

This paper is dedicated to the centenary  
of Academician Viktor Ivanovich Spitsyn

## Preparation of Technetium Metal for Transmutation into Ruthenium

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**Abstract**—Methods for fabricating Tc metal through reduction of ammonium pertechnetate or technetium dioxide by hydrogen, as well as through thermal decomposition of pertechnetates with organic cations, are surveyed. The kinetics and mechanisms of corresponding heterogeneous processes are described. Metallic technetium is shown to be a candidate for neutron-driven transmutation to stable ruthenium.

Technetium, the first artificial element, was synthesized in 1937. This element has found noticeable practical use. The short-lived isotope  $^{99m}\text{Tc}$  ( $T_{1/2} = 6\text{ h}$ ) is the most used radionuclide in nuclear medicine among all developed countries [1]. More than one hundred thousand injections of radiopharmaceuticals of 12 types, containing different complexes and organic compounds of short-lived technetium-99m, are produced in Russia for medical treatment and diagnosis of some diseases [2].

The most abundant technetium isotope is long-lived  $^{99}\text{Tc}$  ( $T_{1/2} = 2.14 \times 10^5$  years). This isotope forms with a high yield (~6%) upon fission of uranium, plutonium, and thorium nuclei and accumulates in the spent fuel of nuclear power plants in a concentration of about 1 kg per fuel tonne. This yields an annual accumulation of 8 tonnes of technetium in the nuclear fuel used throughout the world (for the period 1998–2000) [3]. The prospects for using long-lived technetium have been studied by different researchers, and the major contribution was made by the teams led by Academician V.I. Spitsyn [4] and Professor G.H. Cartledge [5]. Dissolved technetium salts were found to be efficient corrosion inhibitors, first of all, for water cooling systems of nuclear reactors. Small technetium additions (a fraction of percent) to steels and alloys significantly increase the resistance of these materials to corrosion. Thin technetium coatings of seacraft parts exposed to seawater prevent their corrosion and fouling. Adding technetium in iron catalysts of large-scale ammonia synthesis [6] and in catalysts of dehydrogenation and other processes of organic synthesis leads to a manifold increase in product yield [7]. Of interest is also superconductivity of technetium, which ranks below only one metal, niobium, in superconducting transition temperature (8.24

and 9.92 K, respectively) [4]. Until the Chernobyl accident (1986), applications of long-lived technetium had been extensively studied. Since then, technetium has been treated only as industrial radioactive waste, which exhibits a dangerously high capacity for migration in air and natural waters due to the high volatility and solubility of technetium(VII) compounds and their low sorption on rocks and minerals. However, a promising new application of long-lived technetium was found soon afterwards—namely, transmutation, i.e., burning of technetium in reactors and accelerators to produce stable ruthenium.

### TRANSMUTATION OF LONG-LIVED TECHNETIUM TO STABLE RUTHENIUM

Transmutation of long-lived nuclides driven by neutrons or some other particles is a promising method for treatment and neutralization of highly radioactive industrial waste [8]. Among long-lived transuranium and fission nuclides, candidates for transmutation, only technetium yields a valuable product upon transmutation:  $^{99}\text{Tc} (n, \gamma) ^{100}\text{Tc} (\beta, T^{1/2} = 17.5\text{ s}) \longrightarrow ^{100}\text{Ru}_{(\text{stab})} (n, \gamma) ^{101}\text{Ru}_{(\text{stab})}$ . Studies on the transmutation of technetium are carried out in some developed countries [9–11].

The feasibility of using technetium as a source for fabricating nonradioactive ruthenium in amounts comparable to those obtained from ores was theoretically based in the 1990s at the Institute of Physical Chemistry, Russian Academy of Sciences (IPC RAS) [12–15]. A high rate of technetium conversion into ruthenium (34% in the first three months) meeting the requirements of industrial transmutation has heretofore been

attained only at the IPC RAS and NIAR State Research Center (Dimitrovgrad) in an SM-3 reactor with a thermal neutron flux of  $(1-2) \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$  [16]. In all transmutation experiments, technetium metal targets were used; being irradiated, technetium converted into a Tc-Ru solid solution. The feasibility of targets made of other materials—technetium carbide, nitride, and dioxide—has been theoretically considered [17]. Herein, we survey the methods for obtaining the above technetium materials and their properties essential for transmutation.

### FABRICATION OF TECHNETIUM METAL

Technetium is obtained from spent nuclear fuel processing waste. Description of the methods for isolating technetium from wastes is beyond the scope of our review. Note that the modern technology for processing the spent fuel at the RT-1 (Mayak) and La Hauge (France) reprocessing plants makes it possible to easily extract technetium on a commercial scale as a nitric acid solution upon washing an organic tributyl phosphate phase containing plutonium and technetium [17, 18]. Because of the absence of constant demand, technetium is produced sporadically. In the 1970s and 1980s, dozens of kilograms of technetium were isolated at the plants in Oak Ridge and Hanford and at the Mayak Research and Production Association (Ozersk), Siberian Chemical Plant (Tomsk), and Mining Chemical Plant (Krasnoyarsk) in Russia. Beginning in the 1950s, different researchers reported on the synthesis of Tc metal in milligram and gram amounts; these methods were overviewed in [4, 19].

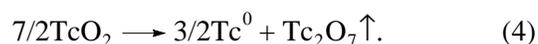
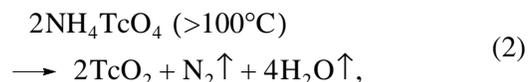
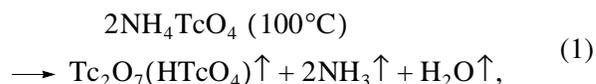
Elemental technetium is chemically inert and is located to the right of copper in the electromotive series. Milligram and gram amounts of Tc metal can be obtained by reacting its compounds with hydrogen, ammonia, carbon monoxide, or ethanol vapor; by thermolysis of double Tc(IV) halides  $M_2TcHal_6$  (M is an alkali-metal ion or ammonium; Hal = Cl, Br, I) or pertechnetates with organic cations; and by electrolysis of technetium solutions. Information on the pilot-plant production of technetium is scant. To the best of our knowledge, preparation of technetium metal in kilogram amounts was described only in the works of the Mayak Production Association and IPC RAS. These data, which were not included in the monographs [4, 19], are considered below.

#### *Synthesis of Technetium Metal from Inorganic Pertechnetates and Technetium Dioxide through Reduction by Hydrogen*

Passing hydrogen over  $Tc_2S_7$ ,  $TcO_2$ ,  $NH_4TcO_4$ ,  $KTcO_4$ , or  $[(C_6H_5)_4As]TcO_4$  at 400–1100°C yields technetium metal. Metal free of impurities of chemical elements constituting the initial compound was prepared only from ammonium pertechnetate and technetium dioxide; these processes were found to be highly

explosive under definite temperature conditions [4, 19]. The Mayak plant produces potassium pertechnetate and technetium dioxide and delivers them as commodity output. The technetium metal obtained by reduction of potassium pertechnetate contains an impurity of potassium oxide. Therefore, the flow chart for preparation of technetium metal for transmutation, developed in the 1990s at the Mayak Production Association and IPC RAS [20–24], begins with cation-exchange conversion of potassium pertechnetate into pertechnetic acid,  $HTcO_4$ , followed by neutralization with ammonia and separation of crystalline ammonium pertechnetate. To find the conditions for the safe synthesis of technetium metal, the kinetics and mechanism of the thermal decomposition of ammonium pertechnetate to dioxide and its reduction to the metal by hydrogen have been studied.

**Thermal decomposition of ammonium pertechnetate** has been mainly studied by thermogravimetry [19, 25, 26]. Relevant data have been interpreted with a varying degree of validity to fit the following reactions:



The slow reaction (1) was detected only in one study based on elemental analysis data after a long-term heating of the salt at 100°C [4]. Reaction (2) was detected in all papers that describe the thermal decomposition of the salt; however, the decomposition temperatures reported by different authors are noticeably different: 325°C in argon [25], 327 and 240°C in nitrogen [19, 26], and 550°C in vacuum [19]. Such a wide scatter of decomposition temperatures is explained not so much by different conditions of recording thermal curves as by the occurrence of different impurities in salt samples [19]. Different “ages” of ammonium pertechnetate samples and, as a result, different absorbed doses due to intrinsic  $\beta$  emission of technetium can also affect thermal decomposition, since this salt, which contains a reducing agent ( $NH_4^+$ ) and a rather strong oxidant ( $TcO_4^-$ ), is characterized by a low radiation resistance compared to alkali-metal pertechnetates [4].

Reaction (3) converts crystalline ammonium pertechnetate and technetium dioxide into the volatile highest oxide; thus, the presence of oxygen reduces the yield of technetium metal from these compounds. That reaction (4) takes place is argued based on thermodynamic calculations [19, 27], which differently interpret

**Table 1.** Thermodynamic characteristics of technetium and its compounds [19, 20]

Substance	$-\Delta G$	$\Delta H_{298}^0$	Heat capacity ( $C_p$ ) <sub>298</sub>		
	kJ/mol		$(C_p)_{298}$	coefficients of the equation $C_p = a + bT$	
				$a$	$b$
Tc <sub>(solid)</sub>	0.0	0.0	25.9	23.4	$8.37 \times 10^{-3}$
TcO <sub>2</sub> (crys)	358.8*	434	54.0	43.5	$38.5 \times 10^{-3}$
	383.2 [19]	457.8 [19]			
NH <sub>4</sub> TcO <sub>4</sub> (crys)	722 [19]	746	154 ( $C_p$ ) <sub>600</sub> = 112**	–	–

\* All the values were taken from [20], unless otherwise specified.

\*\* Calculated on the assumption that NH<sub>4</sub>TcO<sub>4</sub> (crist) has the same temperature dependence of the heat capacity as NH<sub>4</sub>ReO<sub>4</sub> (crist).

the experimental data on the congruent sublimation of technetium dioxide at 900–950°C. Taking into account the vapor pressure of manganese, rhenium, and other elements, the authors of [19, 27] arrived at the conclusion that the congruent sublimation of technetium dioxide at 900–1000°C is unlikely; they explained the experimental data on sublimation [28] by the occurrence of reaction (4), followed by reduction of Tc<sub>2</sub>O<sub>7</sub> to TcO<sub>2</sub> at colder parts of a setup, as was the case with sublimation of ReO<sub>2</sub> [19]. A partial sublimation of NH<sub>4</sub>TcO<sub>4</sub> and TcO<sub>2</sub> was observed in an argon flow at 1000°C accompanied by accumulation of small amounts of metallic technetium in the starting compound, which was attributed to the reducing action of ammonium ion and nascent intermediate nitrogen-containing technetium compounds [25].

Therefore, the major stage of the thermal decomposition of ammonium pertechnetate to dioxide takes place at a temperature of 325°C or higher and is described by reaction (2). This reaction is exothermic and is accompanied by the release of 141.5 kJ/mol TcO<sub>2</sub>. Reaction (2) results in rapid self-heating (1–3 min) of NH<sub>4</sub>TcO<sub>4</sub> from 325 to 500°C and higher and in vigorous liberation of 2.5 mol of gases (N<sub>2</sub>, H<sub>2</sub>O) per mole of the salt. If tens or hundreds of grams of the salt are subjected to decomposition, and in the absence of heat removal, this gas release leads to the explosion or throwing of the starting salt into the cold portion of the reactor [20]. The kinetics of process (2) points to the autocatalytic character of the decomposition of ammonium pertechnetate in an inert medium; the kinetic curves are S-shaped and are adequately described by the Erofeev equation [29]:

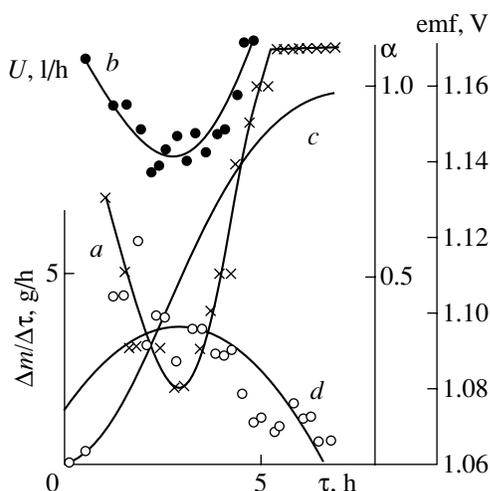
$$\alpha = 1 - (1 - \alpha_0) \exp(-k^2 \tau^2), \quad (5)$$

where  $\alpha$  is the fraction of the intact ammonium pertechnetate at the moment  $\tau$  ( $\alpha = \Delta m_\tau / \Delta m_\infty$ ,  $\Delta m_\tau$  is the change in the sample mass by the time  $\tau$ ;  $\Delta m_\infty$  is the ultimate mass change by time  $\infty$ ) and  $k$  is the rate constant of reaction (2).

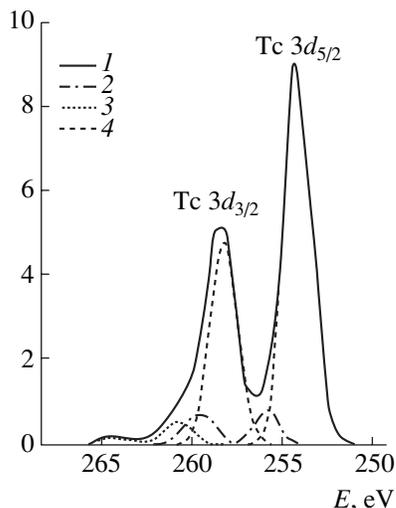
The rate constant of the decomposition of ammonium pertechnetate was studied as a function of temperature in the range 195–300°C, and the corresponding activation energy was determined to be 140 kJ/mol. To find the regime that guarantees safe thermal decomposition of ammonium pertechnetate, the heat balance of the process was calculated based on the kinetics and heat of the exothermic decomposition of the salt and the heat capacities of the initial and ultimate reaction products and the heat-transfer agent argon. The thermodynamic parameters of technetium compounds used in calculations are listed in Table 1.

The argon flow rate that ensures heat removal and safe thermal decomposition of ammonium pertechnetate under isothermal conditions has been calculated (2.8 cm<sup>3</sup> s<sup>-1</sup> per gram of the salt at 250–320°C). This rate makes it possible to place 180 g of ammonium pertechnetate (100 g of Tc) into the reactor and to accomplish the thermal decomposition of the salt in 3 h. An original dosimetric method for monitoring the thermal decomposition of the salt was elaborated. The process is monitored by continuously measuring the exposure dose rate (EDR) of the technetium preparation to be reduced. The EDR method is based on the fact that the dose rate of bremsstrahlung associated with deceleration of technetium  $\beta$ -particles in the sample increases with an increase in the sample density or mean nucleus charge. It was found that the volumes of the initial reagent (NH<sub>4</sub>TcO<sub>4</sub>) and ultimate product (TcO<sub>2</sub>) are virtually the same, while the increase in the mean nucleus charge of the sample (due to H<sub>2</sub>O and N<sub>2</sub> removal) leads to a 38% increase in EDR. This makes it possible to continuously monitor the conversion of pertechnetate into dioxide by measuring EDR with a microdosimeter. The EDR method appeared to be more accurate and convenient than the method based on measuring the water content of the exhaust by means of gas analyzers.

**Reduction of technetium dioxide to the metal by hydrogen.** This method has been used since the 1950s. Currently it is more frequently used for preparation of technetium metal than the other available methods [4, 30–32]. However, the kinetics and mechanism of this



**Fig. 1.** Isotherms of reduction of  $\text{TcO}_2$  by an Ar–7%  $\text{H}_2$  mixture [20, 23]: (a) emf, (b) gas flow rate at the outlet of the reactor ( $U$ ), (c) conversion  $\alpha$ , and (d) water condensation rate  $\Delta m/\Delta\tau$ .



**Fig. 2.** XPS spectrum of the amorphous (for X-ray diffraction) solid product of tetraethylammonium pertechnetate decomposition at  $400^\circ\text{C}$ : (1) experimental spectrum, (2)  $\text{Tc}^{4+}$ , (3)  $\text{Tc}^{7+}$ , and (4)  $\text{Tc}^0$ .

heterogeneous reaction were studied only in the 1990s at the Mayak plant and Institute of Physical Chemistry. These studies resulted in finding optimal conditions for this reaction to occur and made it possible to considerably increase the mass of technetium dioxide loaded into a setup for reduction [20, 22–24]. The isotherms of reduction of technetium dioxide by an argon–hydrogen mixture at 673–1118 K (Fig. 1) are typical kinetic curves of topochemical reactions [20, 22, 23]. The maximal reduction rate corresponding to the inflection point on the integral curve (Fig. 1) is attained at the conversion of about 0.4 of the initial technetium dioxide.

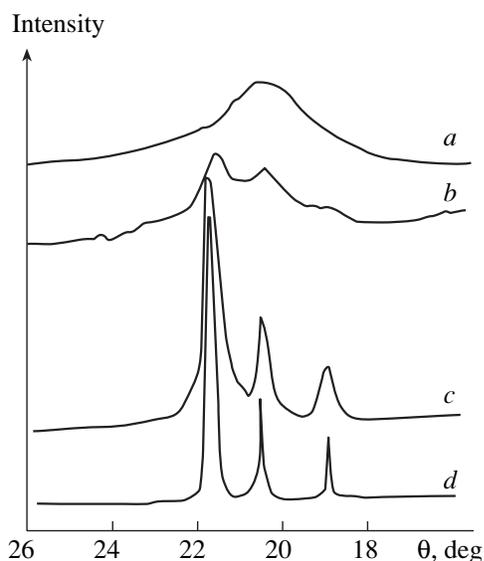
The experimental reduction kinetic data are adequately described by the Erofeev equation (5). The

reaction rate constant at a fixed temperature depends on the argon–hydrogen flow rate and composition and on the weight of the technetium dioxide load. With an increase in temperature, the reaction rate constant increases, passes through a maximum at about 1000 K, and then decreases. The apparent activation energy was estimated from the Arrhenius equation for the ascending branch of the temperature dependence to be 22.6 J/mol. This value is close to the calculated melting heat of technetium metal at these temperatures.

The resulting kinetic parameters and other reaction characteristics permitted the conclusion that the rate-limiting stage of reduction is the crystallization of the metal from the pseudoamorphous phase of technetium metal that forms at the surface of technetium dioxide upon its reaction with hydrogen. Using the optimal temperature and reducing gas flow rate made it possible to considerably reduce the time it takes for the sample to be completely reduced, exclude the stage of recrystallization anneal, and increase the load weight per boat to 100 g of metal.

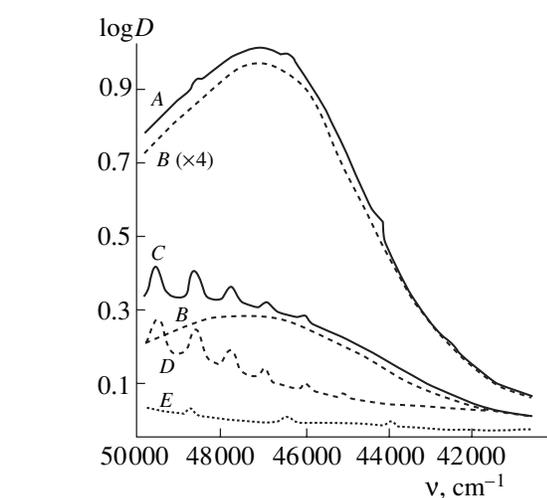
**Synthesis of technetium metal and carbide from pertechnetates with organic cations.** In a series of works, V.I. Spitsyn, A.F. Kuzina and K.E. Guerman considered the possibility of obtaining the metal from pertechnetates with different organic cations. In early experiments, tetraphenylarsonium pertechnetate was suggested for this purpose; however, this cation was shown to be a source of a hard-to-remove arsenic impurity [4]. Thus, further efforts were concentrated on the search for cations containing only C, H, O, and N atoms and ensuring a low solubility of pertechnetates in aqueous nitric acid and nitrate alkaline solutions (for isolation of technetium in the solid state from liquid radioactive waste).

Studying the properties and thermal decomposition of tetraalkylammonium pertechnetates  $[(\text{C}_n\text{H}_{2n+1})_4\text{N}][\text{TcO}_4]$  ( $1 \leq n \leq 5$ ) showed that their decomposition in an argon atmosphere containing 5% of hydrogen at  $300^\circ\text{C}$ , followed by crystallization anneal at  $600$ – $1500^\circ\text{C}$ , yields pure technetium metal of required dispersity [33, 34]. The mechanism of the decomposition of tetraalkylammonium pertechnetates was established based on the results of studying solid and gaseous reaction products. Tetraalkylammonium pertechnetate samples subjected to thermal decomposition under different conditions were studied by X-ray powder diffraction [34]. ESCA evidence shows that thermal decomposition of tetraethylammonium directly yields the metal ( $\geq 90\%$ ) (Fig. 2), in contrast to tetraphenylarsonium and triphenylguanidium pertechnetates, whose decomposition at temperatures below  $400^\circ\text{C}$  results in technetium dioxide [4]. The nascent technetium metal is amorphous to X-ray powder diffraction (Fig. 3). This is due to the high degree of its dispersion: the technetium recrystallization temperature is  $T_{\text{recryst}} = T_m/2 \approx 1360$  K; thus, the metal crystal growth rate under given conditions is very low. Because of its high dispersity and, hence, enhanced reactivity,



**Fig. 3.** X-ray powder diffraction patterns of the solid products of tetraethylammonium pertechnetate decomposition subjected to isothermal annealing at different temperatures: (a) 450, (b) 550, (c) 700, and (d) 900°C.

tiny particles of the nascent metal can either conglomerate upon further heating to give stabler compact metal samples or react with the gaseous decomposition products to produce technetium carbide, which is stabler under given conditions. The first process takes place at a high argon (or argon–6% hydrogen mixture) flow rate and moderate heating rates or when the samples contain 1–5% of occluded water serving to remove the gaseous decomposition products as aerosols. The second process takes place at low argon flow rates, high heating rates, and in the thermolysis of preliminarily dehy-



**Fig. 4.** Representative UV spectrum of a mixture of gaseous products of thermal decomposition of tetraethylammonium pertechnetate: (A) the gaseous products of thermal decomposition at 350°C, (B) the spectrum of triethylamine [36], (C) the gaseous products of thermal decomposition at 500°C, (D) the spectrum of ammonia [36], and (E) the subtraction (A – B) spectrum.

drated samples. The exhaust (Fig. 4) contains CO<sub>2</sub>, H<sub>2</sub>O, R<sub>3</sub>N, and some unidentified products; among solid decomposition products, Tc, TcC, TcO<sub>2</sub>, and C are identified (Table 2). As was shown later, the thermolysis of almost all technetium compounds with tetraalkylammonium cations leads to the formation of technetium metal [35].

Thermal decomposition of tetraalkylammonium pertechnetates [(C<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>N][TcO<sub>4</sub>] (4 ≤ n ≤ 6) in a pure argon atmosphere at 500°C, followed by crystallization

**Table 2.** Synthetic conditions and analysis of technetium metal obtained through thermal decomposition of tetraalkylammonium pertechnetates [34]

Initial compound	Initial moisture content of a sample	Heating rate, K/min	Gas flow rate, l/h	Tc yield, %	Impurity and its content, %
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	15	15	99	<1
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.5	15	15	99	<1
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	15	20	99.5	<1
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	15	5	90	TcC (10)
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	10	15	10	95	TcO <sub>2</sub> (5)
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	5	15	99	<1
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	40	15	90	TcC (5) C (5)
(CH <sub>3</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	25	15	99	<1
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	15	15	99.5	<1
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NTcO <sub>4</sub>	1.0	15	15	99.5	<1
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NTcO <sub>4</sub>	10	15	15	95	TcO <sub>2</sub> (5)
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	2	15	99.5	<1
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NTcO <sub>4</sub>	0.0	40	15	92	TcC (8)

annealing at 600–1500°C results in technetium monocarbide [34].

#### PROSPECTS FOR THE TRANSMUTATION OF TECHNETIUM AND FABRICATION OF ARTIFICIAL RUTHENIUM

Available data on the transmutation of 16% of technetium in one and a half years in the Petten reactor [10] and on the transmutation of 34% Tc in 3 months in the SM-3 reactor (Dimitrovgrad) [16] demonstrate the feasibility of fabrication of artificial ruthenium from radioactive technetium-99. The cost of artificial ruthenium includes the costs of technetium-99, its irradiation, and separation of the resulting alloy into residual technetium and nascent ruthenium. At the moment, this overall cost exceeds the cost of ruthenium extracted from ores. However, poor world resources of ruthenium in ores (3000–5000 tonnes) will lead to its deficiency in the near future. The transmutation of technetium will serve not only as a method for burning the dangerous radioactive waste of Tc-99 but also as an important source of ruthenium. The methods for obtaining technetium metal will be a necessary step in the flow chart of transmutation of the radioactive technetium waste into the artificial precious ruthenium metal.

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