O_8^{2-}$. The applied dose forms Np(V) concentration that is equal to $B G_{eq} \cdot E \times 10^3 / (100 N)$ where E is the dose in eV g^{-1} , N is the Avogadro number, and

$$B = k_{26}[Np(VI)] / (k_{26}[Np(VI)] + k_{41}[O_2] + k_{42}[S_2O_8^{2-}]).$$

Taking into account that $k_{26} = 2 \times 10^{10}$, $k_{41} = 2 \times 10^{10}$, and $k_{42} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982) and $[O_2] = 2 \times 10^{-4} \text{ M}$; $B = 0.164$, $[Np(V)] = 2.5 \times 10^{-6} \text{ M}$ for the experimental conditions, and $A = 0.88$. The derived mean values of k and k_{49} for solutions with different concentrations of LiOH are shown in Table 5-10.

As seen from Table 5-10, the k_{49} value is constant [about $(2.1 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$] when the LiOH concentration decreases from 2.1 to 0.21 M.

The kinetics of reaction (52) was investigated by measuring light absorption at 430 nm in 1 M LiOH, $(1 \text{ to } 2) \times 10^{-4}$ M Np(V), and 0.02 M $\text{K}_2\text{S}_2\text{O}_8$ solution. Treatment of the experimental data according to equation (51) gives $k_{52} = (2.1 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Table 5-10. Rate Constants of The Reaction Between Np(VI) and O_3^- .

$[\text{Np(VI)}] \times 10^5, \text{ M}$	$[\text{LiOH}], \text{ M}$	$[\text{K}_2\text{S}_2\text{O}_8] \times 10^2, \text{ M}$	$k \times 10^{-2}, \text{ s}^{-1}$	$k_{49} \times 10^{-5}, \text{ M}^{-1} \text{ s}^{-1}$
0	2	2	4	-
0	1	2	3.3	-
0	0.5	2	3.0	-
0	0.2	2	2.3	-
2.25	2.15	10	8.7	2.1
2.06	1.66	2	8.5	2.2
2.0	1.06	2	7.5	2.1
2.25	1.0	8.7	7.3	1.8
2.0	1.0	2	6.5	1.6
2.0	0.53	2	6.2	1.6
2.0	0.42	10	8.3	2.6
2.8	0.31	10	9.0	2.4
2.0	0.22	10	6.8	2.2
1.0	0.21	10	4.6	2.3

5.1.2.4 Rate Constants of CO_3^- Reaction with Np(VI) and Np(V). It is known that the addition of Na_2CO_3 up to 1.5 M into a 0.2 M solution of NaOH has no effect on the value of the potential for the Np(VII)/(VI) pair (Simakin and Matyashchuk 1969). The redox potential of the $\text{CO}_3/\text{CO}_3^{2-}$ pair is 1.5 V (Henglein 1980). Because of it, there is a possibility for reaction (53) to occur:

Reaction (53) was studied by pulse radiolysis (Gogolev et al. 1989a).

The kinetics of reaction (53) was investigated from the decrease in optical density at 600 nm (the peak of the optical absorption band of CO_3^-). It was suggested that the value of k_{53} is comparable to or lower than the value of k_{31} . Thus, the concentration of Np(VI) should be sufficiently high for the observation of reaction (53), and at the same time it should also ensure the condition $k_{33}[\text{CO}_3^{2-}] \gg k_{31}[\text{Np(VI)}]$. For instance, in 0.1 M NaOH, $k_{33} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (see above consideration) and $k_{31} = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Weeks and Rabani 1966). At 0.05 M Na_2CO_3 and $2 \times 10^{-3} \text{ M Np(VI)}$, it is possible to neglect reaction (31).

The species e_{aq}^- was scavenged by 0.1 M $\text{K}_2\text{S}_2\text{O}_8$. Saturation of a solution with N_2O was used to suppress reaction (31).

Studies showed that the presence of $2.5 \times 10^{-3} \text{ M Np(VI)}$ in a solution containing 0.5 M Na_2CO_3 , 0.5 to 1.0 M NaOH, and 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ and saturated with N_2O accelerates the decay of CO_3^- . The reactions (17) to (20), (30), (35), (42), (43), (54), and (55) occur in the solution immediately after the pulse:

The rate constant of reaction (43) is $7.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Chalwa and Fessenden 1975); the value of k_{55} is unknown. Even if k_{55} were as high as 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$, it is possible to neglect reaction (55) because the OH^- concentration is three orders of magnitude higher than the Np(VI) concentration. Therefore, OH^- , e_{aq}^- , and H are converted to the CO_3^- radical ion.

In the presence of Np(VI) , the rate of decreasing CO_3^- optical absorption follows the first-order law; in the absence of Np(VI) , the CO_3^- radical ions decay according to a second-order reaction

Treatment of the experimental data using an equation similar to equation (51) gives the value k_{53} of $(9.0 \pm 1.5) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. In carbonate solutions with lower alkali concentration, where the solubility of Np(VI) is lower, the same values of k_{53} were obtained.

In carbonate solutions containing $\text{K}_2\text{S}_2\text{O}_8$ and N_2O , the presence of Np(VI) has no effect on the kinetics of the CO_3^- decay, i.e., reaction (53) does not occur. The absence of Np(VI) oxidation in carbonate solution is explained by the high potential of the Np(VII)/(VI) pair and also by the fact that Np(VI) under these conditions exists in the relatively stable $\text{NpO}_2(\text{CO}_3)_3^{4-}$

form. The ion $\text{NpO}_4(\text{H}_2\text{O})_2^{2-}$ appears upon the addition of alkali, and the radical ion CO_3^- reacts with this form. Probably, the oxidation process consists in the electron transfer from Np(VI) to CO_3^- .

The reaction

was also studied in carbonate-alkaline solutions via the decrease in optical density at 600 nm. The measured values of k_{57} are presented in Table 5-11. The moderate increase in the rate constant with increasing alkali concentration is connected with the decrease in the potential of the Np(VI)/(V) pair upon the transition from 0.2 to 1.0 M solution of NaOH (Simakin and Matyashchuk 1973).

Table 5-11. The Rate Constants of Reaction Between Np(V) and CO_3^- .

[NaOH], M	[Na_2CO_3], M	$k_{57} \times 10^{-7}, \text{M}^{-1} \text{s}^{-1}$
0.2	0.5	1.8
0.5	0.5	2.4
1.0	0.5	4.4

5.1.2.5 Kinetics of Reaction of Np(VII) with Np(V) . The optical absorption of Np(VII) decreases within 50 microseconds after the pulse (Pikaev and Shilov 1978). The decrease probably is because of the reaction

Neptunium(V) is formed in reactions (26) and (36) and also in reactions (20), (59), and (60):

Hydrogen peroxide can react with Np(VII) . However, initially the Np(VI) concentration greatly exceeds Np(VII) concentration; when a sufficient amount of Np(VII) is accumulated, H_2O_2 is already consumed in reactions (59) and (60).

The total yield of Np(V) is comparable with the yield of Np(VII); because of it the coordinates $1/D$ vs. time were used for the determination of reduction rate law. It was found that the experimental points lie satisfactorily on a straight line in these coordinates. Hence, the reaction rate is second order; first order each in Np(VII) and Np(V). The k_{58} values were calculated by the known equation

$$k_{58} = \epsilon b \tan(\varphi) \quad (61)$$

where ϵ is the molar extinction coefficient of Np(VII), b is the length of the light path, and $\tan(\varphi)$ is the tangent of the slope of the straight line in coordinates $1/D$ vs. time. The resulting values are shown in Table 5-12.

Unlike the situation in solutions of LiOH, the optical absorption connected with Np(VII) in solutions of NaOH does not decay in the period 2 to 3 ms after the pulse. However, the solution after the experiment was colorless. Hence, in solutions of NaOH, Np(VII) reacts with Np(V) slower than in the solutions of LiOH. This feature seems to be caused by the different forms of Np(VII) and Np(V) which exist in the solutions of NaOH and LiOH.

5.2 γ -RADIOLYSIS OF ALKALINE SOLUTIONS OF NEPTUNIUM AND PLUTONIUM IONS

Studies performed on radiolysis of solutions of actinide ions showed that the pathways of radiolytic conversions considerably depend on the irradiation conditions. By choosing the radiolytic source, it is possible to conduct oxidation or reduction of actinide ions in different valent states. This selectivity is illustrated by the development of the radiation-chemical method of preparation of Np(VII) and Pu(VII).

5.2.1 Radiation-Induced Oxidation of Np(VI) Ions in Alkaline Solutions

The radiation-chemical method of the preparation of Np(VII) was described shortly after the discovery of Np(VII) (Pikaev et al. 1969). To conduct the preparation, a 2×10^{-4} M solution of Np(VI) perchlorate in 1 M NaOH was saturated with N_2O and irradiated with ^{60}Co γ -rays. The formation of Np(VII) taking place as a result of irradiation was monitored spectrophotometrically. Later the process was studied in more detail (Pikaev et al. 1970; Pikaev et al. 1980).

Studies showed that the oxidation of Np(VI) occurs only in alkaline solutions saturated with N_2O . In alkaline solutions containing air or saturated with argon, Np(VII) is not formed. The addition of 0.1 M NO_3^- ions completely suppresses Np(VI) oxidation. Similar attempts to prepare Np(VII) in neutral and slightly-acid (around pH 4) media were unsuccessful.

From the dependence of the concentration of Np(VII) product on absorbed dose for a 2.1×10^{-4} M solution of Np(VI) in 1 M NaOH saturated with N_2O , it was found that practically complete conversion of Np(VI) to Np(VII) occurs at doses of $(5 \text{ to } 6.5) \times 10^2$ Gy (dose rate 2.8 Gy s^{-1}).

One feature of the process is the presence of a short induction period. The most probable reason for the induction period is the presence of impurities in the solutions used. The impurities can compete with Np(VI) for $O^\cdot$ radical ions formed upon water decomposition.

Table 5-12. The Rate Constants of Reaction Between Np(VII) and Np(V).

[LiOH], M	[Np(VI)] $\times 10^3$, M	$k_{58} \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$
2.0	9.4	2.0
1.03	9.4	1.6
0.24	8.1	1.4
0.072	5.4	2.7
0.033	4.1	2.5

Taking into account the induction period, the initial yield of Np(VII) is 5.1 ions/100 eV. The yield does not depend upon the Np(VI) concentration within the range of $(2 \text{ to } 5) \times 10^{-4}$ M. In more dilute solutions, the yield decreases somewhat. The concentration of NaOH within the range of 1 to 3 M affects the radiation-induced formation of Np(VII) slightly. At lower and higher concentrations of alkali, $G[\text{Np(VII)}]$ decreases noticeably. An eight-fold decrease in dose rate does not change $G[\text{Np(VII)}]$.

At low absorbed doses, reactions (17) to (20), (48), (31), (26), (40), (58) to (60), (62) and (63)

occur in the system, i.e., the $O^\cdot$ radical ion oxidizes Np(VI). Reaction (32) begins to compete with reaction (31) upon the accumulation of Np(VII) and the appearance of O_2 in the solutions as a result of reactions (60) and (63). It is useful to compare the contributions of reactions (31) and (32). The contributions are proportional to $k_{31}[\text{Np(VI)}]$ and $k_{32}[\text{O}_2]$, respectively. Taking into account the yields of Np(VII) and O_2 (5.1 and 0.75 molecule/100 eV, respectively), then the concentration of O_2 to the time required for the formation of about 5×10^{-5} M Np(VII) is about 7×10^{-6} M. Using values of k_{31} and k_{32}

equal to 5×10^7 (Pikaev and Shilov 1978) and $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982), respectively, it is found that more than 70% of the O^- radical ions are consumed in reaction (32). The coincidence of experimental and calculated

$$(\text{G}[\text{Np(VII)}] = \text{G}_{\text{OH}} + \text{G}_{\text{e}_{\text{aq}}} + \text{G}_{\text{H}} - 2 \text{G}_{\text{H}_2\text{O}_2} = 5.0 \text{ ion/100 eV})$$

yields of Np(VII) leads to the conclusion that at $2 \times 10^{-4} \text{ M Np(VI)}$ and at about 22°C , all the O^- and O_3^- radical ions take part in reaction (49).

The dependence of the Np(VII) yield on dose is linear up to the accumulation of $1 \times 10^{-4} \text{ M Np(VII)}$. From that point, a deviation from linearity is observed. For the segment where $(1.2 \text{ to } 0.4) \times 10^{-4} \text{ M Np(VI)}$ remains, $\text{G}[\text{Np(VII)}] = 4.0 \text{ ion/100 eV}$. The decrease in Np(VII) yield is due to side-reactions of O_3^- .

The decrease in $\text{G}[\text{Np(VII)}]$ at less than 1 M NaOH is explained by the acceleration of O_3^- decay (Gogolev et al. 1989b). The diminution of $\text{G}[\text{Np(VII)}]$ in solutions with 3 to 5 M NaOH is attributed to the same cause as the induction period noted for the Np(VI) oxidation, i.e., impurities. It is possible also that the decrease in the solubility of N_2O [it can cause the incomplete participation of e_{aq}^- in reaction (30)] contributes to the diminution of the yield. Besides, it is also possible that in strongly-alkaline solutions, the life-time of N_2O^- (it is an intermediate product of reaction between e_{aq}^- and N_2O) increases, so that it can take part to some extent in the reaction with Np(VI) :

This reaction leads to a decrease in the $\text{G}[\text{Np(VII)}]$.

5.2.2 Radiation-Induced Reduction of Np(VII) Ions in Alkaline Solutions

Neptunium(VI) is formed upon irradiation of aerated alkaline solutions of Np(VII) . The respective data for a $4.3 \times 10^{-4} \text{ M}$ solution of Np(VII) in 2 M NaOH show that a linear dependence of Np(VII) reduction on the concentration of Np(VII) is observed at doses higher than about 300 Gy (Pikaev et al. 1970). For this part of the dependence, $\text{G}[\text{Np(VII)}]$ is 2.4 ion/100 eV.

The most likely mechanism of Np(VII) reduction at doses higher than 320 Gy includes reactions (17) to (20), (25), (26), (31), (41), (48), (49), (58) to (60), (62), (63), and (65)

On the basis of the proposed mechanism it is possible to obtain the following equation:

$$G[-\text{Np(VII)}] = G_{e_{aq}^-} + G_H + 2 G_{\text{H}_2\text{O}_2} - G_{\text{OH}} \quad (66)$$

The use of known values for the yields of primary products of water radiolysis indicates that $G[-\text{Np(VII)}]$ should be 2.2 ion/100 eV, i.e. the experimental and calculated values coincide.

At low doses, when the Np(VI) concentration is small, the side reactions of O_3 giving rise to the formation of HO_2 and O_2 compete with reaction (49). The by-products, HO_2 and O_2 , reduce an additional amount of Np(VII) leading to a higher value of $G[-\text{Np(VII)}]$.

Additional experiments on radiation-induced reduction of Np(VII) in aerated alkaline solutions showed that the yield of this process depends on the alkali concentration (Pikaev et al. 1983):

$[\text{NaOH}], \text{ M}$	0.22	0.50	1.0	2.0
$G[-\text{Np(VII)}], \text{ ion/100 eV}$	3.1	2.4	2.2	2.1

The possible reason for the increase in the value of $G[-\text{Np(VII)}]$ is the acceleration of the O_3 decay with the formation of the O_2 radical ion in diluted alkaline solutions.

5.2.3 Radiation-Induced Oxidation of Np(VI) in Alkaline Solutions Containing Persulfate, Periodate, Hypobromite, or Perbromate

In addition to N_2O , scavengers of e_{aq}^- include $\text{S}_2\text{O}_8^{2-}$, $\text{H}_3\text{IO}_6^{2-}$, BrO^- and BrO_4^- . Although Np(VI) is oxidized by the first three of these ions even without irradiation, the process proceeds effectively only at temperatures higher than 50 °C and in solutions with high concentrations of oxidizing agent (Krot et al. 1977).

Experiments showed that irradiation (dose rate 3.2 Gy s⁻¹) of aerated alkaline 2.1 x 10⁻⁴ M solutions of Np(VI) containing 0.02 M $\text{K}_2\text{S}_2\text{O}_8$ leads to the formation of Np(VII) (Shilov et al. 1979). The initial yield of Np(VII) was determined from the dependence of its concentration on dose. As in the case of irradiation of the solutions saturated with N_2O , a short induction period was observed. It is caused by the impurities present in the alkali solution. The results obtained at different alkali concentrations are shown in Table 5-13. The yield increases with increasing alkali concentration and reaches 4.5 ion/100 eV for 2 M NaOH .

The values of the yield may be calculated on the basis of the mechanism involving reactions (17) to (20), (26), (31), (32), (41), (42), (48), (49), (58) to (60), (62), (63), and (65). For this mechanism

$$G[\text{Np(VII)}] = G_{\text{OH}} + B(G_{e_{\text{aq}}} + AG_{\text{H}}) - (1 - B)(G_{e_{\text{aq}}} + AG_{\text{H}}) - (1 - A)G_{\text{H}} - 2 G_{\text{H}_2\text{O}_2} \quad (67)$$

where

$$A = k_{18}[\text{OH}^-]/(k_{18}[\text{OH}^-] + k_{65}[\text{O}_2]) \text{ and}$$

$$B = k_{42}[\text{S}_2\text{O}_8^{2-}]/(k_{42}[\text{S}_2\text{O}_8^{2-}] + k_{26}[\text{Np(VII)}] + k_{41}[\text{O}_2]).$$

Table 5-13. The Dependence of $G[\text{Np(VII)}]$ on Concentration of Alkali
 $([\text{K}_2\text{S}_2\text{O}_8]_0 = 0.02 \text{ M}, [\text{Np(VI)}]_0 = 2.1 \times 10^{-4} \text{ M}).$

[NaOH], M	$G[\text{Np(VII)}]$, ion/100 eV	$[\text{O}_2] \times 10^4$, M	A	B	$G[\text{Np(VII)}]_{\text{calc}}$, ion/100 eV
0.05	1.70	1.70	0.17	0.94	3.75
0.20	2.10	2.3	0.48	0.94	4.06
0.45	2.70	2.0	0.70	0.95	4.35
0.50	2.80	2.0	0.72	0.95	4.36
0.95	3.75	1.7	0.86	0.96	4.58
1.0	3.85	1.7	0.86	0.96	4.58
2.0	4.50	1.0	0.95	0.98	4.76

Taking into account that k_{18} and k_{65} are equal to 2.1×10^7 and $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; k_{42} , k_{41} , and k_{26} are equal to 8×10^9 , 2×10^{10} , and $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982); and that aerated 2 M NaOH contains $1 \times 10^{-4} \text{ M O}_2$; $A = 0.95$ and $B = 0.98$. Using the value of $G_{\text{H}_2\text{O}_2} = 0.75 \text{ molecule/100 eV}$ and the above values for yields of G_{OH} , $G_{e_{\text{aq}}}$, and G_{H} , $G[\text{Np(VII)}] = 4.76 \text{ ion/100 eV}$. This yield coincides with the experimental yield (within the limits of the experimental error) for 2 M NaOH. The experimental values of Np(VII) yield in solutions with lower concentration of alkali are less than the calculated values. The possible reason is the occurrence of O_3 side-reactions that are accelerated in dilute solutions of alkali.

Neptunium(VII) is also formed upon γ -irradiation of aerated alkaline solutions of Np(VI) containing 0.02 M periodate, hypobromite, or perbromate. The initial yields of Np(VII) at different alkali concentrations are presented in Table 5-14.

Table 5-14. The Influence of the Solution Composition on G[Np(VII)]
(Shilov et al. 1979 and Gusev et al. 1974).

Scavenger (S)	[S]x10 ² , M	[Np(VI)] ₀ x 10 ⁴ , M	[NaOH], M	[KOH], M	G[Np(VII)], ion/100 eV	[Np(VII)] _∞ , as a % of [Np(VI)] ₀
H ₃ IO ₆ ²⁻	2	2.1	0.08	-	3.0	64
	2	2.1	0.50	-	4.0	83
	2	2.1	1.07	-	2.1	85
	2	2.1	-	0.20	1.4	75
	2	2.1	-	0.50	2.5	77
	2	2.1	-	1.00	1.4	75
	2	2.1	-	2.00	1.4	30
BrO ⁻	2	3.3	1.0	-	5.3	~100
	2	3.3	2.0	-	6.8	~100
	2	3.3	3.0	-	7.0	~100
BrO ₄ ⁻	2	2.2	0.2	-	2.0	~100
	2	2.2	0.5	-	2.5	~100
	2	2.2	1.1	-	2.9	~100
	2	2.2	2.0	-	3.2	~100
	2	2.2	3.8	-	3.5	~100
	1	2.2	1.1	-	2.5	~100
	4	2.2	1.1	-	2.7	~100
	8	2.2	1.1	-	2.9	~100

In the case of periodate, the yield value goes through a maximum in 0.5 M NaOH or KOH. Neptunium(VI) is not oxidized completely. The observed features may be explained as follows. Reactions (16) to (20), (25), (26), (31), (41), (49), (65), and (68)

occur upon γ -irradiation of the solution containing periodate. Radical ion O^- reacts with O_2 [reaction (32)] and with I(VII):

The species IO_4 forms a complex with I(VII); the complex decays to I(V), I(VII), and O_2 (Klänning and Sehested 1978). It is not excluded that reducing agents are present among the products of the IO_4 decay. Probably, I(VI) and IO_4 are able to oxidize Np(VI), for example, via reaction:

The nature of the alkali and its concentration have an effect on the form of I(VII) existence and, as a consequence, on reaction (69), and on the conversion of IO_4 .

In the presence of BrO^- , the oxidation of Np(VI) also occurs at less than 1 M NaOH. In such solutions, part of Np(VI) coagulates after irradiation, but Np(VII) is not precipitated.

From Table 5-14 it follows that in solutions containing BrO^- , the yields of Np(VII) are considerably higher than in solutions containing other e_{aq}^- scavengers. It is possible to explain this observation by the occurrence of reactions:

and also reactions of O^- with O_2 and BrO^- :

The rate constant of reaction (75) at pH 12 to 13 is $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982); because of it, the oxidizing agent for Np(VI) is not O_3 but P, since the BrO^- concentration greatly exceeds the concentration of O_2 :

Neptunium(V) formed in reaction (26) is oxidized by hypobromite. Thus, the yield of Np(VII) should be:

$$G[\text{Np(VII)}] = G_{e_{aq}^-} + G_{\text{OH}} + G_{\text{H}} \quad (77)$$

i.e., 6.5 ion/100 eV. The decrease in the $G[\text{Np(VII)}]$ yield in 1 M NaOH is due to side reactions or to the deceleration of reaction (72).

Perbromate reacts with e_{aq}^- with a high rate ($k = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7). The radical ion O^- and BrO_3^- are formed in this reaction:

If hydrated electrons in the presence of either BrO_4^- and $\text{S}_2\text{O}_8^{2-}$ are converted predominantly to O^- radical ions, then the yields of Np(VII) in these systems should be close. This result is observed in 0.2 M NaOH. The yield of Np(VII) in the presence of BrO_4^- increases with increasing alkali concentration at a slower rate than in the presence of $\text{S}_2\text{O}_8^{2-}$. The reason is not clear. It is only possible to suggest that BrO_4^- is decomposed partially with the formation of some reducing agents, and the decomposition depends on the NaOH concentration. It is not excluded that the decrease in the yield is connected with the reaction of the intermediate species BrO_4^{2-} with Np(VI) and Np(VII).

5.2.4 Radiolysis of Carbonate-Alkaline Solutions of Np(VI)

γ -Irradiation of bicarbonate and carbonate solutions of $2.4 \times 10^{-4} \text{ M}$ Np(VI) saturated with N_2O and also solutions containing 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ does not lead to the formation of Np(VII). A small amount of Np(VII) appears in γ -irradiation of Np(VI) solutions containing 0.5 M Na_2CO_3 and 0.01 M NaOH. Increase in the concentration of NaOH to 0.02 M leads to the formation of $3 \times 10^{-5} \text{ M}$ Np(VII); in solutions with 0.03 M NaOH, neptunium (VI) is converted to Np(VII) completely (Gogolev et al. 1989a).

The formation of Np(VII) in solutions saturated with N_2O occurs without an induction period. Complete conversion of Np(VI) to Np(VII) is observed at about 600 Gy dose. The initial yield of Np(VII) increases as NaOH concentration increases from 0.02 to 0.1 M; the Np(VII) yield then decreases somewhat (see Table 5-15).

The value of the yield can be calculated if we take into account the reactions (17) to (20), (25), (26), (30), (33), (48), (49), (53), (56), (58) to (60), (62), (63), and (79):

Hence,

$$G[\text{Np(VII)}] = G_{\text{OH}} + A(G_{\text{e}_a^-} + G_{\text{H}}) - (1 - A)(G_{\text{e}_a^-} + G_{\text{H}}) - 2 G_{\text{H}_2\text{O}_2} \quad (80)$$

where

$$A = k_{30} [\text{N}_2\text{O}] / (k_{30} [\text{N}_2\text{O}] + k_{26} [\text{Np(VI)}]).$$

Table 5-15. The Influence of Solution Composition on Np(VII) Yield ($[\text{Np(VI)}]_0 = 2.4 \times 10^{-4} \text{ M}$, Dose Rate = $9.17 \times 10^{-2} \text{ Gy s}^{-1}$).

$[\text{Na}_2\text{CO}_3], \text{ M}$	$[\text{NaOH}], \text{ M}$	$G[\text{Np(VII)}], \text{ ion/100 eV}$
0.50	0.02	0.7
0.50	0.03	4.1
0.50	0.10	4.75
0.05	0.10	4.8
0.50	0.50	4.35
0.05	0.50	4.30
0.50	1.0	4.1
0.05	1.0	4.2

The solubility of N_2O in 1 M KOH at about 25 °C is approximately 0.02 M (Handbook of Chemist 1971). The solubility in a solution of 0.5 M Na_2CO_3 and 0.1 M NaOH is about the same level. The rate constant k_{30} is $8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982) and k_{27} is $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev et al. 1974; Pikaev et al. 1973). With these data, the yield for a $2.4 \times 10^{-4} \text{ M}$ solution of Np(VI) is 4.8 ion/100 eV.

The coincidence of experimental and calculated yields in solutions containing 0.05 to 0.5 M Na_2CO_3 and 0.1 M NaOH is indicative of the small role of reaction (56). Taking into account that for 0.1 M NaOH, k_{31} is $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Shilov 1978) and

k_{79} is $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Weeks and Rabani 1966), we can neglect reaction (31) already at $0.05 \text{ M Na}_2\text{CO}_3$. Although k_{32} is $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Pikaev and Kabakchi 1982), it is also possible to neglect reaction (32), since the concentration of O_2 at the initial stage of the oxidation is about 10^{-5} M ; because of it, $k_{79}[\text{CO}_3^{2-}]$ is much greater than $k_{32}[\text{O}_2]$. Therefore, the oxidation of Np(VI) occurs by way of reaction (53).

5.2.5 γ -Radiolysis of Alkaline Solutions of Plutonium Ions

Ions of Pu(VII) are formed upon γ -radiolysis of alkaline aqueous solutions of Pu(VI) . The oxidation was initially observed in irradiation of alkaline solutions of Pu(VI) saturated with N_2O (Pikaev et al. 1969). Later the process was studied in detail (Zakharova et al. 1971).

The source of radiation in later studies was the linear electron accelerator U-12 (Zakharova et al. 1971). The bremsstrahlung X-radiation generated by a tungsten target was utilized. The mean dose rate was about 3 Gy s^{-1} . Since the accelerator generated the pulses with 400 Hz frequency (the pulse duration was $2.3 \mu\text{s}$), the instantaneous dose rate was 3 kGy s^{-1} . The maximal dose rate of the self-generated α -radiation of ^{239}Pu (about $1.1 \times 10^{-3} \text{ Gy s}^{-1}$) was negligible in comparison with the mean dose rate of X-radiation.

A solution of Pu(VII) in 1 M NaOH saturated with N_2O was irradiated. Preliminary determinations of the rate of auto-reduction of Pu(VII) (i.e. of its reaction with water) were conducted for the solutions to be used in the studies. The half-time of the auto-reduction for the $1.4 \times 10^{-3} \text{ M}$ solution of Pu(VII) in 1 M NaOH was 8 hours. Because of the auto-reduction, experiments on radiation-induced oxidation of Pu(VI) were performed such that the interval between the beginning of irradiation and the determination of the formed Pu(VII) concentration was not longer than 10 to 12 min. During this time, the concentration of Pu(VII) decreases by not more than 3 to 4% due to reaction with water.

It was found that Pu(VII) is formed only upon irradiation of alkaline solutions saturated with N_2O . For a $4.4 \times 10^{-4} \text{ M}$ solution of Pu(VI) in 1 M NaOH , the virtually complete conversion of Pu(VI) to Pu(VII) takes place at doses of 1.2 to 1.3 kGy. As in the case of Np(VI) oxidation in alkaline solutions (see above consideration), a short induction period is observed. Apparently, it is due to the presence of impurities which can compete with Pu(VI) for $\text{O}^\cdot$ radical ions formed upon water radiolysis. Taking this effect into account, the initial yield of Pu(VII) formation is 5.4 ion/100 eV. The yield of Pu(VII) does not depend on the Pu(VI) concentration within the range of 2×10^{-4} to $1.7 \times 10^{-3} \text{ M}$.

The mechanism of radiation-induced oxidation of Pu(VI) in alkaline solutions is similar to the mechanism for Np(VI). It involves reactions (17) to (20), (28) to (30), (32), (48), and (81) to (87):

For the initial part of the oxidation, it is possible to neglect reaction (28); then

$$\begin{aligned} G[\text{Pu(VII)}] &= G_{\text{OH}} + A(G_{e_{\text{aq}}}^- + G_{\text{H}}) - \\ &\quad (1 - A)(G_{e_{\text{aq}}}^- + G_{\text{H}}) - 2 G_{\text{H}_2\text{O}_2} \end{aligned} \quad (88)$$

where

$$A = k_{30}[\text{N}_2\text{O}]/(k_{30}[\text{N}_2\text{O}] + k_{29}[\text{Pu(VI)}]).$$

If the concentrations of N_2O and Pu(VI) ; the values of k_{29} and k_{30} ; and the values of OH , e_{aq}^- , H , and H_2O_2 yields (Table 5-1) are inserted into equation (88), $G[\text{Pu(VII)}]$ is found to be 4.7 ion/100 eV. The somewhat higher experimental value may be caused by using the pulse radiation as described in the original study (Zakharova et al. 1971).

The formation of Pu(VII) takes place also upon γ -radiolysis of Pu(VI) solutions in 1 M NaOH in the presence of $\text{S}_2\text{O}_8^{2-}$ ions (Bhattacharyya et al. 1981; Saini and Bhattacharyya 1984). It was found that $G[\text{Pu(VII)}]$ is 4.0 ion/100 eV at 5.1×10^{-4} M Pu(VI) and 0.07 M $\text{S}_2\text{O}_8^{2-}$. It coincides with the Np(VII) yield in 1 M NaOH containing $\text{S}_2\text{O}_8^{2-}$ (see

Table 5-13). As in the case of neptunium, the experimental value of Pu(VII) is lower than the calculated value; the lower value is caused by the side reactions of the O_3 radical ion. At a constant concentration of $S_2O_8^{2-}$ (0.025 M), the yield initially increases with increasing concentration of Pu(VI), then decreases [by as much as 2 ion/100 eV at 5×10^{-3} M Pu(VI)]. The initial increase in the yield is predominantly due to the increase in the role of reaction (87), and the decrease is mainly caused by the occurrence of reaction (29) [i.e. of e_{aq}^- with Pu(VI)].

5.3 α -RADIOLYSIS OF AMERICIUM IONS IN CARBONATE MEDIA

Americium(VI) in $NaHCO_3$ or Na_2CO_3 solutions is reduced to Am(V) upon α -irradiation. The yield for ^{241}Am α -particles is 4 ions/100 eV (Coleman et al. 1963). This yield is close to the yield observed in perchloric acid solutions (Pikaev et al. 1983). The dose rate was approximately 0.05 to 0.15 Gy s^{-1} .

However, Am(III) in carbonate solutions is oxidized to Am(IV) upon intense α -irradiation (Osipov et al. 1977). A mixture of the radionuclides ^{242}Cm and ^{244}Cm was used as the source of α -radiation. The experiments were carried out by the following procedure.

Hydroxides, oxalates, and nitrates of Am(III) and Cm(III) were dissolved in a concentrated solution of K_2CO_3 and stored at room temperature. The concentration of K_2CO_3 in the experimental solutions was 3 to 5.5 M, that of americium 0.02 to 0.10 M, and curium 0.04 to 0.12 M. The dose rate, mainly caused by the decay of curium, was within the range of $(1 \text{ to } 3) \times 10^2$ Gy s^{-1} .

Within a short time after the beginning of experiment (usually within one hour), the color of the solution changed from yellow-pink to brown-red. Turbidity of the solution then was observed and the formation of a precipitate took place. Over the following 20 to 30 hours, the precipitation was completed, and the brown-red color of the mother solution disappeared. The precipitate was separated and dissolved in nitric acid. Spectrophotometric measurements showed that the americium was in the pentavalent state, i.e., the precipitate was a binary carbonate of americium(V) and potassium. This conclusion was confirmed by X-ray crystal structure analysis.

High concentrations of CO_3^{2-} and Am(III) lead to the capture of OH radicals from spurs. As a result, H_2O_2 yield decreases. The Am(IV) was formed via reactions (33), (79), (89), and (90):

Americium (IV) in carbonate solutions disproportionates (Shilov and Yusov 1993):

The rate constant of the process decreases from 450 to $0.15 \text{ M}^{-1} \text{ s}^{-1}$ by increasing the K_2CO_3 concentration from 1.5 to 5.8 M.

5.4 α -RADIOLYSIS OF PLUTONIUM HYDROXIDES IN ALKALINE MEDIA

The behavior of Pu(IV) and Pu(VI) in 1 to 15 M solutions of NaOH in experiments lasting 2 years was studied (Delegard 1987). It was found that Pu(V) accumulated over a precipitate of Pu(IV) hydroxide. With time, the concentration of Pu in solution decreased. The Pu(V) concentration in 1 M NaOH began to decrease in 1 to 2 days, in 2 to 9 M NaOH within 7 days, in 10 M NaOH within 20 days, and in 15 M NaOH within 56 days. The role of possible oxidizing agents was not considered (Delegard 1987); the decrease was attributed to the change in the crystallinity of Pu(IV) hydroxide.

In our opinion, two processes occurred; the oxidation of Pu(IV) on the precipitate surface and the reduction of Pu(V) in the bulk of the solution. The oxidizing agents are O_2 , water radiolysis products ($\text{O}^\cdot$ and $\text{HO}_2^\cdot$), and also NO_3 and NO_2 present in the solution. To consider possible Pu(V) reducing agents, the yield of Pu(V) decrease may be evaluated with the formula:

$$G[-\text{Pu(V)}] = k \frac{100}{0.693 A} \quad (92)$$

where $k = -2.3 \log [\text{Pu(V)}]/dt$ (in days^{-1}) and $A = \sum g_i E_\alpha / (100 T_{1/2})$ and where g_i is the percentage of the given nuclide in a mixture, E_α is the energy of α -particles, in eV, and $T_{1/2}$ is the half-life period in days. The A value was calculated using the values shown in Table 5-16 and was found to be 0.765.

The initial values of $\text{Pu(V)}_{\text{max}}$ and Pu(V) through Δt time (days) and the yields of Pu(V) reduction for the same solutions of NaOH ($G[-\text{Pu(V)}]$) are shown in Table 5-17. It is noted that the true reduction yields will differ from the yields presented in the table, because, besides reduction, oxidation occurred.

Table 5-16. Nuclide Composition for Plutonium Used (Delegard 1987) and Nuclide Characteristics (Gorbachev et al. 1975).

Nuclide atomic mass	Percentage	T _{1/2} , years	E _α , MeV
238	0.034	86.41	5.499 (71.5%), 5.456 (28.4%)
239	90.9	24.38x10 ³	5.156 (72%), 5.143 (10.8%), 5.105 (11.2%)
240	8.40	6.62x10 ³	5.168 (75.5%), 5.123 (24.4%)
241	0.54	14	-
242	0.11	3.869x10 ⁵	4.904 (75%), 4.859 (25%)

The reducing agents for Pu(V) can be e_{aq}^- , H, and NO_3^- . The latter species is formed in the reaction:

In the solutions studied, NO_3^- concentration was much greater than 0.02 M; nitrate partially captures the precursors of H_2 from spurs. The high reduction yield may be caused by the fact that not only Pu(V) ions but also colloid particles of Pu(IV) and Pu(V) contribute to radiolysis.

Plutonium(VI) added to the alkaline solutions exists in ionic form and is gradually reduced. The reduction occurs as a result of radiation-induced processes. The initial yield of the Pu(VI) reduction can be evaluated from the change in the Pu(VI) concentration with time (Delegard 1987). In figure 3 of the cited report (Delegard 1987), Pu(VI) concentrations are given for solutions of different compositions through 7, 35, and more days. It is interesting to note that, in the solution with a_{NaOH} of 25 to 26 (about 9 M NaOH), the concentration of Pu(VI) did not change in the initial 7 days. The stability in solution concentration is due to either the low degree of the Pu(VI) reduction or to the high solubility of Pu(V) (for instance, owing to the formation of a peroxide complex [Musicas 1971]).

The calculation of G[-Pu(VI)] was conducted on the formula for G[-Pu(VI)]. The initial values, taken from the cited report (Delegard 1987), are shown in Table 5-18. In performing the calculation it was supposed that the initial concentration of Pu(VI) was the same in all the solutions and was about 4.4×10^{-3} M. It was also assumed that Pu(VI) was the predominant oxidation state present in the solutions through 7 days.

Table 5-17. The Influence of the NaOH Concentration on the Yield of the Pu(V) Reduction.

[NaOH], M	[Pu(V)] _{max} , M	Δt, day	[Pu(V)], M	k x 10 ² , day ⁻¹	G[-Pu(V)], ion/100 eV
1	9.25x10 ⁻⁸	5	6.12x10 ⁻⁸	8.24	15.5
2	3.42x10 ⁻⁷	13	1.60x10 ⁻⁷	5.84	11.0
4	1.84x10 ⁻⁶	13	0.98x10 ⁻⁶	4.70	8.8
6	1.0x10 ⁻⁵	13	5.4x10 ⁻⁶	4.66	8.8
8	3.6x10 ⁻⁵	13	2.38x10 ⁻⁵	3.06	5.8
10	1.35x10 ⁻⁴	36	7.75x10 ⁻⁵	1.54	2.9
15	5.33x10 ⁻³	96	1.42x10 ⁻³	1.38	2.6

The decrease in Pu(VI) concentration occurs as a result of reactions (29) and (81) to (87). If the yields of primary products of water α-radiolysis in alkaline media are the same as in perchloric acid or sulphuric acid solutions, then the yield of the Pu(VI) reduction to Pu(V) should be about 3 ion/100 eV (Pikaev et al. 1983). The higher yields testify to the participation of impurities in the process. One of them is NO₃. Organic compounds, introduced into the solution with distilled water, alkali, and also from the walls of polyethylene vessels in which the long-time experiments were performed, also could act as reducing agents. One more possible reason is the co-precipitation of Pu(VI) with Pu(V).

Table 5-18. Initial Yields of the Pu(VI) Reduction
([Pu(VI)]₀ = 4.4 x 10⁻³ M) (Delegard 1987).

a _{NaOH}	[Pu(VI)] x 10 ³ through 7 days, M	k x 10 ² , day ⁻¹	G[-Pu(VI)], ion/100 eV
0.6	1.72	13.4	25.2
1.3	2.57	7.7	14.4
2.2	2.88	6.1	11.5
3.4	4.00	1.38	2.6

Plutonium(V) in the precipitate captures e_{aq}^- from spurs

After some period, part of the Pu(V) is converted to Pu(IV) and leads to the observed change in the color of the precipitate (Delegard 1987).

5.5 RADIOLYSIS OF ALKALINE SOLUTIONS OF TECHNETIUM IONS

The radiolysis of alkaline solutions of technetium ions was studied on only a fragmentary basis. There are data on the preparation of Tc(VI) ions from TcO_4^- and the investigation of some properties of Tc(VI) ions within a wide range of pH values by pulse radiolysis (Pikaev et al. 1977b; Deutsch et al. 1978; Kryuchkov et al. 1979).

It was found that TcO_4^{2-} is formed in reactions (Pikaev et al. 1977b):

The optical absorption parameters of Tc(VI) were found to depend on the pH value of the solution (Pikaev et al. 1977b; Kryuchkov et al. 1979) (see Table 5-19). It was proposed that this feature is due to the existence of Tc(VI) in different forms:

The values of pK_1 and pK_2 were found to be ≥ -0.5 and 8.7, respectively (Kryuchkov et al. 1979). The pulse radiolysis method allowed measurement of several reaction rate constants occurring in the system under consideration. The respective data are shown in Table 5-20.

Table 5-19. Molar Extinction Coefficients (ϵ) of Tc(VI) Ions in Aqueous Solutions (Pikaev et al. 1977b and Kryuchkov et al. 1979).

Ion	Wavelength, nm	ϵ , M ⁻¹ cm ⁻¹
HTcO ₄ ⁻	295	2.6 x 10 ³
	360	6.0 x 10 ²
	500	~75
TcO ₄ ²⁻	360	3.8 x 10 ²
	500	2.8 x 10 ²
	500-600	~2.5 x 10 ² ^a

^aFrom (Deutsch et al. 1978)

In deaerated solutions, Tc(VI) decays by two second-order reactions and forms from disproportionation of Tc(V):

In solutions containing tertiary butyl alcohol (it is an effective scavenger of hydroxyl radicals), reaction (98) is suppressed, and only disproportionation of Tc(VI) occurs; the respective rate constants are given in Table 5-20. As seen from the table, the rate of TcO₄²⁻ disproportionation is less than that for the other Tc(VI) forms. The highest rate is for the reaction:

which seems to be a process of simple electron transfer from HTcO₄⁻ to TcO₄²⁻. Note that Tc(VI) in alkaline medium has a lifetime on the order of milliseconds (Deutsch et al. 1978). This observation coincides with other measurements (Kryuchkov et al. 1979).

Table 5-20. Rate Constants of Reactions in Irradiated Solutions of TcO_4^- .

Reaction	Medium	k, $\text{M}^{-1} \text{s}^{-1}$	Reference ^a
$\text{e}_{\text{aq}}^- + \text{TcO}_4^-$	Neutral or slightly acid	1.3×10^{10}	[1]
	0.1 M NaOH	2.5×10^{10}	[2]
$\text{OH} + \text{TcO}_4^{2-}$	Neutral or slightly acid	2×10^9	[1]
Disproportionation of Tc(VI)	pH < 2	$\sim 3 \times 10^6$	[3]
	pH ~ 8	3.8×10^7	[3]
	pH > 9	$\sim 2 \times 10^6$	[3]

^aReferences:

- [1] Pikaev et al. 1977b
- [2] Deutsch et al. 1978
- [3] Kryuchkov et al. 1979

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6.0 METHODS OF ISOLATION OF ACTINIDES AND TECHNETIUM FROM ALKALINE MEDIA WITHOUT ACIDIFICATION

Actinides in alkaline media form solid phases and can also form colloids, pseudocolloids, molecular neutral species, and anions. Solid phases are separated by filtration and centrifugation and colloids are separated by ultrafiltration through membranes and filters with small-sized pores. Coprecipitation, sorption, extraction, and electroprecipitation are used for the separation of molecular and ionic forms.

6.1 COPRECIPITATION

The coprecipitation of microamounts of radionuclides, including actinides, has been applied from the first days of existence of radiochemistry and plays a comparatively important role at the present time. Hydroxides, sulfates, phosphates, carbonates, and organic compounds were used as carriers. However, the reported developments concerned acid, neutral, and sometimes carbonate media (Seaborg and Katz 1954; Katz and Seaborg 1957; Milyukova et al. 1965; Metz and Waterbury 1962; and Myasoedov et al. 1972). No published material on the coprecipitation of actinides from alkaline media was found. Nevertheless, concentrating and separating actinides from alkaline media by the coprecipitation method with use of hydroxides of d-elements has been applied in the past 20 years in the laboratory of transuranium elements of the Institute of Physical Chemistry of the Russian Academy of Sciences (the head of laboratory is Professor N. N. Krot). Although the method allows one to separate the bulk of the actinide activity, and the radioactivity level in effluent water is within the approved level for processing at a purification plant, many of the parameters of the method have not been studied. The coprecipitation of Np(VI), Pu(V), and Am(VI) as a function of the alkali concentration, the influence of chemical constituents such as NO_3^- , SO_4^{2-} , CO_3^{2-} , EDTA, and $\text{C}_2\text{O}_4^{2-}$ on coprecipitation, and the behavior of colloids and pseudocolloids upon coprecipitation have not been studied and are unknown.

6.2 SORPTION

The sorption of actinides in alkaline solutions on various sorbents has been studied since the time of the discovery of heptavalent states of neptunium and plutonium. The behavior of Np(VII) in contact with anion exchange resins AB-17, Amberlite¹ IRA-400, and Dowex-1² was studied (Novikov et al. 1972a). Equilibrium upon sorption is achieved during 25, 50 and 75 hours in the cases of IRA-400, Dowex-1x10 and Dowex-1x8, respectively. The distribution coefficient, K_d , is defined:

¹Amberlite is a trademark of Rohm & Haas, Philadelphia, Pennsylvania.

²Dowex is a trademark of Dow Chemical USA, Midland, Michigan.

$$K_d = \frac{(C_{in} - C_{eq})V}{C_{eq} m} \quad (1)$$

where C_{in} is the initial concentration of the radioactive species in solution, C_{eq} is the equilibrium concentration, V is the total volume of the solution (in mL), and m is the weight of sorbent (in g). For Np(VII) at equilibrium the K_d s are >2400, about 2300, almost 1800, about 500 and >400 for Dowex-1x4, AB-17, Dowex-1x8, Dowex-1x10, and IRA-400, respectively.

The highest K_d values are found in 0.1 M NaOH. The K_d value decreases with increasing NaOH concentration. The completeness of the Np sorption on the solid phase depends on the ratio of the volume of alkaline solution to the weight of the sorbent and on the nature of the sorbent. The maximum capacity with respect to neptunium is about 5.9×10^{-2} and about 3.8×10^{-2} mol g⁻¹ for Dowex-1x4 and AB-17, respectively. Desorption of neptunium from anion exchangers by solutions of NaOH, NaClO₄, or their mixtures does not occur. Np(VII) in the desorbates was not found. The results are consistent with the hypothesis that the transition of Np(VII) into the solid phase upon long contact with organic sorbents is accompanied by the simultaneous reduction to Np(VI).

In addition to anion exchangers, cation exchanger KU-2, active carbon, and titanium oxide were used as sorbents for Np(VII). All these sorbents separate Np(VII) from 0.1 M NaOH. The K_d value for active carbon is about 10^3 (the equilibrium is established in 5 hours [Novikov et al. 1972a]). Absorption of Np(VII) on TiO₂ occurs without change in Np valency.

Inorganic sorbents are promising for the separation of Np(VII) from alkaline solutions (Zakharova et al. 1974). Hydroxides of La, Th, Zr, Ti, and Mg, and sodium uranate, which were frozen to prepare a grainy precipitate, were used as sorbents. The sorption of Np(VII) was studied in static and dynamic regimes.

Under static conditions, Np(VII) is adsorbed from 0.2 to 1 M NaOH on La, Th, and U(VI) hydroxides. The sorption of Np(VII) on Mg, Zr, Ti, and Bi hydroxides is small. The sorption of Np(VII) decreases with increasing NaOH concentration. The K_d value is the highest for La(OH)₃ (about 10^3 for 1 M NaOH and about 5×10^2 for 3.5 M NaOH). The experimental data for La(OH)₃ and Th(OH)₄ are reproducible. In the case of uranates, the results are not reproducible. The inconsistency seems to be connected with the variable composition of the solid phase.

The sorption of Np(VII) by hydroxide precipitates is reversible. It is caused by the formation of poorly-soluble compounds:

The chemical nature of the sorbent has a large influence on the sorption of Np(VII). It is due to the differences in the bond strengths for OH⁻ ions with metals in hydroxide precipitates, and in the solubilities of the formed compounds of Np(VII). Only negligible exclusion of OH⁻ ions from Zr, Ti, and Bi occurs, and the sorption of Np(VII) is small. In the case of Mg(OH)₂, the OH⁻ exclusion proceeds easily, but Np(VII) does not form poorly-soluble compounds with Mg²⁺. Therefore Np(VII) sorption on Mg(OH)₂ is also small. The most favorable relation between the ease of OH⁻ exclusion and the solubility of the Np(VII) compound with sorbent takes place in the case of La(OH)₃.

A dark-green layer with a clear interface is formed in a column upon the sorption of Np(VII) from 0.5 to 1 M NaOH on La(OH)₃ or Th(OH)₄ under dynamic conditions. The interface moves down as the sorbent becomes saturated. After complete saturation of the column, the molar ratio of La or Th to Np(VII) in the sorbent phase is close to 10:1.

The desorption of Np(VII) from the column can be conducted by 5 M NaOH. Neptunium in the desorbate is only in the heptavalent state. Np(VII) is desorbed virtually completely after passing a sufficient amount of concentrated alkali solution through the column (for example, the Th(OH)₄ layer contains 5 to 7% neptunium after 30 column volumes).

For the separation of Np(VII) from Np(VI) and Np(V), the solution containing neptunium and 0.5 to 1.7 M NaOH was passed through a column of aluminum oxide (the size of grains was 70-230 mesh) (Shiokawa et al. 1982). The column diameter was 0.6 cm and the length was 10 cm. Upon passing the alkaline solution, greater than 98% Np(V) sorption was observed with considerable sorption of Np(VI), but little Np(VII) sorption. The sorbed Np(VII) is the first that is washed from the column upon passing more alkaline solution through the column.

If the initial solution contains only Np(VII) and Np(VI), then the chromatography on aluminum oxide allows one to prepare separated samples of Np(VII) and Np(VI).

The sorption of trace amounts of plutonium and americium on sodium titanate was used for the purification of spent alkaline solutions (Schulz 1979). The solution α-activity concentration decreases to less than 6 to 7 nCi g⁻¹ (220 to 260 Bq g⁻¹) as a result of slow passage of the solution through the layer of sodium titanate.

In a recent review, it was noted that inorganic sorbents are used for the separation of actinides from alkaline media and that studies in this direction are being continued (March 1993).

Technetium in alkaline solutions exists in the form of TcO_4^- (see Section 2.0 of this survey). In contrast with many anions, TcO_4^- is highly sorbed on the strong base anion exchangers (Lavrukina et al. 1966; and Spitsyn et al. 1981). The K_d value for technetium sorption on the anion exchange resin Dowex-1 from 0.25 M NaOH decreases with increasing NO_3^- concentration (see Table 6-1).

Table 6-1. The Distribution Coefficients (K_d) of TcO_4^- Upon Sorption on the Anion Exchange Resin Dowex-1 from 0.25 M NaOH (Rimshaw and Malling 1961).

$[\text{NaNO}_3], \text{ M}$	K_d	$[\text{NaNO}_3], \text{ M}$	K_d
0	4500	2.0	190
0.5	575	3.0	142
1.0	340	5.0	122

The sorption of Np(V), Np(VI), Pu(VI), and Tc(VII) from 1 to 4 M NaOH on the macroporous strong-basic anion exchange resin VP-1AP (a vinylpyridine) was studied in the laboratory of electrochemistry of actinides and technetium of the Institute of Physical Chemistry of Russian Academy of Sciences (the head of laboratory is Professor V. F. Peretrukhin). The data are shown in Table 6-2. It is seen that all the studied elements are anionic in alkaline solutions and have high affinity for the anion exchange resin.

Table 6-2. Distribution Coefficients (K_d) of Actinides(V), Actinides(VI), and Technetium(VII) for NaOH Solutions and the Anion Exchange Resin VP-1AP.

Element	Concentration of NaOH, M			
	1	2	3	4
Np(V)	32	94	132	177
Np(VI)	325	152	61	30
Pu(VI)	368	143	76	32
Tc(VII)	6233	6155	5683	5193

6.3 EXTRACTION

The discovery of Np(VII) and Pu(VII) stimulated the study of extraction from alkaline solutions. In the first work on this topic, it was found that Np(VII) is not extracted from

0.1 to 4 M NaOH by solutions of the salts of organic cations (of butyl rhodamine and tetraphenyl arsonium) in CHCl_3 and $\text{C}_2\text{H}_4\text{Cl}_2$ (Novikov et al. 1972b). Butyl and isopropyl alcohols, diethyl ketone, and amyl and butyl acetates were also ineffective extractants.

A considerable transfer of neptunium into the organic phase is observed upon contacting alkaline solutions of Np(VII) with solutions of dibenzoylmethane (DBM) in butyl acetate, diethyl ether, and diethyl ketone. The best diluent for DBM is butyl acetate. Under otherwise similar conditions, the maximum isolation of neptunium takes place from 0.6 M NaOH. The completeness of extraction increases with increasing extractant concentration. With 0.1 M DBM, neptunium is transferred into the organic phase virtually completely. The distribution coefficient, D , does not depend on the neptunium concentration within the range of 9×10^{-5} to 3.6×10^{-4} M.

The neptunium in the organic phase is hexavalent. The back-extraction of neptunium proceeds with 4 M NaOH. No Np(VII) was detected in the back-extract. Hence, Np(VII) is transferred into the DBM organic phase where it is reduced to Np(VI) to form a complex. The composition of the extracting complex (metal:ligand) is 1:2.

The behavior of Pu(VII) upon extraction from alkaline media by DBM solutions in butyl acetate is analogous to that of Np(VII) (Vaidyanathan et al. 1972). The distribution coefficient of Pu(VII) between the organic phase and 0.6 M NaOH is not dependent on Pu(VII) concentration within the range of $(1 \text{ to } 3) \times 10^{-4}$ M. The distribution coefficient increases with increasing extractant concentration within the range of 2×10^{-3} to 5×10^{-2} M, reaching the value of 475 for 0.05 M DBM. The dependence of D on extractant concentration corresponds to the formation of a compound with the ratio Pu:DBM of 1:2 in the organic phase. Taking into account the potentials of the pairs Pu(VII)/Pu(VI) and Np(VII)/Np(VI) , and the behavior of Np(VII) upon the contact with the DBM solution, it is possible to suggest that Pu(VII) is reduced to Pu(VI) upon extraction.

The D value for Pu(VI) extraction under the same conditions is about 16 (Vaidyanathan et al. 1972). It follows that initially the Pu(VII) is transferred into the organic phase where the Pu(VII) then is reduced.

The extraction of Pu(VII) from alkaline solutions by various compounds was studied (Rozen et al. 1990; Karalova et al. 1990a; Karalova et al. 1992a; and Karalova et al. 1992b). The neutral extractants (tributyl phosphate (TBP), and trioctyl phosphine oxide, TOPO) do not extract Np(VII) (Rozen et al. 1990). Dicyclohexyl-18-crown-6 (1 M) in 100% TBP is also ineffective; the D value for 2 M KOH is about 0.005. Tetratolylmethylenediphosphine dioxide (1 M) in 100% TBP extracts Np(VII) from 1.7 M NaOH with a distribution coefficient of 0.012. The same result was obtained when methyl isobutyl ketone was used as a diluent (Rozen et al. 1990).

The extraction of Np(VII) by different solvents in the presence of tetrazolium salts was also studied. In this case, the transition of neptunium into the organic phase is also small (the D value for 0.5 M KOH is 0.001 to 0.1) (Karalova et al. 1990a).

Some success was achieved using alkylphenols RC_6H_4OH (where R is C_7 to C_9), *p*-*tert*-butylphenol, and polyalkylphenols (Rozen et al. 1990). Alkylphenolic extractants were studied in more detail (Karalova et al. 1990a; Karalova et al. 1992a; and Karalova et al. 1992b). The extractants used and the D values obtained are shown in Table 6-3.

All the tested systems extract neptunium into the organic phase. HABA and YB transfer neptunium more completely into the organic phase. The composition of the aqueous phase has a considerable effect on the D values for neptunium. The maximal D value of about 10 is achieved in 0.5 and 1.0 M solutions of NaOH in the cases of HABA and YB respectively. Further increase in the alkali concentration in the case of HABA gives rise to a more dramatic decrease in the D values than in the case of YB. At the same time HABA can be used in a wider range of NaOH concentrations in comparison with YB, although the isolation of neptunium by HABA from 5 M NaOH does not exceed 5%.

Table 6-3. The Distribution Coefficients (D) of Neptunium for the System Phenolic Extractant - 0.5 M NaOH (Karalova et al. 1990a).

Extractant	Abbreviated name	Molecular mass	Solvent	D
4-(α,α -Dioctylethyl)-pyrocatechol	DOEP	362	Toluene	0.92
2-Hydroxy-5-alkylbenzyl-diethanolamine	HABD	320	Hexane	0.89
Bis(2-hydroxy-5-alkyl-benzyl)amine	HABA	465	CCl_4	8.14
Nitrogen-containing oligomer of alkylphenol	Yarrezine B (YB)	460	Toluene	4.83
Sulfur-containing oligomer of alkylphenol	Octophor 10S	1150	Toluene	1.36
Oxygen-containing oligomer of alkylphenol	Reagent 101K	520	Toluene	0.98

The completeness of extraction increases with increasing contact with the extractant and with increasing duration of the phase contact. The D values for neptunium increase with time; the rate of establishment of the equilibrium depends on the alkali concentration. Ten minutes are required for equilibrium upon extraction by oligomer YB from 0.5 M NaOH, and not less than 30 minutes are required from 2 M NaOH.

The composition of the extracting compound has a metal:ligand ratio of 1:1 (Karalova et al. 1990a; and Karalova et al. 1992a). The D values for neptunium between 0.1 M YB in toluene and 1 M NaOH do not depend on the initial concentration of neptunium within the range of 10^{-5} to 10^{-3} M (Karalova et al. 1990a).

In the case of HABA, the D values for neptunium do not depend on its initial concentration (up to 10^{-4} M); at higher concentrations they decrease. The coefficients do not change with increasing the speed of stirring. This indicates that the role of diffusion upon extraction is negligible. Increase in temperature from 20 to 40 °C improves the extraction of neptunium.

Study of the isotherm of extraction of neptunium from 0.5 to 2.0 M NaOH by HABA was carried out to determine the capacity of the extractant for neptunium. The concentration of neptunium in the organic phase increases with increasing concentration in the aqueous phase and reaches a maximum at the concentration of 1.89 g/L in the aqueous phase. The capacity of the extractant (0.1 M HABA in CCl_4) was found to be 0.5 g Np/L.

Salts have a considerable effect on the extraction of Np(VII) by HABA solution. The addition of KCl increases the extraction; K_2CO_3 decreases the extraction (Karalova et al. 1992a; and Karalova et al. 1992b).

Neptunium(VI) in the NaOH solution - HABA system is extracted slower, and with a lower value of D , than Np(VII). For instance, Np(VI) requires 3.5 hours to achieve equilibrium (D is about 3) in the system 0.1 M HABA in CCl_4 - 0.5 M NaOH; Np(VII) requires 0.5 hours (D is about 10) (Karalova et al. 1992a; and Karalova et al. 1992b).

The stability of Np(VII) during extraction was studied by spectrophotometry. Np(VII) is not reduced to Np(VI) by short contact of its alkaline solutions with HABA. The reduction of Np(VII) to Np(VI) occurs in the organic phase after extraction. In the organic phase, the neptunium is only in the hexavalent state; Np(VII) was not detected in the back-extract. The shape of the NMR ^{13}C spectra of the loaded alkylphenolic extractants indicates that neptunium complexes form by substituting for protons in the hydroxyl groups of the extractant; the complex has paramagnetic properties. These observations confirm the presence of the hexavalent state (Karalova et al. 1992a; and Karalova et al. 1992b).

The degree of neptunium back-extraction by alkaline solution does not exceed 50% and is independent of the duration of the phase contact, the extractant concentration, and the time of standing of the extracts. Good back-extraction of neptunium occurs by mineral acid solutions (Karalova et al. 1992a).

Extraction of easily-hydrolyzed species, such as the tri- and tetravalent actinides, from alkaline solutions is possible only in the presence of complexing ligands capable of retaining these elements in alkaline media in the form of the stable anionic complexes. Organic ligands (α -hydroxycarboxylates and aminopolycarboxylates) and inorganic carbonate ligands are used as complexing agents.

To date, extraction systems with quaternary ammonium bases (QAB), primary amines, β -diketones, alkylpyrocatechols, alkyl derivatives of aminoalcohols, and condensed alkylaminophenols have been studied (Pal'shin et al. 1978; Karalova et al. 1978; Karalova et al. 1979; Nekrasova et al. 1979; Myasoedov et al. 1979; Myasoedov et al. 1980a; Nekrasova et al. 1981; Karalova et al. 1982; Bukina et al. 1983;

Karalova and Myasoedov 1984; Karalova et al. 1985a; Karalova et al. 1985b; Mahajan et al. 1986; Karalova et al. 1989c; Karalova et al. 1983a; Karalova et al. 1985c; Myasoedov et al. 1980b; Karalova et al. 1981; Karalova et al. 1983b; Karalova et al. 1984a; Karalova et al. 1984b; Karalova et al. 1987b; Karalova et al. 1986; Karalova et al. 1987c; Karalova et al. 1987a; Karalova et al. 1989b; Karalova et al. 1989a; Bukina et al. 1990; Karalova et al. 1991; and Lavrinovich et al. 1993). The results obtained with these systems are considered briefly.

6.3.1 Extraction by Aliquat-336³

Aliquat-336 (i.e., trialkylmethylammonium chloride, where alkyl is C₈ to C₁₀) was one of the QABs studied. The behavior of Am(III), Am(V), La(III), Eu(III), Th(IV), Pu(IV), U(VI), and some other elements upon extraction by Aliquat-336 solutions in cyclohexane or xylene from alkaline solutions was studied (Pal'shin et al. 1978; Karalova et al. 1978; Karalova et al. 1979; Nekrasova et al. 1979; Myasoedov et al. 1979; Myasoedov et al. 1980a; Nekrasova et al. 1981; Karalova et al. 1982; Bukina et al. 1983; Karalova and Myasoedov 1984; Karalova et al. 1985a; Karalova et al. 1985b; Mahajan et al. 1986; and Karalova et al. 1989c). Micro- and macroamounts of Am(III) and Eu(III) are extracted most completely by 0.1 M Aliquat-336 solution in cyclohexane in the presence of 2.5×10^{-2} M tartrate or trihydroxyglutarate in 0.15 to 0.5 M NaOH. Further increase in the NaOH concentration decreases the isolation degree (R, %) of the element into the organic phase. Extraction from 0.5 M NaOH decreases with increasing α -hydroxycarboxylate concentration.

Hydroxydicarboxylates (tartrate, trihydroxyglutarate) provide better extraction by Aliquat-336 from the more concentrated alkaline solutions than hydroxymonocarboxylates (glycerate, gluconate).

Extraction of 10^{-6} M Pu(IV) from NaOH solutions in the presence of tartrate by a 20% solution of Aliquat-336 in xylene was investigated (Mahajan et al. 1986). The R value for Pu(IV) at 0.2 M NaOH increases from 32 to 98% by increasing the Aliquat-336 concentration from 0.04 to 0.2 M. Increase in the NaOH concentration from 0.2 to 0.5 M (at 0.4 M tartrate) decreases the R value from 89 to 4.2%.

The dependence of logD on log extractant concentration shows that a solvate with 3 molecules of extractant is extracted into the organic phase.

Penta- and hexavalent actinides are extracted less effectively than the trivalent actinides. For instance, the D values for Am(V) upon extraction from NaOH solutions containing 2.5×10^{-2} M tartrate are less by an order of magnitude than the values for Am(III).

³Aliquat is a trademark of Henkel Corporation, Gulph Mills, Pennsylvania.

Study of the extraction of Am(III) and other elements in the presence of chelating agents has shown that the D value depends on NaOH concentration (see Figure 6-1). The nature of the chelating agent has a considerable effect on the extraction of ions such as Am(III) and Eu(III). Aromatic hydroxy-functionalized chelating agents allow extraction within a wider range of alkali concentration in comparison with extraction by aliphatic hydroxy-functionalized chelating agents. The derivatives of polymethylene diaminetetraacetate (dihydroxydiaminobutanetetraacetate, DHBTA; and hydroxydiethylenetriaminetetraacetate, HDETTA) are more effective than chelating agents containing hydroxyalkyl groups (hydroxyethyldiethylenetriaminetetraacetate, HEDTTA; and hydroxyethylethylenediaminetriacetate, HEDTA).

Figure 6-1. Extraction of Actinides from Alkaline Solutions.

Extractant: 0.2 M Aliquat-336 in cyclohexane.

Medium: NaOH and 2×10^{-3} M DHBTA (dihydroxydiaminobutanetetraacetate).

The behavior of Am(III), Cm(III), and Eu(III) in the system: Aliquat-336 - NaOH - EDTA was studied in an extraction-chromatographic technique (Bukina et al. 1983). The influence of the concentration of NaOH and EDTA on the D values was considered. For instance, the D value for Am(III) with 0.01 M EDTA decreases from 30 to 2.5 when NaOH concentration increases from 0.1 to 1 M.

6.3.2 Extraction by Amines

Tri-, tetra-, and hexavalent actinides are extracted from carbonate solutions by alkylamines in chloroform, xylene, cyclohexane, and other diluents (Karalova et al. 1983a; and Karalova et al. 1985c). The most effective extractants are the salts of primary amines.

6.3.3 Extraction by Alkylpyrocatechols

Alkylpyrocatechols are effective extractants for the isolation of many elements from alkaline and carbonate solutions (Myasoedov et al. 1980a; Karalova et al. 1982; Karalova and Myasoedov 1984; Karalova et al. 1985b; Karalova et al. 1985a; Karalova et al. 1989c; Myasoedov et al. 1980; Karalova et al. 1981; Karalova et al. 1983; Karalova et al. 1984a; Karalova et al. 1984b; Karalova et al. 1987b). Extraction of lanthanides and actinides by means of 4-(α,α -dioctylethyl)pyrocatechol (DOP) and the mixture of mono- and didecylpyrocatechols (TAP) in toluene and cyclohexane was investigated.

DOP is one of the few reagents isolating microamounts of Am(III) and Eu(III) from concentrated alkaline solutions in the absence of complexing agents. Almost complete extractions are obtained (96 to 97% by means of 0.04 M DOP in toluene from 0.5 to 5 M NaOH within 30 min) when freshly-prepared solutions are used. In the presence of tartrate, the D value for Am(III) increases dramatically with increasing NaOH concentration from 0.1 to 9.5 M; extraction reaches a maximum at 2 M NaOH and remains constant up to 10 M NaOH.

Extraction of Eu(III) from dilute alkaline solutions depends upon the nature of the diluent. The D value decreases in the order: cyclohexane > toluene > chloroform > octyl alcohol. Eu(III) is extracted to 99% from 5 M NaOH independent of the nature of diluent (excluding octyl alcohol).

Extraction of Pu(IV), Th(IV), U(VI), Fe(III), Ru(III), Zr(IV), Nb(V), and Cs(I) by DOP was studied. It was found that tetravalent elements in 0.5 to 3 M NaOH in the presence of 1×10^{-4} M diethylenetriaminopentaacetate have higher D values than trivalent elements. The D values of pentavalent elements are very low. Fe(III) is extracted with a high D value.

Figure 6-2. Extraction of Am(III) and Eu(III) from Alkaline Solutions with DOP ([4(α,α)dioctylethyl] pyrocatechol).
0.4 M DOP Solution in Toluene.

Curves 1 and 2: K_2CO_3 Solution without NaOH.

Curve 3: K_2CO_3 Solution with 0.5 M NaOH.

Curve 4: K_2CO_3 Solution with 2 M NaOH.

DOP isolates trivalent lanthanides and transplutonium elements from carbonate solutions. Figure 6-2 shows the dependencies of the D values for Am(III) and Eu(III) extraction by a 0.4 M solution of DOP in toluene on the carbonate and hydroxide aqueous concentrations. These elements are extracted well from the solutions with less than 0.5 M K_2CO_3 . Increasing the K_2CO_3 concentration to 3 M leads to a two-order decrease in the D value.

Extraction increases dramatically with the addition of NaOH. At NaOH concentrations greater than 0.5 M, the D value is 500 within a wide range of K_2CO_3 concentrations.

Similar dependencies were obtained with the use of mixtures of mono- and bidecylpyrocatechol solutions in chloroform, cyclohexane, or toluene.

6.3.4 Extraction by β -Diketones

Extraction of U(VI), Th(IV), Pu(IV), Am(III), Cm(III), and Eu(III) from $KHCO_3$ and K_2CO_3 solutions by means of thenoyltrifluoroacetone and 1-phenyl-3-methyl-4-benzoylpyrazolone-5 in methyl isobutyl ketone was studied (Karalova et al. 1986; and Karalova et al. 1987c). The composition of the extracted compounds was established. β -Diketones isolate many elements almost completely within a wide range of CO_3^{2-} concentrations. Extractions of actinides decrease in the order: M(III) > M(IV) > M(VI).

6.3.5 Extraction by Alkylaminoalcohols and Alkylphenols

To isolate lanthanides and actinides from alkaline solutions in the presence of tartrate and carbonate, it is possible to use alkyl derivatives of aminoalcohols (Karalova et al. 1987a; Karalova et al. 1989b; Karalova 1989a; Bukina et al. 1990; Karalova et al. 1990b; and Lavrinovich et al. 1993). Extraction of Am(III), Eu(III), U(VI), and other elements by 2-hydroxy-5-alkylbenzyl-diethanolamine (HABD) in different solvents was investigated. Am(III) is extracted completely from tartrate alkaline solutions by 0.1 M HABD in hexane. Increase in the NaOH concentration from 0.01 to 10 M gives rise to an increase in the D value from 10 to about 30 in (1×10^{-2} M tartrate). The nature of the diluent has an effect on the D value in the case of low alkali concentration. The D value decreases in the row: cyclohexane > hexane > chloroform > isoamyl alcohol. Change of diluent upon extraction from 2 M NaOH has a small influence on the D values (excluding isoamyl alcohol).

Increase in the sodium tartrate concentration from 0.001 to 0.1 M slightly changes the D values for Am(III) and Eu(III). Further increase in the tartrate concentration (to 1 M) decreases extraction.

Change of conditions slightly influences extraction of U(VI), Ru(IV), Cr(III), Zr(IV); their distribution coefficients are low.

Am(III) and Eu(III) are extracted rather completely by 0.1 M HABD from 0.01 to 0.1 M K_2CO_3 ($R = 95$ to 98%). Increase in the K_2CO_3 concentration decreases the extraction of the metals into the organic phase; at 1 M K_2CO_3 , both elements remain in the aqueous phase. The addition of KOH promotes extraction of Am(III) and Eu(III).

The phenolic-type extractants (HABA, YB and others, see Table 6-3) isolate not only Np(VII) from alkaline media, but also actinides in different oxidation states from carbonate solutions. In the case of Am(III), the D values increase with increasing pH. The maximal value of D is observed for 1 M K_2CO_3 . Both decrease and increase in the K_2CO_3 concentration decrease the D values. Tetra-, penta- and hexavalent actinides are extracted considerably worse (by 2 to 3 orders of magnitude) than the trivalent actinides.

6.3.6 Extraction of Technetium

Many types of organic compounds have been used as extractants for the isolation of Tc(VII) from alkaline solutions (Lavrukhina and Pozdnyakov 1966; and Spitsyn and Kuzina 1981). Tc(VII) is poorly extracted by aliphatic and aromatic hydrocarbons, their halogenated derivatives, and carboxylic acids. Some respective data are shown in Table 6-4.

In a homologous series of alcohols, aldehydes, or ketones, extraction decreases with an increase in the number of carbon atoms in the chain. Some examples are shown in Table 6-4.

Nitrogen-containing extractants (in particular, pyridine and its derivatives) are effective for technetium isolation.

Tributyl phosphate is one of the most important phosphorus-containing extractants. The D value for 1 M NaOH is 7.5.

Extraction of Tc(VII) by pyridine depends on the presence of nitrate and other ions. Diffusion coefficients decrease considerably with increase in the nitrate concentration.

The possibility of isolation of Tc(VII) from 0.1 to 3.0 M NaOH by use of phenolic extractants was studied (Karalova et al. 1990a). The distribution coefficients for all such extractants are low. Therefore, these extractants are not used for isolation of TcO_4^- from alkaline solutions.

Extraction of Tc(VII) in the form of the adducts with tetrazolium salts (previously used for the isolation of rhenium from alkaline solution) was also investigated (Karalova et al. 1990a; and Karalova et al. 1991a). The advantage of tetrazolium salts in comparison with organic cations such as tetraphenylarsonium and tetraphenylphosphonium is that they extract well even in very concentrated alkali solutions. Technetium is extracted by 5×10^{-4} M tetrazolium salt (especially, 2,3,5-triphenyltetrazolium chloride) in chloroform. The distribution coefficient increases from about 10 for 0.1 M NaOH to 30 for 1.5 M NaOH.

Extraction of Tc(VII) from alkaline solutions by crown compounds in different solvents was studied (Jalhoom 1986). The D values depend on the nature of alkali, increasing in the row: LiOH < NaOH < KOH. Increase in the alkali concentration leads to an increase in the D value. The efficiency of extraction depends on the nature of the diluent; it increases in the row: trichlorobenzene < benzene < chloroform < chlorobenzene < *o*-dichlorobenzene < 1,2-dichloroethane < nitrobenzene. The distribution coefficient for extraction by 0.01 M dibenzo-18-crown-6 in nitrobenzene from 4 M NaOH is about 10.

Table 6-4. Extraction of Tc(VII) from Solutions of NaOH.

Extractant	[NaOH], M	D
Benzene	1	0.037
Toluene	1	0.014
Dichloroethane	1	0.007
Mixture of carboxylic acids	1	0.001
<i>n</i> -Butyl alcohol	1	0.6
Isoamyl alcohol	1	0.1
Acetone	2	61.2
Methyl ethyl ketone	2	47.9
Methyl <i>n</i> -propyl ketone	2	2.9
Cyclohexanone	1	6.7
Methyl isobutyl ketone	2	0.27
Pyridine	3	239
α -Picoline (2-methylpyridine)	3	1970
Lutiodine (2,4-dimethylpyridine)	3	1670
Aldehydine (5-ethyl-2-methylpyridine)	3	930
Quinoline (benzo[<i>b</i>]pyridine)	3	356

6.4 ELECTROCHEMICAL METHODS OF ACTINIDE AND TECHNETIUM ISOLATION FROM ALKALINE SOLUTIONS

Electrochemical methods can be used for electrodeposition of actinides and technetium and for the destruction of nitrate and nitrite ions contained in alkaline wastes.

6.4.1 Electrodeposition of Actinides and Technetium and Their Cementation by Metals from Alkaline Solutions

Electrodeposition of mixed uranium(V,IV) hydroxides has been demonstrated from solutions of 0.5 to 4.0 M NaOH and 5×10^{-5} M U(VI) on platinum or stainless steel cathodes with a current density of 0.4 to 0.5 A cm⁻² at 25 to 60 °C. The ratio of catholyte volume to cathode area was 12 cm, and 98 to 100% of the uranium was electrodeposited on the cathode after 40 min electrolysis (Zantuti et al. 1991). The presence of 0.5 M Na₂CO₃, 2.0 M NaNO₃, 2.0 M NaNO₂, 0.2 M NaF, and 0.5 M H₂O₂ in alkaline solution did not decrease the uranium yield (Zantuti et al. 1991; and Gurevich and Koval'skaya-Yachenko 1958). Uranium(V) and uranium(IV) have been determined in the electrodeposited film. The decrease in the current density from 0.4 to 0.02 A cm⁻² resulted in increasing the electrolysis duration to 4 hours and decreasing the uranium yield as much as 90%. Trace quantities of carrier-free ²³⁹Pu, ²³⁴Th, and ¹⁴⁴Ce were added to the uranium solution. It has been shown that electrodeposition yields of these radionuclides are equal to the uranium yield for the duration of the electrolysis (Zantuti et al. 1991).

The electrodeposition of plutonium from solutions of 1.6 to 1.9 M NaOH and 10⁻⁵ M Pu(VI) has been studied by two groups of authors. The yield of plutonium on platinum and stainless steel was as high as 90 to 96% at a current density of 25 mA cm⁻² after 4 hours electrolysis (Milyukova et al. 1969) and near 100% at current density 40 mA cm⁻² after 2 hours electrolysis (Miller and Brouns 1952).

Some time ago it was shown that technetium can be electrodeposited from a solution of 1 to 2 M NaOH, and 10⁻⁴ M Tc(VII), at the cathode potential -0.86 V (vs NHE) as Tc(IV) hydroxide (Rogers 1949). The yield of technetium electrodeposition from alkaline solution was not reported. Others indicated that Tc(IV) formed by the polarographical reduction of TcO₄ in 1 M NaOH is dissolved within 2 seconds after the formation (Founta et al. 1987). They explained this fact by the conversion of Tc(VII) electroreduction product to TcO₂·xH₂O or by the existence of Tc(IV) amphoteric species stable thermodynamically in alkaline media. The published data are not sufficient to choose conditions for the quantitative electrodeposition of Tc from alkaline solutions.

The deposition of Np(V), Np(IV), and Pu(IV) hydroxides can be carried out from alkaline media, without an external electrical source, on aluminum and zinc foils. Films of Np(V,IV) hydroxides on Al foil with thicknesses up to 0.6 mg cm⁻² have been prepared by the plunging of Al foil into solutions of 0.3 to 0.5 M NaOH and 10⁻³ to 10⁻² M Np(VII) for 10 to 20 minutes (Dzyubenko and Peretruxhin 1977). Thin films of Pu(IV) hydroxides have been

prepared on Al and Zn foils from solutions of 0.5 to 1.0 M NaOH and 10^{-4} M Pu(VI) (Peretrukhin 1981). The films are uniform and have a good adhesion to Al and Zn pieces of any geometrical form. These investigations were carried out to develop techniques for actinide oxide film preparation. These works also indicate a possible method to separate actinides and technetium from alkaline wastes by electrodeposition or metal cementation. The simultaneous reduction of CrO_4^{2-} and other major components of alkaline wastes remains a problem to be investigated.

6.4.2 Electrochemical Denitration of Alkaline Waste

The electrolytic reduction of NO_3^- and NO_2^- in 1 to 3 M NaOH solutions has been studied on platinum, nickel, and stainless steel cathodes (Horanyi and Rizmayer 1985; and Li et al. 1988). Two reduction processes have been reported for nitrate in alkaline solution:

Nitrite can be reduced to nitrogen at the less negative cathode potential, E_{cat} , of -0.60 V. The reduction of nitrate to N_2 in 3 M NaOH takes place at a current density of less than 0.107 A cm^{-2} , and ammonia becomes the major electrolysis product at current densities greater than 0.466 A cm^{-2} (Li et al. 1988). Denitration with N_2 evolution is more suitable for industrial application because mixtures of ammonia with oxygen can be explosive.

The current efficiency of the NO_3^- conversion to N_2 in 3 M NaOH is high (up to 86%) when the nitrogen is used for ventilation of the cell and up to 94% when an air stream is used for ventilation. Oxygen increases the current efficiency due to its reduction at the cathode to form HO_2^- ; HO_2^- seems to react rapidly with nitrate. The presence of 0.25 M Na_2CO_3 in the NaOH solution has no influence on the efficiency of electrolytic denitration. The effect of ruthenium, present in the NaOH solution, on the denitration process is described in reports (Alter et al. 1957; and Messing and Higgins 1957) not available in Russia.

The presence of 1×10^{-4} M Tc(VII) facilitates denitration in 1 to 4 M NaOH solution when the ratio of catholyte volume to the cathode area is 20 cm (Silin and Peretrukhin 1994). But the formation of hydroxide films of U, Np, Pu, and Am should be expected on the surface of the cathode during the denitration of alkaline wastes. The effect of actinide and other metal oxide films on the electrolytical denitration of alkaline waste has not been reported.

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7.0 CONCLUSION

Consideration of published data on the chemistry of transuranium elements and technetium in alkaline media allows us to draw the following conclusions and recommendations.

1. The thermodynamically-stable forms of actinide hydroxides, including Pu(V), and of technetium in 0.1 to 15 M NaOH were determined. It was shown that, in addition to the sparingly-soluble hydroxides of U(IV), Np(IV), and Tc(IV), hydroxides of Pu(IV) and Am(III) can be oxidized to the more soluble pentavalent and, in some cases, hexavalent states by mild oxidizing agents present in the alkaline tanked wastes of the Hanford Site. The ventilation of tanks by nitrogen (instead of air) can be recommended as one measure to decrease the actinide concentration in the solutions.
2. Data on the solubilities and the forms of existence of the hydroxide compounds of the actinides and technetium in alkaline media are incomplete and sometimes contradictory. Significantly, the solubilities of hydroxides of lanthanides, actinides, and technetium in alkali increase considerably in the presence of complexing agents. One of the important problems to be solved is the determination of the solubility of plutonium.
3. Consideration of the redox reactions of actinides in alkaline media allows one to choose reagents for the fast preparation of hydroxide compounds of actinides in valent states from VII to III in "pure" alkaline media. However, realization of the methods in the case of multi-component alkaline wastes requires experimental examination.
4. Information on the radiation-chemical properties of hydroxide compounds of actinides in valent states of V, IV, and III in alkaline media is absent; the same information for technetium is incomplete. There is an interesting possibility to use the radiation field of liquid wastes in Hanford tanks for the conversion of Pu(V), Tc(VII) and, apparently, Np(V) to sparingly-soluble hydroxides of actinides(IV) and technetium(IV) by using additives which are scavengers of the oxidative components of radiolysis. Conversely, conditions for oxidation of actinides in the lower valent states to actinides in higher valent states can be created by the addition of scavengers of the reductive components of radiolysis. In general, use of the respective additive may allow preparation of actinides in any desired oxidation state.
5. Electrochemical methods may be used to isolate actinides and technetium from alkaline solutions by electrodeposition, and by cementation on metals (e.g., Al, Zn). Electroanalytical determination of these elements in solutions also may be performed.
6. Coprecipitation with hydroxides of d-elements (e.g., Mn, Fe), sorption on inorganic sorbents and strong-base macroporous anion exchange resins (e.g., vinylpyridines), and extraction can also be used for the separation of actinides and technetium from alkaline solutions.

7. It is necessary to emphasize that all the isolation methods have been developed and studied for "pure" alkaline solutions. The behaviors of actinides and technetium in the presence of large amounts of NO_3 , CrO_4^{2-} , aluminates, EDTA, and other complexing agents have not been investigated. The respective studies are required to develop technology for the isolation of actinides and technetium from real alkaline wastes.

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