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Physicochemical Behavior of Uranium and Technetium in Some New Stages of the Nuclear Fuel Cycle

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Abstract—Recently published results of the cooperative studies executed by the Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences (IPCE RAS), Research Center Vallée du Rhone (CEA, France), Institute of Nuclear Physics Orsay and University Bordeaux I [Centre Nationale de Recherches Scientifiques (CNRS), France] are reviewed. The review includes data obtained for the first time on the electrochemical properties and anodic dissolution of uranium monocarbide considered among possible bases of the fuel for the reactors of the IVth generation. The results of the investigations in the field of the synthesis of tetraalkyl ammonium pertechnetates, their physicochemical properties and thermal decomposition with formation of Tc metal and Tc monocarbide are summarized. The electrochemical reactions with participation of Tc ions in various oxidation states and their application in the nuclear fuel cycle are described. The behavior of technetium in natural waters near the locations of the radwastes long-term storage and in the areas surrounding nuclear power plants in RF and France was studied.

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INTRODUCTION

The Russian-French scientific collaboration in radiochemistry is of long date; it has started since A.H. Becquerel, Pierre and Marie Curie, D.I. Mendellev, and V.I. Vernadskii. At present this collaboration involves Universities of both States, Russian Academy of Sciences and Centre Nationale de Recherches Scientifiques (CNRS), France, Rosatom and Commission of Atomic Energy (France) [1]. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences takes active part in collaboration on a series of problems in keeping with the existing agreements between the Institute and Commission of Atomic Energy (France) (Research Center Marcoule, Vallée du Rhone, Institute of Nuclear Physics Orsay, and University Bordeaux I). Here a review is presented of joint research carried out by the above research institutions in recent years in the field of development of the nuclear fuel cycle concerning the reprocessing of the irradiated fuel of the atomic power plants.

At present uranium dioxide is the main fuel for atomic power engineering, but both in France and in Russia as a promising fuel of the IVth generation *triso*-fuel is regarded based on UO_2, UC, or UN [2, 3]. This fact poses a problem for radiochemists with respect to development of scientific base of the reprocessing of the used *triso*-fuel [4] based on uranium carbide; separation of plutonium and “small actinides” from the fission products of high β, γ-activity; subsequent refabrication of the *triso*-fuel based on (U, Pu)C, and neutralization of wastes. First stage of processing is the dissolution of the carbide fuel in nitric acid. The study of this process, including the identification of the organic products of dissolution, was one of the problems of collaboration of IPCE with the Institute of

Nuclear Physics Orsay and the Research Center Marcoule. The other part of the collaboration consists in the study of chemistry of technetium, the radioactive element whose existence was predicted by D.I. Mendeleev under the name of eca-manganese. It was the first chemical element artificially produced in 1937. The short-lived isotope ^{99m}Tc ($T_{1/2}$ = 6.02 h) is nowadays in all developed countries the most desired among the radionuclides for nuclear medicine in therapy and diagnostics of a number of diseases [5]. The most abundant and problematic for processing is the long-lived technetium isotope ^{99}Tc ($T_{1/2} = 2.14 \times 10^5$ years). It forms in relatively high yield (~6%) at fission of uranium and plutonium nuclei, and it accumulates in the used fuel of atomic power plants in amount of 1 kg per 1 ton of the fuel [6]. The long-lived ^{99}Tc is among the most dangerous components of the highly active wastes. Its compounds of oxidation state (+7) are volatile and soluble in natural water, and they are weakly sorbed by rocks and minerals.

In reprocessing of the used fuel the technetium is not separated from the overall flow of highly active waste. Its immobilization is performed together with the other highly active radionuclides (^{137}Cs, ^{90}Sr, ^{237}Np, $^{241, 243}$Am, ^{244}Cm) with subsequent storage of the glass in cans in specially designed deep underground depositories. However here also technetium as well as the other long-lived nuclides is environmentally dangerous for hundred thousands of years due to possible leaching with natural water followed by migration. The efficient procedure of technetium neutralization is not the commonly used immobilization in glass, but the currently under development transmutation or nuclear burning in reactors and accelerators. The recent research carried out in IPCE, Research Institute of Atomic Reactors (Dmitrovgrad), and Combine "Mayak" demonstrated that the transmutation simultaneously would become a method of production from technetium of artificial stable ruthenium comparable in amount with mining ruthenium from ores and thus spare the small natural source of this precious metal [7–9]. According to the transmutation procedure technetium is first isolated from wastes and recovered into metal or other materials fit for irradiation in the reactor. Therefore the study of technetium behavior in process solutions and wastes, preparation of its compounds suitable for isolation from solutions and irradiation in reactors, investigation of its migration in natural water are urgent problems, and they were selected for collaboration of IPCE with the above cited French institutions.

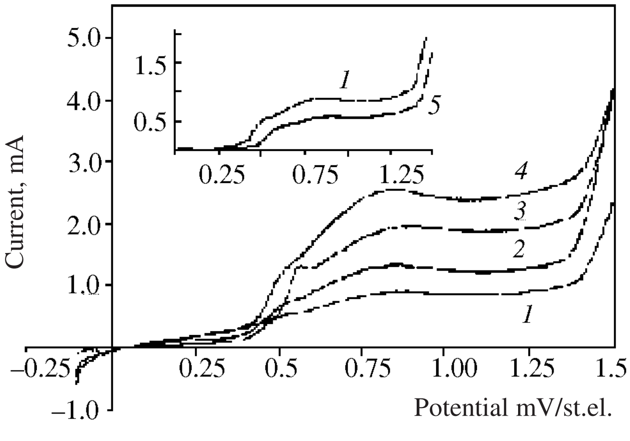

Fig. 1. Cyclic voltammetry of UC in solutions of HNO_3 and $HClO_4$ [11]: 22°C, $S = 0.4$ cm^2; $V = 10$ ml; dE/dt = 10 mV s^{-1}; (*1*) 0.1 mol l^{-1} HNO_3, (*2*) 0.5 mol l^{-1} HNO_3, (*3*) 1.0 mol l^{-1} HNO_3, (*4*) 2.0 mol l^{-1} HNO_3; (*5*) 0.1 mol l^{-1} $HClO_4$.

Investigation of Physicochemical Characteristics of Uranium Carbide

Preparation and Mechanical Properties

Uranium monocarbide (UC) was produced by arc melting of a mixture of uranium turnings and graphite using a tungsten electrode and a copper bottom cooled with water [10]. UC ingots were mechanically powdered in air to the particle size 50–100 mm. The X-ray phase analysis found in the samples a single phase, face-centered cubic UC (a = 4.961 ± 0.005 Å) [11]. The scanning electron microscopy revealed the presence on the carbide powder surface uranium oxycarbide UC_xO_y ($x < 1$, $y < 2$) [12, 13]. By comparison of the edges of the X-ray absorption spectra (XANES) of the uranium metal powder (100–150 mm) and UC we discovered for the first time that in the uranium monocarbide the uranium is present in the oxidation state $0 < x < 3$ [14].

Electrochemical Properties of UC in Acid Solutions

In the study of electrochemical oxidation of uranium carbide by means of linear voltammetry it was shown for the first time [11] that at the anodic dissolution of UC on an electrode in acid solutions (0.1–4.0 mol l^{-1} $HClO_4$; 0.5–6.0 mol l^{-1} HNO_3) the rate of UC oxidation changed stepwise as a function of the applied potential (Fig. 1) from slow ($E < 400$ mV/st.el.)

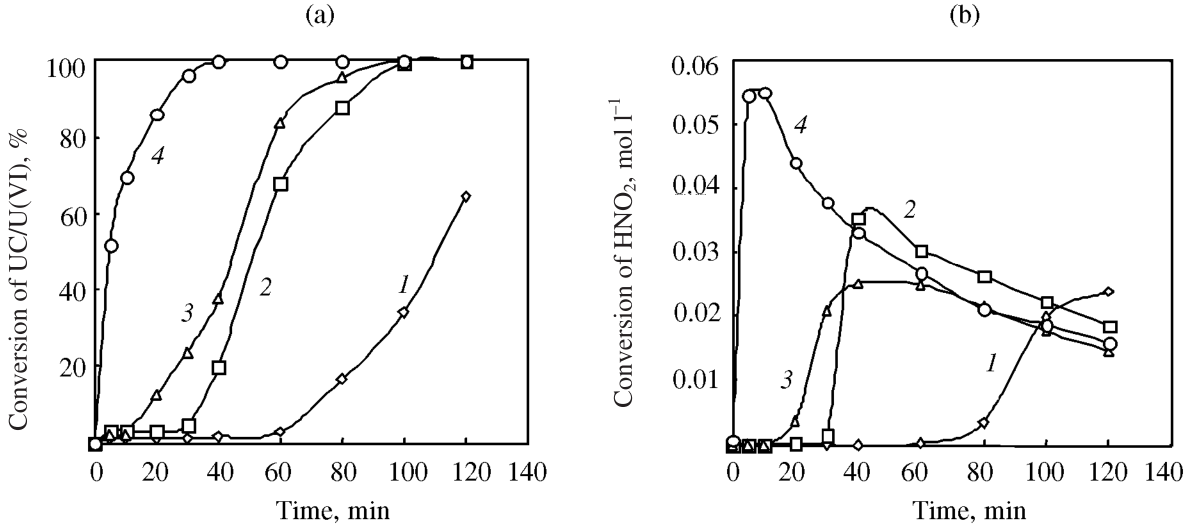

Fig. 2. Conversion of uranium carbide into U(VI) (a) and variation of HNO_2 concentration (b) in the course of UC dissolution in nitric acid [12]. HNO_3 concentration: (*1*) 2.0 M, (*2*) 3.0 M, (*3*) 4.0 M, (*4*) 6.0 M. Conditions of dissolution: 22°C, S/L = 1.1–2.0 g l^{-1}, $V = 10$ ml, stirring rate 100 $\min^{-1}$.

to moderate ($400 < E < 1300$ mV/st.el.) to large ($E > 1300$ mV/st.el.).

At slow UC oxidation apparently formed uranium oxycarbide ($UC_{1-x}O_y$) and products of carbon oxidation sparingly soluble in acid solutions. The moderate rate of electrochemical oxidation of UC corresponds to a stationary state of the electrode surface when simultaneously forms a protective $UC_{1-x}O_y$ film and proceeds its deeper oxidation to products soluble in acid solutions, those containing U(VI) and carbon (CO_2). At potentials $E > 1300$ mV/st.el. the oxidation rate of the protective film is likely far greater than its rate of formation resulting in efficient dissolution of UC. The increase in the acid concentration in the electrolyte results in a higher current density that corresponds to the plateau of the moderate rate of UC dissolution in $HClO_4$ and HNO_3. This may be caused by reduced resistance (thickness) of the protective film on the electrode surface at growing acidity. In HNO_3 solutions the absolute values of the current at the plateau of the moderate UC dissolution rate were higher than the respective values in the $HClO_4$ solutions of the corresponding concentration. This difference may be due to the chemical oxidation of UC and of primary products of its electrochemical oxidation with NO_3^- ions (1) and with nitrous acid formed along reaction (1) and by electrochemical reduction of NO_3^- ions at $E < 700$ mV/st.el. by reaction (3).

$$UC(UC_xO_y) + 5NO_3^- + 7H^+ \rightarrow UO_2^{2+} + 5HNO_2 + CO_2(HOC)^* + H_2O, \quad (1)$$

$$UC(UC_xO_y) + 10HNO_2 + 2H^+ \rightarrow UO_2^{2+} + 10NO + CO_2(HOC)^* + 6H_2O, \quad (2)$$

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O, \quad (3)$$

where * are unidentified organic compounds.

Reactions (1) and (2) result in the formation of a layer of poorly soluble products of UC oxidation with a lesser ohmic resistance than the products arising in $HClO_4$ solutions of the corresponding concentration. An efficient dissolution of UC is possible in water solutions of an oxidative potential $E_h > 400$ mV/st.el.

Oxidation of UC with Nitrous Acid in HNO_3 and $HClO_4$ Solutions

In reaction of UC with nitric acid of a concentration below 4.0 mol l^{-1} ($E_h > 650$ mV/st.el.) the UC dissolution was preceded by an inductive period whose time decreased with the growing HNO_3 concentration (Fig. 2) [12]. Within the inductive period grew the concentration of HNO_2. The oxidation rate of UC considerably increased at concentration of $HNO_2 > 0.005$ mol l^{-1}. At room temperature the 100% yield of U(VI) on dissolution of UC in 3.0–6.0 mol l^{-1} HNO_3 was reached in 30–40 min.

Therewith the HNO_2 concentration first grew to 0.02–0.2 mol l^{-1} depending on the initial concentration of HNO_3 and on the solid/liquid (S/L) ratio, and then decreased because of HNO_2 disproportionation. At room temperature in 2.0–3.0 mol l^{-1} HNO_3 solutions the uranium contained in UC was quantitatively oxidized into U(VI) at HNO_2 concentration over 0,005 mol l^{-1}. It is likely due to the necessity to destroy the surface film of $UC_{1-x}O_y$ [12, 13] by reactions (1) and (2); therewith the rate of reaction (2) is notably higher than that of reaction (1). The destruction of the $UC_{1-x}O_y$ film favored the acceleration of reactions (1) and (2). The kinetics of variation of HNO_2 concentration in the course of UC dissolution in the nitric acid is complex, and we failed to formulate the kinetic description of the process with accounting for the contribution of NO_3^- ions and HNO_2. To estimate the partial oxidation rate constants of UC in acid solutions a dissolution of UC was studied in 0.5–6.0 mol l^{-1} $HClO_4$ solutions in the presence of HNO_2.

At interaction of UC powder (50–60 mm) with 0.5–6.0 M $HClO_4$ (E_h in the range from –0.2 to +0.05 V/st.el.) the conversion of UC into U(VI) did not exceed 2.0% at the initial ratio S/L in the range 0.1–0.2 mg ml^{-1}. The increase in HNO_2 concentration to 0.1 mol l^{-1} increased E_h to 500 mV/st.el.; the yield of uranium carbide dissolution reached 90% and more in 6.0 mol l^{-1} $HClO_4$ [13]. On dissolution of UC in solutions with HNO_2 concentration higher than 0.05 mol l^{-1} the decrease in its concentration followed the first order kinetic equation with a rate constant k_{SD}. The kinetic equation of UC dissolution in $HClO_4$ solutions containing over 0.05 mol l^{-1} HNO_2 was presented as expression (4). The equation takes into account the contribution into the observed dissolution rate of reactions of uranium carbide oxidation with protons (k_{H^+}, n_{H^+}), HNO_2 (k_{HNO_2}, n_{HNO_2}) by reaction (2), and NO_3^- ions (k_{NO_3}, n_{NO_3}) by reaction (1)

$$\frac{\Delta m}{m} = \left(k_{H}+[H^+]^{n_{H+}} + k_{HNO_2} \left\{ [HNO_2]_0 \exp\left(k^{SD}_{HNO_2}\, t\right) \right\}^{n_{HNO_2}} + k_{NO_3^-} \left[\frac{[HNO_2]_0}{3} \left\{ 1 - \exp(-k^{SD}_{HNO_2} t) \right\} \right]^{n_{HNO_3}} \right) t^n. \qquad (4)$$

The results of approximation [14] of the experimental kinetic curves of UC dissolution showed that the suggested kinetic model sufficiently described the dissolution process under the chosen conditions. Applying the model the apparent partial oxidation rate constants k_{HNO_2}, k_{H^+}, and k_{NO_3} were calculated, and also the reaction orders with respect to the reagents and the overall order of dissolution. The rate constant k_{HNO_2} (~2–12 $mol^{-1.8}$ $min^{-1.8}$) is 50–80 times higher that k_{NO_3} (~0.02–0.15 mol^{-1} min^{-1}); hence the oxidation of UC with nitrous acid occurs considerably faster than with NO_3^- ions. The first order (n) in equation (4) for the overall reaction of UC dissolution indicates that the dissolution rate is limited by mass transfer process. In the course of UC dissolution in $HClO_4$ and HNO_3 containing HNO_2 60–85% of carbon was oxidized to CO_2. The rest of carbon was distributed between the solution and insoluble residue. The ratio of "oxidizable carbon" to U(VI) in solution was reduced from 0.5 to 0.1 mg-equiv mol^{-1} at growing concentrations in the solution of HNO_2 and H^+, and in the insoluble residue this ratio increased from 3.0 to 15.0.

Synthesis of New Technetium Compounds

The selection of a procedure for technetium(VII) separation from the process solutions into a solid phase is difficult because of high solubility of pertechnetates with the most inorganic cations. In the publications of IPCE and Research Center "Marcoule" [15–17] a precipitation process and physicochemical investigation is described of sparingly soluble compounds of technetium(VII) and rhenium(VII) with organic cations, in particular, those from the tetraalkylammonium series. Some characteristics of these compounds are compiled in Table 1. The synthesized tetrapropyl-, tetrapentyl-, and tetrahexylammonium pertechnetates and perrhenates $(C_nH_{2n+1})_4NMeO_4$ (n = 3, 5, 6; Me = Tc, Re) were investigated by various physicochemical methods, the heat resistance of their polymorphous modifications was estimated, the solubility, solubility product, and association constants K_1 of formation of ionic associate $[(C_5H_{11})_4N^+)\cdots(TcO_4^-)]$ were measured.

The purification factors of technetium from ^{239}Pu and ^{106}Ru were measured [(1.2–2.5) × 10^2 and (6.8–8.5) × 10^2 respectively] at precipitation in the form of $(C_3H_7)_4NTcO_4$ and $(C_5H_{11})_4NTcO_4$. The optimum composition of compounds with five carbon atoms in the chain was found suitable for separation of technetium(VII) from solution into the solid phase. At the precipitation of $(C_6H_{13})_4NMeO_4$ from nitric acid solutions into the solid phase a considerable amount of nitrate is cocrystallized, therefore this compound cannot be recommended for Tc separation. The thermal decomposition of compounds under considera-tion may be used in practice for production of technetium

Table 1.

Run. no.	Pertechnetates and perrhenates with organic cations	Solubility in water at 25°C, mol l^{-1}	Density, g cm^{-3}	Association constant in water, l mol^{-1}
1	Tetramethylammonium pertechnetate	0.135 ± 0.005	1.67	–
2	Tetraethylammonium pertechnetate	$(2.5 \pm 0.7) \times 10^{-2}$	1.34	–
3	Tetrapropylammonium pertechnetate	$(8.7 \pm 0.2) \times 10^{-3}$	1.26	2.6 ± 0.4
4	Tetrapropylammonium perrhenate	$(8.9 \pm 0.2) \times 10^{-3}$	1.57	2.5 ± 0.3
5	Tetrabutylammonium pertechnetate	$(4.3 \pm 0.20) \times 10^{-3}$	1.17	15 ± 3
6	Tetrabutylammonium perrhenate	$(7.9 \pm 0.2) \times 10^{-4}$	1.12	27 ± 5
7	Tetrapentylammonium pertechnetate	$(8.0 \pm 0.2) \times 10^{-4}$	1.33	36 ± 5
8	Tetrahexylammonium pertechnetate	$(7.1 \pm 0.5) \times 10^{-5}$	1.07	40 ± 5
9	Tetraheptylammonium pertechnetate	$(8.8 \pm 0.8) \times 10^{-6}$	1.03	52 ± 5
10	Triphenylguanidinium pertechnetate	$(3.9 \pm 0.3) \times 10^{-3}$	~1.0	–
11	4',4-trimethyldipiperidine pertechnetate	$(4.9 \pm 0.3) \times 10^{-4}$	~1.0	–
12	Dimethylaminoantipyrinium pertechnetate	$(1.1 \pm 0.1) \times 10^{-3}$	~1.08	–
13	Tetraphenylarsonium pertechnetate	$(4.0 \pm 0.2) \times 10^{-4}$	~1.1	40 ± 5
14	Cetylpyridinium pertechnetate	$(3.9 \pm 0.3) \times 10^{-3}$	~1.12	–
15	Cetyltrimethylammonium perechnetate	$(6.8 \pm 0.5) \times 10^{-3}$	~1.15	–

in the form of metal or carbide, materials suitable for long storage or for targets of technetium transmutation into ruthenium.

The character of phases arising in Tc metal interacting with carbon is poorly understood and is of interest in various respects: starting with Tc behavior in carbide nuclear fuel and during the pyrotechnical reprocessing of the oxide fuel of high burnout [18–20] and up to the interpretation of electronic spectra of Tc and the analysis of its daughter element, Ru, in interstellar dust [21]. It is clear now that the phases of metal and of carbide proper can form with a variable carbon content and in some events with distortions of symmetry that has caused different interpretations discussed in [22]. We used two methods for preparation of technetium-carbon phases: direct reaction of the metal with carbon and the thermolysis of technetium tetraalkylammonium salts under an inert atmosphere. The first procedure makes it possible to control with higher accuracy the conditions of the formation, the composition and properties of the carbon-containing phases, and to refine the data on the phase diagram in the system Tc–P. The second procedure is more feasible for development of processing Tc conversion into the metal or the carbide for subsequent transmutation into the stable Ru. By the first method the carbon-containing technetium phases were obtained by reacting finely dispersed metallic Tc with pure graphite at various ratios of the components and temperatures. The formation of a metastable orthorhombic modification of metallic technetium was discovered for the first time, the mechanism of technetium carbide formation was determined. A significant increase (~10%) in the specific volume of Tc metal in the presence of small, up to при 2 wt %, carbon impurities was proved (Fig. 3). This fact is very important for predicting the behavior of these materials on neutrons irradiation in a reactor.

It was found by the second method that under an inert atmosphere (argon or helium) $(C_5H_{11})_4NTcO_4$ at 300–600°C decomposed with the formation of a mixed phase of technetium carbide deficient in carbon and intercrystallite pyrographite ($Fm3m$, a = 3.98 Å) of a composition TcC_{1-x}, where $0,61 < x < 0,85$ and depended on the flow rate of the inert gas. The gaseous reaction products were triamylamine, CO_2, and water.

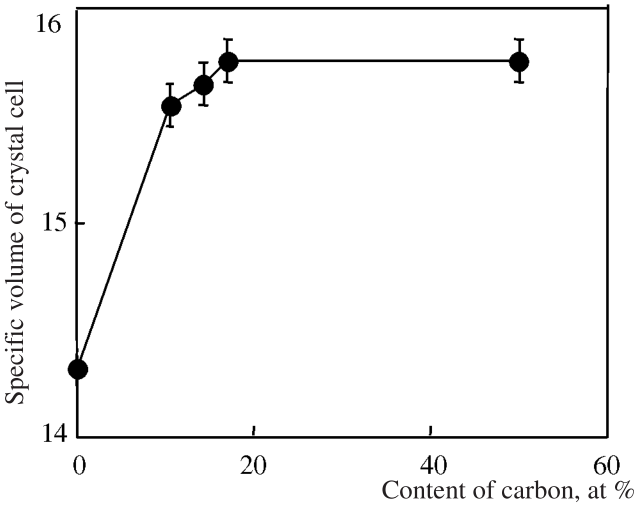

Fig. 3. Dependence of specific volume of crystal cells of technetium-carbon phases on the carbon content.

The presence of a controllable amount of carbon in the phase makes it possible to use the neutrons in transmutation more efficiently due to their deceleration at the collision with the carbon nuclei within the target. In a weakly reductive medium (94% Ar + 6% H_2) $(C_5H_{11})_4NTcO_4$ underwent thermal decomposition into a pure metal.

IPCE carried out joint studies with the Research Center "Marcoule" and Institute of Nuclear Physics Orsay in the field of development of synthetic procedures, investigation of the structure and properties of new technetium compounds with actinides (uranium, neptunium, and plutonium). For the complex compound of neptunyl and pertechnetate synthesized for the first time the X-ray and spectroscopic analysis demonstrated that the neptunyl groups formed two types of complexing centers, and the pertechnetate served a bidentate ligand [23]. By the data of powder X-rayograms we succeeded to find the isostructural character of a series of pertechnetates and perrenates of actinides (Np, U) and to suggest a general formula for the coordination type first discovered in the neptunyl pertechnetate $[(AnO_2)_2(MO_4)_4\cdot 3H_2O]_n$ where M = Tc, Re and An = U, Np [3–9]. This structure proved to be a new coordination type of anions around the uranyl ion; it was not predicted by the system of V.N. Serezhkin et al. [24]. The proof of an existence of similar complexes in solutions was obtained by spectroscopic investigation of the complex cation $[UO_2(TcO_4)(DPPMO_2)_2]^+$ [25]. According to spectroscopy in IR and visible region the formation of such compounds is not characteristic of plutonium(VI).

Electrochemical Reactions of Technetium in Nuclear Fuel Cycle

Dissolution of "White Inclusions"

In the course of burnout of the oxide nuclear fuel the arising technetium isotopes crystallize with molybdenum and with the metals of Ru subgroup forming "white inclusions," alloys Mo–Tc–Ru–Rh–Pd. Their content in the used fuel grows with burnout and attains 5–10 kg t^{-1} of U [26–28]. The dissolution of these alloys in nitric acid occurs slowly and incompletely [29]. Therefore about 10% of technetium remains in the insoluble residues after fuel dissolution [30].

By means of linear voltammetry [31] and electrolysis at a controlled potential [32] an electrochemical dissolution of double alloys (at %): 52.5 Mo–47.5 Re and 90.0 Mo–10.0 Ru in 0.5–6.0 mol l^{-1} HNO_3 was investigated. Taking into account the similarity of the electrochemical characteristics of technetium and rhenium and complete analogy of their alloys [33] the simulation of the behavior of "white inclusions" was performed in this study using rhenium instead of technetium.

The overpassivation potentials of metallic Mo, Re, Ru and alloys Mo–Re and Mo–Ru in nitric acid solutions were estimated by means of linear voltammetry (Table 2). It was shown that with growing concentration of nitric acid the overpassivation potentials moved to the positive values. The overpassivation potentials of alloys fall in the interval between the potentials of pure metals; therewith the overpassivation potential of Mo–Ru alloy was shifted to the metal ruthenium potential.

The peak of current on the curves of linear voltammetry for all electrodes containing Mo was observed at potentials around 1.6 V/st.el. and was related to the secondary passivation of electrodes owing to the accumulation in the diffusion layer of a poorly soluble Mo(VI) hydroxide [34]. The linear voltammetry data showed that the rates of the anodic dissolution of pure metals and alloys increased with the growing concentration of HNO_3 and electrode potential up to E = 1.6 V/st.el., and they amounted to 1.85–2.20 mg cm^{-2} h^{-1} for the alloy 52.5 Mo + 47.5 Re and 0.58–0.64 mg cm^{-2} h^{-1} for the alloy 90 Mo + 10 Ru. More accurate values of the rate constants of dissolution were obtained in the

Table 2. Overpassivation potentials of pure Mo, Re, Ru, and their alloys [31]

$[HNO_3]$, mol l^{-1}	Potential of dissolution in 0.5–6.0 mol l^{-1} HNO_3, V/st.el.				
	Mo	52.5Mo–47.5Re	Re	90.0 Mo–10Ru	Ru
0.5	0.393	0.456	0.697	0.498	1.158
1.0	0.407	0.478	0.743	0.924	1.168
2.0	0.416	0.500	0.764	0.924	1.237
4.0	0.437	0.511	0.793	0.971	1.252
6.0	0.478	0.580	0.812	1.076	1.273

Table 3. Rate constants of dissolution of molybdenum alloys in nitric acid in the course of controlled potential electrolysis [32]

Alloy composition, at%	Potential, V/st.el.	Rate constant of dissolution, $mg \cdot cm^{-2} \cdot h^{-1}$		
		2 mol l^{-1} HNO_3	4 mol l^{-1} HNO_3	6 mol l^{-1} HNO_3
52.5Mo–47.5Re	1.0	507	717	1058
90Mo–10Ru	1.2	167	149	189
	1.6	187	227	117
	2.0	283	279	159

study of electrochemical dissolution of alloys at a controlled potential.

The kinetics of dissolution of pure Mo, Re, Ru and alloys 52.5 Mo + 47.5 Re and 90 Mo + 10 Ru in 0.5–6.0 mol l^{-1} HNO_3 was studied at 22°C [32]. It was shown that the dissolution of the alloys occurred congruently and the reaction of the electrochemical dissolution is of zero order with respect to the metal ions concentration in the solution. The rates of electrochemical oxidation of the Mo–Re at the potential of 1.2 V/st.el. steadily grew from 1.33×10^{-3} to 7.60×10^{-3} mol (Mo + Re) cm^{-2} h^{-1} with the increasing HNO_3 concentration in the electrolyte from 0.5 to 6.0 mol l^{-1}. Yet maximum dissolution rates of the alloy Mo–Ru from 2.21×10^{-3} to 3.28×10^{-3} mol (Mo + Ru) cm^{-2} h^{-1} were observed in 2.0–4.0 mol l^{-1} HNO_3 at the electrolysis potential 1.6 V/st.el. (Table 3).

The increased electrolysis potential and electrolyte acidity reduce the rate of dissolution due to the formation of a passive film of hydrated RuO_2 on the electrode surface. On further oxidation of RuO_2 the film is destroyed with the formation of volatile RuO_4 soluble in water solutions. The oxidant in these processes is oxygen formed from water on the anode [35]. The occurrence of this electrochemical reaction on the electrodes containing considerable amount of molybdenum metal is impeded since the overpotential of oxygen evolution on these electrodes reaches about 3.7 V/st.el. [34, 36]. Therefore at dissolution of "white inclusions" the ruthenium content governs the rate of the electrochemical dissolution of the alloy. The negative effect of the passive film of hydrated RuO_2 on the rate of electrochemical dissolution of "white inclusions" can be considerably decreased by adding into the electrolyte anions forming complexes with Ru(IV). It was shown that electrochemical dissolution of the alloy Mo–Ru in 2.0 mol l^{-1} HNO_3 containing 0.2–0.4 mol l^{-1} $H_2C_2O_4$ occurred without electrode passivation with a rate 4.45×10^{-3} mol (Mo + Ru) cm^{-2} h^{-1}. The rates of electrochemical dissolution of the alloys simulating the "white inclusions" are over 1000 times faster than their oxidation in boiling 7.5 mol l^{-1} HNO_3 [29]. The investigation performed of the electrochemical properties and the dissolution of the alloys simulating the "white inclusions" showed the fundamental possibility of applying electrochemical procedures to dissolution of "white inclusions."

Electrochemical Behavior of Technetium in Complexing Media. Isolation of ^{99}Tc from Solutions of PUREX Process

The electrochemical reduction of Tc(VII) in solutions of 0.1–1.0 mol l^{-1} HNO_3 [37] and in buffer solutions of acetic and formic acids [38–40] forming stable complexes of technetium [6, 41, 42], was carried out in the framework of the international program SPIN (Separation-Partitioning-Incineration) [43]. The goal of the program was the development of methods for isolation of the "smaller actinides" and the long-lived fission products from the solutions of the nuclear fuel cycle, in particular, isolation of ^{99}Tc from the additional raffinate of the 1st cycle of the PUREX process for the long storage and/or "burning out" of ^{99}Tc in nuclear installations with a high neutron flux [7, 8].

The studies demonstrated that the electrochemical reduction of Tc(VII) on a stationary dropping mercury electrode (SDME) and on graphite electrode (GE) in nitric acid solutions proceeded with the formation of Tc(III) [37]. The half-wave potential ($E_{1/2}$) of this process on SDME decreased from 0.06 V to –0.25 V/st.el.

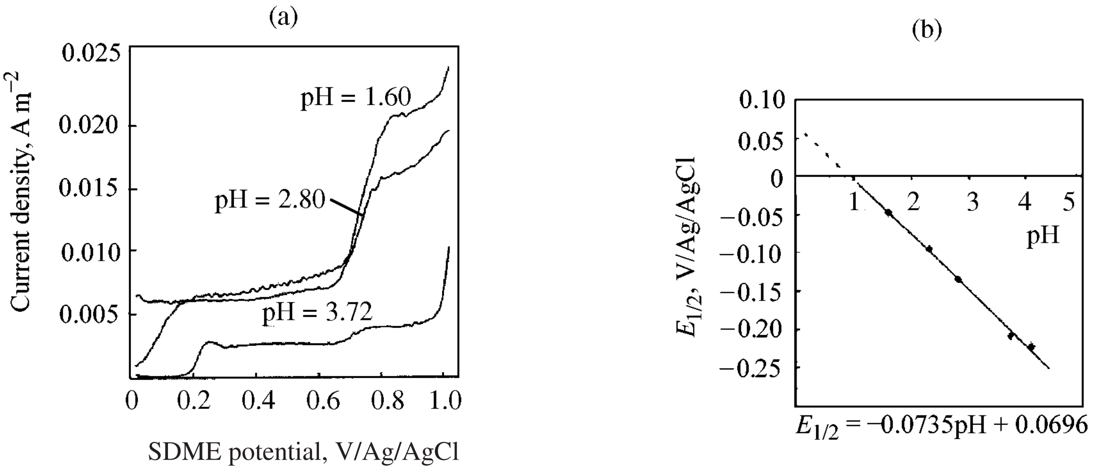

Fig. 4. Electrochemical reduction of ions TcO_4^- on SDME at various pH values [37]: (a) in 0.1 M HNO_3 + KNO_3 solution, (b) half-wave potential for reduction of Tc(VII)/Tc(III).

on increasing the HNO_3 concentration from 0.1 to 1.0 mol l^{-1} (Fig. 4b).

At potentials $E < -0{,}7$ V on the curves $I(E)$ on SDME (Fig. 4a) and GE the current density sharply increased, the reduction of NO_3^- ions and formation of nitrous acid occurred [see Eq. (3)]. The linear dependence of the limiting current of NO_3^- ions reduction on the Tc(VII) concentration suggests that this process is catalyzed by Tc(III) ions that suffer fast oxidation with HNO_2 to Tc(IV) and Tc(V) and again are reduced to Tc(III) on the electrode. The cited reactions at the potentials $E < -0.7$ V decrease the concentration of protons and NO_3^-. At the same time Tc(IV) and Tc(V) undergo hydrolysis in the diffusion layer of the electrode forming hydroxocomplexes of low solubility and partially deposit on the electrode (Table 4).

The study performed showed that the direct electrochemical isolation of technetium by its reduction in the nitric acid solutions cannot proceed sufficiently completely. At the same time the studied processes might be applied to the denitration of the nitric acid solutions containing technetium.

To increase the yield of the electrodeposition of technetium in the form of Tc(IV) hydroxide the application of buffer electrolytes was suggested that formed stable complexes with technetium in the oxidation state (+3)–(+5). The study of the electrochemical reduction of Tc(VII) on SDME in an acetate buffer (pH 4.5–4.6) showed [38] that in the range of potentials from –0.3 V to –0.5 V/st.el. the electrode reaction gave as product Tc(V) well soluble in this electrolyte. The measurements of the capacity

Table 4. Effect of Tc(VII) on electrochemical denitration of HNO_3 and output of Tc electrodeposition under conditions of controlled potential electrolysis at various potentials on graphite cathode [37] (25°C, S/V = 2500 m^{-1}, electrolysis duration 2 h)

Measured parameters	GE potential, V/st.el.				
	0.5	0.65	0.8	1.0	1.2
$[HNO_3]_{t=2\text{ h}}$, mol l^{-1} Without technetium [Tc(VII)] = 0	3.76	3.76	3.12	3.18	3.18
[Tc(VII)] = 2 × 10^{-4} mol l^{-1}	3.98	3.98	2.49	2.48	2.48
Current efficiency, F/1 M HNO_3					
Without technetium [Tc(VII)] = 0	3.76	3.76	3.12	3.18	3.18
[Tc(VII)] = 2 × 10^{-4} mol l^{-1}	3.98	3.98	2.49	2.48	2.48
Current efficiency of Tc electrodeposition, %	9.05	12.4	23.5	34.1	35.0

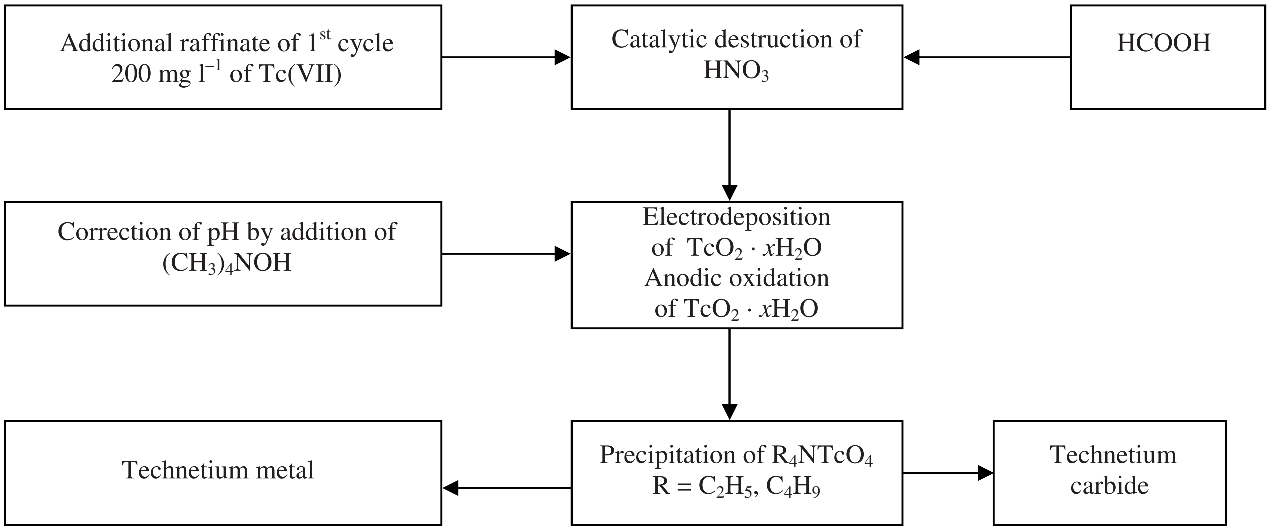

Fig. 5. Flow diagram of technetium and its monocarbide production by electrochemical processing of additional raffinate of PUREX process [45].

of the double electric layer as a function of SDME potential demonstrated that at the potentials more negative than –0.7 V/st.el. a considerable adsorption was observed of insoluble Tc(IV) and Tc(III) compounds on the SDME surface. This result underlies the electrochemical method for Tc separation from the solutions of PUREX process.

For the electrochemical isolation of technetium from the additional raffinate of the PUREX process an electriochemical procedure has been developed and patented [44] that is schematically represented on Fig. 5.

In the first stage the initial solution containing 2.0–4.0 mol l^{-1} of HNO_3 and (1.0–2.0) × 10^{-3} mol l^{-1} of Tc(VII) is subjected to catalytic denitration with formic acid [45]. The solution obtained is neutralized for preparation of a formiate electrolyte. The electrolysis of this solution is carried out on a graphite electrode at potentials from –1.0 V to 1.4 V/st.el. in an electrolytic tank with a cathode and anode departments separated by a cation-exchanger membrane [37, 39, 40, 44]. Intermediate electrolysis products, formiate complexes containing Tc_2^{8+} and Tc_2^{7+} groups [39–42], decelerate the hydrolysis of Tc(V) and Tc(IV) in the diffusion layer of the electrode. The electrolysis at the cathode current density 70–100 mA cm^{-2} led to the formation on the GE surface of a layer of hydrated TcO_2 up to 3.0 mg cm^{-2}. At the optimum electrolysis conditions the deposition on the electrode of 95% of Tc was attained in 2.0 h (Table 5). The obtained $TcO_2 \cdot xH_2O$ is dissolved in 0.1–0.5 mol l^{-1} HNO_3 at potentials on GE 0.3–0.5 V/st.el. to yield 0.2–0.5 mol l^{-1} Tc(VII) solution. This solution is the starting material for precipitation of tetraalkylammonium pertechnetates [15–17] used further for preparation of metallic Tc [18] or TcC [22].

Development of Electroanalytical Chemistry of Technetium

The study of electrochemical properties of Tc(VII) in water solutions [6, 37, 38, 46, 47] show that methods like tast polarography (TP) and differential pulse polarography (DPP) may find extensive application to quantitative estimation of technetium concentration in the liquid radioactive wastes. High sensitivity, (2.0–5.0) × 10^{-7} mol l^{-1}, simple procedure and low cost of the analysis make the electroanalytical methods competitive with ICP MS and X-ray fluorometric analysis, traditional procedures for technetium determination.

Electrochemical Reactions of Tc(VII) in NaOH Solutions

Electrochemical reduction of Tc(VII) on SDME in 0.1–4.0 mol l^{-1} NaOH solutions was investigated by TP and DPP methods. In 0.1 mol l^{-1} NaOH solution [48] the reduction of Tc(VII) was characterized by a reduction wave (DPP peak) at $E_{1/2}$ = –0.80 V/st.el. (E_p = –0.775 V/st.el.) (Table 6).

Table 5. Kinetic parameters of $TcO_2 \cdot xH_2O$ electrodeposition from formiate solutions. Conditions of deposition: 1 mol l^{-1} of $(CH_3)_4CH_3COO$ (pH = 7.32) $[Tc(VII)]_o = 2 \times 10^{-3}$ mol l^{-1}; $E_{cath} = -1.4$ V/st.el., electrolysis duration 2 h

pH	S/V, cm^{-1}	$k_{obs} \times 10^4$, s^{-1}	$[Tc]_{\infty} \times 10^3$, M	Output of electrodeposition, %
3.95	0.25	6.47 ± 0.29	0.85 ± 0.01	57.5 ± 1.8
5.39	0.25	6.18 ± 0.14	0.45 ± 0.01	77.5 ± 2.6
7.37	0.25	4.02 ± 0.15	0.32 ± 0.02	84.0 ± 2.4
7.37	0.50	8.83 ± 0.12	0.086 ± 0.005	95.7 ± 2.6

Table 6. Electrochemical parameters of Tc(VII) reduction on SDME according to TP and DPP data

NaOH concentration, mol l^{-1}	Tast polarography			DPP	
	$E_{1/2}$, V/st.el.	αn[a]	n by Cottrel equation	E_p, V/st.el.	αn[b]
0.1	–0.775	1.05 ± 0.06	3.09 ± 0.05	–0.775	0.90
0.5	–0.735	1.13 ± 0.09	2.89 ± 0.05	–0.733	0.95
1.0	–0.705	1.24 ± 0.05	2.81 ± 0.02	–0.715	0.95
2.0	–0.696	1.47 ± 0.07	2.69 ± 0.06	–0.700	0.95
4.0	–0.694	2.08 ± 0.08	2.34 ± 0.09	–0.690	1.29

[a] Obtained by log analysis of waves of tast polarography. [b] Calculated by equation $W_{1/2} = 90.4$ mV/n (where $W_{1/2}$ is the width of DPP peak at $I = 0.5I_p$)

The increase in the alkali concentration to 4.0 mol l^{-1} of NaOH led to the growth of the reduction potential to 0.69 V/st.el. The number of electrons involved into the electrode reaction (n) was calculated from the TP data by Cottrel equation [49] and by logarithmic analysis of the reduction waves, and also from the data of DPP using equation $W_{1/2} = 90{,}4$ mV/n (where $W_{1/2}$ was the width of the DPP peak at $I = 0.5I_p$) [50]. The analysis of DPP curves and TP waves in the log coordinates showed that the value (n) grew from 1.0 in 0.1 mol l^{-1} NaOH to 2.5 in 4.0 mol l^{-1} NaOH. At the same time the values of n estimated from Cottrel equation decreased from 3.24 to 2.44 at growing NaOH concentration from 0.1 to 4.0 mol l^{-1}. The data obtained demonstrated the decisive role of the disproportionation of Tc(VI) and Tc(V) in the electrode reduction of Tc(VII) on SDME and the increased resistance of Tc(V) against further electrochemical reduction in solutions containing more than 2.0 mol l^{-1} NaOH. It was shown that by DPP method technetium can be quantitatively determined in NaOH solutions with an accuracy of 5–7%. The detection limit is 1.0×10^{-7} mol l^{-1} in the presence of anions NO_3^-, NO_2^-, CO_3^{2-}, F^-, and AlO_2^- [48].

The DPP procedure was applied to simultaneous quantitative estimation of U(VI), Tc(VII), and Cr(VI) concentrations in alkaline solutions of radioactive wastes. The method developed made it possible to determine Cr(VI) and Tc(VII) in the concentration range from 10^{-7} to 10^{-4} and U(VI), from 10^{-6} to 10^{-4} mol l^{-1}, with an accuracy from 14 to 2.0% depending on the concentration of the element in the solution [51]. The detection limits according to the calibration curves amounted to 8.0×10^{-8} for Tc(VII), 3.0×10^{-7} for Cr(VI), and 8.0×10^{-7} for U(VI). Due to the close values of the reduction potential in alkaline solutions the simultaneous measurement of concentrations of uranium and technetium is possible when the ratio [U(VI)]/[Tc(VII)] in the solution is less than 350. To mask Tc(VII) at U(VI) determination it was suggested to reduce Tc(VII) into Tc(IV) with hydrazine (Fig. 6). The simultaneous determination of uranium and chromium (U+Cr) is possible at their ratio in solutions [U(VI)]/[Cr(VI)] > 1.0, and the estimation of Cr(VI) is possible in solutions containing 15-fold excess of uranium.

Tc-Ionoselective Electrodes

In order to develop a cheap express-method for potentiometric determination of Tc in solutions a ionoselective electrode (ISE) was made and investigated with a plasticized poly(vinyl chloride)

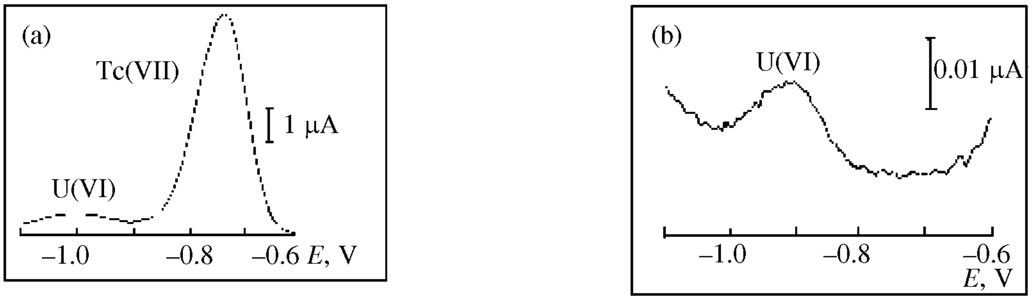

Fig. 6. DPP of solution containing uranium and technetium: 5×10^{-6} mol l^{-1} U(VI) and 5.0×10^{-4} mol l^{-1} Tc(VII) in 2.0 mol l^{-1} NaOH (a) before and (b) after addition of 0.001 mol l^{-1} N_2H_4.

membrane containing dodecyltrimethylammonium pertechnetate (DDTMAP) selective toward pertechnetate ions [52, 53]. The membrane for the electrode was prepared by dissolving DDTMAP, plasicizer, and PVC in tetrahydrofuran followed by slow evaporation of the solvent in air. The comparison of the electrode based on DDTMAP we developed [52, 53] with the liquid electrode based on tetradecylphosphonium described in [54] showed that the lower limit of detection is identical in both electrodes (2.0×10^{-6} mol Tc l^{-1}), and the selectivity of the new ISE is no worse and in some cases, in particular, in the presence of nitrate ions, is better than the selectivity of the electrode based on tetradecylphosphonium.

Investigation of Technetium Behavior in the Natural Waters in the Vicinity of Depositories of Radioactive Wastes and Nuclear Power Plants

The behavior of technetium in natural waters in the contact with the rocks in the vicinity of in the underground laboratories-depositories for radioactive wastes under construction in Meuse/Haut-Marne (France), Monte Terri (Switzerland) [55, 56], and in reservoirs near Kalinin NPP (Russia) was studied [57]. The first stage of this research was the prediction of technetium behavior in the natural systems in question based on the published geochemical data on the composition and properties of natural waters and rocks in the regions under study. Both rocks in France and Switzerland contain minerals possessing Fe(II) and organic carbon, their overall reducing ability is 4.7–4.9 mg-equiv/g of rock, and the natural waters at the depth 400–410 m under anaerobic conditions have pH 7–8, $E_h < 0.1$ V/saturated hydrogen electrode. [58, 59]. Proceeding from these data and from the published information on the stability of the technetium oxidation states in solutions and their sorption on clays and minerals [60, 61] it was concluded that in the systems under study “natural waters–clays” under anaerobic conditions Tc(VII) would be reduced by iron(II) into Tc(IV) and would be completely sorbed on the clays and minerals. The prediction was checked and proved experimentally. It was found that Tc(VII) was not sorbed by the tested clays from France and Switzerland under aerobic conditions, but it was completely sorbed in the absence of oxygen. The sorbtion rate has a zero order in Tc concentration in the concentration range 10^{-7}–10^{-5} mol l^{-1}, and it increases 2.2 times for each 10°C in the range 30–90°C (Fig. 7).

The limiting stage of the sorption process is the reduction of Tc(VII) to Tc(IV) by compounds of Fe(II) contained in the rocks. At the air access oxidation of Fe(II) and Tc(IV) begins, and the formed Tc(VII) undergoes desorption. It was therefore demonstrated that the studied rocks from the regions Meuse/Haut-Marne (France) and Monte Terri (Switzerland) sorbed and immobilized technetium from the natural waters only under anaerobic conditions, and at the access of air the migration of technetium recommenced [55–57]. Therefore we tested minerals-candidates for immobilizing sorbents of technetium from the natural waters under the aerobic conditions. Most of minerals virtually do not sorb the pertechnetate ion TcO_4^- from natural waters, but certain sulfide-containing minerals are prone to chemosorption by transforming TcO_4^- into poorly soluble sulfides Tc_2S_7 or TcS_2 [61].

Stibnite Sb_2S_3, the most wide-spread antimony mineral, is a known good sorbent of technetium with a large sorption coefficient $Kd \sim 10^4$ in neutral medium under aerobic conditions [62, 63]. Stibnite colloids are used in the nuclear medicine to transport technetium in

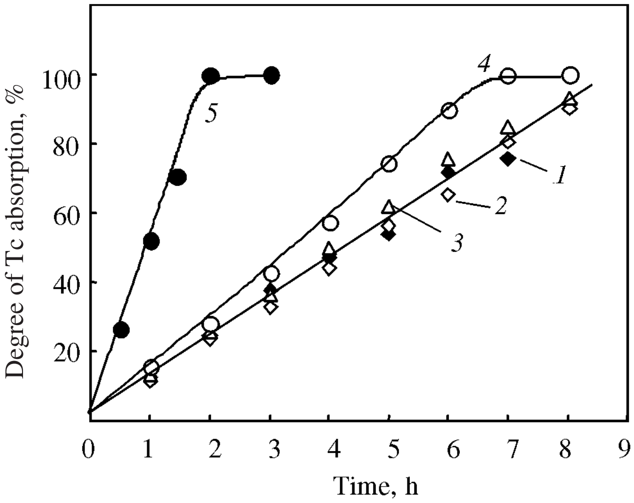

Fig. 7. Kinetics of sorption of technetium **VII** from solutions imitating natural water by clays under anaerobic conditions: 90°C; S/L = 0.6 g ml^{-1}, initial concentration of Tc(VII) 5 × 10^{-7} mol l^{-1}; (*1*–*4*) clays from the regions Meuse/Haute-Marne; (*5*) clay of Monte Terri.

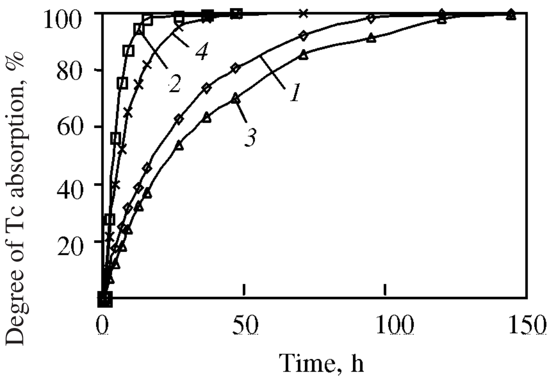

Fig. 8. Technetium sorption with the powder of stibnite mineral: 30°C; initial concentration of introduced Tc(VII) 5 × 10^{-7} mol l^{-1}; size of powder particles 0.05–0.1 mm; S/L = 10 g l^{-1}. (*1*, *2*) imitator solution of natural water; (*3*, *4*) natural water from the depth of 400 m from the region regions Meuse/Haute-Marne: (*1*, *3*) aerobic conditions; (*2, 4*) anaerobic conditions.

the body from the injection place to the ill organ [64, 65]. However the kinetics and mechanism of Tc sorption by stibnite from the natural waters, the effect of the temperature, boundary conditions of the sorption, and the possibility to use stibnite as a component of an engineering barrier precluding the technetium migration from the depository of the radioactive wastes were not investigated. We studied the sorption of ^{99}Tc(VII) from the natural waters on powder and polished surface of stibnite mineral at 25–90°C [66]. We found that the sorption of technetium (VII) from imitation solutions [10^{-7}–10^{-6} M Tc(VII), pH 5–7] and from the natural water of the region Meuse/Haut-Marne (France) on stibnite powder was complete and occurred quickly at m/V = 5 g l^{-1} both in air and under anaerobic conditions. The Tc sorption rate is greater under anaerobic conditions than in air (Fig. 8).

This fact suggests that pertechnetate anion is converted into technetium sulfide in the course of chemisorption according to an equation:

$$2TcO_4^- + 7S^{2-} + 16H^+ \rightarrow Tc_2S_7 + 8H_2O. \qquad (5)$$

The increase of the temperature by 10°C accelerated the sorption of Tc 2.1 and 3.0 times under the anaerobic and aerobic conditions respectively. The difference found in the temperature factors is due to the decrease in the oxygen solubility in water with growing temperature. The sorption of technetium on stibnite powder is irreversible both under anaerobic conditions and in air. The sorption on a polished stibnite surface resulted in technetium layers of the thickness 1–12 mg Tc cm^{-2} at pH 4–8. The investigation of stibnite surface after technetium adsorption was performed on the accelerator of the Center of Nuclear Research at Bordeaux-Gradignan. The scanning with a protons beam of the energy 2.5 MeV and registering of the induced X-ray emission of the main, impurity elements, and sorbed technetium (line K–L$_{2,3}$ of energy 18.320 eV) revealed that the layers of the sorbed technetium were nonuniform in thiskness due to the presence in the mineral of FeS, FeS$_2$, SiO$_2$ etc., impurities. The difference in the thickness of the Tc layer on the main mineral and the impurities corresponded to the known sorption factors of technetium on these materials. For instance, the absence of technetium layer on the grains of SiO$_2$-impurity in the stibnite mineral (Fig. 9) corresponds to the known published extremely low sorption factors of Tc(VII) on quartz [61].

At pH > 9 the degradation of stibnite surface was observed due to hydrolysis and to formation of colloid with technetium sorbed on it. Thus stibnite is an efficient sorbent for technetium capable of preventing migration of this radioelement in natural waters under aerobic and anaerobic conditions in neutral and acid media, but not in alkaline solutions because of hydrolytic deterioration of the mineral [66]. Pyrite mineral FeS_2 proved to be less efficient and kinetically slow sorbent compared to stibnite under the same conditions.

Physicochemical and microbiological components of Tc(VII) sorption from the natural waters were studied under aerobic conditions on the samples of bottom sediments of reservoirs of the region of Kalinin NPP (pH 7.0; E_h = –0.20 V/saturated hydrogen electrode; the parameters did not change within 73 days). It was found that the rate of Tc transition from the water phase onto the bottom sediments of Khomutovka creek was about 8% in 24 h, for eutrophic lake Kezadra, 5%, and for dystrophic lake Navolok, 3% in 24 h in summer at equal temperature, the sediment to the water volume ratio m/V = 10 g l^{-1}, and the initial concentration $[TcO_4^-]_0 = 5 \times 10^{-7}$ mol l^{-1} [57]. The sterilization of sediments decelerated Tc uptake 10–15-fold. An inhibiting effect was found at addition of sodium sulfates and nitrates in concentrations over 70 mg l^{-1} on the biouptake of Tc by bottom sediments for an interval necessary for destruction of the inhibitor ion (~5 days). The probable mechanism of Tc(VII) uptake with bottom sediments consists in its reduction to Tc(IV) and fixing of the latter in the intercellular structures.

CONCLUSION

The length of this article does not permit the inclusion of all results obtained in recent years in the framework of the scientific collaboration between IPCE RAS and French radiochemical institutions. It should be noted in short that in the laboratories of Professors A.M. Fedoseev, G.V. Ionova, M.S. Grigor'ev, and Academician B.F. Myasoedov the research is actively carried out together with Research Center Marcoule and Institute of Nuclear Physics Orsay. The studies performed in the laboratories of A.M. Fedoseev and M.S. Grigor'ev concern the development of synthetic procedures and studies of the structure of single crystals of new compounds of actinides and lanthanides [67–74]. In the quantum chemical laboratory of Professor G.V. Ionova in collaboration with Professor F. David (Institute of Nuclear Physics Orsay) a large number of data was obtained on thermodynamic properties of hydrated actinide ions [75–78], a theoretical study was carried out on the extraction separation of lanthanides(III) and actinides(III) [79–82]. A significant contribution was made by Academician B.F. Myasoedov and the researchers of his laboratory in the framework of program SPIN [43]: They suggested to use hexacyanoferrate complexes for separation of lanthanides and actinides [83].

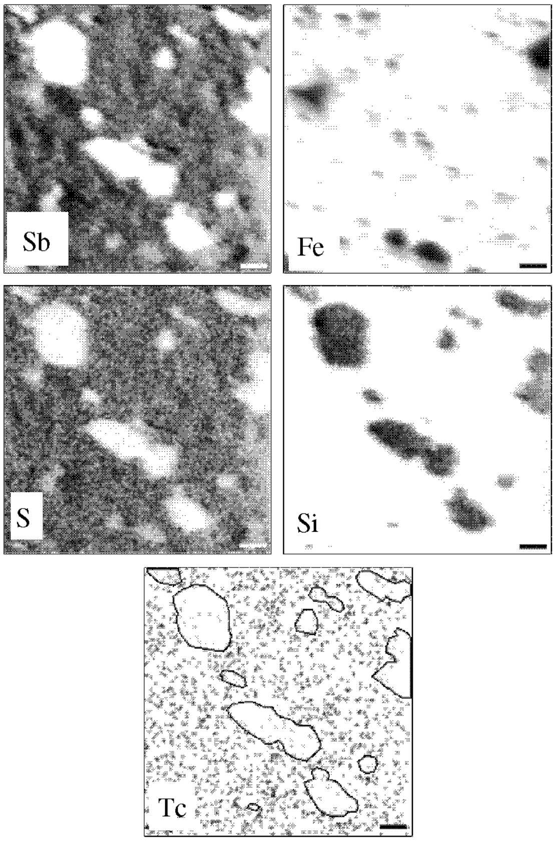

Fig. 9. Map of the distribution of chemical elements in the surface layer (140 μm) of polished stibnite mineral after sorption of Tc from natural water. White color corresponds to the minimal content of the element, black color, to the maximal content.

The short review of results of joint research of IPCE RAS and the enterprises of the Commission of Atomic Energy and Centre Nationale de Recherches Scientifiques (CNRS), France, shows that the collaboration started over 30 years ago [1] continues to develop efficiently. The results of collaboration make an essential contribution into the development of scientific fundamentals for the reprocessing of new types of nuclear fuel, refining of the methods of isolation and analysis of long-lived fission products from the solutions of the nuclear fuel cycle, and in improvement of environmental safety in handling the radioactive wastes.

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