



Redox reactions of neptunium and plutonium in alkaline aqueous solutions upon gamma radiolysis

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Abstract

The paper is a brief review of data obtained by the authors from the study on redox reactions of neptunium and plutonium ions upon γ -radiolysis of their aerated alkaline aqueous solutions. It includes the information on radiolytic reduction of Np(V), Np(VI), and Pu(VI) ions under various experimental conditions. It was found that the values of Np(VI) and Pu(VI) reduction yields do not depend on alkali concentration. The values considerably increase in the presence of some organic compounds (EDTA and formate were investigated). The formation of the Np(V) peroxy complex was observed in the γ -radiolysis of alkaline aqueous solutions of Np(VI) and Np(V) in the presence of nitrate. The mechanism of radiolytic redox reactions of the ions is discussed in some detail. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Some high-level radioactive wastes formed upon reprocessing of irradiated nuclear fuel and the separation of valuable radionuclides are alkaline aqueous solutions. The various radiolytic processes caused by the action of α -, β - and γ -radiations of radionuclides present in the wastes occur upon their long-term storage in tanks, geological strata and so on. Actinide ions also participate in such processes. In this relation, it is obvious that for successful management of the wastes under consideration and for prediction of the behaviour of actinides in the environment as a result of possible accidents on the respective storage facilities and the migration of actinides from underground repositories, it is necessary to know the features of their radiolytic redox reactions in alkaline media.

However, the existing information on radiation chemistry of aqueous solutions of actinides is con-

nected predominantly with acid media (see, for example, Pikaev et al., 1983; Vladimirova, 1983). The data on radiolysis of their alkaline solutions are fragmentary (see Pikaev et al., 1983, 1997). There is an information on radiolytic oxidation of hexavalent neptunium, plutonium, and americium to their heptavalent states in alkaline solutions, on reduction of heptavalent neptunium and plutonium in the same solutions, on oxidation of Am(III) in carbonate medium, on reactivity of actinide ions towards water radiolysis products and some other free radicals.

Taking into account the significance of the information on radiolysis of alkaline aqueous solutions of actinide ions, we have undertaken the detailed study on the features of radiolytic redox reactions of neptunium and plutonium ions in these media. The present paper briefly summarizes our data on γ -radiolysis of aerated alkaline aqueous solutions of Np(V), Np(VI) and Pu(VI) under various experimental conditions. Some of them were published earlier (Gogolev et al., 1996, 1997a,b, 1998a,b).

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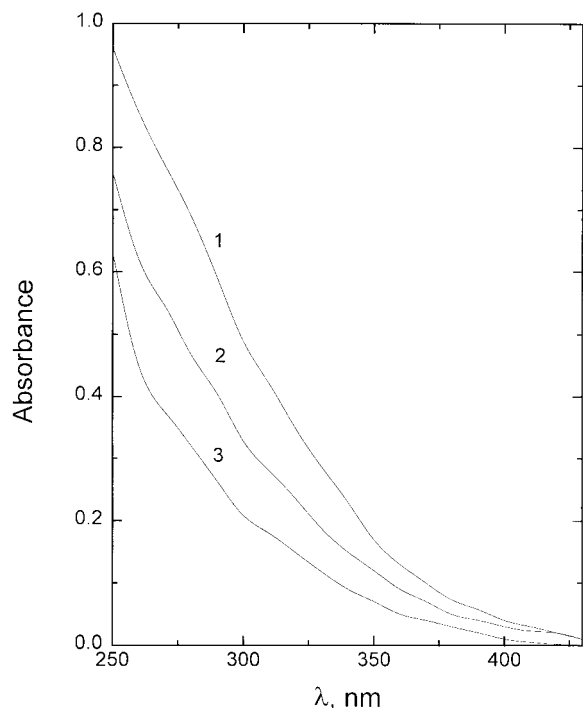


Fig. 1. Optical absorption spectra of aerated aqueous solutions containing 2.74×10^{-4} mol/l Np(VI) and 3.6 mol/l NaOH irradiated to doses (kGy): 1, 0; 2, 0.47; 3, 0.94.

2. Experimental

The details of preparation of alkaline solutions of neptunium and plutonium ions, spectrophotometric analysis of these ions in the solutions, techniques of their γ -irradiation and dosimetry were described earlier (Gogolev et al., 1997b, 1998a,b). Note that the maximum Np(VI) concentration in alkaline solutions used in the experiments was 5.8×10^{-4} mol/l. At higher Np(VI) concentrations, the solutions (especially in 1–2 mol/l NaOH) form precipitates. The maximum concentration of Pu(VI) in alkaline solutions, restricted by its solubility, was 1×10^{-3} mol/l.

Table 1

The yields of Np(VI) reduction, $G[-\text{Np(VI)}]$, upon γ -radiolysis of aerated alkaline aqueous solutions of Np(VI) ($[\text{Np(VI)}]_0 = (2.7\text{--}3.6) \times 10^{-4}$ mol/l)

[NaOH] (mol/l)	Additive and its concentration (mol/l)	Dose (Gy)	$G[-\text{Np(VI)}]$ (ion/100 eV)
0.9	–	≤ 650	1.4
1.5	0.26 mol/l HCOO^-	≤ 250	5.8
1.8	–	960	1.6
2.0	0.013 mol/l EDTA	109	8.5
3.65	–	≤ 650	1.4
7.0	–	≤ 200	3.4
7.0	–	270–650	1.5

A cobalt-60 γ -radiation source with maximum dose rate 15 kGy/h was used. All the experiments were conducted with aerated solutions.

3. Radiolytic redox reactions of neptunium ions

Below, the data on γ -radiolysis of aerated alkaline solutions of Np(VI) and Np(V) in the absence and in the presence of some inorganic and organic compounds are summarized.

3.1. Aerated alkaline Np(VI) solutions in the absence of additives

It was found that several processes occur upon the action of γ -radiation on aerated alkaline aqueous solutions of Np(VI). Decrease in optical absorption in 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 (0.9–8.5 mol/l). Fig. 1 shows the change in Np(VI) optical absorption as a result of γ -irradiation.

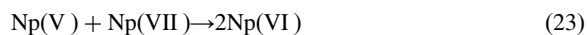
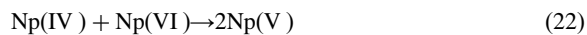
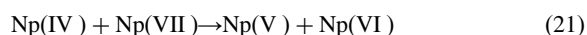
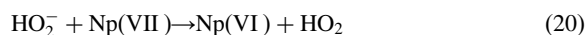
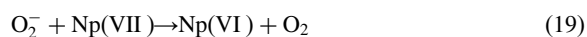
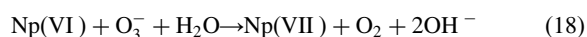
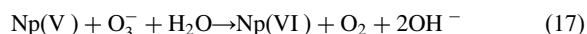
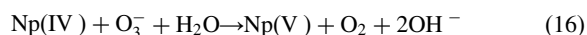
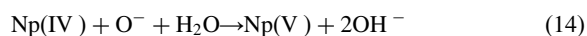
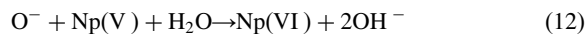
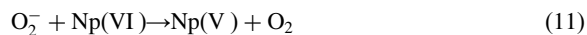
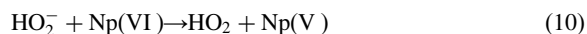
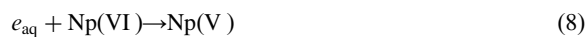
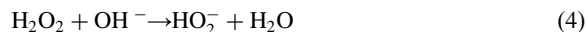
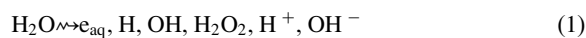
The values of radiation-chemical yields of Np(VI) reduction, $G[-\text{Np(VI)}]$, at various NaOH concentrations are given in Table 1. It is seen that concentration of alkali has only slight influence on the yield. However, at low doses (it was studied in 7 mol/l solution of NaOH) the yield is considerably higher. Apparently, this effect is due to the presence of organic microimpurities in the alkali used.

The spectra of solutions irradiated to doses of 400–800 Gy are stable for at least 20 h after irradiation. However, further irradiation of the solutions (to doses over 8 kGy) increases the optical absorption in the UV- and visible regions. Standing the irradiated solution gives rise to the decrease in optical absorption. If the solution is again irradiated, the repeated increase in the absorption is observed. Thus, a type of peculiar “oscillation” process takes part.

The increased optical absorption occurring at doses

over 8 kGy is due to the formation of more or less stable (depending on alkali concentration) fine dispersed suspensions. This conclusion is confirmed by the presence of a Tyndal cone, caused by light scattering on fine dispersed particles, and by the decrease in the absorption intensity with increasing centrifugation or standing time of the irradiated solution. Both Np(V) and Np(IV) are formed upon irradiation to doses over 8 kGy. It follows from optical absorption spectra of solutions which were prepared by dissolution of precipitates, separated by centrifugation of irradiated solutions, in HClO₄ solution. For example, the ratio [Np(IV)]/[Np(V)] in solution, prepared by dissolution in 2.1 mol/l HClO₄, of precipitate obtained by centrifugation (2 h after irradiation) of irradiated (25 kGy) aerated solution containing initially 2.74 × 10⁻⁴ mol/l Np(VI) and 7 mol/l NaOH is equal to 8. Significantly, no Np(VI) in precipitate was observed by spectrophotometry. Note that if centrifugation is carried out at longer time after irradiation, the ratio under consideration is less. For instance, if centrifugation is conducted 24 h after irradiation, the ratio is 2.3. This effect can be explained by slow oxidation of Np(IV) by atmospheric oxygen. Such a process was observed in unirradiated systems (Shilov et al., 1997). In summary, Np(IV) precipitates are formed in solutions irradiated to dose of ≥8 kGy; the precipitates after irradiation can be oxidized by oxygen from atmospheric air on standing and exposure to air.

The following main reactions can occur upon γ-radiolysis of aerated alkaline aqueous solutions of Np(VI) [expression (1) shows the primary products of water γ-radiolysis which reacting with solutes perform their various conversions including redox reactions; e_{aq} is hydrated electron]:



Based on literature data (Pikaev and Kabakchi, 1982; Pikaev, 1983; Pikaev et al., 1997) on reactivity of Np(VI) ions towards primary products of water radiolysis, it is possible to conclude that e_{aq} , O_2^- and HO_2^- can reduce these ions. Radical ion O^- , reacting with Np(VI) and oxygen, forms Np(VII) and O_3^- , respectively. Neptunium(VII) and O_3^- can oxidize Np(V); Np(VII) also can react with O_2^- and HO_2^- . At relatively high doses, reaction (9) can take part; Np(IV), which is a product of this reaction, is slightly-soluble and appears in the form of fine-dispersed solid phase. Because of it reactions (14), (16), (21), (22) and also interaction of Np(IV) with oxygen of air and hydrogen peroxide formed upon radiolysis proceed slowly, and Np(IV) is accumulated in the form of solid phase upon γ-radiolysis of alkaline aqueous solutions of Np(VI). Note that reaction (10) seems to proceed via the stage of formation of Np(VI) peroxo complex (Shilov et al., 1998).

At low doses, Np(VI) can be reduced to Np(V) via

Table 2

The yields of Pu(VI) reduction, $G[-\text{Pu(VI)}]$, upon γ -radiolysis of aerated alkaline aqueous solutions of Pu(VI)

[Pu(VI)] $\times 10^4$ (mol/l)	[NaOH] (mol/l)	$G[-\text{Pu(VI)}]$ (ion/100 eV)
2.2	1.3	1.4
3.3	6.3	1.3
2.0	6.9	1.5

reactions (8), (10), and (11). Radical ions O^- and O_3^- oxidize Np(VI) to Np(VII) [reactions (15) and (18)]. Neptunium(VII) formed reacts with Np(V). Under these conditions, the reduction of Np(VI) to Np(IV) is not observed. Because of it the $G[-\text{Np(VI)}]$ value at low doses is described by equation:

$$G[-\text{Np(VI)}] = G[\text{Np(V)}] \\ = G_{e_{\text{aq}}} + G_{\text{H}} + 2G_{\text{H}_2\text{O}_2} - G_{\text{OH}} \quad (24)$$

At relatively high doses, the reduction of Np(V) by hydrated electron [reaction (9)] occurs. Hence,

$$G[-\text{Np(VI)}] = G[\text{Np(IV)}] < (G_{e_{\text{aq}}} + G_{\text{H}} + 2G_{\text{H}_2\text{O}_2} \\ - G_{\text{OH}}) \quad (25)$$

In the literature (see, for example, Pikaev, 1986) there are the data on the yields of primary products of water radiolysis at pH 12–13. Using these data for the solutions studied, it is possible to find by means of Eq. (24) that the $G[-\text{Np(VI)}]$ values at low doses should be equal to 2.2 ion/100 eV. However, experimental values (see Table 2), excluding 7 mol/l solution of NaOH at doses < 200 Gy, even at low doses are < 2.2 ions/100 eV. It can be explained mainly by the occurrence (to some extent) of reaction between e_{aq} and HO_2^- . Note that reactions of HO_2^- with O^- , O_3^- and Np(VII) have no effect on the yield of Np(VI) reduction.

As mentioned, at doses ≤ 200 Gy $G[-\text{Np(VI)}]$ in 7 mol/l NaOH has a relatively high value. It is explained by the presence of microimpurities of organic compounds. They react with radical ions O^- , partially suppressing reactions (12), (14), and (15). At sufficiently high doses, these impurities are decomposed, and $G[-\text{Np(VI)}]$ decreases.

3.2. Formation of Np(V) peroxo complex

It can be expected that because of the low reactivity of hydrogen peroxide towards Np(V) and Np(VI) and also the formation of Np(IV) precipitate, HO_2^- can be accumulated in the solution as a result of irradiation. If it is so, it is possible to postulate that at sufficiently high doses when a considerable part of Np(VI) was

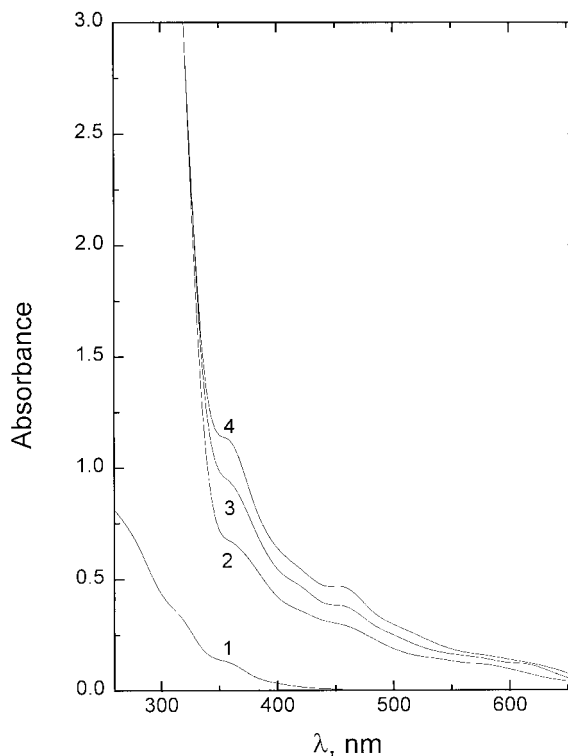


Fig. 2. Optical absorption spectra of aerated solution containing 2.74×10^{-4} mol/l Np(VI) and 8.5 mol/l NaOH (1) and aerated solution containing 3.2×10^{-4} mol/l Np(VI), 0.7 mol/l NaNO_3 and 7.7 mol/l NaOH irradiated to dose (kGy): 2, 15.2; 3, 42.2; 4, 58.8.

reduced the Np(V) peroxo complex described earlier (Musicas, 1970) can appear. However, it was found that the formation of the complex does not occur. Apparently, hydrogen peroxide is decomposed in reactions with other products of water radiolysis [mainly with O_3^- , O^- and Np(VII)], and under these conditions reaction (10) does not take part at all.

It was obtained that the complex is formed upon radiolysis of aerated alkaline Np(VI) solutions containing nitrate ions. In these solutions, the reduction of Np(VI) could not be obtained at doses of < 2 kGy. The reason consists in the fact that nitrate absorbs the light in UV-region. Because of it the change in Np(VI) concentration could not be detected from its charge-transfer band, and Np(VI) was analysed via optical absorption of carbonate complex. The latter is characterized by relatively intense optical absorption in visible region where neither nitrate nor nitrite absorb the light. For analysis, potassium bicarbonate, in quantities exceeding the equivalent amount of alkali present in solution, was added to the unirradiated and irradiated Np(VI) solutions. After this procedure, the absorption of prepared solution was measured at

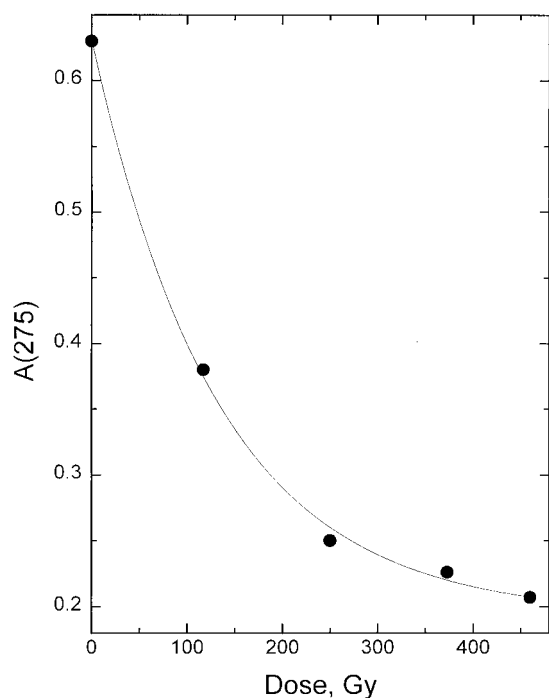


Fig. 3. Dependence of optical absorption (at 275 nm) $A(275)$ of aerated aqueous solution, containing 2.74×10^{-4} mol/l Np(VI), 2 mol/l NaOH and 0.013 mol/l EDTA on dose.

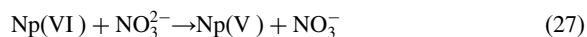
425 nm. At above-mentioned doses, the Np(VI) reduction seems to proceed with low yield, and the described method of analysis is not so sensitive to detect such a small change in Np(VI) concentration.

However, at higher doses the solution became a yellow-brown color. The spectrum of the solution in visible region coincided with the spectrum of Np(V) peroxy complex prepared by conventional chemical method (Musicas, 1970). The respective results are shown in Fig. 2. The same spectrum appears when 2×10^{-4} mol/l solution of Np(V) in 4 mol/l NaOH is added to irradiated (19 kGy) solution containing 0.8 mol/l NaNO_3 and 3.6 mol/l NaOH. The acidification of irradiated solution by perchloric acid leads to the decomposition of the complex and formation of Np(V). Peroxy complex prepared by the addition of a small excess of hydrogen peroxide to alkaline Np(V) solution is decomposed upon irradiation. The complex formation in the Np(VI) solution containing nitrate upon irradiation is inhibited by addition of nitrite or EDTA to the solution.

The formation of Np(V) peroxy complex can be explained qualitatively as follows. Because in the solutions used the concentration of nitrate is considerably higher than the concentrations of oxygen and Np(VI), all the hydrated electrons react with nitrate ions:



Radical ions formed react with O^- , O_3^- and Np(VII), partially or completely suppressing the reactions of them with hydrogen peroxide. Because of it Np(V) appeared in reactions (10), (11) and (27):



The Np(V) appeared can react with hydrogen peroxide forming peroxy complex. It is also not excluded that the complex partially is the product of reaction (10).

3.3. Aerated alkaline Np(VI) solutions in the presence of organic additives

Some high-level radioactive wastes are alkaline and, together with other compounds, contain actinides and organic substances. It was one of the reasons to study γ -radiolysis of aerated alkaline aqueous solutions of Np(VI) in the presence of organic additives such as formate and EDTA (sodium salt).

It was found that, as in the absence of organic additives, irradiation of aerated alkaline solutions of Np(VI) containing formate or EDTA leads to the reduction of Np(VI). As an example, Fig. 3 shows the dependence of optical absorption of aerated Np(VI) solution containing 2 mol/l NaOH and 0.013 mol/l EDTA on dose. It is seen that there is a considerable decrease in optical absorption with increasing the dose. The decrease strongly depends on dose. It is caused by the high values of the yield (see Table 1) and, as a consequence, an appearance of fine dispersed particles, scattering the light, at considerably lower doses than in the case of the solutions not containing organic additives.

As it is seen from Table 1, the yields in the presence of organic additives are higher by several times in comparison with the yields in the absence of these additives.

The main difference in radiolysis of the solutions containing organic compound from radiolysis of the solutions in the absence of this compound, consists in the interaction of the latter with radical ions O^- and, as a result, the suppression of oxidation of Np(V), Np(VI) and Np(IV) by these radical ions. Besides, since the used concentration of organic compound is considerably higher than the concentration of oxygen present in the solution, the reaction of O^- with O_2 giving rise to O_3^- formation does not occur. In reaction of O^- with organic compound, organic free radical R' (e.g., COO^- in the case of HCOO^-), which is reducing species, is formed. The radical is able to reduce Np(VI) and, possibly, Np(V). Note that oxygen can react with R' forming peroxide radical (in the case of EDTA) or O_2^- (in the case of formate) which can reduce Np(VI).

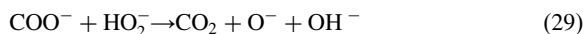
At low doses, reduction of Np(VI) proceeds to Np(V). Because of it the reduction yield under such conditions should be expressed by equation:

$$G[-\text{Np(VI)}] = G[\text{Np(V)}] \\ = G_{e_{\text{aq}}} + G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} \quad (28)$$

Using the values of the yields of primary products of water radiolysis at pH 12–13 (see, for example, Pikaev, 1986), we can find that $G[-\text{Np(VI)}]$ should be equal to 8 ion/100 eV. The experimental value of the yield for the solution containing EDTA is close to the value calculated via equation (28).

At high doses the reduction yield decreases. It was observed in solutions containing EDTA. Apparently, this effect is caused by further reduction of Np(V) to Np(IV).

In the case of HCOO^- , the experimental value is considerably less. Because reaction (10) is comparatively slow, it can be due to the decomposition of hydrogen peroxide in reaction:



If it is true, the value of the Np(VI) reduction yield in the presence of formate at low doses should be:

$$G[-\text{Np(VI)}] = G[\text{Np(V)}] = G_{e_{\text{aq}}} + G_{\text{H}} + G_{\text{OH}} \quad (30)$$

i.e. 6.5 ion/100 eV. The experimental value is comparatively close to this value.

In the solutions with organic compounds even at relatively low doses (~ 300 Gy), fine dispersed particles appear. It seems to be caused by formation of insoluble Np(IV) hydroxide. After radiolysis, the suspension is dissolved fastly (for 10–15 min). The most probable reason is the oxidation of Np(IV) by oxygen of air. As it was mentioned, this non-radiolytic process was described earlier (Shilov et al., 1997). The precipitate formed at higher doses (e.g. at ~ 3 kGy) is not dissolved even for 3 weeks after irradiation. This effect can be connected with the formation (at high doses) of the precipitate consisting of relatively large particles.

Therefore, the presence of organic compounds in the solution intensifies radiolytic reduction of Np(VI).

3.4. Aerated alkaline Np(V) solutions

It was found that Np(V) in aerated alkaline aqueous solutions is reduced to Np(IV) upon γ -irradiation. This behaviour was demonstrated by the formation, even at low doses, of fine dispersed suspensions similar to those appearing in aerated alkaline aqueous solutions of Np(VI) at higher doses. This phenomenon is illustrated by Fig. 4 for aerated alkaline Np(V) solution containing some amount of Np(VI). The figure shows

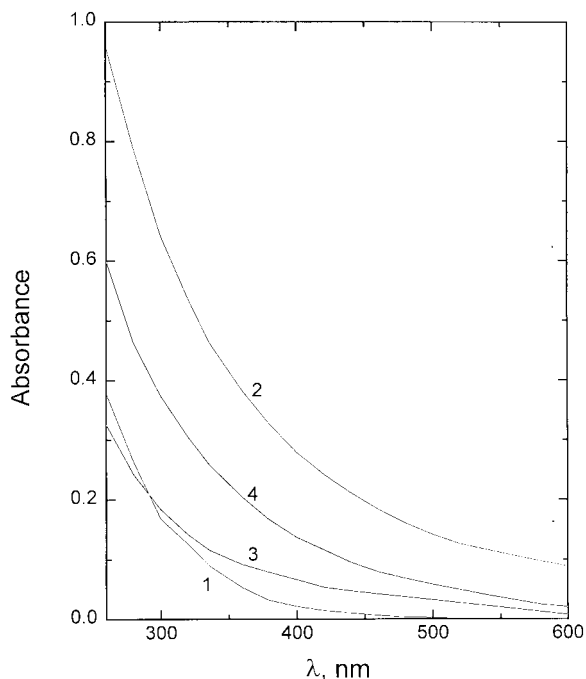


Fig. 4. Optical absorption spectra of aerated solutions containing 1.54×10^{-4} mol/l Np(V), 1.2×10^{-4} mol/l Np(VI) and 6.9 mol/l NaOH: 1, unirradiated solution; 2, solution irradiated to dose 13 kGy; 3, as in 2, but after standing 17 h 10 min; 4, as in 3, but further irradiated to dose 15 kGy.

that the optical absorption of the solution increases as a result of irradiation (because of light scattering on dispersed particles); on aging, optical absorption decreases (because the suspension coagulates, and precipitate is formed). Additional irradiation again increases the optical absorption, since Np(V) is reduced further, and a fine dispersed suspension appears. 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. For example, the ratio $[\text{Np(IV)}]/[\text{Np(V)}]$ in solution prepared by dissolution, in 2.1 mol/l HClO_4 , of precipitate obtained by centrifugation of aerated solution containing 2.7×10^{-4} mol/l Np(V), 0.16 mol/l HCOO^- and 4.5 mol/l NaOH irradiated to dose 21.5 kGy is equal to 6. The presence of Np(V) seems to be caused by its capture by the precipitate upon the formation of the latter.

Obviously, Np(V) is reduced by hydrated electrons [reaction (9)]. Note that in the alkaline solutions studied, virtually all H atoms are converted to hydrated electrons [reaction (2)]; reaction (5) plays a negligible role because of very high alkali concentrations in comparison with oxygen concentration. Hence, the total yield of hydrated electrons is the sum of initial yields

of e_{aq} and H. Hydrated electrons also react with oxygen [reaction (6)]. The fraction f of hydrated electrons participating in reaction (9) is:

$$f = 1/(1 + k_6[O_2]/k_9[Np(V)]) \quad (31)$$

where k_6 and k_9 are rate constants of reactions (6) and (9).

The values of these rate constants are known (see, for example, Pikaev and Kabakchi, 1982; Pikaev et al., 1983, 1997). The concentrations of alkali and oxygen are also known. Therefore, equation (31) can be used to calculate f values. For instance, f is about 0.2 for aerated 1 mol/l solution of NaOH containing 2.7×10^{-4} mol/l Np(V).

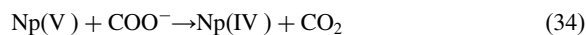
Because O_2^- and HO_2^- cannot reduce Np(V), the yield of Np(IV) in aerated alkaline Np(V) solutions in the absence of additives is expressed by equation:

$$G[Np(IV)] = f(G_{e_{aq}} + G_H) \quad (32)$$

Radical ions O^- and O_3^- which is formed in reaction (13) oxidize Np(V) to Np(VI). Hydrogen peroxide and radical ions O_2^- reduce the Np(VI) formed. Neptunium(IV) is slightly-soluble. Therefore, the reactions of Np(IV), present in solid phase, with O^- , O_3^- , and Np(VI) proceed to an insignificant extent. At sufficiently high doses, hydrated electrons can also reduce Np(VI). Hence, equation (32) expresses the maximum value of the yield. The experimental values can be described by the following expression:

$$G[Np(IV)] < f(G_{e_{aq}} + G_H) \quad (33)$$

The presence of formate causes COO^- radical ion formation. These radical ions can reduce Np(V) [reaction (34)] and react with oxygen [reaction (35)]:



Because of it the fraction f_1 of COO^- radical ions participating in Np(V) reduction is:

$$f_1 = 1/(1 + k_{35}[O_2]/k_{34}[Np(V)]) \quad (36)$$

where k_{34} and k_{35} are rate constants of reactions (34) and (35).

Neptunium(IV) can be oxidized to a small extent back to Np(V) by atmospheric oxygen, and hydrated electrons can participate also to a small extent in Np(VI) reduction (especially at high doses). The experimental values of Np(IV) yield in the presence of formate is described by the following expression:

$$G[Np(IV)] < f(G_{e_{aq}} + G_H) + f_1 G_{OH} \quad (37)$$

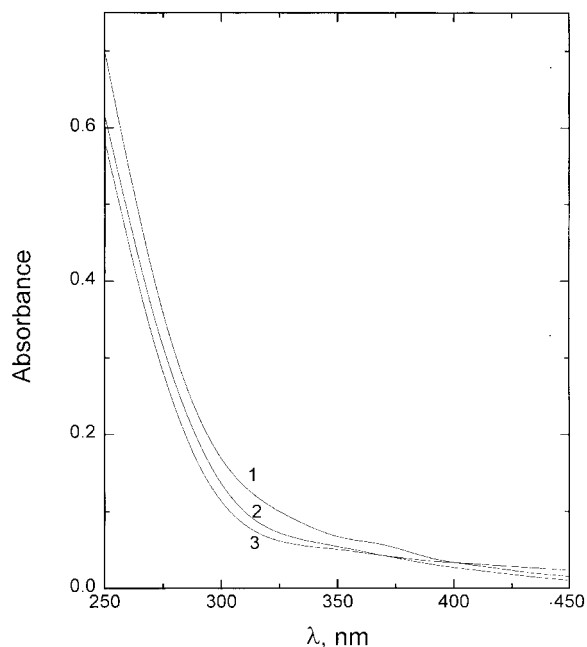


Fig. 5. Optical absorption spectra of aerated solutions containing 1.9×10^{-4} mol/l Pu(VI) and 6.9 mol/l NaOH irradiated to dose (kGy): 1, 0; 2, 0.23; 3, 0.45.

Note also that Np(IV) hydroxide is not stable after irradiation, and it is slowly oxidized in the irradiated solution to Np(V) by oxygen of air and, possibly, radiolytically-produced hydrogen peroxide.

The formation of fine dispersed suspension even at low doses did not allow us to determine the exact values of Np(V) reduction yield by spectrophotometric measurements. The approximative evaluation of the yields via the weights of Np(IV) hydroxide precipitates showed that the order of magnitude for their values is several hundredth of ion per 100 eV, being several times higher for the solution containing formate.

Gamma radiolysis of aerated alkaline Np(V) solutions containing nitrate, as of similar Np(VI) solutions, led to formation of Np(V) peroxo complex. As for Np(VI), this phenomenon is explained by the protection of Np(V) by NO_3^- to reduction.

Note that Np(IV) is not formed upon γ -radiolysis of alkaline Np(V) solutions containing nitrate. The same effect is observed in the presence of nitrite. In the last case, as in Np(VI) solutions, γ -radiolysis did not lead to the formation of Np(V) peroxo complex. The absence of the complex formation is explained by reaction of HO_2^- with nitrite.

4. Radiolytic redox reactions of plutonium ions

Because of instability of Pu(V) in the solutions and insolubility of Pu(IV) in alkaline media, only γ -radioly-

sis of aerated alkaline Pu(VI) solutions with no additives and in the presence of some additives was studied.

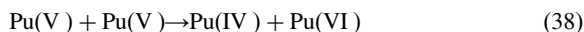
Research showed that Pu(VI) in aerated alkaline aqueous solutions is reduced upon γ -radiolysis. This conclusion follows from the decrease in optical absorption of its solutions as a result of irradiation (see Fig. 5). The reduction yields, $G[-\text{Pu(VI)}]$, measured at doses < 1 kGy, are presented in Table 2. It is seen that the yields do not depend on alkali concentration.

At sufficiently high doses (over ~ 2 kGy), the solutions became turbid because of the formation of fine dispersed suspension. It is difficult to separate the suspension; its stability increases with increasing alkali concentration. In the case of 1.9×10^{-4} mol/l solution of Pu(VI) in 1.3 mol/l NaOH irradiated to dose 4 kGy, the suspension is precipitated simultaneously for 24 h. The suspension is also separated after prolonged (over 40 min) centrifugation.

The precipitation of dispersed species leads to the decrease in optical absorption of the solution. However, the repeated irradiation again causes the appearance of the suspension and, as a consequence, the increase in optical absorption. Therefore, as upon γ -radiolysis of Np(VI) and Np(V) solutions, we deal with the peculiar “oscillation” process.

The precipitates predominantly consist of Pu(IV) hydroxide with a small admixture of Pu(VI). For example, the concentration ratio $[\text{Pu(IV)}]/[\text{Pu(VI)}]$ in solution prepared by dissolution, in nitric or perchloric acid solution, of precipitates obtained by centrifugation of irradiated (10 kGy) aerated solution containing 1.9×10^{-4} mol/l Pu(VI) and 1.3 mol/l NaOH was ≥ 12 . There was no Pu(VI) in the precipitate which was separated from the solution irradiated to dose 20 kGy. Hence, at sufficiently high doses, the complete reduction of Pu(VI) to Pu(IV) occurs.

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:



On the base of this mechanism, it is possible to write that the Pu(VI) reduction yield should be equal:

$$\begin{aligned} G[-\text{Pu(VI)}] &= G[\text{Pu(IV)}] \\ &= 1/2(G_{e_{\text{aq}}} + G_{\text{H}} + 2G_{\text{H}_2\text{O}_2} - G_{\text{OH}}) \end{aligned} \quad (39)$$

i.e. 1.1 ion/100 eV. The experimental value for 1.3 mol/l solution NaOH is somewhat higher (see Table 2) that can be connected with the influence of microimpurities of organic compounds present in alkali.

The fine dispersed suspensions are also formed upon γ -radiolysis of alkaline Pu(VI) solutions containing

nitrate or nitrite. As in the solutions with no additives, the dissolution of the precipitates, separated from the irradiated solution by centrifugation, in perchloric or nitric acid gives rise to the acid solutions of Pu(IV) with a small admixture of Pu(VI). The similar effect is also observed upon γ -radiolysis of the solutions containing EDTA.

In the presence of nitrate or nitrite [their concentrations are considerably higher than concentrations of Pu(VI)], all the hydrated electrons react with these compounds forming NO_3^{2-} or NO_2^{2-} . The reduction of Pu(VI) occurs in reactions with HO_2^- , O_2^- and NO_3^{2-} (in the presence of nitrate) or HO_2^- , O_2^- and NO_2^{2-} (in the presence of nitrite). In the solutions containing EDTA, the reduction of Pu(VI) proceeds in reactions with e_{aq} , O_2^- , HO_2^- , and organic radicals formed in reaction of O^- with EDTA. Unfortunately, the determination of the yields for Pu(VI) reduction in the solutions containing the additives is very complicated because of the formation of fine dispersed suspension even at low doses.

Note that unlike nitrate-alkaline Np(VI) solutions, we could not observe the appearance of Pu(V) peroxy complex, described earlier (Musicas, 1971), upon γ -radiolysis of alkaline Pu(VI) solutions containing nitrate. Apparently, Pu(V) peroxy complex has a low stability at room temperature (in particular, it was mentioned earlier (Musicas, 1971) and/or the rate of Pu(V) disproportionation under studied conditions is higher than that of the complex formation.

5. Conclusions

The data obtained allow us to draw the following conclusions:

1. Upon γ -radiolysis, Np(VI) in aerated alkaline aqueous solutions is reduced initially to Np(V) and, at higher doses, to Np(IV).
2. In the presence of organic compounds (EDTA or HCOO^-), the yield of Np(VI) reduction increases considerably.
3. The Np(IV) generated in the reduction forms fine dispersed suspension that coagulates into a precipitate. This effect is observed at comparatively high doses.
4. After irradiation, Np(IV) is slowly oxidized to Np(V) by heterogeneous reaction with oxygen of air present in the solution.
5. Similar to Np(VI), Np(V) in aerated alkaline aqueous solutions is reduced by irradiation. Suspensions and precipitates containing Np(IV) are observed at lower doses than in the case of Np(VI). After radiolysis, Np(IV) is slowly oxidized by oxygen of air and, possibly, hydrogen peroxide accumu-

lated by irradiation.

6. The Np(V) peroxy complex is formed from γ -radiolysis of aerated alkaline aqueous solutions of Np(V) or Np(VI) under certain experimental conditions such as in the presence of nitrate. Under the same conditions, Pu(V) peroxy complex is not detected upon irradiation of Pu(VI) solutions.
7. Like Np(VI), Pu(VI) is reduced by irradiation. Plutonium(V) formed is unstable, disproportionating to Pu(IV) and Pu(VI).
8. Because Pu(IV) is insoluble, fine dispersed suspensions and then precipitates are formed even at low doses.

Acknowledgements

This work was supported by Department of Energy of the USA, Office of Science and Technology, under the Office of Environmental Management. We thank in particular Drs T. Fryberger, J. Watson and T. Albert for their advice and support. We express the sincere gratitude to Mr C. Delegard for the fruitful and useful work as a scientific coordinator of the respective contract.

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