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Technetium: behaviour during reprocessing of spent nuclear fuel and in environmental objects

N N Popova, I G Tananaev, S I Rovnyi, B F Myasoedov

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Abstract. The review surveys main chemical properties of technetium, methods of its isolation and determination and its behaviour during reprocessing of spent nuclear fuel and in environmental objects. Methods for extraction and isolation of technetium as a hazardous long-lived radionuclide are described. Prospects of using technetium in industrial processes and in medicine are considered. The bibliography includes 276 references.

I. Introduction

Technetium is a Group VII element, which was first prepared by nuclear synthesis in the mid-twentieth century. The characteristic feature of technetium is that all its isotopes with mass numbers from 90 to 110 are radioactive. Technetium is an artificial element and does not occur in nature. However, more than 60 tonnes of Tc have accumulated in the world because spent nuclear fuel (SNF) has a high Tc content (0.6 g per kilogram of ^{235}U in the case of 50% burn-up).[1] Large amounts of fission products (FP), including Tc, were released into the environment from nuclear weapon production and nuclear power engineering. Since the ^{99}Tc isotope has a long half-life, it is a very hazardous radioactive element. Besides, technetium shows a high migration ability and some of its compounds are volatile.

The main chemical and physicochemical properties of technetium are well known and were described in monographs and reviews [2–9] as well as in the handbook published in 1999.[10] However, many new studies published in recent years require generalisation. Besides, progress in nuclear power engineering has generated a need for additional studies of the behaviour of Tc during reprocessing of spent nuclear fuel and in environmental objects. The lack of the necessary information on important radiochemical properties and behaviour of technetium in natural objects has already led to contamination of the environment by a large amount of Tc.

The present review surveys the main properties of technetium responsible for its behaviour during reprocessing of SNF and in environmental objects. These data may be of use for improvements in present-day technologies for reprocessing of SNF from the viewpoint of optimisation and complete extraction of Tc as well as for the prediction of its behaviour in natural objects.

N N Popova, I G Tananaev, B F Myasoedov V I Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, 119991 Moscow, Russian Federation.
Fax (7-095) 938 20 54. Tel. (7-095) 939 70 07.
E-mail: popova@geokhi.ru (N N Popova).
Tel. (7-095) 939 70 98. E-mail: tananaev@geokhi.ru (I G Tananaev).
Tel. (7-095) 237 80 81. E-mail: bf@geokhi.ru (B F Myasoedov)
S I Rovnyi State Scientific Centre of the Russian Federation 'Mayak Plant', ul. Lenina 31, 456780 Ozersk, Chelyabinsk Region, Russian Federation. Fax (7-351) 712 69 45. Tel. (7-351) 712 89 45.
E-mail: rel@envc.chel-65-chel.su

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II. Discovery, methods of preparation and main properties of technetium

D I Mendeleev was the first to suppose that a chemical element with the atomic mass of 99 should be present between manganese and rhenium in the Periodic Table (and gave it the name ekamanganese).[11, 12] However, the discovery of this element in manganese-containing ores and minerals appeared to be a difficult problem. All attempts to isolate the new element with the atomic number 43 failed. The Russian chemist Shchukarev [13] and German physicist Mattauch [14] formulated the 'prohibition rule' stating that the isobars of two adjacent elements in the Periodic Table cannot be stable, *i.e.*, one of these elements is necessarily radioactive. This led to the conclusion that the element with the atomic number 43 could not have stable isotopes and, consequently, could not occur in nature.

1. Preparation and nuclear properties of technetium isotopes

In 1937, Perrier and Segre [15, 16] carried out the first experiments on isolation of the element with the atomic number 43 from a molybdenum target bombarded with deuterons on a cyclotron according to the reaction

$$^{A}Mo_{42}\,(d,n)^{A+1}Tc_{43}\,.$$

The new element was named technetium (for the Greek word 'τεχνηοσ', which means artificial).

Later on, another procedure was developed for the preparation of Tc by irradiation of molybdenum-containing samples in slow neutron flux [17]

$$^{98}Mo(n,\gamma)\,^{99}Mo^{\beta-} \longrightarrow {}^{99m}Tc^{\gamma} \longrightarrow {}^{99}Tc.$$

Kilogramme amounts of either spectrally pure MoO_3 or molybdenum metal are used as a target. The target is irradiated in a reactor for one year and kept until the parent ^{99}Mo isotope completely decays. Irradiation of 1 kg of molybdenum with a flux of 8×10^{13} neutrons cm^{-2} s^{-1} makes it possible to accumulate up to 60 mg of Tc. Isolation of technetium must be carried out in 'hot' chambers operating under remote control at a hot laboratory, whereas the yields remain low.

In this connection, isolation of technetium in the course of SNF reprocessing is presently a more convenient procedure, because technetium is a fission product accumulated upon irradiation of nuclear fuel in a reactor. The accumulation of Tc depends on the nature of the fissionable nuclide and the depth of burn-up and reaches $\sim$1 kg per tonne of fuel in fast-neutron reactors.[18] The yield of ^{99}Tc during fission of ^{235}U or ^{239}Pu is about 6.1%.[19] Other Tc isotopes with the mass numbers from 99 to 110 inclusive were also found among fission products of uranium. These isotopes are produced through β^--decay or neutron capture.[8] However, nuclear reactors produce these isotopes in insignificant yields.

Of technetium isotopes, the long-lived ^{99}Tc isotope ($\tau_{1/2} = 2.14 \times 10^5$ years) is of particular importance. This isotope serves as a β-ray emitter with the energy $E_{\beta max} = 292$ keV, and its decay is not accompanied by γ-radiation.[20] The ^{99m}Tc isotope ($\tau_{1/2} = 6.6$ h) is widely used in medicine. This radionuclide is most commonly isolated with the use of chromatographic,[21] extraction[22] or sublimation[23,24] generators based on ^{99}Mo. Generators based on sublimation separation of Tc outperform generators of other types in many respects. Their construction assumes heating of MoO_3 to 850 °C in a flow of O_2. The yield of ^{99m}Tc obtained by sublimation of volatile technetium oxide and its condensation in a cooled receiver followed by dissolution of the condensate reaches 1 Ci ml^{-1}. The type of ^{99m}Tc decay is the isomeric transition of the nucleus from a metastable state to a lower-energy level. In studies of ^{99m}Tc, it was demonstrated that the chemical state of the element has only a slight effect on the rate of decay of an unstable nucleus. Thus, the half-life of technetium metal is 1.003 times longer than that of $KTcO_4$.[25]

For technetium, 21 isotopes with the mass numbers from ^{90}Tc to ^{110}Tc are known, seven of these isotopes being isomers. Most Tc isotopes have short half-lives (from 0.81 s for ^{110}Tc to 61.2 days for ^{97m}Tc). The exceptions are the above-mentioned ^{99}Tc isotope and two long-lived isotopes, *viz*., ^{97}Tc ($\tau_{1/2} = 2.6 \times 10^6$ years) and ^{98}Tc ($\tau_{1/2} = 4.2 \times 10^6$ years), which are prepared by irradiation of molybdenum with deuterons or protons.

2. Technetium metal

The main properties of technetium metal were studied predominantly in the 1960s. It was demonstrated that it has a hexagonal close-packed structure with the parameters $a = 2.7409$, $c = 4.3983$ Å.[19,26] In polycrystalline films prepared by ion deposition at liquid nitrogen temperature, technetium has a face-centred cubic structure with the lattice parameter $a = 3.68 \pm 0.05$ Å.[27]

The hexagonal crystal lattice of technetium has a small number of easy-slip planes due to which the as-cast metal is brittle and cracks even at small degrees of reduction upon rolling at 20 °C. Nevertheless, technetium was prepared as rods, strips, foil and wire by the corresponding technological processing.[28]

Technetium is a refractory metal with the melting point of > 2000 °C.[29] It forms continuous series of solid solutions with metals, which crystallise in the hexagonal system, *viz*., with ruthenium, osmium and rhenium (analogue of Tc).[30] Technetium is a superconductor ($T_c = 8.24$ K). The magnetic susceptibility of Tc remains constant in the temperature range of 80 – 1300 K and is close to that of rhenium.[31]

Technetium metal is generally prepared by thermal decomposition of pertechnetates with organic cations under a stream of inert gas[32,33] or thermolysis of other Tc compounds (for example, of NH_4TcO_4) in a reducing medium.[34–37]

The metal thus prepared is insoluble in HCl or H_2SO_4. However, it is readily oxidised with nitric acid.

$$3\,Tc + 7\,HNO_3 = 3\,HTcO_4 + 7\,NO + 2\,H_2O.$$

3. Behaviour of technetium in solutions

The electronic structure of the Tc atom ($[Rn]3d^{10}4s^24p^64d^65s^1$) is responsible for its transition-metal properties. Due to such an electron shell structure, technetium can exist in a wide range of oxidation states from +7 to −1 and has a tendency to disproportionation. Besides, equilibrium systems containing Tc in different oxidation states can occur in solutions. This is manifested in the behaviour of technetium in chemical reactions and different technological processes.

The scheme of the Latimer potentials in an acidic medium was reported in the study:[38]

$$Tc \overset{-0.240\,V}{\underset{-0.472\,V}{\overset{-0.782\,V}{\overset{\frown}{\underset{\smile}{}}}}} TcO_2 \overset{-0.8\,V}{\underset{}{}} TcO_3 \overset{-0.7\,V}{\underset{}{}} TcO_4^-$$

The formal oxidation potentials of technetium [relative to the normal hydrogen electrode (NHE)] in acidic and alkaline media are given below.[39]

Medium	+7/+6	+6/+5	+6/+4	+5/+4	+4/0	−1/0
$HClO_4$ (1 mol $litre^{-1}$)	0.56	–	1.39	0.71	0.28	−0.5
NaOH (1 mol $litre^{-1}$)	−0.64	−0.1	–	−0.88	−1.35	–

The standard oxidation potential E for the Tc(VII)/Tc(IV) pair is 0.738 V (*vs*. NHE).[40]

In HNO_3 solutions, the stability of Tc ions increases in the following series: Tc(VII) > Tc(IV) > Tc(V) > Tc(VI).[41]

In acidic media, Tc(IV) is stable only in the presence of complex-forming compounds. For example, Tc(IV) forms the well-studied $TcCl_6^{2-}$ complex in HCl solutions (6 mol $litre^{-1}$).[42]

Technetium(V) is unstable and undergoes disproportionation in acidic media according to the following scheme:

$$3\,Tc(V) = Tc(VII) + 2\,Tc(IV).$$

In the HCl + NaCl system (ionic strength $\mu = 1.0$), the reaction rate is proportional to the square of the Tc(V) concentration.[18] Although prone to disproportionation, pentavalent technetium is more stable than hexavalent technetium and its compounds can be isolated from aqueous solutions.[43–44] Technetium(VI) also undergoes disproportionation according to the reaction

$$3\,Tc(VI) = 2\,Tc(VII) + Tc(IV),$$

the reaction proceeding with a very high rate (at 25 °C, the rate constant is $\sim 3 \times 10^6$ litre mol^{-1} s^{-1}).[18] The stability of technetate ions in aprotic solvents provides evidence that its disproportionation proceeds with the involvement of protons.[45]

The pertechnetate ion is stable in solutions. This ion acts as a rather strong oxidising agent and can be reduced with a number of reducing agents, such as ascorbic acid,[46–49] hydroxylamine,[50,51] urea[52] and the chloride, bromide and iodide ions.[53–55] In an alkaline medium, the TcO_4^- ion is catalytically reduced in the presence of $PdCl_2$ (0.001 mol $litre^{-1}$) to Tc(IV) at 65 °C during 4 days.[56]

Reduction of pertechnetate ions with different reagents in the presence of complex-forming agents is used in many procedures for the qualitative and quantitative determination of Tc.[57]

Only Tc(VII) and Tc(IV) compounds are of practical importance, because these ions are thermodynamically stable and can exist in solution. It is in these oxidation states that technetium can be present both in wastes of radiochemical production facilities and in environmental objects. Unstable and reactive intermediate

forms, *viz*., Tc(V) and Tc(VI), cannot exist under normal conditions but can be involved in redox reactions.

4. Chemical and physicochemical properties of selected technetium compounds

Abundant data on the synthesis, investigation and use of a number of simple and complex technetium compounds are available in the literature (see, for example, the recent review [58]). Hence, we shall take a quick look at the properties of technetium compounds, which determine the behaviour of technetium in nuclear technology and environmental objects. Special attention is given to technetates and Tc(IV) compounds.

The TcO_4^- anion is stable in acidic, neutral and alkaline media.[41] Pertechnetates $MTcO_4$ belong to a class of ionic crystals stabilised primarily through Coulombic interactions between ions.[59] Since the electronic structure of TcO_4^- and its size are similar to those of ReO_4^-, pertechnetates are analogues of perrhenates and, in some cases, these compounds are isostructural. Pertechnetates are more similar to permanganates in thermal stability rather than to perrhenates. The physicochemical properties of polycrystalline $MTcO_4$ depend substantially on the nature of the M cation. Probably, this is partially associated with a distortion of the tetrahedral symmetry of the pertechnetate ion and the type of the crystal system. According to the data from vibrational spectroscopy and ^{17}O and ^{99}Tc NMR spectroscopy, the pertechnetate ion in aqueous and non-aqueous solutions has a regular tetrahedral symmetry regardless of the nature of the cation.[60] According to the results of vibrational spectroscopy and X-ray diffraction studies, the island anionic polyhedron TcO_4^- in crystals is distorted, the degree of distortion being decreased with increasing cation radius.

Pertechnetates may be divided into three groups.[60–62]

1. Pertechnetates of alkali metals (Na, K, Rb) whose crystals have scheelite-like structures and are characterised by a small angular distortion of the TcO_4^- anion (1–2 °).

2. Ammonium pertechnetate whose tetragonal lattice is built from the isolated TcO_4^- and NH_4^+ groups linked through hydrogen bonds. The unit cell parameters of NH_4TcO_4 vary substantially in the temperature range of 100–340 K.

3. Pertechnetates with onium cations whose structures are poorly known (except for Me_4NTcO_4, in which the anionic polyhedron TcO_4^- is strongly distorted); the Tc–O bond lengths in these compounds differ by 0.04 Å and the bond angles are 105.5 and 111.7 °.[60]

Alkali metal pertechnetates are readily soluble in water. Thus, the solubility of $NaTcO_4$ is 11.3 mol litre^{-1} at 20 °C.[39]

Technetium(IV) dioxide TcO_2, which is the most important and stable Tc(IV) compound, occurs as a paramagnetic black powder with a density of 6.9 g cm^{-3}. At 298.16 °C, this compound is characterised by the following thermodynamic parameters: $-\Delta H_{form} = 434.59$ kJ mol^{-1}; $S^\circ = 62.5$ J mol^{-1} deg^{-1}; $-\Delta S^\circ = 173.9$ J mol^{-1} deg^{-1}; $-\Delta G^\circ_{form} = 382.76$ kJ mol^{-1}. Technetium(IV) dioxide TcO_2 crystallises in the monoclinic system with the following unit cell parameters: $a = 5.53$, $b = 4.79$, $c = 5.53$ Å, $\beta = 120$ °.[63] According to the results of EXAFS measurements, the Tc–Tc distance in the structure of TcO_2 is 2.61 Å.[64]

Technetium(IV) dioxide is quite stable in air at 20 °C. In deaerated neutral and acidic aqueous solutions, this compound is stable, whereas in aerated aqueous solutions, TcO_2 rapidly oxidises with subsequent dissolution (with a rate of ~1 mass % during 10 days) to give $Tc^{VII}O_4^-$.[65]

Technetium(IV) dioxide occurs in two forms, *viz*., nonhydrated (TcO_2) and hydrated ($TcO_2 \cdot n H_2O$). The hydrated form is less stable (compared to TcO_2) both in solutions and in air.

In alkali solutions, TcO_2 dissolves to give $Tc(OH)_6^{2-}$ ions, which have a characteristic orange colour. The hydroxo technetate ions, whose solutions absorb light at $\lambda = 410$ nm, are readily oxidised with atmospheric oxygen to Tc(VII).

The solubility of $TcO_2 \cdot n H_2O$ at pH 7–10 in the absence of oxidising and complex-forming agents is close to 10^{-8}–10^{-9} mol litre^{-1} and increases substantially as the pH of the solutions increases. In air, the solubility of $TcO_2 \cdot n H_2O$ in a NaOH solution (1–3.6 mol litre^{-1}) containing N_2H_4 (0.02 mol litre^{-1}) is $(1.1 \pm 0.1) \times 10^{-5}$ mol litre^{-1}. Under the same conditions, the solubility of $Tc_2O_5 \cdot n H_2O$ is 6.1×10^{-6} mol litre^{-1}.[41,66]

III. Methods of isolation of technetium from solutions

1. Liquid–liquid extraction

Liquid-liquid extraction is most commonly used for the isolation of technetium from solutions with different compositions. Abundant data on the extraction properties of Tc(VII) have been accumulated. Different extractants were proposed for extracting technetium from acidic, neutral and alkaline solutions, among which are alcohols, ketones, ethers, nitro compounds, organophosphorus compounds,[67,68] nitriles, amines,[69] *etc*.[70–72]

The extractants characterised by the best distribution coefficients of Tc(VII) in acidic media are listed in Table 1.

Table 1. Distribution coefficients of Tc(VII) (D_{Tc}) in acidic media.

Extractant	Acid	Concentration /mol litre^{-1}	D_{Tc}	Ref.
Triisooctylamine (0.2 mol litre^{-1}) in syntin	HNO_3	1	270	39
Acyldimethylbenzylammonium chloride	H_2SO_4	1	105	73
Diisopentyl methylphosphonate	HNO_3	0.1	117	39
Tri-n-octylamine (0.1 mol litre^{-1}) in cyclohexane	H_2SO_4	1	110	73
Tri-n-octylphosphine oxide (0.5 mol litre^{-1})	HNO_3	0.1	78	39
Cyclohexanol	H_2SO_4	1	32	73

A solution of tetraphenylarsonium chloride in chloroform (10^{-4} mol litre^{-1}) is the most efficient extractant in neutral and weakly alkaline media. The distribution coefficient $D_{Tc(VII)}$ for this agent is 106 (Na_2CO_3, pH 10).[74,75]

α-Picoline ($D = 1840$), 5-ethyl-2-methylpyridine ($D = 1000$), 2,4-dimethylpyridine ($D = 700$) and quinoline ($D = 523$) are the most promising extractants for the extraction of technetium from alkaline solutions (0.5 mol litre^{-1} NaOH + 1 mol litre^{-1} Na_2CO_3).[75]

2. Sorption and extraction chromatography

Data on sorption extraction of technetium(VII) by both synthetic organic sorbents and inorganic materials are available in the literature.

It was demonstrated that Tc(VII) as the TcO_4^- ion has a high affinity for different granulated anion-exchange resins. Strongly basic anion-exchange resins of the AV-17 type, Dowex-1 × 8 or vinylpyridine ion-exchange resins show the highest efficiency for absorption of Tc(VII). Polyfunctional ion-exchange resins, for example, EDE-10, are less efficient for absorption of Tc(VII).[76] The plot of the distribution coefficient [$K_d^{Tc(VII)}$] *vs*. the pH of the solution for sorption of Tc(VII) with the AV-17 anion-exchange resin [77] is shown in Fig. 1.

The distribution coefficient $K_d^{Tc(VII)}$ for sorption of TcO_4^- from NaOH solutions (0.25 mol litre^{-1}) by the Dowex-1 × 8 ion-exchange resin is 4500 cm^3 g^{-1}, but this coefficient decreases substantially as the salt background increases. Thus, an increase in the concentration of $NaNO_3$ from 0.5 to 5.0 mol litre^{-1} leads

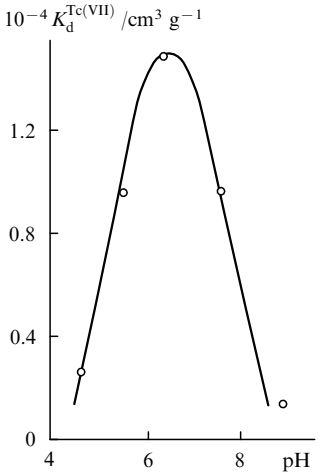


Figure 1. Plot of $K_d^{Tc(VII)}$ *vs.* pH upon sorption on the AV-17 anion-exchange resin in the Cl form.[77]

to a decrease in $K_d^{Tc(VII)}$ from 575 to 122 cm^3 g^{-1}, all other factors being the same. In the case of sorption of Tc(VII) on the VP-1AP anion-exchange resin, the distribution coefficient $K_d^{Tc(VII)}$ changes from 6233 to 5193 cm^3 g^{-1} in the range of the NaOH concentrations from 1 to 4 mol litre^{-1}.[39]

Sorption of technetium(VII) from aqueous solutions with pH 2–12 by granulated monofunctional AV-17-based anion-exchange resins containing amine and amide functional groups or nitrogen heterocycles was studied. It was demonstrated that the AV-17 anion-exchange resin and resins containing different functional groups can be arranged in the following order of increasing affinity for the pertechnetate ion: AV-17 > $NC(O)Et_2$ > $NC(O)Bu^n_2$ > $S(CH_2)_2NMe_2$ > NMe_2. The pH of solutions providing the maximum sorption of technetium increases in the same order. Thus, the maximum distribution coefficients of Tc(VII) (in cm^3 g^{-1}) corresponding to the maximum pH are as follows: 1.3×10^4 at pH 5 [$NC(O)Et_2$], 1.2×10^4 at pH 4 [$NC(O)Bu^n_2$], 1.1×10^4 at pH 3 [$S(CH_2)_2NMe_2$] and 0.4×10^4 at pH 2.5 (NMe_2).[77]

Sorption of TcO_4^- from acidic solutions should be considered as an acid–base interaction according to the reaction

$$R\sim + H^+_W + (TcO_4^-)_W = RHTcO_4,$$

where R~ is the functional group of the resin.

Sorption of technetic acid by basic anion-exchange resins is accompanied by localisation of the proton at the functional group giving rise to $RH^+\cdots TcO_4^-$ ion pairs. The logarithm of the constant of proton association in the HCl–LiCl system (μ = 5) is 0.033.[77, 78]

Sorption of the TcO_4^- ions was studied[79] on the radiation-stable styrene–vinylpyridine anion-exchange resin Reillen^{TM}–HPQ (30–60 mesh granules) containing 75% of highly basic methylated ion-exchange amino groups and 25% of weakly basic non-methylated ion-exchange amino groups. If the equilibrium was established within 30 min, the distribution coefficients $K_d^{Tc(VII)}$ in HNO_3 solutions with concentrations of 10, 5 and 1 mol litre^{-1} were estimated at 11.5, 55.7 and 415 cm^3 g^{-1}, respectively. These values are substantially higher than the corresponding values for the commercial Dowex-1 × 8 anion-exchange resin (under the same conditions, 5, 15 and 135 cm^3 g^{-1}, respectively). The Reillen^{TM}–HPQ sorbent can also be used for the extraction of technetium(VII) from salt solutions. Thus, the distribution coefficients K_d of TcO_4^- with the use of this sorbent at an HNO_3 concentration of 0.001 mol litre^{-1} are 162 cm^3 g^{-1} (in a solution containing 4 mol litre^{-1} of $NaNO_3$), 515 cm^3 g^{-1} (1 mol litre^{-1} of $NaNO_3$) and 138 cm^3 g^{-1} (4 mol litre^{-1} of $LiNO_3$). At an HNO_3 concentration of 0.5 mol litre^{-1}, K_d are 109 cm^3 g^{-1} (4 mol litre^{-1} of $NaNO_3$), 553 cm^3 g^{-1} (1 mol litre^{-1} of $NaNO_3$) and 423 cm^3 g^{-1} (1 mol litre^{-1} of $LiNO_3$).[79]

Not only granulated ion-exchange resins but also fibrous complex-forming sorbents are used in procedures for isolation and extraction of technetium. The latter sorbents exhibit high selectivity for particular ions. Such sorbents have advantages over granulated materials, because they not only possess high selectivity for metal ions but also have a large surface, which ensures their good kinetic properties. In addition to traditional fibrous complex-forming sorbents prepared by a modification of the starting matrices, fibrous materials filled with powdered complex-forming sorbents also show promise. The latter sorbents are composed of fine porous polyacrylonitrile fibers (30–40 μm in diameter), within which a complex-forming sorbent or an ion-exchange agent (filling agent) is held. Fibrous complex-forming sorbents are used for the extraction of rare and noble metals[80–82] as well as of transuranium elements.[83, 84] Fibrous complex-forming agents of the POLYORGS type, which were developed at the V I Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, were also used for the sorption of Tc(VII) from acidic, neutral and alkaline media.[85] Data on extraction of technetium from solutions with different compositions are given in Table 2. The filled fibrous complex-forming sorbents AV-17 and POLYORGS-17 virtually completely absorb trace amounts of Tc both from acidic and alkaline solutions. Other known sorbents also extract technetium from acidic solutions, though to a lesser degree. Under the optimum conditions, the equilibrium distribution coefficients [$K_d^{Tc(VII)}$] for the filled fibrous sorbents of choice are $\geqslant 10^4$ cm^3 g^{-1}, and these sorbents are highly competitive with commercial granulated materials (Table 3).

Table 2. Sorption of Tc(VII) by various fibrous 'filled' sorbents.[85]

Sorbent	Functional groups	Degree of sorption (%)	
		HNO_3 (see [a])	NaOH [a]
AV-17	quaternary ammonium	92	91
AN-31	secondary and tertiary amine	88	23
POLYORGS-17	1,(3)5-dimethylpyrazole	96	96
POLYORGS-33	amidoxime and hydrazide	67	6
POLYORGS-35	hydrazide	79	0

Note. V/m = 100 cm^3 g^{-1}, 20 °C, the contact time was 2 h.
[a] The concentration was 0.1 mol litre^{-1}.

Table 3. Sorption of Tc(VII) by fibrous 'filled' sorbents.[85]

Solution	Concentration /mol litre^{-1}	$K_d^{Tc(VII)}$ /cm^3 g^{-1}	
		AV-17	POLYORGS-17
HNO_3	10^{-3}	3.7×10^4	1.0×10^3
	10^{-2}	1.3×10^4	2.5×10^3
	0.1	1.2×10^3	2.2×10^3
	0.5	382	189
NaOH	0.1	1.0×10^3	277
	1.0	900	–
$NaNO_3$	0.1	861	432

Note. V/m = 100 cm^3 g^{-1}, 20 °C, the contact time was 2 h.

Fibrous sorbents of the POLYORGS type were used for the extraction of technetium from water samples from the Karachai Lake (Russia) located in the territory of the Mayak Production Association and also from wells located in the neighbourhood of this lake.[86]

It was noted that Tc(VII) is efficiently sorbed by activated carbon from acidic solutions, which model compositions of high-level radioactive waste.[87] The distribution coefficient $K_d^{Tc(VII)}$ in solutions containing HNO_3 at a concentration of 0.5 mol litre^{-1} is $\sim 10^3$ cm^3 g^{-1}. For comparison, the sorption of Tc(VII) on other inorganic sorbents, including SiO_2, Al_2O_3 and aluminosilicates, was also studied. Activated carbon appeared to be the sorbent of choice, the use of activated carbon being most efficient in strongly acidic media. The mechanism of sorption and the possibility of the recovery of activated carbon were discussed.[87] The authors of the cited study believed that activated carbon acts as an ion-exchange agent, anion-exchange centres being formed on its surface in solutions with pH 2–5 resulting in an increase in $K_d^{Tc(VII)}$. An increase in the salt background leads to a $\sim$100-fold decrease in the sorption of Tc.[87]

Sorption of Tc(VII) and Tc(IV) on aluminium hydroxide was investigated.[88] The experiments were carried out under an atmosphere of N_2. Under experimental conditions, the sorption of technetium was insignificant and K_d decreased to zero at pH > 7. In hydrochloric solutions, Tc(IV) is sorbed on $Al(OH)_3$ as the $TcCl_6^{2-}$ anions. The sorption maximum is observed in neutral media.

The distribution coefficient $K_d^{Tc(VII)}$ for extraction of Tc(VII) from a solution of HNO_3 (0.05 mol litre^{-1}) with the use of a solid extractant, which is composed of a Polysorb-1 or Chromosorb-W matrix incorporating a solution of trioctylphosphine oxide in cyclohexanone, is $\sim$3500 cm^3 g^{-1}. An increase in the concentration of HNO_3 to 1 mol litre^{-1} causes a decrease in the distribution coefficient to 1060 cm^3 g^{-1}. In solutions containing HCl (1 mol litre^{-1}) and $SnCl_2$ (0.03 mol litre^{-1}), $K_d^{Tc(VII)}$ is 2.8. The distribution coefficient $K_d^{Tc(VII)}$ of Tc(IV) in solutions containing HCl (5 mol litre^{-1}) and $SnCl_2$ (0.3 mol litre^{-1}) is even lower (< 1). In neutral and alkaline media, $K_d^{Tc(VII)}$ are 110 cm^3 g^{-1} (pH 6.4) and 10 cm^3 g^{-1} (0.5 mol litre^{-1} of NaOH + 2.5 mol litre^{-1} of $NaNO_3$).[70]

With the aim of isolating technetium from plant materials, the sorption of the following anions was studied: TcO_4^-, technetium diethylenetriaminepentaacetate as well as the $[Tc^VO_2(1,4,8,11\text{-tetraazacyclotetradecane})]^+$ cationic complex on polydextran gel Sephadex G-25, hydrophilic silica gel Zorbax GF-250 and polymeric gel HEMA-SEC BIO1000. It was found that HEMA-SEC BIO1000 is the matrix of choice for isolation of Tc(VII). In solutions of NaCl with a concentration of 0.04 mol litre^{-1}, $K_d^{Tc(VII)}$ for these ions have close values (4, 1.5 and 0.8 cm^3 g^{-1}, respectively).[89]

The sorption of Tc on TiO_2, cadmium sulfide, zirconium phosphate and complex inorganic materials[90] was studied upon contact between a sorbing material (1 g) and a solution of Tc(VII) (10 ml) at 20 °C (Table 4). At pH 6.5, Termoxid-34 and GSK (see Table 4) are the most efficient sorbents. After irradiation of samples using a ^{60}Co γ-source ($\sim 10^7$ rad) at 20 °C for 20 h, their total sorption capacity was almost halved.

Table 4. Distribution coefficients $K_d^{Tc(VII)}$ for different composites.[90]

Sorbent	$K_d^{Tc(VII)}$/cm^3 g^{-1}		
	pH 1.27	pH ~6.5	pH 12.7
GSK (crystalline CdS)	11.0	13.4	2.16
Termoxid-34 (high-density crystalline TiO_2)	5.3	31.3	0.73
SPSK ($Sb_2O_5 \cdot n\,SiO_2 \cdot m\,P_2O_5$)	4.7	9.4	< 0.1
ISMA ($n\,LiO \cdot m\,MnO_2 \cdot l\,Al_2O_3 \cdot k\,H_2O$)	4.0	10.25	~1

Sorption methods are being developed for the extraction of technetium from alkaline wastes (pulps) of radiochemical production facilities. It is known that high-level radioactive wastes were accumulated during 50 years as a result of weapon plutonium production and still remain unreprocessed both in Russia (Mayak Production Association, Ozersk)[91] and abroad, particularly, in the USA (Hanford Site, Savannah River Site, Idaho National Engineering and Environmental Laboratory, West Valley Staffing Group and Oak Ridge National Laboratory).[92–94] Thus, thousands of tonnes of alkaline pulps, which have the overall activity of $\sim 2 \times 10^5$ Ci and contain Np (50–100 kg), Pu (540–860 kg), Am ($\sim$30 kg) and Tc ($\sim$2 t), were accumulated at the Hanford Site of the Westinghouse Hanford Company (Richland, USA).[92–94] It is also necessary to extract technetium during reprocessing of alkaline pulps followed by burial of hazardous long-lived radionuclides. Main problems associated with the development of sorption methods for the extraction of technetium from these wastes are a high concentration of alkali ($[OH^-] \approx 1$–4 mol litre^{-1}), high salt background ($[Na^+] \approx$ 2–5 mol litre^{-1}, $[Al^{3+}] \approx 0.8$ mol litre^{-1}; $[K^+] \approx 0.1$ mol litre^{-1}; $[NO_3^-] \approx 1.6$ mol litre^{-1}; $[NO_2^-] \approx 1$ mol litre^{-1}), high density of the liquid phase ($\approx$1.1–1.3 cm^3 g^{-1}) and high radiation background.

Selective organic granulated anion-exchange resins and inorganic materials (including metals) are used for the extraction of technetium from alkaline solutions with high salt concentrations.

The SuperLig 639 sorbent was specially constructed for the extraction of technetium from alkaline high-level radioactive waste stored at the Hanford Site (USA). This sorbent was tested on real solutions from the waste tanks AN-103 ($[Na^+] \approx$ 4.9 mol litre^{-1}, $[NO_3^-] \approx 1.6$ mol litre^{-1}, $[OH^-] \approx 1.9$ mol litre^{-1}), AZ-102 ($[Na^+] \approx 2.7$ mol litre^{-1}, $[NO_3^-] \approx$ 0.27 mol litre^{-1}, $[OH^-] \approx$ 0.1 mol litre^{-1}) and AN-102 ($[Na^+] \approx 5.3$ mol litre^{-1}, $[NO_3^-] \approx 1.5$ mol litre^{-1}, $[OH^-] \approx$ 1.25 mol litre^{-1}).[95] This sorbent occurs as 20–70 mesh granules (200–800 μm) and is made up of the groups of crown ether DCH-18-C-6 covalently bonded to a polystyrene matrix. The distribution coefficients $K_d^{Tc(VII)}$ for sorption of technetium from radioactive wastes from the tanks AN-103, AZ-102 and AN-102 with the use of this anion-exchange resin are 530, 886 and 287 cm^3 g^{-1}, respectively.

Extraction chromatography was applied to the isolation of technetium from alkaline wastes with the use of the ABEC™-5000 ion-exchange resin made up of monomethylated poly(ethylene glycol) (PEG-5000) covalently bonded to a polystyrene support, which efficiently adsorbed TcO_4^- from solutions. Sorption of Tc(VII) was carried out from NaOH solutions (2–4 mol litre^{-1}). The desorption of Tc followed by its concentration were performed with the use of distilled water. The addition of the NO_3^- and NO_2^- ions to the eluent leads to an increase in the rate of elution of TcO_4^- from a sorbent layer. By contrast, the citrate, carbonate and aluminate ions facilitate the retention of TcO_4^- by the resin. An increase in the temperature from 25 to 40 °C has only a slight effect on this process. The ABEC™-5000 ion-exchange resin appeared to be resistant to ^{60}Co γ-irradiation up to the dose of 131 mrad.[96]

3. Currentless electrochemical deposition

The static contact between granulated Zn metal and solutions containing 0.5, 2.0 or 3.5 mol litre^{-1} of NaOH and $(6 \pm 3) \times 10^{-5}$ mol litre^{-1} of Tc(VII) in the presence of complex-forming agents led to sorption of technetium on the metal surface with $K_d^{Tc(VII)}$ of 1.4, 3.9 and 5.7 cm^3 g^{-1}, respectively.[97] In the dynamic mode, the distribution coefficients $K_d^{Tc(VII)}$ were 1.9, 4.7 and 8.9 cm^3 g^{-1}, respectively (Fig. 2). The sorption of technetium from NaOH solutions with concentrations from 0.5 to 3.5 mol litre^{-1} with the use of Cr or Sn metals both in the static or dynamic modes in the presence of complex-forming agents is characterised by low distribution coefficients $K_d^{Tc(VII)}$ (< 1.2 cm^3 g^{-1}). The authors of the cited study[97] believed that interactions of Zn, Cr or Sn with Tc in alkaline solutions caused reduction of Tc(VII) to Tc(IV) followed by sorption of the resulting $TcO_2 \cdot n\,H_2O$ on the metal surface. The solubility of $TcO_2 \cdot n\,H_2O$ thus precipitated in a deaerated NaOH solution (4 mol litre^{-1})

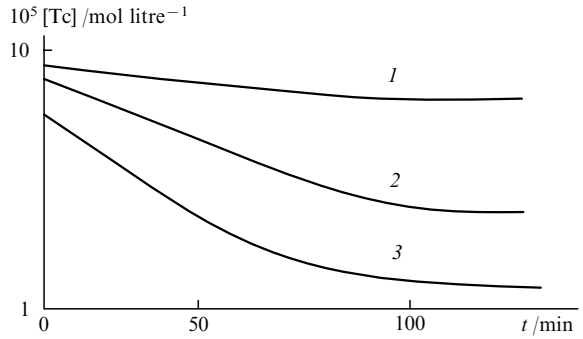


Figure 2. Sorption of Tc(VII) on zinc granules depending on the duration of the contact between the granules and a NaOH solution.[97]
(*1*) 1M NaOH, (*2*) 2M NaOH, (*3*) 4M NaOH.

was nearly 6×10^{-7} mol litre^{-1}, which is 50 times lower than the solubility of $TcO_2 \cdot n\,H_2O$ prepared by reduction of Tc(VII) with hydrazine. The high reactivities of the metals used (Zn, Cr, Sn, Pb and Sb) are associated with the fact that these metals do not form oxide films (which hinder the contact) in alkaline media. Because of this, the oxidation potentials of these metals are sufficient for reduction of Tc(VII) to $TcO_2 \cdot n\,H_2O$. The degree of Tc deposition (contrast to actinides) increases with increasing NaOH concentration. An increase in the temperature from 20 to 60 °C and the removal of dissolved O_2 have virtually no effect on the final results.

4. Electrochemical separation

Electrochemical methods are used along with traditional chemical methods for the preparation of solutions with the aim of stabilising technetium and actinides in the desired oxidation states when using the extraction technology of reprocessing of spent nuclear fuel.[98,99] It was demonstrated that the rate of electrolytic oxidation of Pu(0) to Pu(IV) and the yield of the product increased in the presence of technetium(VII) ions. Thus, the addition of Tc(VII) (70 mg litre^{-1}) to a solution containing Pu(III) and hydrazine caused acceleration of oxidation of plutonium by a factor of ~ 1.5 due, apparently, to catalytic decomposition of hydrazine with technetium ions.[18] Electrolysis of solutions of Tc(VII) in H_2SO_4 (1 mol litre^{-1}) in a diaphragm cell led to reduction of technetium partially to metal that deposited on the cathode and partially to Tc(IV) accumulated in the electrolyte as a colloidal suspension of TcO_2.

Data on the electrochemical separation of technetium from solutions which model compositions of liquid radioactive wastes were reported in the study.[100] In HNO_3 solutions (0.1–1.0 mol litre^{-1}), electrochemical reduction of Tc(VII) to Tc(III) involves two electrode reactions. The first reaction proceeds at 0.069 to -0.205 V (relative to SHE) and is associated with reduction of technetium. The second reaction proceeds at -0.71 V and results in decomposition of nitric acid catalysed by Tc(III) cations. Electrochemical reduction of the pertechnetate ions by polarographic methods on a mercury electrode in an acetate buffer (pH 3.5–6.0) was studied. It was noted that the Tc(VII)/Tc(III) reduction proceeded through the formation of Tc(V) followed by its disproportionation to give water-insoluble suspensions of Tc(IV) compounds. Technetium(IV) present in precipitates adsorbed on the electrode was reduced to Tc(III). An original scheme of separation of technetium from solutions which model wastes from the PUREX process ([Tc(VII)] = 200 mg litre^{-1}, [HNO_3] = 2–4 mol litre^{-1}) was proposed in the study.[100] This method involves denitration of the starting solution with formic acid on heterogeneous platinum catalysts followed by electrolytic reduction of technetium on a graphite electrode at -1.3 ± 0.1 V to give $TcO_2 \cdot n\,H_2O$ (pH 6.0–7.5, the ionic strength was 0.5–1.0 mol litre^{-1}, the yield was 92%–95%).[100]

5. Precipitation and coprecipitation

It is known that Tc(VII) is efficiently precipitated with hydrazine in the presence of $FeCl_3$. The presence of complex-forming agents (for example, of sodium phosphate or sodium ethylenediaminetetraacetate at concentrations of 0.01 and 0.1 mol litre^{-1}, respectively) leads to a decrease in the degree of precipitation of technetium.[101] Reduction of Tc(VII) with hydrazine can be accompanied by sorption of technetium on metals, such as Zn or Al.[41] Up to 99.5% of Tc was precipitated in alkaline media (0.5–4.0 mol litre^{-1} of NaOH) in the presence of $N_2H_4 \cdot H_2O$ (0.17 mol litre^{-1}) and $FeCl_3$ (0.025–0.15 mol litre^{-1}). However, only 76% of Tc was extracted from model solutions of high-level radioactive wastes under analogous conditions, which indicates that Tc(VII) is only partially reduced in the presence of salts.[101] In some cases, technetium was successfully isolated as Tc(IV),(V) hydroxides.[102]

In wastes of radiochemical production facilities, Tc is present together with platinum-group elements. A procedure was developed for the separation of Tc from these elements using denitration of a solution of nitric acid with formic acid.[87,103,104] Under these conditions, Pd and Rh are reduced with formic acid to metals, and Tc is reduced to Tc(IV) and is isolated as hydrated dioxide. It was found that more than 90% of Tc was precipitated in the presence of Pd and Rh (> 0.005 mol litre^{-1}) at a concentration ratio $HCOOH/HNO_3 > 1.8$. Then technetium(IV) dioxide is dissolved in the presence of different oxidising agents. Refluxing of technetium(IV) dioxide in the presence of O_2, O_3, H_2O_2 or HNO_3 afforded Tc(VII) in 23%, 34%, 76% or 90% yields, respectively. Storage with sodium hydroxide during 24 h afforded Tc(VII) in only 6% yield. Hence, nitric acid proved to be the most efficient oxidising agent.

The coprecipitation of Tc(VII) and Re(VII) with FeS belonging to the tetragonal system was studied.[105] In this process, TcO_4^- was reduced to Tc(IV) to give a TcS_2-like phase.

The separation of technetium from Mo and Ru was achieved by its coprecipitation in the presence of tetraphenylarsonium.[41] It was also demonstrated that technetium(VII) was reduced to Tc(IV) and Tc(V) and coprecipitated with the latter upon contact with $Mn(OH)_2$, $Co(OH)_2$ or $Cr(OH)_3$, which allowed one to separate ^{99}Tc from impurities of ^{137}Cs.

IV. Methods of determination of technetium

1. Radiometry

Generally, ^{95m}Tc and ^{99m}Tc are detected from their γ-activity.[106] In a number of studies, ^{99}Tc was determined from the β-activity on a Packard 2750 TR/LL scintillation counter.[106–108] A scheme was proposed for the determination of ^{99}Tc in natural samples. This scheme involves annealing of a sample at 550 °C and treatment of the residue with solutions of nitric acid followed by extraction of technetium with a 5% solution of tri-n-octylamine in xylene. In an aqueous reextract, Tc is concentrated by the anion-exchange method, the concentrate is dissolved in a scintillation cocktail and the ^{99}Tc content is determined from its β-activity in the sample.

At low concentrations in natural samples, Tc is isolated with the use of carriers (generally, ^{99m}Tc). The radiometric determination of the initial ^{99}Tc is performed only after the complete decay of the carrier within two weeks. The sensitivity of the method is 1.7 Bq kg^{-1}. The sample weight necessary for the determination of Tc is ~ 10 g.

2. Spectrophotometry

Spectrophotometry is used for the determination of the oxidation state of technetium. Thus, the state of Tc(V) in complicated complex compounds was studied by spectrophotometry.[109,110] The spectrophotometric determination of technetium as complexes with thiourea after separation on a strongly basic anion-exchange resin was described in the studies.[111,112]

To determine the concentration of technetium in sea water, it is concentrated in aqueous samples by coprecipitation with $Fe(OH)_3$. After two purification cycles, *viz*., the extraction and chromatographic purification, Tc is determined in the raffinate by spectrophotometry.[113]

A combination of photocalorimetry and potentiometry was used for calculating the thermodynamic characteristics of technetium and its compounds. The heat of formation of Tc_2O_7 was determined (1115.0 ± 10.9 kJ mol^{-1}) and the standard oxidation potential of the TcO_4^-/TcO_2 pair was measured (-0.782 ± 0.011 V).[38]

3. Other methods

The X-ray fluorescence method is used for the detection of technetium in different technological solutions. The sensitivity of serial X-ray fluorescence instruments to Tc is $\sim$2 mg litre^{-1}. The level of sensitivity to technetium is increased to 90 μg litre^{-1} with the use of a paper backing. However, this leads to an increase in the time of analysis.[114]

A method for the crystalless X-ray fluorescence determination of technetium was described in the study.[114] This method has a substantially lower threshold of sensitivity due to scattering of the exciting radiation in the analysed sample. The sample volume is 3.5 cm^3. Technetium cannot be detected in the presence of a large amount of plutonium due to overlapping of the peaks of the excited radiation of these elements. In mixtures with uranium, Tc is reliably determined up to the U/Tc concentration ratio of $\sim$100.

The technetium concentrations of an order of several μBq litre^{-1} are determined by inductively coupled plasma mass spectrometry (ICP-MS).[115, 116] The concentrations of stable ruthenium in samples are generally much higher than the concentrations of Tc, which hinders the determination of the latter element. Hence, the complete removal of ^{99}Ru as well as of ^{98}Mo and ^{100}Mo is essential for the successful determination of Tc. Initially, technetium is concentrated by chromatography using the TEVA^{TM} Spec resin sorbent and then Tc is determined by ICP-MS. The limit of determination of technetium in samples is 0.3 μBq g^{-1}.[115, 117]

Electrothermal vaporisation inductively coupled plasma mass spectrometry (ETV-ICP-MS) holds the most promise for determining the Tc concentrations in samples. The main advantage of this method is that ultrasmall volumes of samples (10–100 μl) are required for the determination of Tc, which is of particular importance in the analysis of biological objects or high-level radioactive samples. This method allows one to determine technetium without separation of ^{99}Ru. After the addition of modifying agents, such as aqueous solutions of HNO_3 (1%) or NaClO (0.7%), to analysed samples, the limit of determination of Tc is 1.4 pg ml^{-1} (0.9 mBq ml^{-1}) in the presence (which is particularly important) of a more than a thousand-fold excess of Ru.[118]

The properties of the $Zn[Tc(OH)Cl_5]$ complex were studied by IR and NMR spectroscopy, powder X-ray diffraction analysis, ESR spectroscopy and thermal analysis and it was demonstrated that this compound is paramagnetic and contains Tc in the oxidation state IV.[119]

A Waters Quanta 4000 capillary electrophoresis system was developed for studying the effect of γ-radiolysis on the oxidation state of technetium in the $K^{99}TcO_4$ compound in solutions modelling groundwaters. This system consists of two electrolytic cells joined to a capillary column 75 μm in diameter and 60 cm long (the potential difference is 30 kV). This method enables one to perform the quantitative separation of Tc(VII) and Tc(IV) in solution.[120, 121]

To establish the crystal structures of pertechnetates with different compositions, the dependence of the quadrupole coupling constant on the temperature in the ^{99}Tc NMR spectra was studied.[59, 122, 123]

The *in situ* behaviour of technetium in radioactive wastes was investigated by Mössbauer absorption spectroscopy.[124, 125] This method was also used to establish the correlation between the observed chemical shifts of technetium in the NMR spectra and its oxidation states. It was noted that the chemical shift of technetium depends on its formal oxidation state.[64]

The state of technetium in a cement matrix, which is used for the isolation of radioactive wastes from the environment, was studied by XAFS Mössbauer absorption spectroscopy. This method not only enables one to determine the oxidation state of Tc in the solid state but also makes it possible to identify the compositions and structures of the resulting technetium-containing compounds. The advantage of this method is that it allows one to determine the element directly without its pre-isolation from the matrix regardless of its crystal structure.[125]

In some cases, the Tc concentrations in natural objects can be estimated from the ^{137}Cs concentrations in the same materials, because these fission products are generated in close yields ($\sim$6%) upon uranium fission. Thus, the levels of technetium contamination in the irradiated exclusion zone surrounding the Chernobyl reactor were estimated from the ^{137}Cs concentration.[126, 127]

V. Behaviour of technetium during reprocessing of spent nuclear fuel

1. Distribution of technetium in the PUREX process

In Russia, spent nuclear fuel is reprocessed with the use of the so-called PUREX process (Fig. 3). This process involves dissolution of irradiated fuel in nitric acid and coextraction of U and Pu with a 30% solution of tributyl phosphate (TBP) in synthetic saturated hydrocarbons followed by reductive reextraction of Pu into an aqueous phase. The process is carried out in a series of mixer-settlers with pulse or mechanical mixing of the phases. Plutonium and uranium are isolated as dioxide and uranyl nitrate, respec-

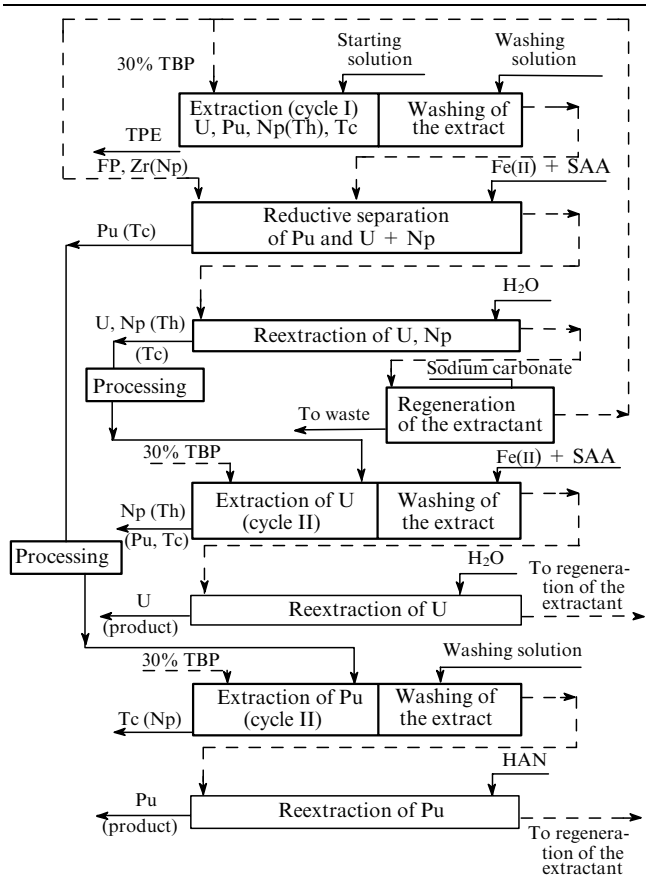


Figure 3. Scheme of the classical strongly acidic PUREX process; SAA is sulfamic acid and HAN is hydroxylamine nitrate.[128] Flows of aqueous and organic solutions are indicated by solid and dashed arrows, respectively.

tively.[91] The process can be performed in two structurally identical modifications ('weakly acidic' and 'strongly acidic').[128]

Upon dissolution of spent nuclear fuel in nitric acid, technetium passes into solution as pertechnetate ions. In the first step of extraction of uranium and plutonium under the conditions of the technological scheme used, technetium(VII) goes into the organic phase. In the Japanese modification of the PUREX process, the degree of extraction varies from 30% (see Ref. 129) to 80% (see Refs 111, 114 and 130) depending on the conditions of the extraction process. In the process performed according to the scheme of the RT-1 plant (Mayak Production Association, Russia), the degree of extraction reaches 94% – 98%.[131] Due to coextraction of Tc(VII) and U(VI), technetium goes into the organic phase as the $UO_2(TcO_4)(NO_3)(TBP)_2$ complex.[132] Data on the extraction of technetium into the organic phase depending on the concentration of nitric acid and composition of the aqueous phase are presented in Fig. 4.[65]

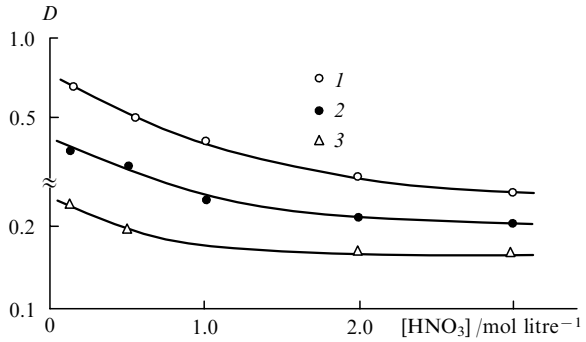


Figure 4. Plots of distribution coefficients D of Tc(VII) *vs.* the HNO_3 concentration and the composition of the aqueous phase upon the extraction with 30% TBP in n-dodecane.[65]
(*1*) 1M $UO_2(NO_3)_2$, (*2*) 1M $UO_2(NO_3)_2$ + 1M NH_4NO_3;
(*3*) 1M $UO_2(NO_3)_2$ + 2M NH_4NO_3.

Technetium forms mixed solvates not only with uranium but also with Pu and Zr.[129] The calculated distribution coefficients of Tc change in parallel with the experimental values, which indicates that coextraction proceeds by the hydration – solvation mechanism.

Technetium also forms a complex with tributyl phosphate

$$H^+ + TcO_4^- + (TBP)_{org} \rightleftharpoons (HTcO_4 - TBP)_{org}.$$

The stability and structural transformations of the latter complex were described in the study.[133]

In the second step of the extraction process, plutonium and uranium are separated from each other. For this purpose, plutonium is subjected to reductive reextraction, generally, with U(IV) or Fe(II) in the presence of hydrazine. This process affords Pu(III), which goes into the aqueous phase, while uranium(VI) remains in the organic phase. In this step, it is very important to choose adequate conditions for stabilisation of U(IV) and Pu(III) in the presence of technetium in the organic phase and, consequently, to calculate the required amount of the reducing agent.[133, 134]

If an aqueous solution of U(IV) is used as the reducing agent, Tc is partially reextracted together with Pu into the aqueous phase and partially remains in the organic phase. The Tc(VII) ions have a strong effect on the stability of low-valence forms of uranium and plutonium in media of nitric acid.

The TcO_4^- anions oxidise U(IV).

$$TcO_4^- + U(IV) \longrightarrow Tc(IV) + U(VI) \text{ (rapidly)},$$

$$Tc(IV) + NO_3^- \longrightarrow Tc(VII) + NO \text{ (slowly)}.$$

The Tc(VII) ions oxidise Pu(III) according to a reaction, whose rate is described by the following equation:

$$-\frac{d[Pu(III)]}{d\tau} = k\,[Pu(III)]\,[Tc(VII)]\,[H^+]^{2.3},$$

where $k = (3.82 \pm 0.11) \times 10^{-2}$ litre$^{3.3}$ mol$^{-3.3}$ at 50 °C and $\mu = 4$.[135]

In addition, the technetium(VII) ions catalyse oxidation of Pu^{3+} with nitric acid according to a reaction described by a first-order equation with respect to both Pu(III) and Tc(VII).[136]

$$Pu^{3+} + HNO_3 + 3H^+ = Pu^{4+} + NO + 2\,H_2O$$

This reaction proceeds also in the presence of hydrazine nitrate ($\sim$0.1 mol litre^{-1}). It was demonstrated that Tc(VII) serves as the catalyst also for oxidation of U(IV) with nitric acid.[133, 134]

Technetium(VII) ions have been proved to catalyse the decomposition of hydrazine used for stabilisation of Pu(III) and U(IV) in the course of the technological process.[134, 137] In solutions, technetium(VII) is successively reduced with hydrazine to Tc(V) and Tc(IV), which are again oxidised with nitric acid to the initial state.[138]

$$N_2H_5^+ + Tc(VII) \longrightarrow Tc(IV) + N_2,$$

$$Tc(IV) + NO_3^- \longrightarrow Tc(VII) + NO.$$

In this process, the concentration of Tc(VII) remains constant, while hydrazine is completely consumed.

For decomposition of hydrazine in the presence of Tc(VII) ions at concentrations of 0.4×10^{-2}, 1.0×10^{-2} and 2.0×10^{-2} mol litre^{-1}, the apparent zero-order rate constants k_0 are 0.0140, 0.0415 and 0.0800 h^{-1} litre^2 mol^{-1}, respectively, and the formal rate constants $k_c = k_0/[Tc(VII)]$ are 3.5, 4.1 and 4.0 h^{-1} litre^2 mol^{-1}, respectively.

The reaction is zero order with respect to hydrazine and first order with respect to technetium, which indicates that oxidation of Tc is, most likely, the rate-determining step of this process.

The rate of Tc oxidation sharply increases with time, and the process becomes autocatalytic. The autocatalytic mechanism assumes that certain products, which accelerate oxidation of hydrazine, are accumulated in the course of the reaction. Apparently, intermediate forms, *viz.*, Tc(V) and Tc(VI), serve as such products. A mathematical model was considered and kinetic calculations were performed for oxidation of hydrazine in solutions of nitric acid catalysed by technetium ions.[139]

Apparently, the above-mentioned reactions proceeding in a heterogeneous system exert an effect on the completeness of reductive reextraction of plutonium by uranium(IV).

If Fe(II) is used as a reducing agent in the step of reextraction of plutonium(III), Tc is virtually completely reextracted together with Pu into the aqueous phase. The concentration of the reducing agent has a substantial effect on the extraction ability of technetium. For example, the yield of the extracted forms of Tc decreases from 28% to 6% as the concentration of Fe(II) increases from 0 to 0.1 mol litre^{-1}, respectively. Under these conditions, technetium is virtually not retained in the uranium-containing organic phase. In the next step of purification of plutonium extracted, Tc passes into aqueous medium-level radioactive wastes, from which Tc can be quantitatively extracted. Thus, from 94% to 98% of Tc is separated in the step of plutonium refining involved in the technology which is employed at the RT-1 plant.[131]

It should be noted that the PUREX process has been initially developed and used instead of the REDOX process for reprocessing of irradiated uranium metal produced for military purposes. The drawback of the REDOX process was accumulation of large quantities of high-salt wastes, which cannot be subjected to reprocessing and utilisation. The aims and problems of reprocessing changed substantially when spent nuclear fuel from nuclear power stations appeared. At nuclear power stations, spent nuclear fuel burns up to a substantial degree (from 0.5 – 1 to 40 – 100 GW days t^{-1}).[128] An increase in the degree of burn-up complicates the extraction and separation of components with the

use of TBP solutions. In the course of the extraction reprocessing of spent nuclear fuel from nuclear power stations, the behaviour of Tc (and Np) in the extraction and redox processes is of importance. Hence, the necessity of achieving the completeness of separation of actinides extracted in the presence of technetium dictates both the modern technological schemes of reprocessing of spent nuclear fuel from nuclear power stations and trends in their development.

The elaboration of the modified PUREX process that met this requirement gave rise to different technological schemes both in Russia and abroad. One of the main aims is to separate and concentrate technetium in a single flux. Of new technologies, noteworthy is a process providing the complete extraction of U, Pu, Tc and the major portion of Np, while Zr passes into a high-level radioactive raffinate due to extensive washing of the extractant.[140, 141] The characteristic feature of this scheme is the involvement of the step of pre-reextraction of Tc with strong acid, in which 80% – 85% of Tc is removed. This makes it possible to perform reductive reextraction of plutonium under the conditions of complete removal of Np together with U followed by their separation in the uranium cycle II.

The technological scheme employed at the RT-2 plant (Russia) holds promise.[142 – 144] This scheme involves the coextraction of U, Np, Pu, Tc and Zr with TBP solutions as the first step, reextraction of Zr (with a portion of Np and Tc), reextraction of Pu and Np with strong acid (Tc remains in the organic phase together with uranium), reductive separation of Pu and Np with the use of U(IV) in the cycle I, reextraction of Np and Tc into a single flux using a salt-free complex-forming agent, *viz*., acetohydroxamic acid (AHA), followed by reextraction of uranium. This is the first scheme of such a type. However, this scheme has some drawbacks, because it is rather cumbersome and has a large number of links within the cycle.

Further progress in these investigations was achieved in the study,[145] in which the authors proposed that the coextraction of U, Pu, Np and Tc with dilute TBP should be followed by reductive reextraction of Np and Tc with n-butanol and separation of Pu and U.

However, actual success was achieved only in the SuperPUREX scheme[128, 146] (Fig. 5) involving the extraction of U, Pu, Np and Tc as well as Zr followed by reextraction of Zr together with Tc and Np under the action of hydrazine at the corresponding concentration of HNO_3. This scheme allows one to perform any modification of isolation of uranium and plutonium, *viz*., either their deep separation and purification within a one-cycle scheme or their simultaneous reextraction in the course of processing of plutonium – uranium fuel for fast-neutron reactors.

It should be noted that the extraction of Zr together with Tc and Np provides the basis for their subsequent incorporation into matrices for radioactive waste immobilisation.[128]

With the aim of intensifying the extraction reprocessing of spent nuclear fuel, scientists are looking into the possibility of using equipment with a high specific output, *viz*., centrifugal extractors and vibrating columns, in the key operations of fuel reprocessing.

Thus, some aspects of the behaviour of U, Tc and Zr in the extraction of uranium from solutions in nitric acid with 30% TBP solutions in n-alkanes were examined on a column-type vibrating extractor. It was demonstrated that the uranium front was shifted to the middle part of the column in the presence of zirconium and the concentration of uranium in the raffinate increased. It was hypothesised that the hydrodynamics of the process in extractors of this type are impaired due to formation of a structure-mechanical barrier on the drop surface and retardation of coalescence. The behaviour of Tc in this process is adequately described by the mechanism of coextraction with uranium and zirconium and by the hydration – solvation mechanism. The degree of Tc extraction was ~80%. The use of hydrogen peroxide in this process leads to a decrease in the degree of Tc extraction and reduces the influence of zirconium on the uranium extraction.[111]

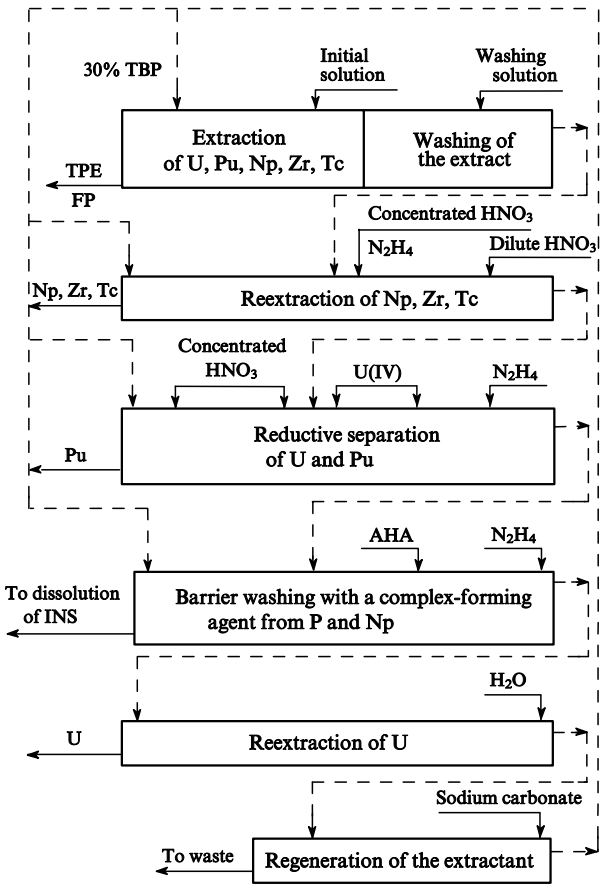


Figure 5. Scheme of the cycle I of reprocessing of spent nuclear fuel from nuclear power stations in the SuperPUREX process.[128]

2. Isolation of technetium during fractionation of radiochemical wastes

All countries that develop their civil nuclear industry face the problem of fractionation of high-level radioactive wastes and separation of long-lived radionuclides. Many procedures were proposed for the extraction fractionation of wastes. Since most of the technologies developed in the last decade have been oriented primarily toward the deep separation of transuranium elements, not all processes of extraction fractionation of high-level radioactive wastes involve the step of separation of the technetium fraction. In this connection, studies of the behaviour of technetium in methods developed for the fractionation of high-level radioactive wastes are of interest.

a. Partitioning of high-level radioactive wastes using organophosphorus acids

The most well-known process of fractionation of high-level radioactive wastes involving organophosphorus acids is the technology developed at the Japan Atomic Energy Research Institute. This technology is based on the use of diisodecylphosphoric acid [(iso-$C_{10}H_{23}O$)P(O)OH, DIDPA] as the extractant.

This extractant is an analogue of the widely known di-2-ethylhexylphosphoric acid (D2EHPA), but it allows one to perform the process in more acidic media.

The recent version of the technological process with the use of DIDPA,[147] whose development was started 24 years ago, provides a way of separating the following factions from radioactive wastes: transuranium elements (TUE); ^{99}Tc + platinum metals (PM); ^{137}Cs + ^{90}Sr and the remaining radionuclides.

This process involves the step of the preliminary correction of the composition of high-level radioactive wastes in the course of which the concentration of nitric acid is decreased from 2–3 mol litre^{-1} to 0.5 mol litre^{-1} by denitration with formic acid. This makes it possible to extract tervalent transplutonium elements (TPE). Then actinides and lanthanides are extracted with a mixture of DIDPA and TBP in n-dodecane. Hydrogen peroxide is added to a solution to improve the extraction of neptunium. Fission and stable elements, including technetium, platinum metals, caesium and strontium, remain primarily in the raffinate. Americium, curium and lanthanides are reextracted from the organic phase with nitric acid (4 mol litre^{-1}). Plutonium and neptunium are reextracted with oxalic acid. Uranium is extracted with sodium carbonate. The acidity of the reextract containing Am, Cm and lanthanides is again decreased from 4 mol litre^{-1} to 0.5 mol litre^{-1} by denitration and then these elements are extracted with a mixture of DIDPA and TBP in n-dodecane. Americium and curium are washed away with a mixture of diethylenetriaminepentaacetic acid (DTPA) and lactic acid. Lanthanides are washed away with nitric acid. In another modification, U and Pu are extracted with tributyl phosphate in the early step of the process and then the acidity is decreased. Then Am and Cm are extracted as described above followed by separation of lanthanides and TPE involving the reextraction of the latter with a mixture of DTPA and lactic acid. The extraction scheme is supplemented by the extraction of ^{99}Tc and platinum metals from the first raffinate after the extraction of all TUE by sorption on a column with activated carbon and subsequent extraction of strontium-90 and caesium-137 by inorganic ion-exchange resins (titanic acid and zeolite, respectively). The extraction affords 99.99% of Am, Cm, Pu and U and 99.95% of Np. After sorption, 99.90% of technetium and more than 99.9% of Cs and Sr are extracted. The overall volume of four fractions is 3.3 times smaller than the volume of vitrified wastes without partitioning.[148, 149]

In the technological CTH process developed in Sweden,[150, 151] D2EHPA is used and another way of decreasing the solution acidity is employed. Initially, U, Pu, Np and major portions of Zr, Nb, Mo and Fe are extracted with a solution of D2EHPA in a hydrocarbon diluent from a solution of high-level radioactive wastes pre-acidified to the HNO_3 concentration of 6 mol litre^{-1}. The organic phase is washed with a solution of a mixture of HNO_3 and HF to remove Zr and Nb. Then actinides are removed by ammonium carbonate. The reextract is concentrated and acidified. Then U, Pu and Np are extracted. The acidity of the first raffinate is decreased from 6 to 0.1 mol litre^{-1} by removing nitric acid with the use of a solution of TBP in the same diluent, Pd, Ru and Tc being removed together with nitric acid. The latter elements are extracted by the ion-exchange method. Thereafter Am, Cm and lanthanides are extracted with a solution of D2EHPA followed by their reextraction with a solution of nitric acid with a rather high concentration. Caesium and strontium are isolated from the raffinate by sorption on inorganic ion-exchange resins. There is also a modification of the process, in which americium and curium are washed away by a mixture of DTPA and lactic acid, while lanthanides are washed away by nitric acid. When this scheme was tested on real high-level radioactive wastes, the factors of purification from α- and β-emitters were $\sim 10^5$ and $\sim 3 \times 10^4$, respectively.

With the aim of excluding the steps of denitration and neutralisation of a raffinate, which are involved in the two above-described processes to decrease the acidity of the high-level radioactive raffinate, a technological scheme was proposed[152] for reprocessing of high-level radioactive wastes with the use of n-alkyl phenylphosphonic acids [PhP(O)(OH)OR, where R = n-C_8H_{17}–$C_{10}H_{21}$, (APPA)] and their zirconium salts.

The latter scheme includes two cycles. In the first of them, transplutonium and rare-earth elements are extracted from high-level radioactive wastes containing nitric acid at a concentration of 2 mol litre^{-1} with a solution of APPA (0.9 mol litre^{-1}) in the RED-1 diluent (preferentially, 0.5 mol litre^{-1}). Transplutonium elements are reextracted with a solution of DTPA in lactic acid. Rare-earth elements are reextracted with HNO_3 (3–5 mol litre^{-1}). In the second cycle, ^{90}Sr and Ca are extracted from solutions of nitric acid with a concentration of 0.1 mol litre^{-1} by zirconium salt of APPA. It is known that zirconium improves the extraction of metals by alkylphosphonic acids.[153] Reextraction of ^{90}Sr and Ca is carried out using HNO_3 solutions (3–4 and 7 mol litre^{-1}, respectivel). Data on the behaviour of molybdenum are lacking in the literature.

The use of APPA instead of D2EHPA made it possible to prevent the precipitation in the organic phase in the course of extraction of iron.

b. Partitioning of high-level radioactive wastes by neutral organophosphorus compounds

Mono- and bidentate neutral organophosphorus compounds (MNOPC and BNOPC, respectively) allow one to extract a series of long-lived radionuclides, including actinides and technetium, from acidic high-level radioactive wastes.

Phosphine oxide bearing different substituents [$R^1R^2R^3P(O)$, PODS], where R^1, R^2 and R^3 are the C_6H_{13}–C_9H_{19} alkyl groups, is one of the most efficient MNOPC.

The technological scheme, which has been developed in China [154, 155] and Germany [156] and tested on real high-level radioactive wastes, provides a way of extracting actinides from high-level radioactive wastes in quantitative yields (99.9%) using solutions of PODS in kerosene. Solutions of high-level radioactive wastes containing nitric acid at concentrations, generally, higher than 2.5 mol litre^{-1}, should be pre-neutralised to a concentration of no higher than 1 mol litre^{-1}. To achieve the complete extraction of neptunium, Np(V) is electrochemically oxidised to Np(IV). Technetium is extracted together with actinides and lanthanides (and also partially, with Zr and Mo), which are selectively washed away from the organic phase. Thus, Am, Cm and lanthanides are washed away with HNO_3 (5.5 mol litre^{-1}), Pu and Np (together with Zr and Mo) are washed away with oxalic acid and U (together with Tc) is washed away with sodium carbonate. The overall purification from α-emitters is $> 10^3$. Different modifications of this process have also been developed in Russia. The advantages of this method are low prices of the reagents and diluent and the possibility of the efficient extraction of Tc along with actinides.

The use of bidentate neutral organophosphorus compounds for the extraction of long-lived radionuclides, *viz*., actinides and technetium, makes it possible to eliminate the main drawbacks of the above-described processes involving alkylphosphoric acids and monodentate neutral organophosphorus compounds, among which are the necessity of performing neutralisation of high-level radioactive wastes before the extraction of actinides and the use of solutions of nitric acid for reextraction of TPE from the organic phase. Bidentate neutral organophosphorus compounds extract actinides from acidic solutions, and TPE are reextracted with dilute solutions of nitric acid. The so-called TRUEX process developed at the Aragon National Laboratory (USA) is based on one of BNOPC, *viz*., octylphenyl(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide (C_8H_{17})PhP(O)CH_2C(O)NBu^i_2 (OctPhBu^i_2).[157] Different versions of this process involving the same reagent were also developed in other countries, primarily in Japan and India.[158, 159] Another BNOPC, *viz*., diphenyl(*N*,*N*-di-n-butylcarbamoylmethyl)phosphine oxide (Ph_2Bu_2), is also often used in this process.

In the TRUEX process, solutions of Oct PhBu^i_2 (0.2 mol litre^{-1}) in a mixture with TBP (1.0–1.4 mol litre^{-1}) in saturated hydrocarbons are used for the extraction of actinides and lanthanides from high-level radioactive wastes containing nitric acid at a concentration of 0.7–5 mol litre^{-1} to which a complex-forming compound (most often, oxalic acid) is added to suppress the extraction of zirconium. After washing of the extract with a solution of a mixture of nitric acid with either aluminium nitrate or oxalic acid, transplutonium elements and lanthanides are

reextracted by dilute solutions of nitric acid. Thereafter plutonium and neptunium are extracted with a solution of ammonium carbonate or a mixture of dilute nitric acid with HF or oxalic acid. If high-level radioactive wastes contain uranium, the latter is washed away by a solution of sodium carbonate (together with Tc). The factor of purification of high-level radioactive wastes from actinides is $> 10^3$. Japanese researchers plan to improve this process with the aim of separating lanthanides and transplutonium elements by selective reextraction of the latter by a DTPA–$NaNO_3$ mixture.[160]

In the Russian version of the TRUEX process developed at the Mayak Production Association, the V I Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences and the V G Khlopin Radium Institute, polar diluents are used. This makes it possible to do away with the addition of TBP and to use cheaper diphenyl(*N*,*N*-di-n-butylcarbamoylmethyl)phosphine oxide.[161] Investigations demonstrated that Ph_2Bu_2 in polar diluents possesses higher extracting ability with respect to actinides and lanthanides than that in a mixture of hydrocarbons with TBP. The higher distribution coefficients are observed throughout the concentration range of nitric acid from 0.01 to 10 mol litre^{-1}.

The U.S. version of the TRUEX process was used for reprocessing of real wastes of different origin and with different compositions, *viz*., wastes of analytical laboratories, wastes from reprocessing of zirconium jackets that hold the fuel rods as well as wastes from the PUREX process employed at the plutonium production plants at the Hanford Site (USA).[157] The Russian version of the TRUEX process was tested at the Mayak Production Association under both dynamic and static conditions with the use of simulators and real solutions of raffinates from the PUREX process and high-level radioactive wastes.[161]

c. Partitioning of high-level radioactive wastes by solutions of diamides

The process of extraction of actinides from high-level radioactive wastes by diamides of the general formula $[R^1R^2NHC(O)]_2CHR^3$, where R^1, R^2 and R^3 are alkyl substituents, is called the DIAMEX process. Di-n-butyl-*N*,*N*′-dimethyl-*N*,*N*′-1,2-tetradecylmalonamide was proposed and used in France.[162,163] The extraction properties of diamides are similar to those of bidentate neutral organophosphorus compounds, in particular, of $OctPhBu^i_2$, used in the TRUEX process.

Actinides(III, IV, VI) together with lanthanides are extracted from solutions of high-level radioactive wastes containing nitric acid at concentrations of 3–5 mol litre^{-1} to which oxomalonic acid and hydrogen peroxide are added to suppress the extraction of zirconium and molybdenum. After washing of the organic phase, actinides together with lanthanides are reextracted with a solution of nitric acid (0.5 mol litre^{-1}) and a solution of potassium nitrate (0.01 mol litre^{-1}). In addition to the DIAMEX process, a technological scheme was developed for the separation of actinides and lanthanides from dilute HNO_3 solutions by solutions of 2,6-bis(1,2,4-triazin-3-yl)pyridine with saturated hydrocarbons and octanol. This process has advantages over the known TALSPEAK and TRAMEX processes (USA) used for the separation of actinides and lanthanides, because it does not require the strict maintenance of pH and the use of salts, whereas the extraction equilibrium is rapidly reached.

d. Extraction of technetium from high-level radioactive wastes

In the best-developed procedures for the extraction of actinides from high-level radioactive wastes, no provision was made for separating fractions of other hazardous long-lived radionuclides (^{99}Tc, ^{90}Sr, ^{137}Cs and ^{129}I) within the framework of a single technological extraction scheme.

In the course of reprocessing of fuel from early Russian fast-neutron reactors, uranium was regenerated by sublimation followed by separation of fluorinated fission products by sorption with the use of fluorine condensers and columns with NaF. Technetium was trapped by a lime absorber, thus being separated from virtually all fission products.[7] Later on, a Russian technology was developed for the extraction of technetium from wastes from nuclear fuel reprocessing based on sorption of technetium on the AV-17 anion-exchange resin from a solution pre-neutralised to pH 7–9. The factor of purification from the fission products was $\sim 2 \times 10^2$. After desorption with concentrated nitric acid and neutralisation of the eluate, technetium was extracted with acetone. Further purification was carried out by precipitation of technetium as poorly soluble Tc_2S_7 and tetraphenylarsonium pertechnetate and their annealing under a stream of hydrogen to reduce these compounds to metal.[164]

In recent years, the PUREX process was supplemented by a scheme of the deep recovery of technetium and neptunium in the course of extraction by tributyl phosphate together with uranium and plutonium followed by their separation and combination with the TPE + REM fraction isolated from the raffinate of the first cycle.[165]

The so-called PARK process (Partitioning Conundrum Key),[166] which is another improved version of the PUREX process, was developed at the Japan Atomic Energy Research Institute. This scheme provides the extraction of neptunium and technetium (together with uranium and plutonium), which are subsequently separated from uranium and plutonium by two successive reextractions by a reducing agent, *viz*., butyraldehyde, and concentrated nitric acid. In the PARK process, iodine is also removed by distillation and sorption concentration.

3. Methods for utilisation and disposal of technetium

Being a long-lived radionuclide, technetium-99 released from nuclear power stations must be extracted and reliably isolated from the biosphere. For this purpose, either the so-called transmutation of Tc, *i.e*., the transformation of Tc into stable isotopes, is performed or Tc is incorporated into the corresponding matrices, which provides reliable isolation for thousands of years until Tc completely decays.

a. Transmutation of technetium

In full measure, technetium can be rendered harmless only by transmutation into stable nuclides under neutron irradiation. Since the ^{99}Tc nucleus has high neutron-capture cross-sections in the thermal and, particularly, epithermal energy ranges (main resonance peaks are in the range of 2–20 eV), thermal reactors, which generally have a sufficient spectral hardness ($\gamma = 0.3 \pm 0.1$), hold promise for burning this radionuclide.[167] In the above-mentioned neutron energy range, the process is described by the following scheme:

$$^{99}\text{Tc} \longrightarrow {}^{100}\text{Tc} \longrightarrow {}^{100}\text{Ru} \longrightarrow {}^{101}\text{Ru} \longrightarrow {}^{102}\text{Ru} \longrightarrow$$

$$\longrightarrow {}^{103}\text{Ru} \longrightarrow \text{short-lived and stable Rh and Pd isotopes.}$$

The contribution of other nuclear reactions is virtually insignificant. The dynamics of transmutation of the ^{99}Tc point target at $\gamma = 0.3$ is shown in Fig. 6.

The ^{100}Ru, ^{101}Ru and ^{102}Ru isotopes are stable. The ^{103}Ru isotope has a half-life of 39.3 days and decays to stable ^{103}Rh. Consequently, after the extraction of non-burned Tc from the irradiated technetium target, the product occurs as stable ruthenium with impurities of rhodium and palladium.[19]

It is presently assumed that technetium metal or its carbide TcC, which are rather stable at high temperatures in the absence of oxygen, are the forms of Tc most probable for transmutation. Graphite, potassium hydride, D_2O, *etc*. were proposed as neutron moderators.[167]

In most cases, calculations of the transmutation of long-lived nuclides in modern reactors are based on the assumption that these reactors provide the conditions for the formation of an appropriate neutron spectrum and/or for an increase in the neutron flux density. Calculations of the transmutation of ^{99}Tc in light-water, thermal-water and fast reactors demonstrated that

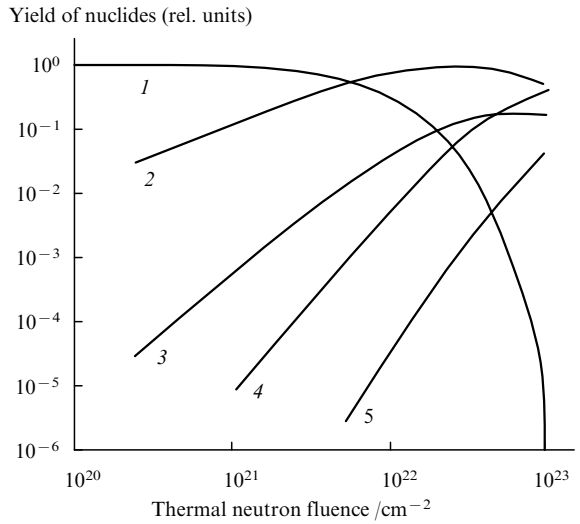


Figure 6. Dynamics of transmutation of ^{99}Tc upon thermal neutron irradiation with the spectrum hardness $\gamma = 0.3$.[167]
(*1*) ^{99}Tc, (*2*) ^{100}Ru, (*3*) ^{101}Ru, (*4*) ^{102}Ru, (*5*) impurities.

this problem cannot be solved in light-water reactors. In thermal-water and fast reactors (neutron moderation), the half-life of ^{99}Tc burning varies in the range of 15–25 years at loadings of 2.5–4.0 t and the rate of transmutation of technetium of 100–140 kg year^{-1}. Simultaneously, ~20 kg of ruthenium are produced per year.[168] These half-lives of burning are close to half of the service life of the reactor. In addition to technetium, it is also planned to burn a series of other radionuclides, including neptunium, americium and other actinides. Energy reactors are of no use for solving this problem of transmutation. This was confirmed by irradiation of a technetium target for 193 days on the HFR research reactor in the Netherlands under conditions more favourable than those provided in a fast-neutron nuclear reactor without substantial construction changes. Irradiation of a technetium target with the use of the total neutron fluence of 1.5×10^{22} cm^{-2} and thermal component of 2.5×10^{21} cm^{-2} led to the burn-up of only ~5% of ^{99}Tc.[169]

Hence, it is necessary to design special fast-flux transmutation systems providing a high rate of transmutation of technetium into stable nuclei to burn-up ^{99}Tc. In the experiments carried out at the Scientific Research Institute of Atomic Reactors (Dimitrovgrad, Russia) on an SM-3 experimental reactor, a much higher degree of technetium burning was achieved (under particular conditions, up to 15%).[170]

Apparently, the full-scale solution of the problem of ^{99}Tc burning should involve one of the modes of transmutation of early actinides using their irradiation with thermal neutron fluxes with the density of 10^{15}–10^{16} cm^{-2} s^{-1}.[171] In the Accelerator-Driven Transmutation of Waste (ATW) Programme (USA) and the ACTINEX Subprogramme of the SPIN Programme of the French National Agency for Radioactive Waste Management,[172] the possibility of the simultaneous burning of minor actinides and ^{99}Tc as well as of some other nuclides was considered.[173, 174] The transmutation of ^{99}Tc not only makes it possible to convert it into the safe form but also serves as a source of the valuable metal of the platinum group, *viz*., stable ruthenium, which is used in the electronics and electrotechnical industry (the price of ruthenium is ~$10 per gramme).[175] The total reserves of ruthenium in ores are estimated at ~3100 t, whereas the world demand for this element is about 7.4 t per year and is close to the rate of accumulation of ^{99}Tc in nuclear power engineering.[176]

b. Incorporation of technetium into solid matrices

One of the procedures for isolating technetium from the biosphere is based on its cementation to form matrices stable on storage. These studies were carried out at the Savannah River Site (USA).[125] It appeared that technetium-containing cement matrices are unstable upon storage because they include Tc as pertechnetate ions readily soluble in water. Hence, cementation of technetium-containing high-level radioactive wastes requires the transformation of technetium into a water-insoluble form, for example, into TcO_2. Either an ash or additives of FeS or Na_2S can be used as reducing agents. These reagents reduce pertechnetate to a stable form with equal ease. However, it was believed [125] that only partial reduction of Tc(VII) to Tc(IV) could be achieved with the use of these reagents. Hence, this process is not sufficiently efficient.

Incorporation of technetium into a cement-like matrix, such as bentonite, also does not lead to stabilisation of Tc. For example, up to 40% of technetium is leached when the matrix is exposed to water during 20 days. Thereafter, the rate of leaching decreases due, apparently, to the formation of a new mineral phase involving technetium.[173, 177] It is believed that cement based on Al oxides without bentonite is more stable than a mixed cement.[173] The best results were obtained with the use of cement annealed in a furnace. However, all the above-mentioned materials appeared to be unstable, as a result of which cementation methods were rejected. Hence, the examination of new ceramic, mineral-like or other matrices for reliable disposal of technetium remains an urgent problem.

VI. Behaviour of technetium in environmental objects

1. Main sources of the release of technetium into the environment

Problems associated with the control of the behaviour of technetium in the environment are becoming increasingly important.[178, 179] The ^{99}Tc isotope has accumulated in the geosphere since the 1950s. This isotope is one of the long-lived radionuclides released into the environment (along with ^{14}C and ^{129}I).

The main sources of the release of Tc into the environment are nuclear weapons testing (180 TBq), wastes from nuclear power stations (4 GBq), atmospheric fallout after the Chernobyl accident (0.75 TBq) and wastes from nuclear fuel processing plants.[180–182] One more source of the release of technetium into the environment to the use of ^{99m}Tc in medicine, the scale of which will increase.[183]

The world annual accumulation of Tc from nuclear power station operation is about 6 t, and ~60 t of Tc have already been produced.[1] An increase in the degree of burn-out of nuclear fuel will lead to further accumulation of technetium. Hence, one would expect that the contribution of technetium to the population radiation dose will be substantially increased with the development of nuclear power engineering. For example, the level of ^{99}Tc contamination of forest soil in the 30-km zone around the Chernobyl reactor is ~1.1–14.1 Bq kg^{-1}.[184–187]

2. Forms of the existence of technetium in environmental objects

Forms of the existence of technetium in a multicomponent system of the geological medium depend primarily on the following factors: the redox potential (E_h) and pH of the system, interactions with inorganic compounds, the influence of organic complex-forming agents and microorganism action.

The redox conditions in the geological medium are responsible for stabilisation of technetium in particular oxidation states and forms of its occurrence. The $Fe^{2+} - e^- = Fe^{3+}$ ($E^\circ = 0.77$ V) and $O_2 + 4e^- + 2H_2O = 4OH^-$ ($E^\circ = 0.401$ V) pairs are the main potential-forming pairs having influence on the redox behaviour of technetium in environmental objects.

Iron is involved in many rock-forming minerals. In the areas with a low water exchange or under anaerobic conditions, iron is stabilised as Fe(II). The reduced form of iron loses stability when exposed to atmospheric oxygen (aerobic conditions) dissolved in

groundwaters in the zone of active water exchange and stabilises in the Fe(III) state.

The formal oxidation potential of the pair

$$TcO_4^- + 4H^+ + 3e^- \longrightarrow TcO_{2(solid)} + 2H_2O$$

is higher than 0.8 V.[101, 188] In the zone of a low water exchange or in its absence, TcO_4^- can be reduced to Tc(IV) in groundwaters according to the reaction

$$TcO_4^- + 3Fe^{2+} + 7H_2O \longrightarrow 3Fe(OH)_3 + TcO_2 + 5H^+.$$

Electrophoresis measurements and atomic absorption spectroscopy revealed the presence of the following forms of Tc(IV) under reducing conditions and at alkaline pH: TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2$, $TcO_2 \cdot 2H_2O$ and $TcO_2 \cdot nH_2O$ (Fig. 7). These forms of technetium would be expected to undergo hydrolytic adsorption or co-precipitation on Fe(III) hydroxide to give complexes with Fe–O–Tc bonds.[189, 190]

Under aerobic conditions, Tc(IV), occurring in the form of TcO_2 in aqueous solutions, is oxidised by atmospheric oxygen to Tc(VII) with a rate of ~1 mass % during two months followed by dissolution of the precipitate.[65] The resulting pertechnetate ions are quite stable under aerobic acidic, neutral or alkaline conditions.

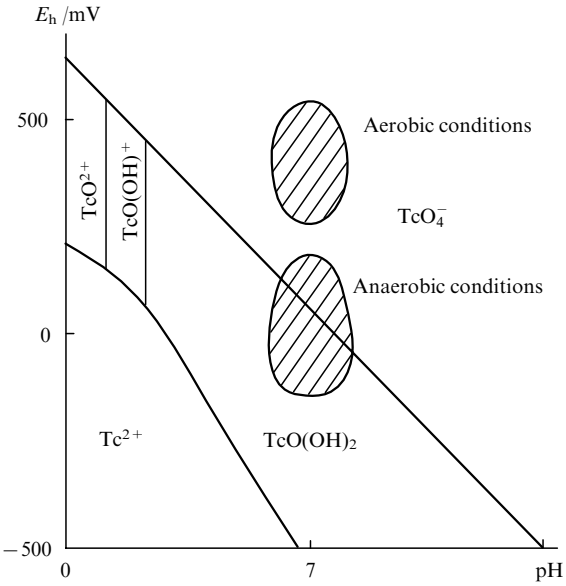


Figure 7. Forms of the existence of technetium in an aqueous solution depending on E_h and pH.[65]

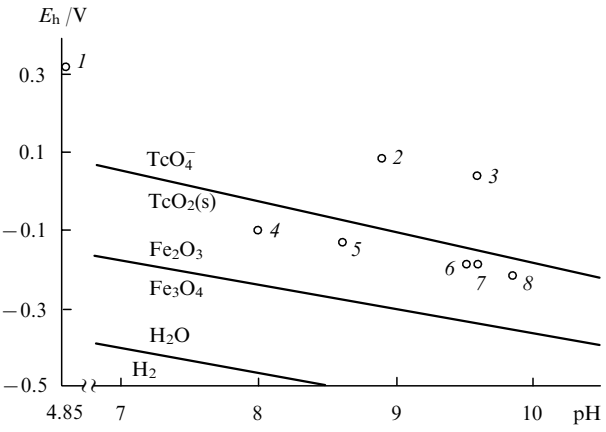


Figure 8. Effect of E_h and pH on the redox equilibrium Tc(VII) ⇌ Tc(IV) in a rock–water system.
Samples of argillaceous slates or clays (Conasauga, USA) (*1–3*); granites: Westerly granite, USA (*4*, *7*); Climax Stock granite, USA (*6*); Sentinel Gap basalts, USA (*5*, *8*).[191]

The data from the E_h–pH diagram are widely used for the prediction of the sorption behaviour of Tc in environmental objects. By way of example, let us consider the results of the determination of the Tc(VII)–Tc(IV) redox equilibrium, which depends on E_h and pH and was calculated taking into account the maximum allowable (in USA) concentration of technetium in drinking water (0.3 μCi litre^{-1}) [191, 192] (Fig. 8). Under real geological conditions, Tc in groundwaters is stabilised in the tetravalent state and is sorbed onto different granites (New Hampshire, USA) and basalts (Mattawan, USA). By contrast, technetium in argillaceous slates or clays (Catasauqua, USA) occurs as pertechnetate ions and is not sorbed onto soils.

Data on the complex formation of technetium with inorganic and organic ligands are of great interest.

a. Sulfide ions

In addition to $TcO_2 \cdot nH_2O$, other stable technetium compounds, for example, Tc sulfides, can also be sorbed onto soil (Fig. 9). Technetium(IV) sulfide TcS_2 is precipitated by hydrogen sulfide generated upon plant degradation. Natural sulfur-containing organic compounds serve as another source of sulfide ions in water-saturated soil.[183, 193]

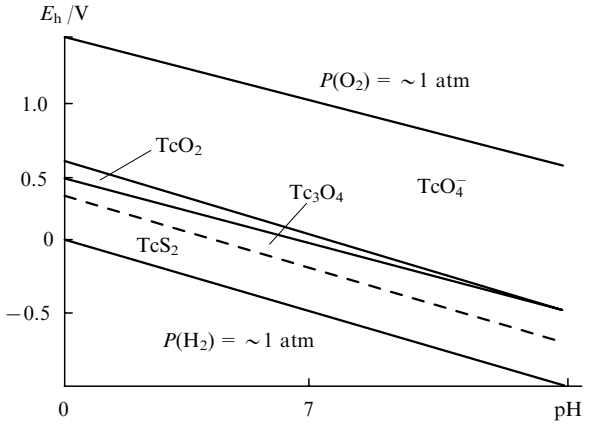


Figure 9. Behaviour of Tc in the Tc–S–OH system, 25 °C, ~1 atm (thermodynamic data).[193]

Technetium(IV) sulfide is also formed upon reductive precipitation of the TcO_4^- ions onto the FeS surface in a rock layer. The structures of the mixed FeS–Tc(VII) and FeS–Tc(IV) compounds were studied by EXAFS spectroscopy and it was found that technetium is present as an individual phase structurally similar to TcS_2 rather than being incorporated into the FeS phase.[191, 194]

The reaction of the TcO_4^- and S^{2-} ions in a solution of Na_2S afforded technetium(VII) sulfide Tc_2S_7, the type of the precipitate being dependent on the concentration of sodium sulfide. If the concentration of $Na_2S > 0.33$ mol litre^{-1}, large precipitate particles form spontaneously. At lower concentrations of sodium sulfide, a suspension of colloidal Tc_2S_7 is produced, the formation of the suspension being completed within ~3 days.[195] The solubility of Tc_2S_7 in water is 0.257 g litre^{-1}.[90]

b. Carbonate ions

Only in carbonates (unlike many other aqueous media), internal γ-irradiation of Tc(VII) samples does not lead to its self-reduction to Tc(IV). The possible reoxidation of Tc(IV) to Tc(VII) is accounted for by the fact that radiolysis in solution affords $CO_3^{\bullet}$ radicals, which can transform technetium into the heptavalent state.[23, 121]

c. Humic acids

It is assumed that technetium in deep beds of groundwater occurs primarily in complexes with humic acids (Tc–HA). Their percentage was estimated at ~50–70% (Fig. 10).[196–199]

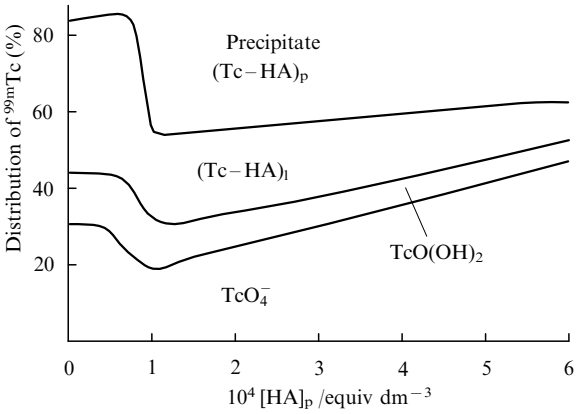


Figure 10. Different forms of the existence of ^{95m}Tc depending on the initial concentration of humic acids $[HA]_o$ at $[Sn^{2+}] = 10^{-5}$ mol litre^{-1}.[196]

The indices 'p' and 'l' correspond to the precipitate and mother liquor, respectively.

The compositions of the complexes depend on the pH of the solution, concentration of humic acids, salt background and the presence of reducing agents. Under aerobic conditions, the Tc–HA complexes in solutions of pH 9–11 occur as poorly soluble precipitates. An increase in the salt background leads to suppression of Tc sorption on minerals. The presence of reducing agents [hydrazine and Fe(II)] gives rise to readily sorbable forms and a precipitate of hydrated TcO_2.[196]

Finally, microorganisms also have an effect on the forms of the existence of Tc in environmental objects. Microorganisms absorb oxygen dissolved in water and shift the redox equilibrium in the system to small E_h.[200, 201]

3. Sorption of technetium on natural materials

In studies of the sorption of technetium by natural systems, the following three types of processes should be taken into account: sorption on the outer surface of solid particles, sorption on porous particles and irreversible precipitation or coprecipitation.[202]

Under aerobic conditions, sorption of technetium by natural minerals is low. At pH 6, the distribution coefficients $K_d^{Tc(VII)}$ were determined for sandstone (2.57 cm^3 g^{-1}), peat (1.89 cm^3 g^{-1}), feldspar (1.66 cm^3 g^{-1}), phosphorite (1.05 cm^3 g^{-1}), bauxite, basalt (0.98–1.01 cm^3 g^{-1}) and pyrite (0.32 cm^3 g^{-1}).[90] At pH 5.8–7.4, the coefficients of sorption of Tc on minerals decrease by a factor of $\sim 10^4$ as E_h in solution increases from 180 to 220 mV (Fig. 11).[65, 203–205]

It is assumed that technetium occurs as the TcO_4^- anions, which are poorly adsorbed on different rocks, in aerated solutions with high E_h. This assumption was supported by studies of the extraction of technetium by tetraphenylarsonium chloride. It was also demonstrated that colloidal particles of Tc do not occur in solution, which was confirmed by ultrafiltration of solutions.[65, 189, 204]

It is known that $K_d^{Tc(VII)}$ is proportional to the initial concentration of TcO_4^- and depends only slightly on the specific surface of the sample. Hence, it was hypothesised[65, 130, 189, 205] that technetium in deep layers is stabilised as $TcO(OH)_2$ or TcO_2 under anaerobic conditions at reduction potentials E_h and its sorption by minerals is, apparently, associated with irreversible precipitation of poorly soluble forms of Tc(IV).[89, 205] To test this assumption, experiments were carried out on sorption of technetium(VII) from flowing groundwater (pH 9; E_h = 158 mV; conductivity 1340 μS cm^{-1}) by finely dispersed (180–850 μm) strongly metamorphised rocks taken from the fracturing zone at a depth of 250 m without contact with the atmosphere.[203] The material filling the column consisted of quartz, alkaline feldspar, plagioclase, biotite, chlorite and trace amounts of magnetite. It was found that about 40% of technetium was sorbed on fractions of ferrous minerals, which are composed primarily of biotite and other so-called mafic minerals, such as hematite, magnetite and iron hydroxides (7% of the overall weight). It was demonstrated that sorption on mafic minerals occurs through chemisorption rather than being due to precipitation in the bulk of groundwater.[203] It can be assumed that sorption of technetium proceeds in two steps, *i.e.*, through reduction of Tc(VII) to Tc(IV) by divalent iron present in rocks and chemisorption on their surfaces. This assumption was confirmed by the results of the studies,[101, 189, 194, 199, 206, 207] in which it was found that technetium(VII) was not sorbed by Fe(III)-containing minerals, whereas sorption of TcO_4^- increased on Fe(II)-containing minerals.

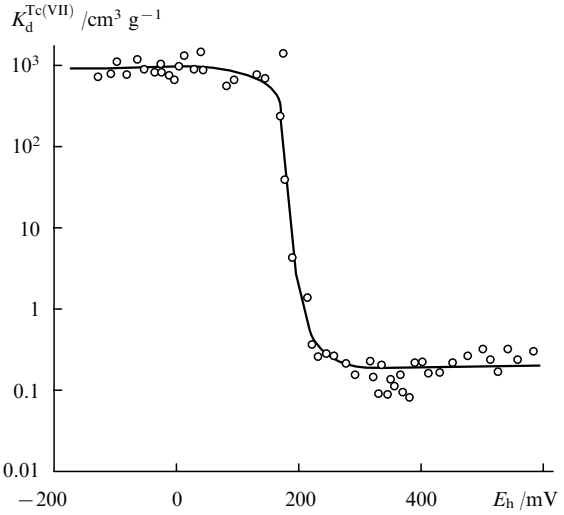


Figure 11. Plot of the coefficient of sorption of technetium by minerals from solutions of groundwaters (pH 5.8–7.4) *vs.* E_h.
$[TcO_4^-] = 10^{-6}$ mol litre^{-1}. The ratio of the volume of the solution to the weight of the sample is 2.5 cm^3 g^{-1}.[65]

Sorption of Tc on samples of soils taken in the region of the production site of the Mayak Production Association was studied (Table 5).[199] It was demonstrated that the distribution coefficients of technetium in water–soil sample systems $[K_d^{Tc(VII)}]$ depend on the content of organic components in the soil. Thus, the distribution coefficients $K_d^{Tc(VII)}$, which are in the range of ~6–

Table 5. Coefficients of sorption of Tc in soil–water systems.[199]

Sample	Organic component (%)	pH after sorption	$K_d^{Tc(VII)}$ /cm^3 g^{-1}
Sand	0	7.1	10
Kaolin clay	0	7.5	12
Loam	2	7.3	14
Grey soil	5	7.3	18
Humus	35	6.9	25
Bottomset bed (Uvildy lake)	43	7.4	30
Deciduous foliage (birch)	52	7.2	140
Mushroom chitin	–	6.5	39

Note. The starting concentration of technetium was 45 mg litre^{-1}, V/m = 50 cm^3 g^{-1}, 20 °C, the duration of the contact was 8 weeks.

12 $cm^3\ g^{-1}$ for samples of sand and kaolin clay devoid of organic compounds, slowly increase as the percentage of the organic component increases. High distribution coefficients of Tc in soil samples were observed for humus (25 $cm^3\ g^{-1}$) and bottomset beds (30 $cm^3\ g^{-1}$) containing organic components (algae, fungi, *etc.*). Biosorption by bacterial cell walls and fungal melanins makes the major contribution to bioaccumulation of Tc. Thus, the anomalously high coefficient $K_d^{Tc(VII)} = 140\ cm^3\ g^{-1}$ was found for deciduous foliage.

Hence, the available experimental data indicate that, occurring in the anionic form at high reduction potentials E_h, technetium is very poorly sorbed by minerals. Apparently, the fixation of technetium by soils and rocks under reductive conditions results, primarily, from chemical precipitation.[208] An increase in $K_d^{Tc(VII)}$ for samples containing organic compounds is proportional to their percentage. Taking into account that organic components of soil are, primarily, humus and various cell organisms and that humus, in turn, consists of humine and humic acids, it was hypothesised[199] that it is these components that are favourable for active fixation of Tc by soil samples.

4. Diffusion properties of technetium

It is commonly assumed that ^{99}Tc possesses high mobility in environmental waters. As mentioned above, oxidised technetium occurs in the water-soluble anionic form and is sorbed by neither minerals nor clay–sand soils to a noticeable degree. According to in-field observations,[203] technetium can be transferred by groundwater through the water-bearing sand bed in the form of TcO_4^- ions.[209] In the case of crystalline rocks, water-filled cracks serve primarily as migration channels. Generally, walls of these cracks are covered with a layer of metamorphised minerals. It was demonstrated that the coefficient of diffusion of $^{99}TcO_4^-$ in samples of metamorphised granite and bentonite taken from the fractured zone of Precambrian batonite at a depth of about 250 m is $1.4 \times 10^{-12}\ m^2\ s^{-1}$.[117,210]

5. Distribution of technetium in the World Ocean

The World Ocean serves as an indicator of the ecological state of the main Earth shells. Hence, data on the presence of particular pollutants, including radionuclides released into the hydrosphere, in the World Ocean are of great importance.

The specific activities of ^{99}Tc in coastal sea waters of the World Ocean are presented in Fig. 12. In seas and the Pacific Ocean, the specific activities are in the ranges of 1.0–7.4 and 0.49–3.33 μBq $litre^{-1}$, respectively. The ^{99}Tc concentrations in the Irish Sea and the North Sea are higher than the average level due to their pollution with industrial wastes from the Sellafield plant, where spent nuclear fuel is reprocessed. The authors of the study [113] believed that the occurrence of Tc in other regions of the World Ocean is associated primarily with the global fallout.

Being constant in different regions of the World Ocean, the activity ratio $^{99}Tc/^{137}Cs = (2.7 \pm 0.6) \times 10^{-4}$ depends on the release of fission products from nuclear explosions, mechanical dispersion of nuclear explosion products and chemical and physical fractionation of radionuclides.

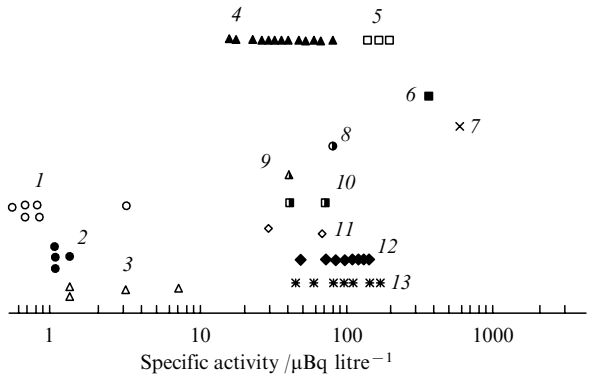


Figure 12. Specific activity of ^{99}Tc in waters from different seas.[113] (*1*–*3*) Pacific Ocean (*1*, 1992; *2* and *3*, 1993); (*4*) and (*5*) Baltic Sea [*4*, 1986, *5*, 1988]; (*6*), Norwegian Sea (1980); (*7*) Barents Sea (1980); (*8*) Greenland Sea (1988); (*9*) Davis Strait (1984); (*10*) Baltic Sea (1983, 1986); (*11*) Mediterranean Sea (1985–1987); (*12*) and (*13*) Japan Sea (1987).

6. Behaviour of technetium in biosystems

The behaviour of technetium in biosystems has been studied in detail. Most of the available data indicate that Tc is readily transferred from soils (or waters) into plants or organisms under anaerobic conditions, which is, apparently, associated with high solubility of pertechnetates and their mobility in soils.[88,210–212] It was demonstrated [106,211,213,214] that the mechanism of transfer of Tc into biosystems involves the transport of TcO_4^- through a plant cell membrane [89] (energy consumption is ~9.4 kJ mol^{-1}) as the first step [211] followed by photoreduction of Tc(VII) to Tc(IV) in chloroplasts by plant gelatin serving as the complex-forming reducing agent present in plants.[106]

The equilibrium concentration of Tc in a biomass, for example, in duckweed *Lemna minor*, is established very rapidly (already within 2 h). The kinetics of bioaccumulation of Tc in plants depends on the intensity of their illumination, the concentrations of technetium and nitrate ions in solution and temperature. At 25 °C, the rate of Tc reduction under solar illumination is close to 200 μmol $m^{-2}\ s^{-1}$.[211]

Generally, the absorption of radionuclides from soil by vegetables is characterised by the transport factor (TF) [126,215,216] or concentration factor (CF), which are determined as the ratio of the radionuclide concentration in a fresh plant to its concentration in dry soil (Bq kg^{-1}). The transport factor is among the most important parameters used for the estimation of the intake of radionuclides into the human body. The transport factors depend on the nature of the plant. For example, the transport factors for foliar vegetables are much higher than those for root vegetables. The transport factors for old leaves are much higher than those for young leaves. Since root and stalk tissues cannot retain technetium that enters into plants, it is transferred to leaves and accumulated there when water is evaporated. Apparently, the transfer of technetium together with photosynthesis products, for example, with carbohydrates, from leaves to tubers, fruits and follicles is insignificant.

As can be seen from Table 6, the transport factor of technetium calculated for the weight of dry samples of the plants under

Table 6. Transport factors of ^{95m}Tc (Bq kg^{-1}) from soil to different organs of vegetables (radionuclide label was introduced into soil when cropping).[215]

Plant	Non-edible part/ edible part	TF /Bq kg^{-1}	
		wet plant	dry plant
Lettuce (*Lactuca sativa L.*)	lower/upper leaves	16/2	340/26
Sweet pepper (*Capsicum annuum L.*)	old leaves/fruits	30/0.03	184/0.03
Aubergine (*Solanum melongena L.*)	old leaves/fruits	5/0.01	22/0.1
Kidney bean (*Phaseolus vulgaris*)	old leaves/follicles	16/0.02	127/0.2
Cauliflower (*Brassica oleracea L. var. botrytis*)	lower leaves/flowers	135/0.1	456/0.9
Yam (*Dioscorea japonica Thunb*)	leaves/tubers	−/1	218/4
Soya (*Glycine max L.*)	leaves/legumes	−/−	1416/0.8

examination changes from 5 to 1416 Bq kg^{-1} (dry soya leaves) [215] and even to 2600 Bq kg^{-1} (dry spinach leaves).[126]

It is reasonable to compare the above-mentioned transport factors of Tc into edible parts of plants with the safe level of technetium recommended by the International Atomic Energy Agency (5 Bq kg^{-1}).

Of sea organisms, annelida (*Fucus serratus*, **I**), crustacea (*Perinereis cultrifera*, **II**) and brown algae (kelps) (*Homarus gammarus*, **III**) intensively accumulate Tc. The corresponding concentration factors are 1500 (**I**), 1200 (**II**) and 1000 Bq kg^{-1} (**III**). The concentration factors for other sea plants and animals (fish, shellfish, phytoplankton, *etc*.) are much lower (1–10 Bq s^{-1} kg^{-1}). In studies of the concentrations of Tc in sea organisms taken in the region of the La Hague Strait (European Continent), the following concentration factors were found: 44.4, 155.4 and 125.8 Bq kg^{-1} for **I**, **II** and **III**, respectively. The concentrations of technetium in fish, for example, in *Blennius pholis* or *Labrus bergulta*, varied from 0.92 to 1.48 Bq kg^{-1}, respectively.[217]

Microorganisms readily adsorb technetium through interactions with the sulfur atoms of amino acids and proteins. From this viewpoint, Tc is similar to iodine, which also readily interacts with microorganisms. For example, the data on bioaccumulation of Tc and other long-lived radionuclides by bottom sediments from different basins under the action of microorganisms were analysed in the studies.[200, 202, 217–223]

7. Influence of radiolysis on the behaviour of Tc in environmental objects

It is known that the migration properties of Tc and other radionuclides in the biosphere can depend on self-irradiation of the samples, which has an effect on the stability of their oxidation state and diffusion in geological formations.[23, 121] For example, γ-irradiation of solutions of Tc(VII) leads to its reduction to Tc(IV) depending on the composition of the medium. It was demonstrated that a neutral solution of TcO_4^- turned brown and TcO_2 or $TcO_2 \cdot n\,H_2O$ colloidal particles with the grain size of 30–130 nm formed at the irradiation dose of 2 kGy. In deaerated solutions, TcO_4^- is reduced at lower doses. It was found that the yield decreased in the course of reduction with increasing concentration of carbonate ions in solution.[224]

VII. Use of technetium in technological processes and medicine

1. Catalytic properties

The catalytic activity of technetium metal has been predicted by Balandin [225] on the basis of a sextet model of dehydrogenation of cyclohexane. Since technetium metal has a hexagonal crystal structure and the smallest distance between the atoms ($\sim$2.74 Å) is in the range of distances for known catalysts (2.49 Å for Ni or 2.77 Å for Pt), it should serve as a catalyst for the transformations of six-membered cyclic hydrocarbons.

It was demonstrated that a catalyst containing 1 mass % of Tc on SiO_2 or Al_2O_3 support, like a rhenium catalyst, accelerates hydrogenation of benzene to form cyclohexane and hydrogenolysis of benzene at 100–350 °C, the best results being achieved with the use of γ-Al_2O_3 as the support.[226] In the above-mentioned processes, the specific catalytic activity of metals changes in the series Ru > Pt > Tc > Pd > Re and Ru > Tc > Re.[227, 228]

The promotion action of technetium was studied in hydrogenation and dehydrogenation of hydrocarbons on applied catalysts based on platinum metals (Pt, Pd, Rh, Ru).[229–231] It was found that the catalytic activity was substantially increased upon the addition of technetium (synergistic effect). The physicochemical properties of technetium-metal catalysts were examined.

Technetium serves as a catalyst for hydrogenation of anhydrides (for example, the transformation of succinaldehyde into tetrahydrofuran [232]), conversion of aliphatic hydrocarbons (for example, dehydrocyclisation of heptane to form toluene [233]) and decomposition of aliphatic alcohols to hydrogen and the corresponding aldehyde.[226]

The Standard Oil Corp. (USA) developed catalysts involving technetium and its dioxide as the activator for petroleum reforming, and these catalysts were covered by patents. The concentration of technetium on an Al_2O_3 support was 0.01%–0.2%. The noble metal served as the major component.[234]

Catalysts based on complex Tc compounds are of particular interest from both the theoretical and practical standpoints. In many cases, these compounds proved to be more efficient than catalysts based on metals or their oxides.[235] One of the most promising applications of complex catalysts is the activation of molecular nitrogen, which opens up possibilities for the direct synthesis of ammonia under mild conditions. For example, the complex technetium compound with composition $TcCl_4(PPh_3)_2$ catalyses reduction of molecular nitrogen to ammonia under the action of lithium naphthalide.[236]

2. Superconducting properties of technetium and its compounds

The superconductivity of technetium was discovered in 1953 when studying the magnetic susceptibility of powdered metal with purity of no lower than 99.9%.[237] The superconducting transition begins at 11.2 K and is completed at 7.7–7.8 K. Hence, technetium is the second best superconductor, exceeded only by niobium ($T_c = 9.25 \pm 0.02$ K). Technetium differs from other metals in the degree of anisotropy of the superconducting properties. Technetium is the only representative of type II superconductors belonging to the hexagonal system.[238] It should be noted that although Tc in the bulk state is somewhat inferior to niobium as a superconductor, its films exhibit better superconducting properties. Superconducting Tc films have obvious advantages over niobium films. That was the reason why technetium was chosen as a material for superconducting RF cavities for an accelerator in the USA.[239]

Technetium is of interest because its alloys combine phases typical of rhenium and manganese. Since technetium alloys can simultaneously possess physical properties exhibited by rhenium and manganese alloys, they can be considered as materials with special properties.[240] The so-called 'rhenium effect' is of obvious interest for superconducting technetium-based materials. This effect lies in the fact that both the strength and plasticity of the metal increase simultaneously upon the addition of Tc or Re.[241]

An alloy containing 5%–75% of Mo is the first commercial Tc-containing alloy (Western Electric Company, USA; covered by a UK patent), which can be used for the construction of electromagnets.[242]

3. Technetium as an inhibitor of corrosion

High inhibiting ability of the pertechnetate ion was first established by Cartledge as early as 1955 [243–245] and then confirmed by investigations of Russian researchers.[246–248] It was demonstrated that the pertechnetate ion (like other known inhibitors of the MO_4^{n-} type, where M = Cr, Mo or W) is among the most efficient inhibitors of corrosion of carbon and stainless steels, the action of TcO_4^- being observed even at a concentration of $\sim 10^{-5}$ mol $litre^{-1}$ at 250 °C.[243] It was established that the mechanism of action of TcO_4^- is identical to that of CrO_4^{2-} and WO_4^{2-}.[249] However, the required protective concentration of the pertechnetate ions is $\sim$10 times lower.[250] Besides, the TcO_4^- ion is more resistant to radiation than the CrO_4^{2-} and WO_4^{2-} ions. These results opened up possibilities for the use of Tc as an inhibitor of corrosion of water-cooled nuclear reactors. Thus, $KTcO_4$ (0.5 kg) was introduced into the bulk of a D_2O core coolant (47 m^3) to prevent corrosion of the CANDU energy reactor with an output of 200 MW.[251]

Technetium coatings were also proposed for the protection of the underside of oceangoing ship hulls from microorganisms.[252] The commercial Technetium Corp. (USA) established in 1976 was

aimed at extending business activity in the design, use, sale and licensing of technetium coatings for their application in marine and industrial media.

4. Use of technetium compounds in medicine

Radionuclide methods of examination and treatment are widely used in different fields of scientific and practical medicine. Radionuclides used in these fields and the corresponding radiopharmaceuticals based on them are classified as diagnostic therapeutic according to the areas of their application. Diagnostic radiopharmaceuticals, in turn, are divided into groups of radionuclides for single photon emission computed tomography (SPECT, γ-emitters with energies in the range of 100 – 200 keV and half-lives from several minutes to several days) and positron emission tomography (β^+-emitters with half-lives from several seconds to several hours). In the last two decades, the overwhelming majority of diagnostic procedures (up to 80%) employing the SPECT technique were carried out with the use of radiopharmaceuticals containing ^{99m}Tc (see Refs 253, 254), which is called the 'work horse' of nuclear medicine.[255]

The ^{99m}Tc isotope belongs to the category of short-lived isotopes, whose application allows one to study the same object repeatedly at short intervals without overirradiation.

Numerous studies demonstrated that ^{99m}Tc can be used for the diagnosis of diseases of the liver, thyroid,[256] kidneys and adrenals,[257] spleen,[256] respiratory system,[258] cerebrum,[256] spinal cord,[259] bone marrow,[260] salivary glands, digestive system,[256] bones and joints of the skeleton [261] and also for studies of the physiological functions of the cardiovascular system,[256] lymphatic system [262] and urological system,[263] investigations of the glomerular filtration rate and plasma volume.[264, 265] In addition, ^{99m}Tc can be used for examining internal cavities,[266] infectious heart diseases,[267] infectious brain diseases,[268] infectious eye diseases,[269] infectious dermal diseases [270] and skin transplantation.[271]

The synthesis of efficient ^{99m}Tc radiopharmaceuticals is of considerable importance for using technetium in medicine. In Russia, a methodology was developed for the design of generators for ^{99m}Tc and technological schedules were applied to the production of various radiopharmaceuticals, among which are $^{99m}TcO_4^-$, ^{99m}Tc citrate, groups of colloidal ^{99m}Tc pharmaceuticals, *etc*.[272, 273]

Pharmaceuticals containing ^{99m}Tc are prepared in different forms specific for particular organs, groups of organs or systems. The possibility of the use of a drug for the diagnosis of diseases of a particular organ depends substantially on both the oxidation state of the radioactive label and the properties of the drug into which it is incorporated.

Radiopharmaceuticals containing ^{99m}Tc can be divided into three groups according to their biological specificity: Na or K pertechnetates, technetium(VII) complexes with various ligands and technetium(IV) complexes with various ligands. Sodium pertechnetate is accumulated primarily in glandular organs of the human body, *viz*., in the thyroid gland, gonads, parotid gland and kidneys.[274] Since the pertechnetate ion is biologically nonspecific, radiopharmaceuticals of the first group can be used for the diagnosis of almost all organs and systems. These pharmaceuticals are removed from the organism during one day.[255] In the radiopharmaceuticals of the second group, which are more biologically specific than pertechnetate, Tc is involved in micelles in the hepta- or tetravalent state.[275, 276] The third group containing the largest number of representatives includes complex compounds, which are prepared by reduction of the pertechnetate ion to lower oxidation states. The biological specificity of Tc complexes is most pronounced. Many of these complexes involve organic compounds of different classes, *viz*., alcohols, sugars, nucleic acids, nucleoproteins, amino sugars, polysaccharides, drugs containing phytin, penicillamine acetazolamide, bleomycin, dihydrothioctic, glucoheptonic, gluconic and other acids [94, 276] as well as Tc chelate complexes.[166]

In Russia, the problem of the production of a standard list of reagent sets has already been solved. These reagents are produced by virtually all corporations. Thus, the Medradiopreparat Plant of the Ministry of Health of the Russian Federation produces reagent sets for the preparation of the drugs Pentatech (^{99m}Tc complex with diethylenetriaminepentaacetic acid used for the determination of glomerular filtration rate in kidney disease or visualisation of brain tumours), Pyrphotech (^{99m}Tc complex with pyrophosphate used for scintigraphy of the skeleton or acute myocardial infarction), Coren (^{99m}Tc complex based on rhenium sulfide used for scintigraphy of the liver, spleen or bone marrow). The Diamed Plant produces the above-mentioned pharmaceuticals along with Technephor (^{99m}Tc complex with oxabiphor used for scintigraphy of the skeleton), *etc*.[253]

Extensive studies are being conducted on the design of new pharmaceuticals based on ^{99m}Tc complexes with the $N_2S_2 - NS_3$, S_3N ligands, carbonyl ligands and peptides.[253]

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