Radiolysis of Actinides and Technetium in Alkaline Media

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ABSTRACT

The γ -radiolysis of aerated alkaline aqueous solutions of Np(V), Np(VI), Pu(VI), Tc(IV), Tc(V), and Tc(VII) was studied in the absence of additives and in the presence of CO_3^{2-} , NO_3^- , NO_2^- , EDTA, formate, and other organic compounds. The radiolytic reduction of Np(V), Np(VI), Pu(VI), and Tc(VII) under different experimental conditions was examined in detail. The addition of EDTA, formate, and alcohols was found to considerably increase the radiation-chemical reduction yields. The formation of the Np(V) peroxo complex was observed in the γ -radiolysis of alkaline aqueous solutions of Np(VI) in the presence of nitrate.

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RADIOLYSIS OF ACTINIDES AND TECHNETIUM IN ALKALINE MEDIA

1.0 INTRODUCTION

Highly radioactive aqueous solutions, including carbonate and alkaline solutions, are produced on reprocessing spent nuclear fuel and the separation of product radionuclides. The products of water radiolysis appear in the solutions as a result of the action of α -, β -, and γ -radiation emanating from actinides, cesium, strontium, rare earths, and other radioactive elements. The radiolysis products react with solutes (including actinides) in various ways and can influence technological operations that use such solutions.

The radioactive waste stored in underground tanks at the Hanford Site are alkaline. To manage such waste successfully, it is necessary to know the features of radiolytic conversions of actinides in alkaline media. The radiolysis-induced behavior of technetium, which is present in the waste solutions, is also of concern.

Information on the radiation-chemical properties of actinides in the V, IV, and III valent states in alkaline media currently is not available. The existing technical literature primarily contains data on radiation-induced oxidations of hexavalent neptunium, plutonium, and americium to their respective heptavalent states in alkaline solutions, reduction of heptavalent states in the same solutions, oxidation of Am(III) in carbonate media, and reactivity of actinide ions towards water radiolysis products and certain other free radicals in carbonate and alkaline solutions (Pikaev et al. 1983 and Peretrukhin et al. 1995). Information on the radiation chemistry of technetium alkaline solutions is limited to the preparation of Tc(VI) ions from TcO₂ and some properties of Tc(VI) ions within a wide pH range studied by pulse radiolysis (Peretrukhin et al. 1995).

The present work is devoted to the study of γ -radiolysis of alkaline and carbonate-alkaline aqueous solutions of penta- and hexavalent neptunium, hexavalent plutonium, and tetra-, penta- and heptavalent technetium. The radiolytic conversions were investigated both in the absence of any additives and in the presence of NO₂, NO₂⁻, EDTA¹, and other organic additives.

¹EDTA is ethylenediaminetetraacetate.

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2.0 EXPERIMENTAL MATERIALS AND METHODS

Double and sometimes triple distilled water and chemically-pure grade sodium hydroxide were used to prepare the solutions. A portion of the initial NaOH solution was first γ -irradiated to about 70 kGy dose to remove possible organic microimpurities. Optical absorption spectra of irradiated and unirradiated NaOH solutions in the ultraviolet (UV)-region at wavelength, λ , greater than 230 nm were virtually the same and did not contain bands that could be attributed to organic impurities. Pure-for-analysis grade formic acid, EDTA (sodium salt), and potassium nitrite, chemically-pure grade perchloric acid and sodium nitrate, and special chemically-pure grade nitric acid were used without additional purification. Sodium carbonate was purified by two recrystallizations from bidistilled water.

The stock solution of neptunyl perchlorate was prepared by the following known procedure. A portion of ^{237}Np was first purified by an ion exchange method. The neptunium solution in nitric acid that desorbed from the column was evaporated to damp salts three times with perchloric acid. The residue was dissolved in 0.085 M HClO_4 , then stored in the dark. Spectrophotometric analysis in the range of 350 to 1,300 nm showed that the solution contained about 1% Np(V) ; the remaining neptunium was hexavalent. The solution spectrum is shown in Figure 2-1. The Np(VI) concentration in the stock solution was 1.4×10^{-2} M. The neptunium concentration was determined by complexometric titration with preliminary reduction to the tetravalent state.

Alkaline Np(VI) solutions were prepared by adding measured amounts of the stock $\text{NpO}_2(\text{ClO}_4)_2$ solution to vigorously stirred aqueous alkali solutions of known concentration in volumetric flasks. The flasks then were filled to volume with the stock alkali solution. The maximum Np(VI) concentration in alkaline solutions used in the experiments was 5.8×10^{-4} M. At higher Np(VI) concentrations, the solutions (especially in 1 to 2 M NaOH) form precipitates.

Perchloric acid solutions of Np(V) were obtained by two methods. The first consisted of γ -irradiation of the stock perchloric acid solutions of Np(VI) . Neptunium(V) is the product of radiolytic Np(VI) reduction in acid aqueous solutions (Pitkaev et al. 1983). Spectrophotometry showed that only Np(V) is present in the solution after γ -irradiation to a dose of about 60 kGy. Adding the prepared acid Np(V) solution to the alkaline solutions produced alkaline solutions of Np(V) . The second consisted of reducing Np(VI) by sodium nitrite; the Np(V) product was precipitated by ammonia solution and the precipitate was separated by centrifugation. The Np(V) precipitate was washed twice with ice-cold bidistilled water. The precipitate then was dissolved in a small excess of HClO_4 solution.

The stock perchloric acid solutions of hexavalent plutonium were prepared by the following standard procedure. An aliquot of ^{239}Pu first was purified by an ion exchange method in nitric acid. The purified acidic plutonium solution desorbed from the column was evaporated with concentrated perchloric acid solution to damp salts. This operation was repeated twice.

Figure 2-1. Optical Absorption Spectrum of the Prepared Stock Np(VI) Solution in 0.085 M HClO₄ (1 cm pathlength).

The residue was dissolved in 0.01 M HClO_4 . The optical absorption spectrum of one of the solutions prepared is shown in Figure 2-2. The spectrum shows that only Pu(VI) is present in the solution. The solution was used within 3 to 4 days, with longer holding times, α -autoradiolysis caused noticeable reduction of Pu(VI) . Fresh solutions of Pu(VI) were prepared as required. Alkaline solutions of plutonium were obtained by the same procedure as alkaline solutions of neptunium. Plutonium(VI) is more readily soluble in alkaline solutions than neptunium(VI) and its maximum concentration used was 1×10^{-3} M.

Potassium pertechnetate (produced at Mayak Production Association, Chelyabinsk), recrystallized twice from bidistilled water and dried to a constant weight at 110°C , was used for the preparation of the solutions used in the study. This salt also served as an initial compound for synthesis of Tc(IV) and Tc(V) oxides.

All the experiments were conducted in aerated solutions.

A cobalt-60 γ -radiation source with maximum dose rate 15 kGy h^{-1} was used in this work. Neptunium and plutonium solutions were irradiated in glass test tubes with ground-glass stoppers. The test tubes were placed in a glass beaker held in a metal container. All manipulations with alkaline technetium solutions were conducted in polyethylene or polypropylene test tubes with ground stoppers. The tubes were soaked in concentrated alkaline solutions for at least 1 week to remove impurities. When technetium oxides were used, small portions were placed into polymeric test tubes to which 5 to 7 mL of distilled water were added. The resulting mixtures were vigorously shaken and then centrifuged. The washings were repeated at least five times to remove possible Tc(VII) impurities that might appear during storage of the technetium oxide specimens.

Dosimetry was performed using dosimetric solutions of ferrousulfate (for dose rates ranging from 500 to 600 Gy h^{-1}) or dichromate (at dose rates 6 to 8 kGy h^{-1}) as described in the technical literature (e.g., Fiksuov 1985). Differences in the densities of dosimetric and investigated solutions were taken into account in calculating delivered dose.

The valent states and concentrations of neptunium and plutonium were determined by optical absorption spectrophotometry. A Shimadzu model UV-3100-PC spectrophotometer (Japan) was used. The wavelengths (λ) and molar extinction coefficients (ϵ) used for these measurements are shown in Table 2-1. Neptunium(V) in alkaline solution has no optical absorption bands suitable for measurements. Therefore, Np(V) was measured by spectrophotometry after alkaline solutions were acidified or Np(V) precipitate, separated by centrifugation, was dissolved in HClO_4 solution. Spectrophotometry of acidified solutions or solids also was used to identify Pu(IV) .

Figure 2-2. Optical Absorption Spectrum of a Prepared Stock Pu(VI) Solution
in 0.01 M HClO₄ (1 cm pathlength).

Table 2-1. Values of λ and ϵ Used to Determine Neptunium and Plutonium Concentrations. ^{1,2,3}

Radioide	Medium	λ , nm	ϵ , M ⁻¹ cm ⁻¹
Np(VI)	2 M HClO ₄	1223	45
Np(VI)	1 M NaOH	275	2,400
Np(VI)	1 M NaOH	275	2,500*
Np(VI)	2 M NaOH	275	2,550*
Np(VI)	4 M NaOH	275	2,450*
Np(VI)	6 M NaOH	275	2,800*
Np(VI)	8.5 M NaOH	275	2,850*
Np(V)	2 M HClO ₄	982	400
Np(IV)	2 M HClO ₄	962	162
Pu(VI)	6-8 M HClO ₄	831	500
Pu(VI)	1 M NaOH	275	2,000
Pu(IV)	6-8.5 M HClO ₄	475-477	50
Pu(IV)	6-7.5 M HNO ₃	475-477	80

Notes:

* The ϵ values found in this work were used in calculations.¹ Cohen (1961)² Nikolskiy et al. (1975)³ Seaborg et al. (1986)

Methods based on the measurements of β radioactivity were used to determine the concentrations of ²³⁷Tc in solution. The measurements were conducted using the automatic counter Tesla NZQ 605. For irradiated systems, the evaluations were made after the suspensions were separated by centrifugation. The soft β radiation of ²³⁷Tc is absorbed strongly by the alkali salts. Correction for this self-absorption was made by methods described elsewhere (Petrushkin et al. 1996).

Disperse particles were separated by centrifugation. The centrifuge had a rotor radius of 26 cm and a frequency of 50 Hz.

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3.0 GAMMA RADIOLYSIS OF AQUEOUS ALKALINE SOLUTIONS OF NEPTUNIUM

The radiolytic conversions of Np(VI) and Np(V) in alkaline aqueous solutions at various concentrations of alkali were studied in the absence of the special additives and in the presence of CO_3^{2-} , NO_3^- , NO_2^- , EDTA, and HCOO^- .

3.1 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF NEPTUNIUM(VI) IN THE ABSENCE OF ADDITIVES

The studies show that the action of γ -radiation on alkaline aqueous solutions of Np(VI) induces several radiolytic processes. Decrease in optical absorption in the UV-region is observed at relatively low doses (to about 2.4 kGy). The decrease, caused by the reduction of Np(VI), occurred over the entire studied range of alkali concentration (0.9 to 8.5 M). Figure 3-1 illustrates the change in Np(VI) optical absorption caused by irradiation. Figure 3-2 shows the dependence of Np(VI) solution concentration on dose.

Values of radiation-chemical yields for these transformations at various NaOH concentrations are given in Table 3-1. These data show that the concentration of alkali has only slight influence on the yield. However, at high alkali concentration, the yield strongly depends on the presence of organic impurities in the solution. Based on findings given in Table 3-1, further tests were conducted. The results of these tests showed that the yield of Np(VI) reduction in 7 M NaOH at low doses is decreased if the initial alkali solution first is irradiated (to dose 70 kGy). Apparently, preliminary irradiation decomposes organic microimpurities present in the solution. This conclusion is supported by the considerable difference in yield observed at relatively low doses (see Figure 3-2).

The spectra of solutions irradiated to doses of 400 to 800 Gy are stable for at least 20 hours after irradiation. However, further irradiation of the solutions (to doses over 8 kGy) increases the optical absorption in the UV and visible regions. Figure 3-3 shows the dependence of Np(VI) concentration in 7 M NaOH on dose. Optical absorption of irradiated solutions also is found to decrease with time stored outside the radiation field. However, further irradiation again increases optical absorption. Thus, a type of "oscillation" process is observed.

Figure 3-1. Optical Absorption Spectra of Solution Containing 2.74×10^{-4} M Np(VI) and 3.6 M NaOH Irradiated to Various Doses.

Dose, kGy: 1 - 0; 2 - 0.47; 3 - 0.94.

Figure 3-2. Dependence of Np(VI) Concentration in 7 M NaOH on Dose.

Alkali solution used for preparation of Np(VI) solutions underwent preliminary irradiation to dose, kGy: 1 - 70; 2 - 0.

Figure 3-3. Dependence of Optical Density at 275 nm for Alkaline Solutions Containing 2.74×10^{-4} M Np(VI) and 7 M NaOH on Dose.

The first 5 points were obtained at 0.47 kGy h⁻¹ dose rate;
the remaining points were obtained at 4.3 kGy h⁻¹ dose rate.

Table 3-1. Radiation-Chemical Yields of Np(VI) Reduction,
G[-Np(VI)], in Aersated Alkaline Aqueous Solutions.
[Np(VI)] = $(2.7 \text{ to } 3.6) \times 10^{-4} \text{ M}$

[NaOH], M	Additive	Dose, Gy	G[-Np(VI)], ion/100 eV
0.9	-	≤ 630	1.4
1.8	-	960	1.6
3.65	-	≤ 630	1.4
7	-	≤ 200	3.4
7	-	270-650	1.5
7	-	≤ 650	0.7
2.4	CO_3^{2-} , 0.67 M	≤ 650	0.7
2	EDTA, 0.013 M	109	8.5
2	EDTA, 0.013 M	436	3.5
1.5	HCOO^- , 0.26 M	≤ 250	5.8

Note:

* The alkali solution was preirradiated to 70 kGy.

The increased optical absorption occurring at doses over 8 kGy is postulated to result from the formation of Np(V) peroxo complexes. To test this hypothesis, alkaline Np(V) peroxo complex solutions were prepared by adding excess H_2O_2 to alkaline Np(V) solutions. The product solution spectrum corresponded to that described in Musikas (1974). However, the absorption spectrum caused by the complex decreased and completely disappeared following γ -irradiation of the alkaline Np(V) peroxo complex solution (see Figure 3-4). Based on these observations, accumulation of appreciable amounts of Np(V) peroxo complex by γ -radiolysis of alkaline solutions of Np(VI) and Np(V) without additives is improbable. With α -autoradiolysis and the attendant higher H_2O_2 yield, formation of peroxo complexes may play an important role.

The increased light absorption observed at doses over 8 kGy was postulated to occur because more or less stable (depending on alkali concentration) fine disperse suspensions were formed. The following facts confirm this suggestion. First, a Tyndall cone, caused by light scattering on fine disperse particles, is observed in such solutions. Second, the intensity of optical absorption depends on the length of time that irradiated solutions are centrifuged. Centrifugation decreased optical absorption over the entire observed spectrum (see Figure 3-5) and a fine settled precipitate accumulated.

Figure 3-4. Optical Absorption Spectra of the Np(V) Peroxo Complex in Solutions Containing 2.74×10^{-4} M Np(V), 3.9×10^{-4} M H_2O_2 and 4.2 M NaOH After γ -Irradiation.

Dose, kGy: 1 - 0; 2 - 2.15; 3 - 4.3; 4, 5 - 6.45; 6 - 12.9.

Figure 3-5. Optical Absorption Spectra of 2.74×10^{-4} M Np(VI) and 7 M NaOH.

Dose, kGy: 1 - 0; 2 - 25; 3 - 25 after 3 Minutes' Centrifugation;
4 - 25 after 13 Minutes' Additional Centrifugation.

Irradiation of low-alkali-concentration solutions of Np(VI) to doses over 8 kGy produces solutions containing Np(IV) and Np(V) in acidified aliquots. Both Np(IV) and Np(V) also were observed in perchloric acid solutions of solids produced by over 8 kGy irradiation of solutions having high alkali concentrations (for example, solids formed by 25 kGy irradiation of alkaline Np(VI) solution). Dissolution of solids, separated by centrifugation 2 hours after irradiation, in 2.1 M HClO₄ yielded solutions with a [Np(IV)]/[Np(V)] ratio of 8:1 (Figure 3-6). Significantly, no Np(VI) (λ_{max} at 1223 nm) was observed by spectrophotometry. Further centrifugation of the balance of the irradiated solution 24 hours after irradiation separated a precipitate which, after dissolution in 2.1 M HClO₄, had a [Np(IV)]/[Np(V)] ratio of 2:3:1 (see Figure 3-7). The lower ratio is explained by the oxidation of Np(IV) by atmospheric oxygen following storage of the irradiated solution. Oxidation of Np(IV) precipitates by atmospheric oxygen in unirradiated solutions has been described (Shulov et al 1996).

In summary, Np(IV) precipitates form in solutions irradiated to over 8 kGy dose; these precipitates then can be oxidized by atmospheric oxygen on standing and exposure to air.

The following reactions may proceed by γ -radiolysis of alkaline aqueous solutions of Np(VI):

Figure 3-6. Optical Absorption Spectrum of the Solution Prepared by Dissolution, in 2.1 M HClO_4 , of Precipitates Obtained by Centrifugation Two Hours After Irradiation of 2.74×10^{-5} M Np(VI) and 7 M NaOH to 25 kGy.

Figure 3-7. Optical Absorption Spectrum of the Solution Prepared by Dissolution, in 2.1 M HClO_4 , of Precipitates Obtained by Centrifugation 24 Hours After Irradiation of 2.74×10^{-4} M Np(VI) and 7 M NaOH to 25 kGy.

Based on the known reactivities of Np(VI) ions, it may be concluded that e_{aq}^- , O_3 , and hydrogen peroxide reduce Np(VI) ions (Pikaev et al. 1983, Peretrukhin et al. 1995, and Gogolev et al. 1996). Note that k_{10} and k_{11} , the rate constants of Reactions 10 and 11, respectively, decrease with increasing alkali concentration. In 1 M LiOH, they are 140 and 80 $M^{-1}s^{-1}$, respectively (Gogolev et al. 1996). The O^- radical ion can react with Np(VI) and oxygen to form Np(VII) and O_2 , respectively; Np(VII) in turn can react with Np(V) to form Np(VI). Neptunium(VII) and O_3 can oxidize Np(V); Np(VII) can also react with O_3 and HO_2 . Neptunium(V) can react with e_{aq}^- at relatively high doses; the product Np(IV) is slightly soluble and is rapidly precipitated to form a finely dispersed solid phase. Because the oxidation of Np(IV) in the solid phase is relatively slow, Np(IV) solid phase accumulates at high dose on γ -radiolysis of alkaline aqueous Np(VI) solutions.

At low doses, Np(VI) is reduced to Np(V) by Reactions 8, 10, and 11. In Reactions 23 and 28, O_2 and O oxidize Np(VI) to Np(VII). The Np(VII) reacts with Np(V). The reduction of Np(V) to Np(IV) is not observed under these conditions. Therefore, the value of $G[-Np(VI)]$ at low doses is described by the following equation:

$$G[-Np(VI)] = G_{H_2} + G_H + 2 G_{H_2O_2} - G_{OH} \quad (29)$$

where G values on the right are initial yields of primary products of water radiolysis.

At relatively high doses, the reduction of Np(V) by hydrated electrons (Reaction 9) occurs, the relevant equation for $G[-Np(VI)]$ is:

$$G[-Np(VI)] = \frac{1}{2} (G_{e_{aq}} + G_H + 2 G_{H_2O_2} - G_{OH}) \quad (30)$$

For alkaline solutions at pH 12 to 13, the individual initial yields are known: $G_{e_{aq}} = 3.05$, $G_H = 0.53$, $G_{OH} = 2.9$, and $G_{H_2O_2} = 0.75$ (see, e.g., Pikaev et al. 1983). Hence, the $G[-Np(VI)]$, calculated from Equations 29 and 30 for solutions with about 1 M alkali should be 2.2 and 1.1 ion/100 eV, respectively. However, experimental values for even low doses, shown in Table 3-1, are lower than 2.2 ion/100 eV. This shortfall can be explained by the occurrence, to some extent, of Reactions 16, 24, and 25. In these reactions, reducing species are consumed.

Because the G values for the primary products of radiolysis in concentrated aqueous alkali solutions are unknown, drawing similar conclusions about the behavior of Np(VI) in strongly alkaline systems is not possible.

Hydrogen peroxide can be expected to accumulate by radiolysis. If so, the Np(V) peroxo complex would be postulated at relatively high doses when most of the Np(VI) is reduced. However, peroxo complexes are not observed. This likely is because hydrogen peroxide decomposes in reactions with other radiolysis products such as $O^{\cdot -}$ and e_{aq}^- .

3.2 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF NEPTUNIUM(VI) IN THE PRESENCE OF ADDITIVES

The effects of carbonate, organic compounds, nitrate, and nitrite on gamma radiolysis of neptunium(VI) were investigated.

3.2.1 Carbonate

The presence of high sodium carbonate concentrations in alkaline aqueous solutions of Np(VI) has a relatively small effect on γ -radiolysis. Figure 3-8 shows the decrease in

optical absorption of a solution containing 3.56×10^{-4} M Np(VI), 2.4 M NaOH, and 0.67 M Na_2CO_3 on γ -irradiation. The dependence of Np(VI) concentration on dose for the same solution is presented in Figure 3-9. The $G[\text{Np(VI)}]$ value, calculated from the data presented in Figures 3-8 and 3-9, is given in Table 3-1 and can be compared with the $G[\text{Np(VI)}]$ values found in alkaline solution without carbonate.

These data show that the radiation-chemical yield of Np(VI) reduction in the absence of carbonate is comparable with, but somewhat higher than, that found in the presence of carbonate. These results indicate that the radical ion $\text{CO}_3^{\cdot -}$ formed in reactions of carbonate with OH and/or $\text{O}^{\cdot -}$ behaves as an oxidizing agent and can participate in the same reactions as the $\text{O}^{\cdot -}$ radical ion.

The small difference existing between radiolysis in the presence and absence of carbonate might be explained by the influence of organic impurities. However, $\text{CO}_3^{\cdot -}$ only reacts slowly with organic compounds to form organic free radicals. Therefore, the reduction of Np(VI) by organic free radicals is improbable. This deduction is confirmed by the fact that the influence of organic impurities in carbonate-alkaline solutions is not as significant as it is in alkaline media.

Figure 3-8. Optical Absorption Spectra of 3.56×10^{-4} M Np(VI) , 0.67 M Na_2CO_3 , and 2.4 M NaOH as a Function of Dose.

Dose, kGy: 1 - 0; 2 - 0.45; 3 - 0.97; 4 - 1.3; 5 - 2

Figure 3-9. Dependence of Np(VI) Concentration on Dose in 0.67 M Na_2CO_3 and 2.4 M NaOH .

3.2.2 Organic Compounds

In general, organic compounds scavenge OH (and O[•]) radicals. The products of the scavenging reactions often can act as reducing agents themselves, increasing the yields of radiation-induced reduction processes. Such a situation is observed for γ -radiolysis of alkaline Np(VI) solutions in the presence of EDTA or HCOO⁻ (formate). Figure 3-10 shows the dependence of Np(VI) concentration on dose in a solution containing 0.013 M EDTA and 2 M NaOH.

The yields of Np(VI) reduction calculated from these studies are presented in Table 3-1. The data show that yields in the presence of EDTA or HCOO⁻ are much higher than in their absence. The following example, for formate, explains the observations. First, the hydroxyl radical reacting with HCOO⁻

forms the radical ion COO^{-•}, a strong reducing agent. The COO^{-•} reduces Np(VI) and, possibly, Np(V) by the following reactions:

Besides Reactions 32 and 33, the COO^{-•} radical ion can participate in the reaction

The radical ion O₂^{-•} is also a reducing agent and can reduce Np(VI). Hence, O₂ has the same effect on the final result of radiolytic reduction of Np(VI) as COO^{-•} does.

The mechanism of Np(VI) reduction in solutions containing EDTA is almost the same. The only exception seems to be the absence of a reaction between the free radical from EDTA and oxygen to form O₂^{-•}.

At sufficiently low doses, reduction of Np(VI) proceeds only to Np(V). The yield may be expressed by the equation

$$G[-\text{Np(VI)}] = G_{\text{e}} + G_{\text{H}} + G_{\text{OH}} + 2 G_{\text{H}_2\text{O}_2} \quad (35)$$

Based on these known G values, the yield for 1 M NaOH should be 8 ion/100 eV.

Figure 3-10. Dependence of Np(VI) Concentration on Dose in 0.013 M EDTA and 2 M NaOH.

In the case of reduction to Np(IV), the corresponding equation is

$$G[-\text{Np(VI)}] = \frac{1}{2} (G_{\text{H}_2} + G_{\text{H}} + G_{\text{OH}} + 2 G_{\text{H}_2\text{O}_2}) \quad (36)$$

and the yield should be 4 ion/100 eV

The experimental yield for the solution containing EDTA at low dose is close to that calculated by equation 35. However, in the case of HCOO^- , the experimental value is noticeably lower. The low value for formate can be explained in the same way as for the reduction of Np(VI) in the absence of additives, i.e., Reactions 16, 24, and 25 also occur and can consume reducing species.

In solutions containing organic additives, turbidity appears after even relatively low (about 300 Gy) doses. The turbidity seems to be caused by the precipitation of insoluble Np(IV) hydroxide. This precipitate is very finely dispersed and redissolves within 10 to 15 minutes after irradiation without stirring. The redissolution is caused by the oxidation of the Np(IV) hydroxide by oxygen present in the solution and by hydrogen peroxide formed by irradiation.

At higher doses (about 2 kGy), in solutions containing 2.74×10^{-4} M Np(VI), 0.26 M HCOO^- and 1.5 M NaOH, a precipitate forms that does not redissolve, even after standing for 3 weeks. Dissolving this 3-week old precipitate in 2.1 M HClO_4 gave a solution with the optical absorption spectrum of Np(V). Bands of Np(VI) and Np(IV) were not detected. Apparently, on storage of such solutions, Np(IV) is oxidized by atmospheric oxygen to the more soluble Np(V).

3.2.3 Nitrite and Nitrate

Reduction of Np(VI) at less than 3 kGy dose was not observed in alkaline solutions containing nitrite. Because nitrite (and nitrate) absorb light in the UV region, measurement of Np(VI) concentration changes cannot be monitored through the Np(VI) charge-transfer band. Instead, Np(VI) concentration was determined by measuring the optical absorbance of the carbonate complex. Potassium bicarbonate, in quantities considerably exceeding the equivalent amount of alkali present in solution, was added to the unirradiated and irradiated Np(VI) solutions. Neptunium(VI) carbonate complexes have relatively intense optical absorption in the visible region (see Figure 3-11). The absence of optical absorption of nitrite (and nitrate) in this visible region allows the Np(VI) concentration to be measured by spectrophotometry at 425 nm. The results obtained showed that both the unirradiated and irradiated (to less than 3 kGy) solution spectra were virtually identical, that is, the reduction of Np(VI) under these conditions did not occur.

The radiolytic reduction of Np(VI) in alkaline solutions containing nitrate could not be detected at less than 2 kGy dose. Under these conditions, the reduction likely proceeds only

Figure 3-11. Optical Absorption Spectra of NaOH, NaNO_2 , NaNO_3 , and Np(VI) Solutions; Carbonate Complexes.

- 1 - 2 M KNO_3 and 0.9 M NaOH ;
- 2 - 0.11 M NaNO_2 and 0.81 M NaOH ;
- 3 - 2.74×10^{-4} M Np(VI) & Np(V) and 2.6 M NaOH ;
- 4 - 2.74×10^{-4} M Np(VI) & Np(V) , 2.8 M KHCO_3 , and 2.6 M NaOH ;
- 5 - 2.74×10^{-4} M Np(VI) & Np(V) , 0.8 M NaNO_3 , 2.8 M KHCO_3 , and 2.6 M NaOH irradiated to 1 kGy

with comparatively low yield. However, the method used to analyze Np(VI) is not sufficiently sensitive to measure a change in Np(VI) concentration. The solution became a yellow brown color at higher doses. The spectra of these solutions in the visible region coincided with the spectra of the Np(V) peroxo complex. The respective data are shown in Figures 3-12 and 3-13. The same spectrum is formed when 2×10^{-4} M Np(V) in 4 M NaOH is added to an equal volume of irradiated (19 kGy) solution containing 0.8 M NaNO_3 and 3.6 M NaOH. Acidification of the irradiated solutions with perchloric acid yielded Np(V) solutions. Adding EDTA or nitrite to the solution containing the Np(V) peroxo complex had no effect on the shape and intensity of the spectrum over 16 hours. However, irradiation (12.9 kGy) of the prepared solutions caused the complete disappearance of the Np(V) peroxo complex. These effects are illustrated by Figures 3-14 and 3-15.

The observed results may be explained qualitatively as follows. First, the hydrated electron reacts readily with NO_3^-

At relatively low doses, the generated $\text{NO}_3^{\cdot -}$ radical ion reacts with oxygen to regenerate nitrate

Reactions of $\text{NO}_3^{\cdot -}$ with O and O_2 are also possible. Hydrogen peroxide seems to decompose by reacting with O . After the dissolved oxygen is exhausted, $\text{NO}_3^{\cdot -}$ can participate in the reaction

and the product Np(V) can react with hydrogen peroxide to form the peroxo complex.

In solutions containing nitrite, the hydrated electron participates in the reaction

The O radical ion also reacts with nitrite

Apparently, hydrogen peroxide can be decomposed by reactions with species formed in Reactions 40 and 41.

Figure 3-12 Optical Absorption Spectra of NaOH, NaNO_2 , NaNO_3 , and Np(VI) Solutions, Formation of Peroxo Complexes

- 1 - 2.74×10^{-4} M Np(VI) and 6.9 M NaOH, unirradiated,
- 2 - same solution as (1) also containing 0.02 M H_2O_2 ,
- 3 - 2.74×10^{-4} M Np(VI) and 8.5 M NaOH, unirradiated,
- 4 - 3.2×10^{-4} M Np(VI) , 0.8 M NaNO_2 , and 7.7 M NaOH irradiated to 12 kGy,
- 5 - 3.2×10^{-4} M Np(VI) , 1.2 M NaNO_2 , and 7.7 M NaOH irradiated to 12 kGy

Figure 3-13. Optical Absorption Spectra of NaOH and Np(VI) Solutions.

- 1 - 2.74×10^{-4} M Np(VI) and 8.5 M NaOH, unirradiated;
2 - 3.2×10^{-4} M Np(VI), 0.7 M NaNO_3 , and 7.7 M NaOH irradiated to 15.2 kGy;
3 - 3.2×10^{-4} M Np(VI), 0.7 M NaNO_3 , and 7.7 M NaOH irradiated to 42.2 kGy;
4 - 3.2×10^{-4} M Np(VI), 0.7 M NaNO_3 , and 7.7 M NaOH irradiated to 58.8 kGy

Figure 3-14. Optical Absorption Spectra of NaOH, NaNO_2 , and Np(VI) Solutions with Added Nitrile.

- 1 - 3.2×10^{-4} M Np(VI) , 0.8 M NaNO_2 , and 7.7 M NaOH , irradiated to 42.9 kGy;
2 - same solution as (1) 16 hours after addition of 2.27 M NaNO_2 ;
3 - same solution as (2) after additional irradiation to 12.9 kGy

Figure 3-15. Optical Absorption Spectra of NaOH, NaNO₃, and Np(VI) Solution with Added EDTA.

- 1 - 3.2×10^{-4} M Np(VI), 0.8 M NaNO₃, and 7.7 M NaOH irradiated to 55.8 kGy;
2 - 2.9×10^{-4} M Np(VI), 0.7 M NaNO₃, and 7 M NaOH irradiated to 42.9 kGy,
4.5 $\times 10^{-3}$ M EDTA added and irradiated further to 12.9 kGy;
3 - solution (2) after centrifugation

3.3 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF NEPTUNIUM(V)

Neptunium(V) in alkaline aqueous solutions is reduced to Np(IV) on γ -irradiation. This behavior was demonstrated by the formation, even at relatively low doses, of finely dispersed suspensions similar to those appearing in alkaline aqueous solutions of Np(VI) at higher doses. This phenomenon is shown in Figure 3-16 for alkaline Np(V) solution containing a small amount of Np(VI). The figure shows that the optical absorption of the solution increases as a result of irradiation (because of light scattering on dispersed particles); on aging, light absorption decreases (because the suspension coagulates and precipitates form). Additional irradiation again increases the light absorption because Np(V) is reduced further and a finely dispersed suspension forms. In other words, as in the case of radiolytic reduction of Np(VI) (see Section 3.1), a peculiar "oscillation" process is observed.

The precipitate consists of predominantly Np(IV) compounds. This conclusion is confirmed by Figure 3-17, which shows the optical absorption spectrum of the solution obtained by dissolving the precipitate in 2.1 M HClO₄. The precipitate was obtained after centrifugation of irradiated (dose 21.5 kGy) solution that originally contained 2.7×10^{-4} M Np(V), 0.16 M HCOO⁻ and 4.5 M NaOH. In this solution, the ratio [Np(IV)]/[Np(V)] is 6:1. The presence of Np(V) seems to be caused by its capture as the precipitate forms.

Obviously, Np(V) is reduced by the hydrated electron (Reaction 9). Note that in the alkaline solutions studied, virtually all H atoms are converted to hydrated electrons by way of Reaction 3; the yield of hydrated electrons formed is thus the sum of the direct hydrated electron yield and the yield of the H atom:

$$G(e_{aq}^-) = G_{e_{aq}^-} + G_H \quad (42)$$

Hydrated electrons also react with oxygen (Reaction 6). The fraction f of hydrated electrons participating in Reaction 9 is:

$$f = \frac{k_9[Np(V)]}{k_9[Np(V)] + k_6[O_2]} = \frac{1}{1 + \frac{k_6[O_2]}{k_9[Np(V)]}} \quad (43)$$

where k_6 and k_9 are rate constants of Reactions 6 and 9. The values of these rate constants are known (see Pikaev et al. 1983 and Pikaev and Kabachnik 1982). Because the concentrations of Np(V) and oxygen are also known, equation 43 can be used to calculate f values. For instance, f is about 0.2 for aerated 1 M NaOH containing 2.7×10^{-4} M Np(V).

Figure 3-16. Optical Absorption Spectra of NaOH, Np(V), and Np(VI) Solutions.

- 1 - 1.54×10^{-4} M Np(V), 1.2×10^{-4} M Np(VI), and 6.9 M NaOH;
- 2 - solution (1) after irradiation to 13 kGy;
- 3 - solution (2) after standing 17 hours, 10 minutes;
- 4 - solution (3) further irradiated by 15 kGy

Figure 3-17. Optical Absorption Spectrum of Dissolved Precipitate from Irradiated Np(V) Solutions.

Precipitate dissolved in 2.1 M HClO_4 ; precipitate produced by centrifugation of solution containing 2.7×10^{-4} M Np(V), 0.16 M HCOO^- , and 4.5 M NaOH and irradiated to 21.5 kGy.

Because O_2 and HO_2 cannot reduce $Np(V)$, the radiation-chemical yield of $Np(IV)$ in aerated alkaline $Np(V)$ solutions in the absence of additives is expressed by the equation:

$$G[Np(IV)] = f(G_{e_{aq}} + G_H) \quad (44)$$

Radical ions O^- and O_2^- (products of Reaction 19) oxidize $Np(V)$ to $Np(VI)$. Neptunium(IV) is slightly soluble; therefore, the reactions of $Np(IV)$, present in solid phase, with O^- , O_2^- , and $Np(VI)$ proceed to an insignificant extent. At fairly high doses, hydrated electrons can also reduce $Np(VI)$. The studies have shown that equation 44 expresses the maximum value of the yield. Experimental yield values can be described by the following expression:

$$G[Np(IV)] < f(G_{e_{aq}} + G_H) \quad (45)$$

The presence of formate, $HCOO^-$, causes COO^- radical ion formation (Reaction 31). These radical ions can reduce $Np(V)$ (Reaction 33) and react with oxygen (Reaction 34). Hence, the fraction, f_1 , of COO^- radical ions participating in $Np(V)$ reduction is:

$$f_1 = \frac{k_{33}[Np(V)]}{k_{33}[Np(V)] + k_{34}[O_2]} = \frac{1}{1 + \frac{k_{34}[O_2]}{k_{33}[Np(V)]}} \quad (46)$$

Neptunium(IV) can be oxidized to a small extent back to $Np(V)$ by atmospheric oxygen; hydrated electrons can participate to small extent in $Np(VI)$ reduction (especially at high doses). The following equation for experimental values of $Np(IV)$ yield in the presence of formate expresses these relationships:

$$G[Np(IV)] < f(G_{e_{aq}} + G_H) + f_1 G_{OH} \quad (47)$$

Note also that $Np(IV)$ is not stable following irradiation and is slowly oxidized in the irradiated solution to $Np(V)$ by oxygen and radiolytically produced hydrogen peroxide.

Gamma radiolysis of alkaline nitrate $Np(V)$ solutions, as for similar $Np(VI)$ solutions, results in $Np(V)$ peroxo complex formation. Nitrite has the same influence for $Np(V)$ as for $Np(VI)$ alkaline solutions. The formation of the $Np(V)$ peroxo complex is shown in Figure 3-18; the inhibiting influence of nitrite is shown in Figure 3-19.

These effects are explained by the "protection" of $Np(V)$ by NO_2^- to reduction and the reaction of nitrite with hydrogen peroxide. Hydrogen peroxide is decomposed by NO_2^- formed in the presence of nitrite by Reaction 40. At relatively high NO_2^- concentrations, the peroxo complex does not appear (see Figure 3-19). Note that $Np(IV)$ is not formed on γ -radiolysis of alkaline $Np(V)$ solutions containing nitrate and/or nitrite.

Figure 3-18. Optical Absorption Spectra of NaOH, NaNO_3 , and Np(V) Solutions.

- 1 - 5.8×10^{-4} M Np(V) , 0.16 M NaNO_3 , and 3 M NaOH ;
2 - solution (1) irradiated to 17.9 kGy

Figure 3-19. Optical Absorption Spectra of NaOH, NaNO_2 , NaNO_3 , Np(V) , and Np(VI) Solutions.

- 1 - 1.8×10^{-4} M Np(VI) & Np(V) , 0.7 M NaNO_3 , and 3.6 M NaOH;
- 2 - solution (1) irradiated to 25.8 kGy;
- 3 - 1.8×10^{-4} M Np(VI) & Np(V) , 0.7 M NaNO_3 , 0.018 M KNO_3 , and 3.6 M NaOH irradiated to 25.8 kGy;
- 4 - 1.8×10^{-4} M Np(VI) & Np(V) , 0.7 M NaNO_3 , 0.16 M KNO_3 and 3.6 M NaOH irradiated to 25.8 kGy

4.0 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF PLUTONIUM

Plutonium(V) is unstable in aqueous solutions and disproportionates to Pu(VI) and Pu(IV). The plutonium(IV) is virtually insoluble in alkaline solutions. Hence, the study was limited to gamma radiolysis of acetated alkaline aqueous Pu(VI) solutions both with no additives and in the presence of some additives.

4.1 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF PLUTONIUM IN THE ABSENCE OF ADDITIVES

Research showed that Pu(VI) in alkaline aqueous solutions is reduced on γ -irradiation. This conclusion follows from the decrease in optical absorption of its solutions after irradiation (see Figure 4-1). At comparatively high doses (over about 2 kGy), the solution became significantly turbid in all solutions studied. Figure 4-2 shows this effect for the solution of Pu(VI) in 1.3 M NaOH. The solid phase formed is very finely dispersed and prolonged centrifugation (over 40 minutes) is required for its separation. The turbidity is especially characteristic of solutions with high alkali concentration. The suspension formed in solution containing 1.9×10^{-4} M Pu(VI) and 1.3 M NaOH irradiated to 4 kGy dose precipitated spontaneously (without centrifugation) after about 24 hours. It is noted that at relatively high doses, complete conversion of Pu(VI) to Pu(IV) occurs.

Dissolving the centrifuge-separated precipitate in 7.5 M HNO₃ (sometimes in 4.2 M HNO₃) or in 8.5 M HClO₄ always gave nitric acid or perchloric acid solutions of Pu(IV) with small admixtures of Pu(VI). For instance, a nitric acid solution with a [Pu(IV)]/[Pu(VI)] ratio of about 12:1 was formed after dissolving the precipitate from the irradiated (dose 10 kGy) 1.3 M NaOH solution in 7.1 M HNO₃ (see Figure 4-3). A solution of the same composition, irradiated to dose 20 kGy, also gave a precipitate. Dissolution of this precipitate in 4.2 M HNO₃ produced Pu(IV) solution containing no Pu(VI) (see Figure 4-4).

Radiation-chemical yields of Pu(VI) reduction were measured at doses of less than 1 kGy for solutions with various concentrations of alkali. The data obtained are shown in Table 4-1. Based on these data, the alkali concentration clearly has little effect on the yield.

Note that optical absorption spectra of the solutions immediately after dissolution of the precipitates differed from the spectra of the solutions prepared from individual Pu(IV) compounds. After the solutions were stored for 16 hours, the spectra became identical to those of individual Pu(IV) compound solutions (see Figure 4-5). This effect likely is caused by the presence of colloid solutions of Pu(IV) in the first stage of precipitate dissolution.

Figure 4-1. Optical Absorption Spectra of 1.9×10^{-4} M Pu(VI) and 6.9 M NaOH Solution as a Function of Dose.

Dose, kGy: 1 - 0; 2 - 0.22; 3 - 0.45

Figure 4-2. Optical Absorption Spectra of 1.9×10^{-4} M Pu(VI) and 1.3 M NaOH Solution as a Function of Dose.

Dose, kGy: 1 - 0; 2 - 4.3; 3 - 8.6

Figure 4-3. Optical Absorption Spectrum of Dissolved Precipitates from 10 kGy irradiated Pu(VI) Solution.

Precipitates dissolved in 7.1 M HNO₃; precipitates produced by 10 kGy irradiation of solution containing 1.9×10^{-4} M Pu(VI) and 1.3 M NaOH.

Figure 4-4. Optical Absorption Spectrum of Dissolved Precipitates from 20 kGy Irradiated Pu(VI) Solution.

Precipitates dissolved in 4.2 M HNO₃; precipitates produced by 20 kGy irradiation of solution containing 1.9×10^{-6} M Pu(VI) and 1.3 M NaOH.

Figure 4-5. Optical Absorption Spectra of Dissolved Precipitates from 20 kGy Irradiated Pu(VI) Solution -- Effect of Dissolution Time.

Precipitates dissolved in 7.5 M HNO₃; precipitates produced by 20 kGy irradiation of solution containing 1×10^{-3} M Pu(VI) and 8.5 M NaOH.

Time after irradiation, hours: 1 - 0; 2 - 16

Table 4-1. Initial Radiation-Chemical Yields of Pu(VI) Reduction, G[-Pu(VI)], in Aerated Alkaline Aqueous Solutions.

[Pu(VI)] $\times 10^4$, M	[NaOH], M	G[-Pu(VI)], ion/100 eV
2.2	1.3	1.4
3.3	6.3	1.3
2.0	6.9	1.5

The mechanism of radiolytic reduction of Pu(VI) is similar to that exhibited by Np(VI). The only difference is that Pu(V) is unstable and disproportionates by the reaction:

The precipitation of Pu(IV) to form a solid phase restricts its reoxidation by water radiolysis products. The radiation-chemical yield of Pu(VI) may be described by the equation:

$$G[-\text{Pu(VI)}] = \frac{1}{2} (G_{\text{e}^-} + G_{\text{H}_2} + 2 G_{\text{H}_2\text{O}_2} - G_{\text{OH}}) \quad (49)$$

which is 1.1 ion/100 eV in alkaline solution. Experimental values are slightly higher.

4.2 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF PLUTONIUM IN THE PRESENCE OF ADDITIVES

The action of γ -radiation on alkaline aqueous solutions of Pu(VI) containing nitrate or nitrite leads to the formation of finely dispersed suspensions. Dissolution of the precipitates, separated from irradiated solutions by centrifugation, in 7.5 M HNO_3 or 8.5 M HClO_4 gave acid solutions of Pu(IV) with small admixtures of Pu(VI). A similar phenomenon was observed in the case of Pu(VI) solutions containing EDTA.

In solutions containing nitrate or nitrite, the produced hydrated electrons react readily with NO_3^- or NO_2^- to form the corresponding radical ions. The Pu(VI) then is reduced by reacting with NO_2^- , $\text{NO}_2^{\cdot -}$, hydrogen peroxide, or similar agents. The Pu(V) peroxo complex identified in the literature (Musikas 1971) was not observed in solutions containing nitrate (possibly because of disproportionation of Pu(V) or because of the reportedly low stability of the complex at room temperature).

In solutions containing EDTA, reduction of Pu(VI) proceeds by reactions with the hydrated electron and hydrogen peroxide. Free radicals from EDTA, produced by its reaction with $\text{OH}^\cdot$ ($\text{O}^\cdot$), apparently do not react with Pu(VI). Unfortunately, the radiation-chemical yields of Pu(VI) reduction in solutions containing the investigated additives could not be determined because, even at low doses, a finely dispersed suspension formed.

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5.6 GAMMA RADIOLYSIS OF ALKALINE AQUEOUS SOLUTIONS OF TECHNETIUM

Radiolytic reduction of pertechnetate under various conditions and the influence of γ -irradiation on the solubility of Tc(IV) and Tc(V) hydroxides in alkaline media were studied in this work.

5.1 RADIOLYTIC REDUCTION OF PERTECHNETATE

In most cases, the concentration of pertechnetate, TcO_4^- , in the experimental solutions used was $5 \times 10^{-3} \text{ M}$. No net reduction of pertechnetate was observed on γ -radiolysis of its aerated alkaline aqueous solutions. A sequence of radiation chemical steps occurs in such solutions. First, the hydrated electron reacts with TcO_4^- .

The formation of TcO_4^{2-} , technetate, on radiolysis of alkaline solutions of pertechnetate has been detected by pulse radiolysis (Pikulev et al. 1977). Radical ions O_2^- react with diatomic oxygen by Reaction 19 to form ozonide (O_3^-). Technetate formed in Reaction 50 disproportionates and is oxidized by ozonide.

Pentavalent technetium is also oxidized by ozonide. Hydrogen peroxide does not reduce Tc(VII) in alkaline solution.

In alkaline media, pertechnetate has been reported to reduce to Tc(V) (Kryuchkov 1983). The yield of TcO_4^- reduction, expressed in the following equation, reflects the effects of Reactions 50 to 52.

$$G(-\text{TcO}_4^-) = \frac{1}{2} (G_{e_{aq}^-} + G_H - G_{OH}) \quad (53)$$

By this calculation, the yield in 1 M NaOH should be 0.35 ion/100 eV. However, the reduction is not observed. Apparently, this is because reactions with hydrogen peroxide occur (in addition to Reactions 50 to 52).

Pertechnetate is reduced in the presence of organic compounds that are effective scavengers of OH (and O⁻) radicals. Scavenger compounds studied were methyl, ethyl, isopropyl, and tertiary-butyl alcohols, and EDTA. Figure 5-1 shows the decrease of TcO₄⁻ concentration in aerated solution containing 0.05 M TcO₄⁻, 4 M NaOH, and 0.04 M EDTA as a function of dose. The reduction yields calculated from such dependencies are listed in Table 5-1. Note that the values of yields are approximate because the precision to determine β-radioactivity reflecting small relative changes in high original pertechnetate concentrations is not high (i.e., not better than 25 to 35%).

Figure 5-1. Dependence of TeO_5 Concentration on Dose in Aerated Aqueous Solution Containing 4 M NaOH and 0.04 M EDTA.

Table 5-1. Radiation-Chemical Yields of TcO_2 Reduction [$G(-\text{TcO}_2)$] in Aqueous Solutions.

$$[\text{TcO}_4^-] = 5 \times 10^{-3} \text{ M}$$

[NaOH], M	Additive	Dose, kGy	$G(-\text{TcO}_2)$, ion/100 eV
4	None	To 20	0
14.6	None	To 20	0
4	CH_3OH , 0.1 M	2.5-5	2.5
14.6	CH_3OH , 0.1 M	2.5-5	2.8
4	$\text{C}_2\text{H}_5\text{OH}$, 0.1 M	1-20	2.7
14.6	$\text{C}_2\text{H}_5\text{OH}$, 0.1 M	5	2.6
14.6	<i>iso</i> - $\text{C}_3\text{H}_7\text{OH}$, 0.1 M	5	1.5
4	<i>tert</i> - $\text{C}_4\text{H}_9\text{OH}$, 0.1 M	1-20	1.0
14.6	<i>tert</i> - $\text{C}_4\text{H}_9\text{OH}$, 0.1 M	1-20	1.4
4	EDTA, 0.04 M	1-20	1.2
14.6	EDTA, 0.04 M	10	1.1

The listed organic compounds react with OH (and $\text{O}^\cdot$) to form radicals that can reduce TcO_4^- . For example, in the case of methyl alcohol, reaction in alkaline media gives the $\text{CH}_2\text{O}^\cdot$ radical ion, a strong reducing agent:

The most probable reaction of this radical ion is:

Similar reactions occur for ethyl and, possibly, isopropyl alcohols.

Oxygen can react to form organic peroxide radicals from the organic free radicals under consideration. However, this reaction in the test solutions is unlikely because the concentration of TcO_4^- is much higher than the concentration of dissolved oxygen (assuming the reactivities of TcO_4^- and oxygen with $\text{CH}_2\text{O}^\cdot$ are similar).

Because hydrogen peroxide does not reduce pertechnetate, the expected reduction yield in the presence of the tested alcohols can be calculated:

$$G(-\text{TcO}_2) = \frac{1}{2} (G_{\text{H}_2\text{O}_2} + G_{\text{H}} + G_{\text{OH}}) \quad (58)$$

i.e., the yield in 1 M NaOH should be 3.3 ion/100 eV. However, the experimental values are lower. Apparently, the shortfall is because of peroxide oxidation of technetate (Reaction 54)

The free radical formed from *tert*-butyl alcohol by the reaction

is not a reducing agent. Hence, the maximum yield of the reduction should be expressed by the equation

$$G(-TcO_4^-) = \frac{1}{2} (G_{\text{max}} + G_{\text{H}_2}) \quad (60)$$

This yield should be 1.8 ion/100 eV. The lower experimental values observed again likely are because of Reaction 54. A similar conclusion can be drawn regarding the mechanism of γ -radiolysis of the solutions containing EDTA.

5.2 RADIOLYTIC OXIDATION OF Tc(IV) AND Tc(V) HYDROXIDES

Pentavalent technetium in alkaline media is sparingly soluble. It exists in the form $TcO_4^- \cdot nH_2O$. The form of existence of tetravalent technetium in these media is $TcO_2 \cdot nH_2O$.

It was found that both hydrated oxides partially dissolve when their suspensions are γ -irradiated in alkaline media. The rates of dissolution depend on the presence of the other species (additives) in the solution. However, taking into account the poor precision of the analytical method used to determine technetium concentration in solution over the precipitate, the following results should be considered at best semiquantitative and sometimes qualitative.

Figure 5-2 shows the dependencies of technetium concentration on γ -irradiation dose of $TcO_2 \cdot nH_2O$ suspensions in solutions with various concentrations of alkali. The dependencies for suspensions of $Tc_2O_7 \cdot nH_2O$ are represented in Figure 5-3. The examples illustrating the effects of nitrate on the hydroxides' dissolutions on irradiation are shown in Figures 5-4 and 5-5. In all experiments, the amount of hydroxides added to the solution was 4 g/L (calculated based on the respective oxide). The samples taken for irradiation contained Tc(VII) formed by oxidation of Tc(IV) or Tc(V) by atmospheric oxygen.

Figure 5-2. Dependence of Technetium Concentration on Dose for Suspensions of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ at Various NaOH Concentrations.

[NaOH], M: 1 - 0.5; 2 - 4; 3 - 8; 4 - 15

Two conclusions are derived from the results presented in Figures 5-2 through 5-5. First, the concentration of dissolved technetium in samples without additives decreases with increasing dose. Second, in the presence of nitrate, the concentration increases with increasing dose. In other experiments, it was established that, when nitrate or carbonate is added, the concentration decreases with increasing dose.

In samples without additives, $\text{OH}^\cdot (\text{O}^\cdot)$ apparently reacts partially with technetium hydroxides, oxidizing them. The technetium hydroxides can also react (though very slowly) with hydrogen peroxide. However, the yield of oxidation is less than the yield of Tc(VII) reduction (for example, by hydrated electrons). The technetium concentration decreases in the presence of nitric because nitric reacts with $\text{OH}^\cdot (\text{O}^\cdot)$ radicals thus excluding their reaction with oxides. In the presence of carbonate, $\text{CO}_3^\cdot$ radical ions are formed, their reactivity is lower than that of $\text{OH}^\cdot (\text{O}^\cdot)$. Nitrate interacts with hydrated electrons suppressing Tc(VII) reduction by these species. In the presence of nitrate, dissolved technetium increases with increased dose.

In summary, the radiation-induced oxidation of Tc(IV) and Tc(V) hydroxides increases in the presence of additives that are scavengers of hydrated electrons and decreases in the presence of additives that are scavengers of $\text{OH}^\cdot (\text{O}^\cdot)$ radicals.

The oxidation of Tc(IV) and Tc(V) hydroxides continues after irradiation. This phenomenon is called post-radiation oxidation. Data on the rates of post-irradiation oxidation under various experimental conditions are shown in Tables 5-2 through 5-9.

The data show that the rates of post-radiation oxidation occasionally differ, but only slightly, from those observed in unirradiated solutions. In some cases (especially at high alkali concentrations), the rate decreases by increasing the dose to which the sample was irradiated. For instance, in the sample containing TcO_2 , nH_2O and 15 M NaOH and irradiated to 20 kGy dose, the rate is approximately half that in unirradiated samples of the same composition (see Table 5-2). Reactions of technetium hydroxides with dissolved atmospheric oxygen and with hydrogen peroxide formed by irradiation might seem to be responsible for post-radiation oxidation. However, the oxidation rates in irradiated and unirradiated solution are similar. On this basis, it appears that hydrogen peroxide does not play an important role. This may be because of low radiation-chemical yields of hydrogen peroxide, or because of its fast decomposition in alkaline media after irradiation. A probable reason for lower oxidation rates in highly concentrated alkali solution is the lower solubility of air in such media.

The additives have slight influence on post-radiation oxidation rates of Tc(IV) and Tc(V) hydroxides. This small effect may only be a reflection of their small influence on the solubility of oxygen in the test solutions because of their relatively low concentrations.

Figure 5-3. Dependence of Technetium Concentration on Dose for Suspensions of $Tc_2O_3 \cdot nH_2O$ at Various NaOH Concentrations.

[NaOH], M: 1 - 0.5; 2 - 4; 3 - 8; 4 - 15

Figure 5-4. Dependence of Technetium Concentration on Dose for Suspensions of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ at Various NaOH Concentrations and 0.04 M NaNO_3 .

[NaOH], M: 1 - 0.5; 2 - 4; 3 - 8; 4 - 15

Figure 5-5. Dependence of Technetium Concentration on Dose for Suspensions of $Tc_2O_7 \cdot nH_2O$ at Various NaOH Concentrations and 0.04 M $NaNO_3$.

[NaOH], M: 1 - 0.5; 2 - 4; 3 - 8; 4 - 15

Table 5-2. Rates, V , of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ Post-Radiation Oxidation at Various NaOH Concentrations and Absorbed Doses.

[NaOH], M	Dose, kGy	$V \times 10^4$, mol L ⁻¹ day ⁻¹
0.5	0	5.8
0.5	2.5	7.2
0.5	5	7.2
0.5	20	7.5
4	0	5.4
4	2.5	4.2
4	5	5.4
4	10	5.9
4	20	3.7
8	0	3.0
8	2.5	3.0
8	5	2.3
8	10	2.2
8	20	2.4
15	0	2.9
15	2.5	2.5
15	5	1.4
15	10	1.6
15	20	2.1

Table 5-3. Rates, V , of $Tc_2O_7 \cdot nH_2O$ Post-Radiation Oxidation at Various NaOH Concentrations and Absorbed Doses.

[NaOH], M	Dose, kGy	$V \times 10^4$, mol L ⁻¹ day ⁻¹
0.5	0	6.0
0.5	2.5	6.0
0.5	5	5.3
0.5	10	8.1
0.5	20	8.2
4	0	7.1
4	2.5	3.9
4	5	3.9
4	20	3.9
8	0	2.2
8	2.5	2.0
8	5	2.4
8	20	2.2
15	0	2.2
15	2.5	2.0
15	5	1.8
15	10	1.9
15	20	1.7

Table 5-4. Rates, V , of $\text{TeO}_2 \cdot n\text{H}_2\text{O}$ Post-Radiation Oxidation in the Presence of 0.04 M NaNO_3 at Various NaOH Concentrations and Absorbed Doses.

$[\text{NaOH}], \text{M}$	Dose, kGy	$V \times 10^4, \text{mol L}^{-1} \text{day}^{-1}$
0.5	0	6.1
0.5	2.5	6.1
0.5	5	6.0
0.5	10	6.9
0.5	20	5.8
4	0	3.6
4	5	2.5
4	10	3.6
4	20	2.2
8	0	1.8
8	5	1.5
8	10	1.9
8	20	1.7
15	0	2.1
15	2.5	4.4
15	5	1.0
15	10	1.0
15	20	0.3

Table 5-5. Rates, V , of $\text{Te}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ Post-Radiation Oxidation in the Presence of 0.04 M NaNO_3 at Various NaOH Concentrations and Absorbed Doses.

$[\text{NaOH}]$, M	Dose, kGy	$V \times 10^3$, mol $\text{L}^{-1} \text{ day}^{-1}$
0.5	2.5	5.7
0.5	5	5.1
0.5	10	5.7
0.5	20	5.3
4	0	3.9
4	10	4.3
8	0	4.0
8	2.5	4.9
8	10	2.8
8	20	4.0
15	0	2.4
15	2.5	1.6
15	10	0.8

Table 5-6. Rates, V , of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ Post-Radiation Oxidation in the Presence of 0.05 M NaNO_3 at Various NaOH Concentrations and Absorbed Doses.

[NaOH], M	Dose, kGy	$V \times 10^4$, mol $\text{L}^{-1} \text{ day}^{-1}$
0.5	0	5.0
0.5	2.5	4.4
0.5	5	3.8
0.5	10	3.4
0.5	20	3.2
4	0	3.7
4	2.5	3.4
4	5	3.2
4	10	3.0
4	20	2.8
8	0	2.9
8	2.5	2.8
8	5	2.7
8	10	2.5
8	20	2.1
15	0	1.5
15	2.5	1.5
15	5	1.3
15	10	1.1
15	20	0.8

Table 5-7. Rates, V , of $Tc_2O_7 \cdot nH_2O$ Post-Radiation Oxidation in the Presence of 0.05 M $NaNO_3$ at Various $NaOH$ Concentrations and Absorbed Doses.

$[NaOH], M$	Dose, kGy	$V \times 10^4, mol L^{-1} day^{-1}$
0.5	0	4.5
0.5	2.5	4.9
0.5	5	5.1
0.5	10	4.9
0.5	20	4.4
4	0	4.3
4	2.5	4.2
4	5	4.0
4	10	3.9
4	20	3.9
8	0	2.8
8	2.5	3.0
8	5	3.2
8	10	3.0
8	20	3.0
15	0	1.7
15	2.5	1.4
15	5	1.0
15	10	1.1
15	20	0.8

Table 5-8. Rates, V , of $\text{TeO}_2 \cdot n\text{H}_2\text{O}$ Post-Radiation Oxidation in the Presence of 0.05 M Na_2CO_3 at Various NaOH Concentrations and Absorbed Doses.

NaOH, M	Dose, Mr	$V \times 10^3, \text{mol l}^{-1} \text{day}^{-1}$
0.5	0	5.0
0.5	2.5	4.4
0.5	5	3.6
0.5	10	3.8
0.5	20	4.5
4	0	3.7
4	2.5	3.3
4	5	3.0
4	10	2.8
4	20	3.4
8	0	2.7
8	2.5	2.5
8	5	2.3
8	10	2.2
8	20	2.8
15	0	2.0
15	2.5	1.6
15	5	1.2
15	10	0.7
15	20	0.8

Table 5-9. Rates, V , of $Tc_2O_5 \cdot nH_2O$ Post-Radiation Oxidation in the Presence of 0.05 M Na_2CO_3 at Various $NaOH$ Concentrations and Absorbed Doses.

[$NaOH$], M	Dose, kGy	$V \times 10^4$, mol $L^{-1} day^{-1}$
0.5	0	5.8
0.5	2.5	4.3
0.5	10	3.3
0.5	20	4.1
4	0	4.0
4	2.5	3.7
4	5	3.2
4	10	2.8
4	20	3.0
8	0	2.5
8	2.5	2.3
8	5	2.2
8	10	2.0
8	20	2.0
15	0	1.4
15	2.5	1.6
15	5	1.5
15	10	1.0
15	20	1.1

6.0 CONCLUSION

As expected, neptunium, plutonium, and technetium ions, on γ -irradiation of their alkaline solutions, participate in various reactions. The pathways of these reactions depend on the valent states of the ions, the dose, and on the presence or absence of additives.

Neptunium(VI) is reduced initially to Np(V) and, at higher doses, to Np(IV). The reduction occurs by reactions of Np(VI) with hydrated electrons, O_2^- radical ions, and hydrogen peroxide to form Np(V) and by continued reaction of Np(V) with hydrated electrons. Oxidation of Np(V) back to Np(VI) occurs by reactions with OH ($O^\cdot$) and O_2^- radicals and with Np(VII) formed in reactions of Np(VI) with OH ($O^\cdot$) and O_2^- . In the presence of organic compounds (EDTA or $HCOO^-$), radiation-chemical yields of Np(VI) reduction increase considerably.

The Np(IV) generated in these reductions forms a finely dispersed suspension that coagulates into a precipitate. This effect is observed at comparatively high doses. After irradiation, Np(IV) is slowly oxidized to Np(V) by heterogeneous reactions with atmospheric oxygen dissolved in solution and by hydrogen peroxide accumulated in small concentrations by irradiation.

Like Np(VI), Np(V) is reduced by irradiation. The reduction occurs by reaction of Np(V) with hydrated electrons. Suspensions and precipitates containing Np(IV) are observed at lower doses than in the case of Np(VI). The Np(V) peroxo complex is observed in the γ -radiolysis of alkaline Np(V) solutions under certain experimental conditions such as in the presence of nitrate [remarkably, the Np(V) peroxo complex is not observed in the γ -radiolysis of Np(VII)]. After irradiation, Np(IV) is slowly oxidized to Np(V) by atmospheric oxygen and, possibly, by hydrogen peroxide.

Plutonium(VI) in alkaline solutions is reduced by reactions with hydrated electrons, O_2^- radical ions, and hydrogen peroxide. The product plutonium(V) is unstable, disproportionating to Pu(IV) and Pu(VI). Because Pu(IV) hydroxide is insoluble, finely dispersed suspensions and then precipitates form even at low doses. After irradiation, Pu(IV) can be oxidized to Pu(V) by slow heterogeneous reactions with atmospheric oxygen and, possibly, hydrogen peroxide. The subsequent disproportionation of Pu(V) gives Pu(VI) and again Pu(IV).

Technetium(VII) in the absence of special additives is not reduced by γ -radiolysis in alkaline solutions. Reduction is observed in the presence of additives that can scavenge OH ($O^\cdot$) radicals. Such scavengers include alcohols (e.g., methanol and *tert*-butanol) and EDTA.

γ -irradiation of alkaline suspensions containing dissolved TeO_3 and Te(IV) or Te(V) hydroxide solids gives rise to reduction of the Te(VII) . Oxidations of the Te(IV) and Te(V) hydroxides are observed if the system contains an additive, such as nitrate, that can scavenge hydrated electrons. The post-irradiation oxidation rates for technetium systems differ only slightly from the rates observed in unirradiated samples.

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