ISSN 1066-3622, Radiochemistry, 2007, Vol. 49, No. 4, pp. 409–414. © Pleiades Publishing, Inc., 2007.
Original Russian Text © O.N. Batuk, S.N. Kalmykov, V.G. Petrov, Yu.A. Teterin, E.V. Zakharova, 2007, published in Radiokhimiya, 2007, Vol. 49, No. 4, pp. 359–363.

Interaction of Neptunium and Technetium with UO_{2+x}

O. N. Batuk[a], S. N. Kalmykov[a], V. G. Petrov[a], Yu. A. Teterin[b], and E. V. Zakharova[c]

[a] *Chemical Faculty, Lomonosov Moscow State University, Moscow, Russia*
[b] *Russian Research Centre Kurchatov Institute, Moscow, Russia*
[c] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

Received March 24, 2007

Abstract—Interaction of uranium dioxide with highly mobile radionuclides ^{237}Np and ^{99}Tc was studied under oxidative conditions. Sorption of these radionuclides at different pH was measured, and the mechanism of redox reaction occurring in the course of their sorption were determined. In alkaline solution, Np(V) is reduced on the UO_{2+x} surface and is sorbed in the form of tetravalent species. In neutral solutions, Np is sorbed in the form of Np(V). This is due to the fact that the stoichiometry of the UO_{2+x} surface corresponds to U_4O_9. In acid solution, U(VI) is leached to form surface UO_2. Although the free surface area of a UO_{2+x} sample is low, the Np distribution coefficients K_d at pH > 6 are relatively high: $\log K_d > 2$. Unlike Np, Tc(VII) is not reduced on the UO_{2+x} surface. However, the sorption capacity of uranium dioxide for Tc(IV) is high.

PACS numbers: 68.43.-h
DOI: 10.1134/S1066362207040157

Large amounts of radioactive waste (RW) have been accumulated at nuclear power plants. In many countries, including Russia, high-level RW is intended to be disposed of in geological formations after partitioning of radionuclides and their immobilization in glass or mineral matrices. A concept of underground repositories of HLRW is based on a multibarrier system restricting or preventing release of radionuclides into the environment. At the same time, depleted uranium (DU) is simultaneously accumulated in production of enriched uranium fuel for atomic power plants (APPs). Depleted uranium is stored in the form of highly toxic UF_6 in surface repositories. At the beginning of the XXI century, the world's resources of DU were estimated [1, 2] to be 1 million tons. Depleted uranium is used for production of mixed oxide (MOX) fuel and fabrication of containers for RW transportation [3]. In this study we examined the possibility of using DU in the form of uranium dioxide as an engineered barrier in repositories of solidified HLW and spent nuclear fuel (SNF). This approach allows safe storage of HLW for a long time and, on the other hand, utilization of DU. To estimate the possibility of using DU at repositories of HLW and SNF, its sorption properties with respect to artificial radionuclides should be studied. Radionuclides ^{99}Tc and ^{237}Np are toxic and environmentally hazardous since they are long-lived and are converted under oxidative conditions into highly mobile water-soluble species. Pertechnetate anion is sorbed only on positively charged, i.e., protonated surface (low pH for most of metal oxides and hydroxides). Neptunyl(V) cation has a low effective charge of +2.2 [4] and hence is poorly sorbed on minerals.

The aim of this study was to examine sorption of Tc and Np on uranium dioxide under oxidative conditions and the influence of redox reactions of these radionuclides on their sorption.

EXPERIMENTAL

Determination of the Composition of a UO_{2+x} Sample

We studied sorption properties of commercial UO_{2+x} (TVEL Joint-Stock Company, Elektrostal, Russia). UO_{2+x} was prepared by heat treatment of UF_6 in an oxygen flow and subsequent treatment of the product in an Ar/H_2 mixture at 650°C. The U/O ratio in the bulk of the UO_{2+x} sample was determined by X-ray phase analysis (XPA) using the linear dependence of the lattice parameter a on x in the range from 0 (UO_2) to 0.25 (U_4O_9) [5]. ThO_2 prepared by calcinations of thorium oxalate at 500°C in an oxygen flow [6] was used as a UO_2 analog stable to oxidation.

The phase composition of UO_{2+x} and ThO_2 was determined by XPA at room temperature in a threeframe focusing monochromator camera (CuK_{α_1} radiation, effective diameter 228 mm). A Johansson bent quartz single crystal was used as monochromator. Germanium was added to the sample, and its lines were used as an internal reference [a = 5.6574(9) Å]. The X-ray patterns were measured on an IZA-2 comparator with an accuracy of ±0.002 mm; the intensity was visually estimated by a 100-point scale [7]. The X-ray pattern was indexed and the lattice parameters were refined using the Powder2 software.

The surface stoichiometry of a UO_{2+x} sample was determined by X-ray photoelectron spectroscopy (XPS) on an MK II VG Scientific electrostatic spectrometer (AlK_α radiation, $h\nu$ = 1486.6 eV) in a high vacuum (1.3×10^{-7} Pa) at room temperature. The resolution of the spectrometer, determined by the halfwidth of the $Au4f_{7/2}$ line, was 1.2 eV. The binding energies of U and O electrons were determined relative to the C1s line (285.0 eV). Carbon sorbed in small amount on the sample surface during drying in a vacuum was used to calibrate the line energy. The half-width of the lines was measured relative to that of the C1s line taken as 1.3 eV. The determination error of binding energies and line width was 0.1 eV. The relative intensity of the line was determined with an accuracy of 10%.

Samples of UO_{2+x} and ThO_2 were also characterized by nitrogen sorption at 77 K. The free surface area and porosity of the samples were calculated by the BET equation. The particle size and the surface morphology were determined by dynamic light scattering and scanning electron microscopy, respectively.

We found that the free surface area of UO_{2+x} sample was low (1.5 $m^2\,g^{-1}$) and its structure was nonporous. As determined by XPA, the stoichiometry of the sample is close to UO_2 [a = 5.4638 Å]; the sample surface is partially oxidized (XPS data) and its composition is close to $UO_{2.25}$ (U_4O_9). The average particle size of the sample is 1.5 μm. The properties of crystalline ThO_2 sample are close to those of UO_{2+x}: low specific surface area (1 $m^2\,g^{-1}$), nonporous structure, average particle size 3.5 μm, lattice parameter a 5.5997(8) Å (calculated from X-ray diffraction patterns).

Sorption Experiments

Sorption of Np(V), Th(IV) and Tc(VII, IV) was performed from deionized water on UO_{2+x} and ThO_2 in plastic vessels to prevent sorption of the radionuclides on the walls. To exclude the influence of atmospheric CO_2 on the sorption, the experiments were performed in a hermetically sealed box filled with N_2. The total radionuclide concentration in all the sorption experiments was 1×10^{-10} M; the solid-to-liquid ratio was 2.5 g l^{-1}. The solid phase was separated by microfiltration on filters with 170-nm pores. To determine a time required to attain the sorption equilibrium, aliquots of the examined suspensions were taken at regular intervals and the concentration of the radionuclides in the filtrate was measured. The sorption equilibrium with all the examined radionuclides was attained within a time shorter than 24 h. Once the sorption equilibrium had been attained, the solid phase was separated and the U/O ratio on the surface of the samples kept at different pH was determined by XPS.

Technetium(IV) was prepared by reduction of Tc(VII) with a Sn(II) solution in 1 M HCl [8]. The oxidation state of the examined elements in the working solutions was determined by liquid extraction. Neptunium(IV) was extracted with 0.5 M solution of 1-(2-thenoyl)-3,3,3-trifluoroacetone in toluene [9]. Technetium(VII) was extracted with 1×10^{-3} M solution of methyltrioctylammonium bromide in toluene. Under these conditions, Tc(IV) is retained in the aqueous phase [10].

To increase the sensitivity of radionuclide detection, we used mixtures of ^{99m}Tc ($T_{1/2}$ = 6.01 h)/^{99}Tc ($T_{1/2} = 2.11 \times 10^5$ years) and ^{239}Np ($T_{1/2}$ = 2.36 days)/^{237}Np ($T_{1/2} = 2.14 \times 10^6$ years). A solution with required $^{99}TcO_4^-$ concentration was prepared by dissolution of metallic Tc in concentrated HNO_3 on heating. ^{99m}Tc was isolated form its mixture with ^{99}Mo by elution of a technetium generator (Institute of Energy Physics, Obninsk). Nitric acid solution of $^{237}NpO_2^+$ was obtained from the Research Institute of Atomic Reactors (Dimitrovgrad). ^{239}Np was isolated from its equilibrium mixture with ^{243}Am by extraction with trioctylamine [11]. γ-Ray radiation of ^{99m}Tc ($E_{\gamma\,max}$ = 140.5 keV, p = 89%) and ^{239}Np ($E_{\gamma\,max}$ = 106.1 keV, p = 27%) was registered using an ultrapure germanium semiconducting detector (GC-3020, Canberra).

We used Th(IV) to simulate the sorption behavior of Np(IV). For this purpose we used ^{234}Th ($T_{1/2}$ = 24.1 days) and ^{232}Th ($T_{1/2} = 1.41 \times 10^{10}$ years). ^{234}Th was recovered from its equilibrium mixture with ^{238}U on a column packed with KU-2 cation exchanger by the procedure described in [12].

RESULTS AND DISCUSSION

Np(V) Sorption

The pH dependence of Np(V) sorption on UO_{2+x} is shown in Fig. 1a. The shape of this dependence is atypical for cation sorption which is probably due to redox reactions in the solution or on the UO_{2+x} surface. The sorption is high in acid solution (pH 2–3.5), decreases to the minimal values in the pH range 3.5–7, and then increases at pH > 7. In acid solutions, Np(V) is probably reduced by the UO_{2+x} surface to Np(IV) which is sorbed. It is known [13, 14] that sorption of tetravalent actinides substantially differs from that of pentavalent actinides. The reactivity and sorption of a cation are determined by its charge which is equal to +4 and +2.2 for An(IV) and An(V), respectively [4]. The oxidation state of Th(IV) does not change in the whole pH range. The fact that Th(IV) is quantitatively sorbed at pH ≥ 2 indirectly confirm the assumption on sorption of Np(IV) species on UO_{2+x} at pH < 3.5 (Fig. 1a). The results of liquid extraction show that only 6% of Np being in the contact with UO_{2+x} is in the tetravalent form at pH 3.0. These results are consistent with thermodynamic calculations (Fig. 2) which also show the presence of pentavalent Np in the solution under conditions of the sorption experiment. The Pourbaix diagram shown in Fig. 2 was constructed using the thermodynamic data for Np recommended by NEA (Nuclear Energy Agency) [15, 16] and the thermodynamic data for U, taken from [17]. We suggest that, in acid solutions, Np(V) is reduced to Np(IV) in the electrical double layer of UO_{2+x} and is stable in the solution. Under these conditions, U(VI) is leached and the surface stoichiometry of UO_{2+x} kept in acid solutions becomes close to UO_2. As the pH increases, the U(VI) solubility decreases [18] and the U(VI)/U(IV) ratio on the sample surface increases.

The change in surface stoichiometry of UO_{2+x} as influenced by pH of the solution was confirmed by XPS. The O2*s*, U6*p*, and U5*f* spectra of a UO_{2+x} sample kept in solutions with pH 2.54 and 7.04 are shown in Fig. 3. The XPS spectrum of U5*f* electrons negligibly involved in chemical bonding contains a relatively sharp band on the low-energy side of the valence band (Figs. 3c, 3d). The intensity of this band determined by the contribution of the U5*f* electrons of U(IV) can be used to separate spectral states of U(IV), U(V), and U(VI) in the U4*f* spectrum (Figs. 3a, 3b). The oxygen coefficient of uranium oxides can be determined from the ratio of the intensities of bands corresponding to different oxidation states of U [19, 20]. The oxygen coefficients of UO_{2+x} samples determined by XPS are presented below. The stoichiometry of uranium dioxide kept at pH 7.04 is close to U_4O_9. The surface stoichiometry of the samples approaches UO_2 with decreasing pH of the solution.

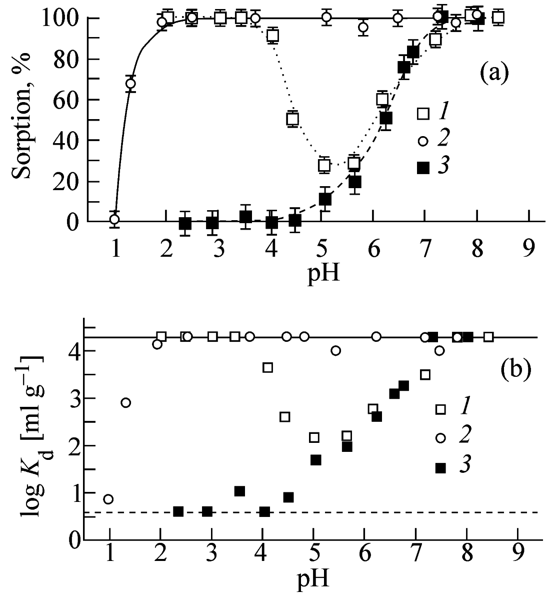

Fig. 1. (a) Fraction of (*1*) Np(V) and (*2*) Th(IV) sorbed on UO_{2+x} and (*3*) fraction of Np(V) sorbed on ThO_2, and (b) logarithm of distribution coefficients of these radionuclides, as functions of pH.

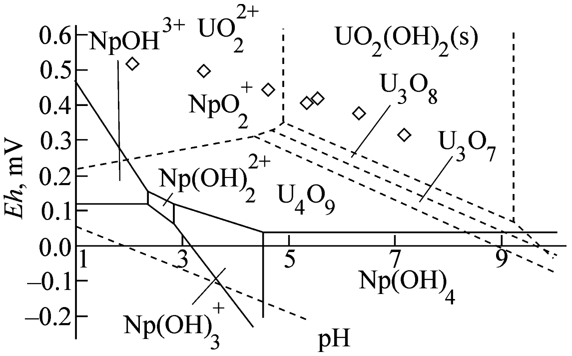

Fig. 2. Pourbaix diagram for Np (continuous line) and U [17] (dashed line). The *Eh* potential is given vs. standard hydrogen electrode. Points denote the conditions of sorption experiments.

pH of solution	Stoichiometry of UO_{2+x} surface
2.54	$UO_{2.14}$
4.35	$UO_{2.17}$
7.04	$UO_{2.22}$

At pH ~4 the U solubility decreases [21] and the reduction potential of the UO_{2+x} surface is insufficient to reduce Np(V) to Np(IV). As a result,

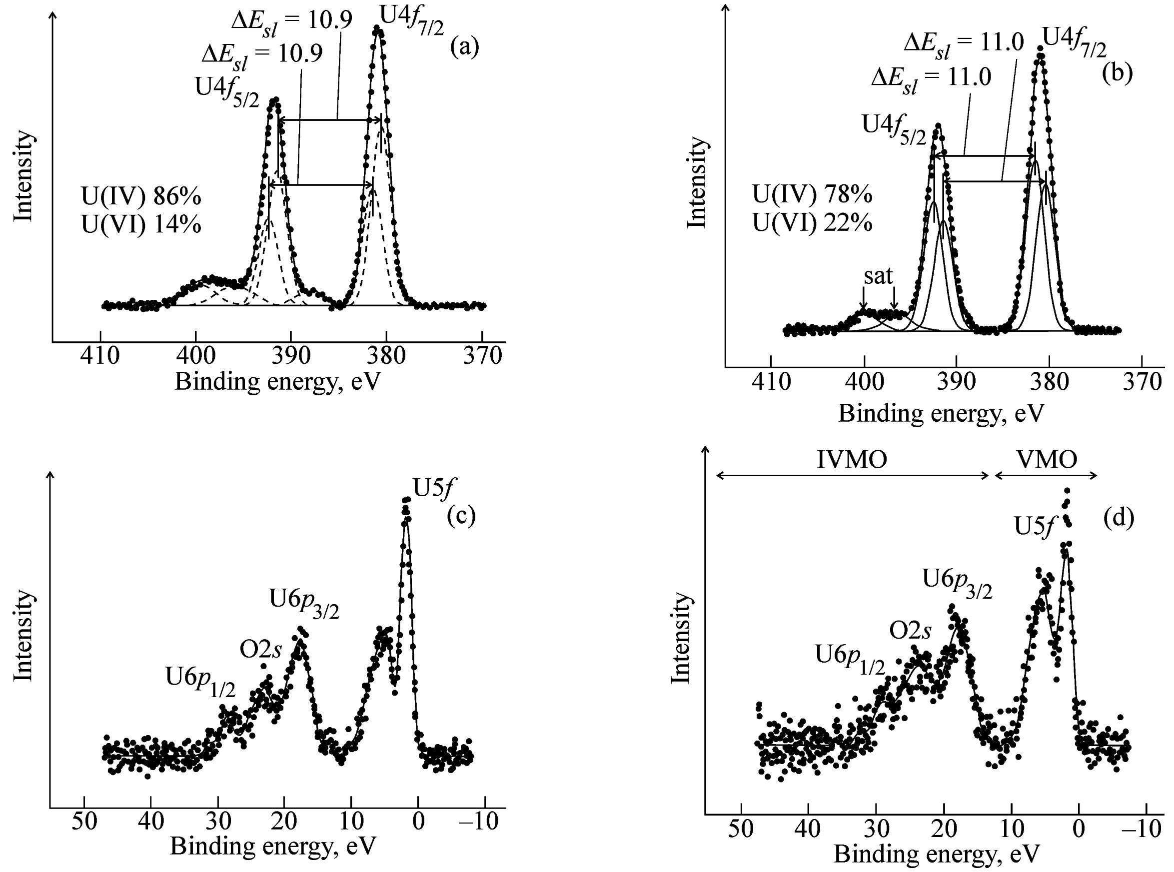

Fig. 3. X-ray photoelectron spectra of (a, b) U4*f* electrons and (c, d) valence electrons of UO_{2+x} samples kept at pH (a, c) 2.54 and (b, d) 7.04. The bands were resolved in the approximation that the samples contain only U(IV) and U(VI).

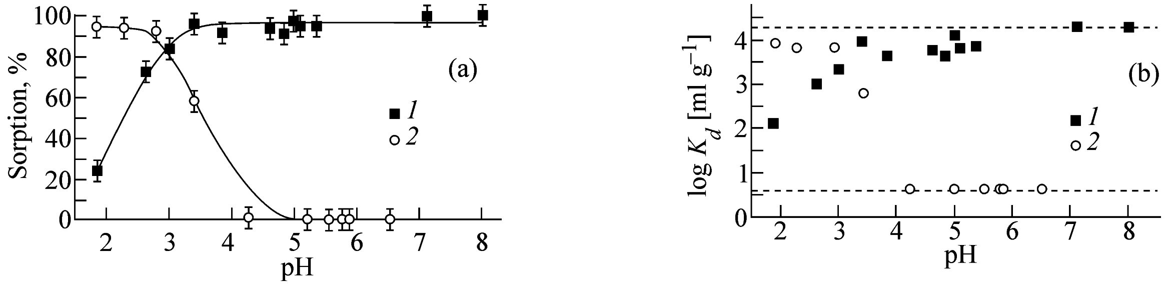

Fig. 4. (a) Fraction of (*1*) Tc(IV) and (*2*) Tc(VII) sorbed on UO_{2+x} and (b) logarithm of distribution coefficients of these species as functions of pH.

the total Np sorption decreases. At pH > 5.5 the Np sorption increases and is probably caused by formation of Np(V) hydroxo complexes on the UO_{2+x} surface. The portion of the pH dependence of the Np sorption (Fig. 1a) at pH > 5.5 can be described by an S-shaped curve typical for cation sorption via formation of complexes with surface hydroxy groups of metal oxides or hydroxides. The assumption that in this pH range Np(V) is sorbed to form complexes with the surface hydroxy groups is confirmed by the shape of the curve of Np(V) sorption on ThO_2 (Fig. 1a) as an oxidation-resistant analog of UO_2.

Although the free surface energy of the UO_{2+x} sample is low, the distribution coefficients K_d of Np at pH > 6 are relatively high ($-\log K_d > 2$) (Fig. 1b). For comparison, $\log K_d$ for sorption of quartz, microcline, and kaolinite is 1.3, 1.5, and 1.0, respectively [22].

Sorption of Tc(VII) and Tc(IV)

The pH dependence of Tc(VII) sorption on UO_{2+x} is shown in Fig. 4a. High Tc(VII) sorption at low pH is due to interation of the TcO_4^- anion with the UO_{2+x}

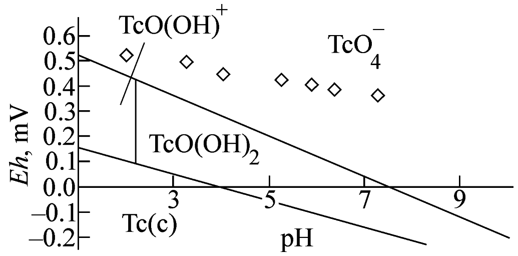

Fig. 5. Pourbaix diagram for Tc. The *Eh* potential is given vs. a standard hydrogen electrode. Points denote the conditions of sorption experiments.

surface protonated in this pH range. At pH 3, the sorption sharply decreases, and at pH > 4.5 TcO_4^- does not interact with the UO_{2+x} surface. Although the potential of the U(IV)/U(VI) couple [23, 24] is sufficient for reduction of Tc(VII) to Tc(IV), Tc(VII) in contrast to Np probably is not reduced in the examined system. However, we deal with heterogeneous reaction on the UO_{2+x} surface. In this case, the contact of Tc(VII) with the U(IV) surface is hindered by electrostatic repulsion between TcO_4^- and the UO_{2+x} surface negatively charged in neutral and alklaine solutions. This conclusion is indirectly confirmed by the shape of the pH dependence of Tc(IV) sorption, which is typical for sorption of cations on metal oxides and hydroxides (Fig. 4a). Although *Eh* potentials of the solution corresponding to the range of TcO_4^- stability in experiments on Tc(IV) sorption are relatively high (Fig. 5), Tc(IV) is rapidly sorbed and is stabilized in the form of tetravalent species. Probably, Tc(IV) oxidation in the solution is slower than its sorption on UO_{2+x}.

The pH dependence of $\log K_d$ of Tc(IV) between the solution and UO_{2+x} is shown in Fig. 4b. As in the case of Np, the sorption capacity of UO_{2+x} for Tc(IV) is high.

Thus, UO_{2+x} is an efficient sorbent of Np(V) from neutral solutions under oxidative conditions typical for underground waters. However, not only oxidative but also reducing conditions can be produced in underground repositories of HLW and SNF owing to corrosion of metal container [25, 26]. Under these conditions, Tc will exist in the tetravalent state. UO_{2+x} efficiently sorbs Np(IV) and Tc(IV) form neutral solutions. Even under the oxidative conditions, Tc(IV) is sorbed on the UO_{2+x} surface without oxidation, i.e., Tc sorption is faster than its oxidation. The results of this study show that uranium dioxide can be used as sorbent to prevent migration of the most environmentally hazardous radionuclides, Np and Tc.

ACKNOWLEDGMENTS

This study was financially supported by International Science and Technology Center (project no. 2694) and the Russian Foundation for Basic Research (project no. 05-03-33028a).

REFERENCES

1. Hamilton, E.I., *Sci. Tot. Environ.*, 2001, vol. 281, pp. 5–21.
2. Haire, M. and Croff, A.G., Deplated Uranium in Repositories, *Report ORNL/CP-95280*, 1998.
3. Management of Depleted Uranium, *A Joint Report by the OECD Neclear Energy Agency and Int. Atomic Energy Agency*, OECD, 2001.
4. Choppin, G.R. and Rao, L.F., *Radiochim. Acta*, 1984, vol. 37, pp. 143–146.
5. Voronov, N.M, Sofronova, R.M., and Voitekhova, E.A., *Vysokotemperaturnaya khimiya okislov urana i ikh soedinenii* (High-Temperature Chemistry of Uranium Oxides and Their Compounds), Moscow: Atomizdat, 1971.
6. Matyukha, V.A. and Matyukha, S.V., *Oksalaty redkozemel'nykh elementov i aktinidov* (Oxalates of Rare-Earth Elements and Actinides), Moscow: Energoatomizdat, 2004, 2nd ed.
7. Puchsharovskii, D.Yu., *Rentgenografiya mineralov* (X-ray Diffraction Analysis of Minerals), Moscow: Geoinformmark, 2000.
8. Spitsyn, V.I. and Kuzina, A.F., *Tekhnetsii* (Technetium), Moscow: Nauka, 1981.
9. Choppin, G.R. and Bond, A.Kh., *Zh. Anal. Khim.*, 1996, vol. 12, pp. 1240–1251.
10. Dzhigirkhanov, M.S.-A., Abramov, A.A., and Iofa, B.Z., *Radiokhimiya*, 2002, vol. 44, no. 1, pp. 14–17.
11. Mikhailov, V.A., *Analiticheskaya khimiya neptuniya* (Analytical Chemistry of Neptunium), Moscow: Nauka, 1971.
12. *Rukovodstvo k prakticheskim zanyatiyam po radiokhimii* (Manual to Practical Course of Radiochemistry), Nesmeyanov, A.N., Ed., Moscow: Khimiya, 1980.
13. Khasanova, A.B., Shcherbina, N.S., Kalmykov, S.N., et al., *Radiokhimiya*, 2007, vol. 49, no. 4, pp. 367–372.
14. Sancluz, A.L., Murray, J.W., Sibley, T.H., et al., *Geochim. Cosmochim. Acta*, 1985, vol. 49, pp. 229–230.
15. Lemire, R.J., Fuger, J., Spahiu, K., et al., *Chemical Thermodynamics of Neptunium and Plutonium*, Amsterdam: Elsevier, 2001.
16. Guillaumont, R., Fanghanel, Th., Neck, V., et al.

Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium, Amsterdam: Elsevier, 2003.

17. Vitorge, P. and Capdevila, H., *Radiochim. Acta*, 2003, vol. 91, pp. 623–631.
18. Batuk, O.N., Kalmykov, St.N., Zakharova, E.V., et al., *J. Nucl. Mater.*, 2006, vol. 352, pp. 241–245.
19. Teterin, Yu.A., Kulakov, V.M., Baev, A.S., et al., *Phys. Chem. Miner.*, 1981, vol. 7, pp. 151–158.
20. Teterin, Yu.A. and Teterin, A.Yu., *Usp. Khim.*, 2004, vol. 73, no. 6, pp. 514–580.
21. Neck, V. and Kim, J.I., *Radiochim. Acta*, 2001, vol. 89, pp. 1–9.
22. Allard, B., Beall, G.W., and Krajewski, T., *Nucl. Technol.*, 1980, vol. 49, pp. 474–480.
23. Rard, J.A., Rand, M.H., Angeregg, G., et al., *Chemical Thermodynamics of Technetium*, Amsterdam: Elsevier, 1999.
24. Grenthe, I., Fuger, J., Kenings, R.J.M., et al., *Chemical Thermodynamics of Uranium*, Amsterdam: Elsevier, 1992.
25. Eriksson, J. and Werme L., Copper Canister with Cast Inner Components, *SKB TR 95-02*, 1995.
26. Cui, D. and Spahiu, K., *Radiochim. Acta*, 2002, vol. 90, pp. 623–628.