Russian Chemical Reviews **64** (9) 831 – 837 (1995)
©1995 Russian Academy of Sciences and Turpion Ltd

UDC 546.799:541.14

The photochemistry of transuranic elements in solution

A B Yusov, V P Shilov

Contents

I. Introduction	831
II. The photochemistry of plutonium and neptunium	831
III. The photochemistry of americium	835
IV. Reversible charge transfer in americium(III) and curium(III) luminescence quenching processes	836
V. Conclusion	836

Abstract. The literature data on the photochemical reactions of neptunium, plutonium, and americium in HNO_3, $HClO_4$, HCl, H_2SO_4, and Na_2CO_3 solutions as well as certain extraction systems are surveyed. The mechanisms of the photochemical reactions are discussed and it is concluded that those proposed in the literature do not account for those reactions in solutions occurring without added oxidants or reductants. The possibilities of the practical application of photochemistry in the processing of spent nuclear fuel are examined. The bibliography includes 53 references.

I. Introduction

Numerous photochemical studies have been devoted to the ions of metals with unfilled electron shells. The photochemical properties of uranyl have already been investigated quite fully. The UO_2^{2+} ion can exist in the excited state for hundreds of microseconds, exhibiting strong oxidising properties. Uranyl photochemistry constitutes a large independent field. The principal data accumulated in this field have been presented in a monograph[1] written more than thirty years ago and also in a review.[2] Uranyl photochemistry continues to develop vigorously at the present time.

In recent years, appreciable attention began to be devoted to the ions of other *f* elements: lanthanides (cerium, europium, and samarium) and actinides [the first transuranic elements (TUE) — neptunium, plutonium, and americium]. The photochemistry of the last three elements will be the subject of the present review.

It may be assumed that the photochemistry of TUE began to develop since 1958 when the photochemical reduction of Np(VI) to Np(V) in perchloric acid solutions was observed.[3] Later, in 1965, Indian investigators[4] showed that Pu(VI) is reduced to Pu(IV) in the extraction of plutonium(VI) from acid solutions with a benzene solution of thenoyltrifluoroacetone under illumination and that this process does not occur in the dark. Systematic studies on the influence of light on the chemical behaviour of plutonium and neptunium in solutions began in the 1970s. Reports concerning the photochemical reactions of americium also appeared subsequently.

A B Yusov, V P Shilov Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, 117915 Moscow, Russian Federation. Fax (7-095) 335 17 78. Tel. (7-095) 330 41 70

Received 31 May 1995
Uspekhi Khimii **64** (9) 888 – 895 (1995); translated by A K Grzybowski

Despite the more than twenty year history of the photochemistry of TUE, the accumulated data, particularly those obtained in recent years, have not been analysed. There have been only brief reviews on the photochemistry of plutonium and on the application of photochemical processes in the processing of irradiated nuclear fuel. The aim of the present review is to give a systematic account of the available data on the photochemistry of all the transuranic elements and to assess the prospects for its further development.

II. The photochemistry of plutonium and neptunium

1. The photochemistry of aqueous acid solutions

a. Nitric acid solutions

Visible light does not affect the chemical behaviour of plutonium in nitric acid solutions in the absence of additives, but on exposure to UV light (mercury lamps were usually employed) plutonium passes to the Pu(VI) state regardless of the initial valence form — Pu(III) or Pu(IV).[5] The reaction takes place both in air and under a CO_2 atmosphere. Pu(III) is oxidised particularly rapidly. With increase in the concentration of acid (up to 3.5 M), the rate of oxidation also increases. According to the data of Duan Yunfu et al.,[6] the rate of the photochemical oxidation of Pu(III) to Pu(IV) is proportional to the concentrations of Pu(III), H^+, and NO_3^-. The authors[6] believe that the comversion of plutonium to the hexavalent state takes place by disproportionation of Pu(IV) to Pu(III) and Pu(VI). In the presence of H_2O_2, plutonium is quantitatively converted into Pu(III) on UV irradiation and at a higher rate than in the dark.

It is believed[7,8] that, on UV irradiation of any valence form of neptunium — Np(IV), Np(V), and Np(VI) — over a wide range of HNO_3 concentrations (0.1 – 6.0 M), the final form is Np(V). However, it has been noted that other photochemical reactions also occur in solution, for example the oxidation of Np(V) to Np(VI) and the reduction of Np(V) to Np(IV).[8] The quantum yields η of various photochemical reactions of neptunium in nitric acid solutions on irradiation with light at λ = 254 nm have been measured.[8] In the absence of additives in 1.0 M (solution I) and 4.0 M (solution II) of HNO_3, the following values of η were obtained:

Process	η for solutions	
	I	II
Reduction of Np(VI) to Np(V)	0.03	0.003
Oxidation of Np(IV) to Np(V)	0.053	0.017
Oxidation of Np(V) to Np(VI)	0.015	0.022

These reactions proceed also under the influence of light at λ = 300 nm but with much lower yields.

Somewhat different results have been obtained by Galkin et al.,[9] although they employed the same light source as Nemodruk et al.[7] Galkin et al.[9] note that Np(V) accumulates only at $[HNO_3] < 1$ M, whereas at $[HNO_3] = 2$ and 4 M, the concentration of Np(V) increases only during the first 5–10 min of irradiation and then falls as a result of the formation of Np(VI). The authors explained this by the reversibility of the reaction

$$2NpO_2^{2+} + HNO_2 + H_2O \rightleftharpoons 2NpO_2^{+} + NO_3^{-} + 3H^{+}. \quad (1)$$

The passage of air through the irradiated solution leads to the quantitative formation of Np(VI). The difference between the results obtained in the above two studies[7,9] at identical acid concentrations may be associated with the influence of factors which have not been taken into account, for example, micro-impurities inhibiting or catalysing the photochemical reactions.

The introduction of various additives into nitric acid solutions with $[HNO_3] = 0.1-4$ M changes the results of the photochemical experiments. In the presence of urea—a substance which removes NO_2^- ions from the system—it is possible to obtain Np(VI) solutions virtually without an admixture of Np(V).[7,9] However, our data have shown that in weakly acid solutions, even those containing many NO_3^- ions, neptunium(VI) is not formed. Thus, when $NpO_2(ClO_4)_2$ is irradiated in 1×10^{-3} M $HClO_4$ + 1 M $LiNO_3$ in the presence of 0.1 M urea, Np(V) is formed quantitatively. The presence of hydrogen peroxide accelerates the photo-chemical oxidation of Np(IV) to Np(V), but the HNO_3 concentration should not then exceed 1 M,[7] while the introduction of hydrazine leads to the photochemical reduction of Np(V) to Np(IV), but the reaction does not go to completion. Its quantum yield in 4 M HNO_3 was found to be 0.006.[8] In ethanol, neptunium(VI) is reduced photochemically to Np(V) in 0.094 yield $\{[HNO_3] = 4$ M$\}$.[8]

The photochemical reactions of neptunium in nitric acid solutions in the presence of uranyl have been investigated in a number of studies (see, for example, Refs 9–11). The aim of these studies was to investigate the possibility of using the photochemical reactions for the separation of neptunium from uranium and plutonium in technological processes. It was observed that at low concentrations ($\sim$5 g litre^{-1}) uranyl does not influence the photochemical reactions and the dark equilibria involving neptunium. However, at high uranyl concentrations ($\geqslant$100 g litre^{-1}), uranyl is photolysed, which increases the yield of pentavalent neptunium. This effect has been attributed to the sensitising effect of uranyl and the photochemical formation of NO_2^- from NO_3^- [9] and to the stabilisation of Np(V) towards oxidation as a result of the formation of the cation–cation complexes between Np(V) and UO_2^{2+}.[11]

In one of the studies, a photocatalyst, namely Pt/TiO_2, was introduced into a nitric acid solution of neptunium $\{[HNO_3] = 3$ M$\}$ before irradiation.[12] In solutions without added urea, the photocatalyst does not affect the results, i.e. the neptunium is entirely converted, and at the same rate, into Np(V). On the other hand, in the presence of urea the photocatalyst accelerates the transition of neptunium to the hexavalent state to the extent of $\sim$30%, ensuring an almost 100% yield of Np(VI). The authors believe that this acceleration is associated with the occurrence of the reactions on the surface of the photocatalyst (PC).

$$PC \xrightarrow{h\nu} h^{+} + e^{-} \text{ (where } h^{+} = \text{hole)}, \quad (2)$$

Hydrated electrons react with the nitrate ion while the hole participates in the oxidation of the neptunium:

$$NpO_2^{+} + h^{+} \longrightarrow NpO_2^{2+}. \quad (3)$$

b. Perchloric acid solutions

Not only oxidation-reduction reactions of plutonium but also its ability to form polymers have been investigated in perchloric acid solutions exposed to light. In contrast to the behaviour in nitric acid solutions, in $HClO_4$ the final result depends on the initial form of the plutonium. When aerated solutions are irradiated, the Pu(III) is partly converted into Pu(IV). Plutonium(VI) remains unchanged on irradiation.[5] These data were obtained at acid concentrations >0.5 M. Our experiments with dilute $HClO_4$ solutions (10^{-3} M) showed that, on exposure to the UV light from the SVD-120a mercury lamps, Pu(VI) is fully converted into Pu(V).

In the presence of reductants, the photochemical behaviour of plutonium in $HClO_4$ changes. The introduction of H_2O_2 stabilises Pu(III), suppressing fully its oxidation to Pu(IV).[5] Oxalic acid reduces Pu(VI) to Pu(IV), which results in the precipitation of Pu(IV) oxalate.[4] Ethanol reduces photochemically both Pu(VI) to Pu(V) and Pu(IV) to Pu(III).[13] The authors[13] were the first to determine the quantum yields of the photochemical reaction involving plutonium. For the reaction

$$PuO_2^{2+} + C_2H_5OH \xrightarrow{h\nu} PuO_2^{+} + C_2H_5O^{\cdot} + H^{+}, \quad (4)$$

[taking into account the disproportionation of the Pu(V) obtained], η was found to be 0.02, while for the reaction

$$Pu^{4+} + C_2H_5OH \xrightarrow{h\nu} Pu^{3+} + C_2H_5O^{\cdot} + H^{+}, \quad (5)$$

the quantum yield was 0.03.

Irradiation with UV light accelerates sharply the disproportionation of Pu(IV) and a pseudoequilibrium is established, differing appreciably from the dark equilibrium: whereas in the dark or with room illumination, the disproportionation of the 9.9×10^{-3} M Pu(IV) solution in 0.47 M $HClO_4$ continues for tens of hours, on irradiation with UV light only a few hours are required and the degree of conversion of Pu(IV) increases appreciably: the pseudoequilibrium constant for the reaction

$$3\,Pu^{4+} + 2\,H_2O \overset{h\nu}{\rightleftharpoons} 2\,Pu^{3+} + PuO_2^{2+} + 4\,H^{+}, \quad (6)$$

is 0.025, whereas the constant for the dark reaction is 0.0086.[13–15] The process is reversible, i.e. when irradiation stops the system returns to the dark equilibrium.

Under the influence of UV light, the degradation of the polymeric forms of Pu(IV) accelerates severalfold in 0.47 M $HClO_4$.[13–15] Such solutions were prepared by precipitating plutonium hydroxide with its subsequent dissolution in $HClO_4$ at the required concentration. Under these conditions, both freshly prepared solutions and solutions kept for some time undergo photochemical decomposition. Furthermore, in solutions at a lower $HClO_4$ concentration (0.13–0.16 M) the dark decomposition of the polymers does not occur at all and only the photochemical decomposition is observed.

In the first study on the photochemistry of neptunium,[3] it was established that the UV irradiation of perchloric acid solutions of Np(VI) results in the reduction of the latter to Np(V). The concentrations of ^{237}Np was 0.045 M, while the concentration of the acid was 0.22–1.00 M. The quantum yield of this reaction was measured ($\eta = 0.032 \pm 0.011$). It has been suggested that the reductant is the photolysis product of water. Our data also indicate that, on irradiation with UV light in dilute $HClO_4$ (10^{-3} M), Np(VI) is fully reduced to Np(V). According to other data,[16] in sufficiently concentrated solutions of perchloric acid Np(IV) is oxidised to Np(V), while the latter is oxidised to Np(VI). Friedman et al.[17] believe that mainly photochemical reactions involving the oxidation of neptunium take place in perchloric acid solution without additives. They found that, following an increase in the $HClO_4$ concentration from 0.1 to 4.0 M, the quantum yield in the oxidation of Np(IV) to Np(V) falls from 0.02 to 0.0049, while the quantum yield in the oxidation

of Np(V) to Np(VI) increases from 0.004 to 0.010 and further (for light at $\lambda = 254$ nm).

In the presence of ethanol (acetaldehyde or other moderately strong reductants), the Np(VI), Np(V), and Np(IV) ions are capable of being photochemically reduced.[16,17] Prolonged irradiation results in the conversion of all the neptunium to the tetravalent state, a process which may be used for analytical purposes.[16] The quantum yields of the reactions of different neptunium ions with ethanol are within the limits from several thousandths to several hundredths.[17]

The photochemical oxidation of Np(V) in perchloric acid solutions with xenon trioxide has been investigated.[18] The ionic strength of the solution was kept constant at 2 with the aid of sodium perchlorate. The reaction is first order relative to XeO_3 and zero order relative to Np(V). It obeys the equation

$$\frac{d[Np(V)]}{dt} = k_1[XeO_3].$$

Thus the photochemically active substance in this reaction is XeO_3 and the rate of reaction is limited by the rate of its photochemical decomposition. It does not change when the $HClO_4$ concentration is raised from 0.5 to 2.0 M. The constant k_1 depends on the intensity of the irradiation and the spectral composition of the light. Under the experimental conditions, the average value of k_1 obtained was 6.28×10^{-6} s^{-1}. In the absence of light, the reaction is very slow and proceeds via a different mechanism.

c. Hydrochloric acid solutions

When hydrochloric acid solutions of Pu(III) with [HCl] = 0.5–5.5 M are irradiated with UV light in air, Pu(IV) gradually accumulates. Under a CO_2 atmosphere, the process is somewhat slower. The oxidation of Pu(IV) to Pu(VI) is not observed under these conditions[5] (plutonium concentration $\sim 10^{-3}$ g ml^{-1}). A mixture of Pu(IV) and Pu(VI) hardly changes on UV irradiation. In the presence of hydrogen peroxide, Pu(VI) is reduced to Pu(IV) and partly to Pu(III).

Under the influence of UV irradiation, Np(V) in hydrochloric acid solutions is oxidised to Np(VI), while Np(IV) is initially oxidised to Np(V) and then to Np(VI).[19] At [HCl] > 3 M, the oxidation to Np(VI) is quantitative. Deaeration of the solution does not affect the course of the reaction. Our results show that, in both perchloric and nitric acid solutions, the final form of neptunium depends not so much on the concentration of the anion as on the concentration of H^+. Thus in a solution containing 1×10^{-3} M HCl, 1 M KCl, and 1×10^{-3} M Np(VI), Np(VI) is converted quantitatively into Np(V) on UV irradiation.

In the presence of hydrogen peroxide, Np(IV) and Np(VI) are converted into Np(V), while in the presence of ethanol Np(V) and Np(VI) are quantitatively converted into Np(IV), a reaction which can be used for analytical determinations.[19]

d. Sulfuric acid solutions

The behaviour of plutonium in sulfuric acid solutions is similar to its behaviour in hydrochloric acid solutions. Plutonium(III) is converted photochemically into Pu(IV) but not into Pu(VI). Even daylight is sufficient for this purpose. Plutonium(VI) is inert in sulfuric acid solution, but in the presence of ethanol it is converted into Pu(IV).[5]

On the whole, UV irradiation intensifies the reduction of Pu(VI) to Pu(IV) in acid media by reagents such as ethanol, hydrogen peroxide, oxalic acid, ethylenediaminetetraacetic acid (EDTA), and probably others.[5] The possibility of using the above reactions, occurring on UV irradiation, for the monitoring of oxidation–reduction reactions in the processing of irradiated nuclear fuel has been briefly discussed in a review.[20]

Neptunium(IV) in H_2SO_4 solutions at concentrations from 1 to 2 M is oxidised photochemically to Np(V) and further to Np(VI), the oxidation being quantitative after prolonged irradiation. At $[H_2SO_4] > 2$ M, Np(IV) is also detected in the reaction mixture after prolonged irradiation and its amount is greater the higher the acid concentration.[21]

Neptunium(V) is oxidised photochemically to Np(VI); the rate of oxidation increased with increase in the H_2SO_4 concentration. At $[H_2SO_4] = 1-3$ M, the oxidation is quantitative. Nemodruk et al.,[21] who used at PRK-7 lamp, required 20 min to complete the reaction.

The introduction of ethanol, suppresses the oxidation of Np(IV) and Np(V) and at ethanol concentrations of several per cent Np(V) is reduced quantitatively to Np(IV).[21]

Novikov[22] considered the photochemical reactions of neptunium in acid solutions from the standpoint of its isolation and determination.

e. The mechanisms of the photochemical reactions in acid solutions

The mechanisms of the photochemical reactions of plutonium and neptunium in acid solutions were not investigated in the studies examined above. Only certain hypotheses were put forward. For example, perchloric acid does not absorb light from the mercury lamp, so that in this medium the reaction should begin with the excitation of plutonium or neptunium ions. It has been suggested[17] that, after the excitation of the Np(III), Np(IV), or Np(V) ions, they are oxidised by the perchlorate ions. It has also been suggested that plutonium ions are also excited in sulfuric acid, since the oxidation of Pu(III) takes place even under the influence of the usual room illumination, where the photolysis of sulfate ions is impossible. On the other hand, in nitric acid, UV light leads to the photolysis of the NO_3^- ion.[7]

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O^\cdot. \qquad (7)$$

This accounts for the accumulation of the Np(V) ions: oxygen oxidises the lower valence forms of neptunium, while the permanent presence of nitrite in solution leads to the reduction of Np(VI).[7]

According to Nemodruk et al.,[19] the oxidation of Np(IV) and Np(V) in hydrochloric acid is associated with the reactions

$$Cl^- \xrightarrow{h\nu} Cl^\cdot + e_{aq}^-, \qquad (8)$$

$$Np^{4+} + Cl^\cdot + 2H_2O \longrightarrow NpO_2^+ + 4H^+ + Cl^-, \qquad (9)$$

$$NpO_2^+ + Cl^\cdot \xrightarrow{h\nu} NpO_2^{2+} + Cl^-. \qquad (10)$$

These reactions result in the formation of hydrated electrons e_{aq}^-, which react with H^+, affording hydrogen atoms, while the latter recombines at a sufficiently high HCl concentration to form H_2. However, one cannot agree with these hypotheses. According to literature data,[23] the rate constant for the interaction of the H atom with Np(VI) is $(4.0 \pm 0.5) \times 10^8$ litre mol^{-1} s^{-1}, which is ~ 500 times smaller than the rate constant for the recombination of H atoms. However, the stationary concentration of H atoms during the irradiation process is lower by many orders of magnitude than the Np(VI) concentration (especially at the end of the reaction), so that Np(VI) is reduced before the recombination of H atoms. Thus the oxidation state of neptunium does not change. A similar situation is characteristic also of other acids.

An alternative explanation of the photochemical reactions of transuranic elements (TUE) may be, in our view, the formation of excimers (dimers) from the excited and unexcited ions. Two TUE ions then participate simultaneously in the reaction, so that the less reactive molecular products are formed instead of radicals. From this standpoint, the oxidation of Pu(III), for example, in perchloric acid solutions can be represented by the reactions

$$Pu(III) \xrightarrow{h\nu} Pu(III)^*, \quad (11)$$

$$Pu(III)^* + Pu(III) \longrightarrow [Pu(III)^*...Pu(III)], \quad (12)$$

$$[Pu(III)^*...Pu(III)] \longrightarrow 2(Pu^{3+}_{aq} \cdot OH) + H_2, \quad (13)$$

$$Pu^{3+}_{aq} \cdot OH + H^+ \longrightarrow Pu^{4+}_{aq}. \quad (14)$$

A similar mechanism is possible also for the oxidation of Pu(III) and Np(III) in hydrochloric and sulfuric acid solutions and also for the reactions of other oxidation states of plutonium or neptunium in these acids, for example, the reduction of Pu(VI) in dilute perchloric acid:

$$Pu(VI) \xrightarrow{h\nu} Pu(VI)^*, \quad (15)$$

$$Pu(VI)^* + Pu(VI) \longrightarrow [Pu(VI)^*...Pu(VI)], \quad (16)$$

$$[Pu(VI)^*...Pu(VI)] \longrightarrow 2Pu(V) + H_2O_2, \quad (17)$$

$$Pu(VI) + H_2O_2 \longrightarrow Pu(V) + HO_2 + H^+, \quad (18)$$

$$Pu(VI) + HO_2 \longrightarrow Pu(V) + O_2. \quad (19)$$

Bearing in mind that in most cases the preferential formation of higher oxidation states of neptunium is observed with increase in the acid concentration, one may postulate that, at low and high H^+ concentrations, the Np(VI) and Np(V) excimers respectively are formed more effectively, which leads to the respective reduction of Np(VI) or oxidation of Np(V).

In nitric acid, the photolysis of the NO_3^- ion with formation of HNO_2 makes an additional contribution. This is the only medium in which Pu(VI) accumulates photochemically, which is evidently associated with the formation of nitrogen compounds capable of oxidising plutonium to the hexavalent state. In dilute HNO_3 solution, the Pu(VI) reduction reaction predominates, which agrees with the hypothesis of the formation of Pu(VI) [as well as Np(VI) excimers] in dilute solutions. The reaction

$$Pu(VI) + HNO_2 \longrightarrow Pu(V), \quad (20)$$

probably also makes its own contribution.

The acceleration of the disproportionation of Pu(IV) in $HClO_4$ solutions is also associated with the excitation of the plutonium ions themselves. In the presence of reductants, mixed mechanisms are possible where plutonium ions are excited and the additive is photolysed simultaneously.

Thus the studies on the photochemistry of plutonium and neptunium have shown that the reactions in acid media involve the excitation of plutonium and neptunium themselves (similarly to the photochemical reactions of uranyl). However, the mechanisms proposed in the literature do not withstand criticism in our view.

2. The photochemistry of alkaline carbonate solutions

a. The flash photolysis of Pu(VI)

There has been only one communication on the flash photolysis of the ions of transuranic elements.[24] This is the photolysis of the PuO_2^{2+} ions in sodium carbonate solution with $[Na_2CO_3] = (5-30) \times 10^{-3}$ M at pH 12.5. The authors[24] designed and constructed a special apparatus for the flash photolysis of the actinides, which included a glove box and a system for the evacuation of the specimens.[25] During flash photolysis,[24] the reaction is similar to the pulse radiolysis of actinide ions, including their radiolysis in carbonate media (see, for example, Gogolev et al.[26]). The authors were able to demonstrate the possibility of the oxidation of Pu(VI) to Pu(VII) by the CO_3^- radical-ion formed on photolysis of the carbonate ion. However, in the medium investigated, Pu(VII) is very unstable and disappears with a rate constant of $(7.61 \pm 0.09) \times 10^2$ s^{-1}. The constant is independent of the pH in the range from 10 to 12.6, of the initial Pu(VI) concentration, and also of the CO_3^{2-} concentration in the range 5–30 mM. In a CO_3^{2-} free medium Pu(VII) is not formed. These results appear somewhat surprising, since in the pulsed radiolysis of N_2O-saturated neptunium(VI) carbonate solutions Gogolev et al.[26] observed the formation of Np(VII) only in the presence of NaOH at a concentration of the latter not less than 0.01 M.

b. The photochemical oxidation of Np(VI)

In the only study on the photochemistry of neptunium in alkaline carbonate solutions,[27] it was reported that Np(VI) had been oxidised to Np(VII) on irradiation with the light from a mercury lamp in a nitrous oxide-saturated solution containing 0.09 M LiOH and 0.28 M K_2CO_3. It is known[28] that neptunium(VII) can be most readily obtained in an alkaline solution, but the photochemical oxidation of Np(VI) to Np(VII) does not occur in an alkaline solution without additives. Under the influence of UV light, the CO_3^{2-} ion is converted into the radical oxidant CO_3^-, while N_2O captures the hydrated electrons, whereupon yet another oxidant is obtained — the radical-ion O^-:

Thus the reaction does not proceed due to the excitation of neptunium itself but is a result of the photochemical decomposition of CO_3^{2-}. The CO_3^- radical-ion or OH is apparently the direct oxidant of Np(VI).

$$CO_3^{2-} \xrightarrow{h\nu} CO_3^- + e^-_{aq}, \quad (21)$$

$$N_2O + e^-_{aq} \longrightarrow N_2 + O^-, \quad (22)$$

$$O^- + H_2O \rightleftharpoons OH^\cdot + OH^-, \quad (23)$$

$$OH + CO_3^{2-} \longrightarrow OH^- + CO_3^-. \quad (24)$$

3. The photochemistry of extraction systems containing plutonium and neptunium

In the extraction systems containing plutonium and neptunium organic substances are present, so that the reduction of higher oxidation states of plutonium and neptunium becomes probable and exposure to light can also lead to the photolysis of the organic compounds. As early as 1952, it was noted that, during the extraction of Pu(VI) in the water–hexane system, the partition coefficient decreases as a function of time. The authors[29] postulated that this is associated with the photochemical reduction of Pu(VI) to Pu(IV). The photochemical reduction of microconcentrations of Pu(VI) to Pu(IV) was achieved in nitrate–perchlorate–benzene–thenoyltrifluoroacetone (TTA) and chloride–perchlorate–benzene–TTA extraction systems,[14] Pu(VI) not being reduced in the dark. Somewhat different results were obtained for Pu(VI) in a TTA solution in toluene with [TTA] = 0.5 M:[30] it is reduced slowly over several days even in the dark; on illumination under room conditions or on irradiation with visible light, the rate of reduction increased sharply and became proportional to the light intensity. In benzene, Pu(VI) is reduced photochemically more slowly, while in heptane it is reduced faster than in toluene. The Pu(V) form is reduced further to Pu(IV). No relation was observed between the relative permittivity of the solvents and the rate of the photochemical reduction of plutonium. The influence of added tributyl phosphate on the rate of reduction of Pu(VI) in TTA-containing extraction systems was also investigated.[30] Tributyl phosphate intensifies the extraction and slows down the reduction of Pu(VI) and Pu(V). Choppin and Saito[30] showed that the products of the photochemical decomposition of TTA have a reducing capacity and that plutonium is reduced not only during irradiation but also in its absence — in TTA solutions subjected to preliminary irradiation. The authors were unable to isolate the reductant itself. There have been reports also about the photochemical reduction of Pu(IV) to Pu(III).[31,32] The reduction of Pu(IV) takes place in the aqueous phase and its rate increases with increase in the concentration of H^+ ions. The reduction mechanism is apparently similar to the mechanism of the reduction of Pu(VI) and Pu(V).[31]

Methods for the photochemical reduction of Pu(IV) have been patented in the USA for use in industry.[33,34] The photochemically active substance is in both cases not plutonium itself but uranyl. According to a patent,[33] the organic phase obtained in the extraction purification of irradiated nuclear fuel and containing tributyl phosphate, U(VI), and Pu(IV) is treated with tributyl phosphite and H_3PO_4 and is irradiated with UV light. Uranyl is then reduced by tributyl phosphite to U(IV), which reduces Pu(IV) to Pu(III). Tributyl phosphite is oxidised in this process by uranium(VI) to tributyl phosphate, as a result of which the re-extraction of plutonium is achieved without introducing additional substances. Another patent[34] describes the use of hydrazine for the photochemical reduction of uranyl to U(IV), the latter reducing in its turn Pu(IV) to Pu(III). These reactions are also employed to separate plutonium from uranium with the aid of the tributyl phosphate extraction system.

Thus, in the extraction systems considered, the photochemical reactions involve the photolysis of the additive — TTA or uranyl, and not the excitation of the plutonium ion itself.

Like plutonium(VI), neptunium(VI) can also be reduced by the TTA photolysis product in extraction systems.[30] Thus in the dark Np(VI) is stable in 0.5 M TTA solution in toluene, but on illumination under room conditions it is reduced in several hours.

4. The use of photochemistry for the extraction of neptunium from irradiated nuclear fuel

The photochemical formation of neptunium(V) in nitric acid solutions, including those having a composition similar to those employed in the purex process, may serve as the basis for the extraction of neptunium from irradiated nuclear fuel.[35-37] (This process has been patented in the USA.[38]) Thus it becomes possible to separate Np(V) from plutonium(IV) and uranium(VI). The krypton-fluoride excimer laser may be used to increase the irradiation intensity. The authors[35-37] prepared the neptunium solutions for irradiation in nitric acid with $[HNO_3] = 0.75-3$ M in the following way: Np(IV) was obtained by reducing Np(V) with iron sulfamate, whilst Np(VI) was prepared by oxidising Np(V) with potassium permanganate. On irradiating these solutions with light from a krypton-fluoride laser, neptunium(V) is formed even in the presence of an excess of oxidant or reductant.[35,37] This makes it possible to introduce the photochemical method into the usual extraction process, for example into the purex process, without its significant modification. Fukasawa et al.[39] investigated the stability and extraction of the Np(VI) obtained photochemically in nitric acid solution with $[HNO_3] = 3$ M in the presence of urea. They showed that a 30% solution of tributyl phosphate in dodecane may be used to extract the Np(VI) obtained photochemically and that irradiation in the course of prolonged extraction improves the results, compensating for the partial reduction of Np(VI) in the organic phase.

The possibility of separating neptunium and plutonium in nitric acid solutions with the aid of photochemical methods has also been considered by Wada et al.[40] When a hydrazine-containing nitric acid solution with $[HNO_3] = 3$ M is irradiated with the light from a 150 W mercury lamp, Pu(III) is oxidised to Pu(IV) to an extent greater than 95%, while neptunium remains as Np(V). This combination is optimal for the separation of neptunium and plutonium by extraction with tributyl phosphate in dodecane.

5. The photochemical dissolution of plutonium dioxide

A familiar radiochemical problem, the difficulty of dissolving plutonium dioxide, led Panigrahi et al.[41] to try to use UV light for this purpose. The dissolution was carried out in hydrochloric acid in the presence of uranyl and hydrazine with exposure to the light from a mercury lamp. The authors were able to achieve the dissolution of PuO_2 even at room temperature. For example, at $[HCl] = 5$ M, $[UO_2^{2+}] = 0.015$ M, and $[N_2H_4] = 0.2$ M, 95.6% of PuO_2 dissolved in 5 h. At a higher hydrochloric acid concentration, the dissolution is impaired. This effect is attributed to the excitation of the PuO_2 surface and also to the photochemical generation of U(IV). The following reactions were postulated:

$$PuO_2^*(\text{solid}) + U(IV) \longrightarrow Pu(III)_{aq} + U(VI), \quad (25)$$

$$PuO_2^*(\text{solid}) + N_2H_4 \longrightarrow Pu(III)_{aq} + N_2. \quad (26)$$

III. The photochemistry of americium

1. The photochemical reactions of americium in bicarbonate–carbonate solutions

The possibility of photochemical reactions with participation of americium was pointed out as early as 1981.[42] It was noted that americium is probably more difficult to photolyse than neptunium and plutonium. The first communication concerning the use of photochemistry for the changing of the oxidation states of americium appeared in 1992.[43] In this[43] and subsequent studies,[44-47] the photochemical behaviour of americium in bicarbonate–carbonate solutions was investigated. It was observed that, on irradiation with the UV light from a mercury lamp, Am(III) may be oxidised in such solutions to Am(IV). The most complete conversion of Am(III) into Am(IV) (up to ~60%) occurs at pH 9–10 and $[CO_3^{2-}] = 1-2$ M, the quantum yield of the reaction reaching 0.3 under these conditions. The further oxidation of Am(IV) to Am(V) and Am(VI) was not observed. At pH 11 and above, Am(III) is not oxidised at all.[45] The characteristic features of the photochemical oxidation of americium(III) in bicarbonate–carbonate solutions in the presence of specially introduced oxidants have been discussed in a number of studies.[44,46,47]

By employing XeO_3 and $S_2O_8^{2-}$, BrO^-, and BrO_3^- ions, it is possible to oxidise americium photochemically in bicarbonate–carbonate media to both the IV and the VI states. The quantum yields in the photochemical oxidation of Am(III) to Am(IV) in bicarbonate–carbonate solutions at pH ~ 9.9 are 1.07 for $S_2O_8^{2-}$, 0.56 for BrO^-, and 0.20 for BrO_3^-.[45] The possibility of the further oxidation of americium depends mainly on the pH of the solution and the carbonate concentration: at pH 9–10 and $[CO_3^{2-}] > 1$ M, Am(IV) is obtained quantitatively, while at pH 11 and above or at low concentrations of the bicarbonate–carbonate solution the product is Am(VI). The results for the sodium and potassium solutions are similar; the only difference is the possibility of obtaining Am(IV) in concentrated K_2CO_3 solutions (4 M and above), whereas only Am(VI) is formed in Na_2CO_3 soutions. Americium(III) is oxidised photochemically to Am(IV) also in bicarbonate–carbonate solutions saturated with N_2O.[47] Thus it is possible to obtain an Am(IV) solution without the addition of extraneous substances. It is noteworthy that, before the employment of photochemistry, the only method for the preparation of Am(IV) in bicarbonate–carbonate solutions remained the electrochemical procedure.[48]

Am(V) is also photochemically reactive in bicarbonate–carbonate solutions. On irradiation with UV light, it disproportionates partly to Am(IV) and Am(VI), traces of Am(III) appearing under these conditions.[49] Ultimately the solution contains a mixture of different oxidation states of americium, which enter into both photochemical and dark reactions with one another. The quantitative formation of any oxidation states is not therefore observed. The quantum yield of the photochemical disproportionation of Am(V) has been estimated as ~0.003.

2. The mechanisms of the photochemical reactions of americium

As mentioned above, the carbonate ion is a photochemically reactive species affording the CO_3^- radical oxidant and e_{aq}^- on photolysis [see Eqn (21)]. This feature has been used for the oxidation of plutonium(VI)[24] and neptunium(VI).[27] The oxidation potential of the CO_3^- radical-ion enables it to oxidise also americium (III) in bicarbonate–carbonate media:

$$Am(III) + CO_3^- \longrightarrow Am(IV) + CO_3^{2-}. \quad (27)$$

This reaction does indeed take place, but it is effective only in the presence of N_2O, which reacts with e_{aq}^- [see Eqn (22)]. On the other hand, in solutions without N_2O or oxidant ions, the same difficulties arise as in acid solutions of neptunium and plutonium, namely e_{aq}^- should ultimately reduce the Am(IV) formed. For this reason, according to Shilov and Yusov,[50] Am(III) is oxidised in this case too via the formation of excimers. Within the excimer, Am(III) is oxidised by water, from which a H_2 molecule, which is a relatively weakly reactive reductant, is split off and the dimer decomposes into two Am(IV) complex species.

$$Am(III)^* + Am(III) \longrightarrow [Am(III)^*...Am(III)], \quad (28)$$

$$[Am(III)^*...Am(III)] \longrightarrow 2\,Am(IV) + H_2. \quad (29)$$

The incomplete oxidation of Am(III) to Am(IV) indicates the occurrence also of the reverse photochemical reaction — the reduction of Am(IV) to Am(III).[50] One cannot rule out the possibility that it too proceeds via a stage involving the formation of excimers.

If the photochemical oxidation of americium takes place in a solution containing XeO_3 or the oxidant ions $S_2O_8^{2-}$, BrO^-, or BrO_3^-, the reaction proceeds as a result of the photolysis of the latter, for example:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2\,SO_4^-, \quad (30)$$

$$BrO^- \xrightarrow{h\nu} Br^\cdot + O^-, \quad (31)$$

$$Br^\cdot + Br^- \longrightarrow Br_2^-, \quad (32)$$

$$Br_2^- + CO_3^{2-} \longrightarrow Br_2 + CO_3^-, \quad (33)$$

$$SO_4^- + CO_3^{2-} \longrightarrow SO_4^{2-} + CO_3^-. \quad (34)$$

This is followed by reaction (27).

3. The photocatalytic properties of Am(III) in bicarbonate–carbonate solutions

Our latest data indicate that Am(III) can serve as a photocatalyst of the oxidation of Np(IV) and Pu(IV) in bicarbonate–carbonate solutions free from other additives. Americium(III) is not itself oxidised quantitatively to Am(IV) under these conditions, but it does catalyse the oxidation of Np(IV) to Np(VI) and of Pu(IV) to Pu(VI).[51,52] The oxidation of neptunium and plutonium is quantitative. The reaction mechanism involves the intermediate formation of Am(IV) (see above) and the subsequent oxidation of Np(IV) and Np(V) or Pu(IV) and Pu(V). Without americium, the photochemical oxidation of Np(IV) or Pu(IV) is not observed.

IV. Reversible charge transfer in americium(III) and curium(III) luminescence quenching processes

It is known that the luminescence of many variable-valence ions may be quenched by an electron transfer mechanism. For example, the luminescence of uranyl is effectvely quenched by many reductants precisely by such a mechanism. This initiates the actual photochemical reduction of uranyl. Reversible electron transfer leading to quenching of the excited states of the Am(III) and Cm(III) ions is a similar reaction. Among the first four transuranic elements, only the ions of these two elements, especially Cm(III), exhibit luminescence in solutions. As a result of the ability of curium and americium to pass to the +4 oxidation state, the luminescence of Cm(III) and Am(III) may be quenched via charge transfer in those cases where the atom of an element capable of being reduced is present in the vicinity of the excited TUE ion. The Am(III) and Cm(III) complexes of unsaturated polytungstate anions of the type $PW_{11}O_{39}^{7-}$ and $SiW_{11}O_{39}^{8-}$, in which the luminescence of curium is significantly weakened while that of americium is altogether absent, may serve as examples. This is associated with the quenching of the luminescence with formation of the Cm(IV)–W(V) or Am(IV)–W(V) charge-transfer state.

An even more pronounced quenching effect with charge transfer is observed in the complexes of the same elements with polymolybdate anions: here there is no luminescence even in the case of curium. As a consequence of the constant close proximity of the TUE and W or Mo ions, the reverse charge transfer takes place after the removal of excitation and ultimately there is no photochemical oxidation of americium or curium. Nevertheless, one cannot rule out the possibility that it may be possible to select conditions under which such a photochemical reaction could be achieved. We emphasise that a reaction of this kind should in fact follow the excitation of the TUE ion and should not be a result of the oxidation of TUE by the products of the photochemical decomposition of the added oxidant. We shall not consider reversible charge transfer here in detail. The reader is referred to a review[53] on the luminescence of TUE, in which there are a series of references to the original studies where the quenching of the luminescence of Am(III) and Cm(III) as a result of charge transfer was investigated.

V. Conclusion

The above survey of the literature permits a series of conclusions.

Firstly, the photochemical method is fairly promising from the standpoint of its application in radiochemical industries. For this reason, its improvement is being continued, including the application of lasers.

Secondly, despite the outward similarity, a significant difference between photochemistry and radiation chemistry should be noted. Oxidation–reduction processes take place in both cases but in radiolysis (be it by γ-quanta, fast electrons, or heavy particles) energy is adsorbed by the medium and the molecules and ions of the latter are excited. On the other hand, in photolysis, the energy entering the system is absorbed preferentially by the solute. The final molecular products in the radiolysis and photolysis of aqueous solutions may be the same: H_2O, H_2O_2, and H_2. However, in radiolysis they are formed as a result of the processes involving the recombination of e_{aq}^-, H, OH, H^+, and OH^- in tracks, whilst in photolysis they are produced by the interaction of the excited molecules with the medium. Certain excited substances decompose, affording radicals. This resembles the situation which obtains on thermal excitation (for example, the decomposition of the $S^2O_8^{2-}$ ions, H_2O_2 molecules, etc.)

Thirdly, the question of the mechanisms of the photochemical reactions in solutions without added oxidants or reductants remains open. We tend to the view that the mechanisms put forward in the literature cannot lead to the occurrence of the observed reactions and believe that the results can be explained by the formation of excimers. However, this hypothesis requires an experimental test.

Fourthly and finally, the photochemistry of transuranic elements has so far been investigated only in acid and carbonate solutions of neptunium and plutonium, in carbonate solutions of americium, and a little in plutonium-containing extraction systems. Thus the possibilities of the photochemistry of TUE have still not been fully discovered and studies involving other media, including neutral, alkaline, complex-forming, etc., may yield very interesting results.

References

1. E Rabinowitch, R L Belford *Spectroscopy and Photochemistry of Uranyl Compounds* (New York: Macmillan, 1964)
2. H D Burrows, T J Kemp *Chem. Soc. Rev.* **3** 139 (1974)
3. A J Zielen, J C Sullivan, D Cohen *J. Inorg. Nucl. Chem.* 7 378 (1958)
4. A S G Mazumdar, C K Sivaramakrishnan *J. Inorg. Nucl. Chem.* **27** 2423 (1965)
5. P N Palei, A A Nemodruk, E V Bezrogova *Radiokhimiya* **11** 300 (1969)
6. Duan Yunfu, Zhang Xianye, Zhou Zhihong, Hu Jinxin, Lin Shuyen *Khekhuasyue Yui Fanshe Khuasyue* **9** 200 (1987); *Ref. Zh. Khim.* 7 B 4506 (1988)
7. A A Nemodruk, E V Bezrogova, S A Ivanova, Yu P Novikov *Zh. Anal. Khim* **27** 2414 (1972)
8. L M Toth, H A Friedman *Radiochim. Acta* **27** 173 (1980)
9. V Ya Galkin, S V Krutitskii, L N Lazarev, K Ya Mishin, V N Romanovskii *Radiokhimiya* **27** 494 (1985)
10. J F Wogner, in *12emes Journees des Actinides* (Orsay: Institute of Nuclear Physics, 1982) p. 64
11. H A Friedman, L M Toth *J. Inorg. Nucl. Chem.* **43** 1611 (1981)
12. T Fukasawa, F Kawamura *J. Nucl. Sci. Technol.* **28** 27 (1991)
13. J T Bell, H A Friedman *J. Inorg. Nucl. Chem.* **38** 831 (1976)
14. H A Friedman, L M Toth, J T Bell *J. Inorg. Nucl. Chem.* **39** 123 (1977)
15. J T Bell, L M Toth, H A Friedman, in *Plutonium Chemistry* ASC Symposium Ser. No 216 (Eds W T Carnall, G R Choppin) (Washington, DC: Am. Chem. Soc., 1983) p. 263
16. A A Nemodruk, E V Bezrogova, S A Ivanova, Yu P Novikov *Zh. Anal. Khim.* **27** 73 (1972)
17. H A Friedman, L M Toth, M M Osborne *J. Inorg. Nucl. Chem.* **41** 1339 (1979)
18. J M Cleveland, G J Werkema *Nature (London)* **215** 732 (1967)
19. A A Nemodruk, E V Bezrogova, S A Ivanova, Yu P Novikov *Zh. Anal. Khim.* **27** 1270 (1972)
20. J T Bell, L M Toth *Radiochim. Acta* **25** 225 (1978)
21. A A Nemodruk, E V Bezrogova, S A Ivanova, Yu P Novikov *Zh. Anal. Khim.* **28** 379 (1973)
22. Yu P Novikov *J. Radioanal. Nucl. Chem.* **21** 519 (1974)
23. V P Shilov, A K Pikaev *Khim. Vys. Energ.* **16** 468 (1982)
24. R D Saini, P K Bhattacharyya *Radiat. Phys. Chem.* **27** 189 (1986)
25. P K Bhattacharyya, R D Saini *Micro-Second Flash Photolysis Apparatus for Actinide Transient Chemistry* (Bombay: Bhabha Atomic Research Center, 1974)
26. A V Gogolev, V P Shilov, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 20 (1989)
27. V P Shilov, E S Stepanova, N N Krot *Radiokhimiya* **22** 53 (1980)
28. N N Krot, A D Gel'man, M P Mefod'eva, V P Shilov, V F Peretrukhin, V I Spitsyn *Semivalentnoe Sostoyanie Neptuniya, Plutoniya, Ameritsiya* (The Heptavalent State of Neptunium, Plutonium, and Americium) (Moscow: Nauka, 1977)
29. L L Burger, I M Rehn, C M Slansky, USAEC Rep. HW-19949 (1952); quoted after Ref. 13
30. G R Choppin, A Saito *Radiochim. Acta* **35** 149 (1984)
31. S K Nayak, R P R Vasudeva, C K Mathews *Radiochemistry and Radiation Chemistry Symposium, Kanpur, 1985* (Bombay, 1986) p. 492; *Ref. Zh. Khim.* 12 B 4351 (1987)
32. P R Natarayan *Lanthanide Actinide Res.* **2** 139 (1988)
33. US P. 3 620 687; *Ref. Zh. Khim.* 18 L 7P (1972)
34. US P. 4 131 527; *Ref. Zh. Khim.* 16 L 6P (1979)
35. J Enokida, A Suzuki, R Kiyose, in *The Third World Congress on Chemical Engineering, Tokyo, 1986* Vol. 1, p. 700
36. J Enokida, A Suzuki, R Kiyose *Annu. Rep. Eng. Res. Inst. Fac. Eng., Univ. Tokyo* **45** 113 (1986)
37. J Enokida, A Suzuki *J. Nucl. Sci. Technol.* **26** 770 (1989)
38. H A Friedman, L M Toth *Photo-Reduction Process for Separating Neptunium from a TBP Solution Containing Uranium, Plutonium and Neptunium* Appl., 1980; quoted after Ref. 11
39. T Fukasawa, T Ikeda, F Kawamura *Eur. J. Solid State Inorg. Chem. (France)* **28** 73 (1991)
40. Y Woda, T Goibuchi, K Morimoto, H Tomiyasu, in *Final Program and Abstracts of the International Conference 'Actinides'93'* (Los Alamos, NM: Los Alamos National Laboratory, 1993) p. 14
41. B S Panigrahi, T G Srinivasan, Rao P R Vasudeva *Radiochim. Acta* **50** 205 (1990)
42. H A Friedman *Energy Res. Abstracts* **6** 5154 (1981)
43. A B Yusov, V P Shilov *Radiokhimiya* **34** 21 (1992)
44. V P Shilov, A B Yusov *Radiokhimiya* **35** 38 (1993)
45. A B Yusov, V P Shilov *Mendeleev Commun.* 83 (1993)
46. A B Yusov, V P Shilov *Radiokhimiya* **35** 38 (1993)
47. V P Shilov, A B Yusov *Radiokhimiya* **35** 61 (1993)
48. D E Hobart, K Samhoun, J R Peterson *Radiochim. Acta* **31** 139 (1982)
49. A B Yusov, V P Shilov *Khim. Vys. Energ.* **29** (1995) (in the press)
50. V P Shilov, A B Yusov *Khim. Vys. Energ.* **29** 378 (1995)
51. V P Shilov, A B Yusov *Radiokhimiya* **37** (1995) (in the press)
52. V P Shilov, L N Astafurova, A B Yusov *Radiokhimiya* **37** (1995) (in the press)
53. A B Yusov *Radiokhimiya* **35** 3 (1993)