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Technetium transmutation and production of artificial stable ruthenium

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Abstract

The recent Russian results on technetium transmutation into ruthenium are summarized, including the first isolation of artificial stable ruthenium from irradiated technetium targets. *To cite this article: V. Peretroukhine et al., C. R. Chimie 7 (2004).*

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Résumé

Transmutation du technétium et production du ruthénium artificiel. Les résultats obtenus en Russie sur la transmutation du technétium en ruthénium artificiel et son isolement des cibles irradiées sont présentés. *Pour citer cet article : V. Peretroukhine et al., C. R. Chimie 7 (2004).*

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1. Introduction

The long-lived radionuclide technetium-99 is one of the most abundant fission products. Its content in spent fuel of nuclear power plants is about 0.8 kg per ton for thermal reactor fuel and about 2 kg per ton for fast reactor fuel. About 8 tons of technetium per year are produced by nuclear power plants in the world, but its demand on the world market does not exceed some hundreds of grams per year for scientific research [1]. The radioactivity of technetium does not exceed $1 \times 10^{-3}\%$ of the total radioactivity of the nuclear fuel wastes in present time. However, its contribution to the

total β-activity of the nuclear wastes of the 20th and 21st centuries will be one of the most important in thousand of years, when most of the short-lived actinides and fission products will have disintegrate. ^{99}Tc in heptavalent state is regarded as mobile and ecologically dangerous radioelement because of its high solubility in natural waters and low sorption by the majority of minerals and rocks. Therefore, the destruction of this long-lived radionuclide is as important as the transmutation of minor actinides is. ^{99}Tc is the only one candidate for transmutation giving the precious product: artificial stable ruthenium after the irradiation.

The duration of irradiation of Tc target has been calculated by different authors to be 10–50 years to achieve 50% burn-up of ^{99}Tc in the majority of modern reactors and accelerators [2,3]. The experimental study of ^{99}Tc transmutation was described by three groups of the researchers from Hanford Site (USA), Petten (Holland) and CERN (Switzerland) before the beginning of our works. A burn-up of 0.67% ^{99}Tc for 10 days has been achieved in Hanford fast reactor, using a metal-hydride moderated environment of the target [4]. The burn-up of 16–18 % for 579.3 days of irradiation has been achieved in Petten reactor, which has a neutron flux with a thermal component of 2×10^{14} cm^{-2} s^{-1} [5]. No information has been published by the three above-mentioned groups about the isolation of artificial ruthenium from technetium target after transmutation. A number of technological concepts have been proposed by the group from Los Alamos for the separation of technetium and ruthenium after the accelerator transmutation of Tc(IV) hydroxide pulp or Tc(VII) solution in D$_2$O. These concepts have been based on the different behaviours of the two elements during the following procedures: cation-exchange sorption of [Ru(NO)NO$_3$]$^+$ from Tc(VII) solution; ozonolysis and removing of RuO$_4$ from neutral aqueous solution of Tc(VII); selective reduction of RuO$_4$ up to RuO$_2$ precipitate and its separation by filtration; magnetic separation of diamagnetic Tc(VII) and paramagnetic Ru(IV) compounds; fluorination of Tc and Ru oxides and separation of Tc and Ru hexafluorides using their different volatility [6]. No information has been found by us about the realization of above mentioned separation concepts both in laboratory and at the industrial scale.

The aim of this article is to demonstrate the possibility of the production of an artificial stable ruthenium

from ^{99}Tc at the Russian high flux reactor SM, provided that the high transmutation rate fits for the process at the industrial scale, and to demonstrate the isolation of artificial ruthenium from the irradiated target.

2. Russian researches on technetium transmutation and on the isolation of ruthenium

2.1. Calculation of ruthenium production

The kinetics of isotopes $^{100-105}$Ru accumulation and that of the radionuclides of rhodium and palladium in Tc target have been calculated at the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC–RAS) for the thermal neutron fluxes with different radiation hardness [7–9]. A necessary set of parameters has been calculated for the industrial production of artificial stable Ru, pure enough for applications in non-nuclear industry. It comprises the minimal thermal-neutron flux (1×10^{15} cm^{-2} s^{-1} and higher), sufficient for transmutation with acceptable rate, optimal burn-up of technetium (about 50% before the recycling of the target); the maximal permissible content of actinides impurity in Tc target (5×10^{-9}–1×10^{-11} g$_{An}$/g$_{Tc}$). The last requirement is based on the possible appearance of radioactive ^{106}Ru ($T_{1/2} = 1.01$ yr) as the fission product, which cannot be separated from the stable ruthenium during chemical isolation from the irradiated target. The necessary decontamination factor of ruthenium from technetium during the reprocessing of the target has been calculated to be about 2×10^8 for the use of artificial ruthenium in non-nuclear industry and about 4×10^7 for the use in nuclear industry [10,11]. The requirements for the irradiation can be met by few modern research reactors only and the requirements for the preparation and reprocessing of the Tc targets can be met easily at radiochemical plants.

2.2. Preparation of technetium targets for transmutation

Russian experimental research of technetium transmutation are based on the isolation of technetium from PUREX waste in production association radiochemical plant 'Mayak' and on the preparation of thin technetium metal targets in IPC–RAS [12–15]. Radioche-

mical plant RT-1 in PA Mayak produces aqueous solutions of rather pure technetium in HNO_3 during the washing of the TBP-phase in the first extraction cycle [13], like at the plants in La Hague and Sellafield. Tc(VII) has been concentrated from nitric acid by sorption on anion-exchange column, followed by its desorption with HNO_3, KNO_3 solution, by evaporation and precipitation of $KTcO_4$. To prepare Tc metal, $KTcO_4$ was converted into $HTcO_4$ on a cation-exchange column and then neutralized to NH_4TcO_4. Obtained solution was concentrated by evaporation, the salt has been precipitated by cooling, calcined to TcO_2 and reduced to powder metal in an hydrogen–argon stream [14,15]. Powder Tc metal has been melted, Tc foil has been prepared by rolling and the targets for transmutation have been cut from the foil.

2.3. Irradiation of the targets in the reactor

More than one hundred technetium targets-discs with a diameter of 6 mm and thickness of 0.3 mm have been irradiated in the high flux reactor SM-3 of the Research Institute of Atomic Reactors, Dimitrovgrad, Russia (RIAR) [16,17]. The flux of thermal neutrons was 1.2×10^{15} n cm^{-2} s^{-1} in the neutron trap inside the target at the beginning of the irradiation and increased to about 15% when Tc burn-up achieved 70%. The epithermal neutron flux in the neutron trap was 1.1×10^{14} cm^{-2} s^{-1} and changed insignificantly during the irradiation. The contribution of epithermal resonance neutrons to the technetium burn-up was important, because the main cross-section peaks of the reaction ^{99}Tc(n,γ)^{100}Tc are in the energy interval 2–20 eV and its resonance integral is much higher than the thermal cross-section [18]. Some parts of the targets have been unloaded when the calculated burn-up achieved 30, 50, and 70%. The Ru content in the targets has shown to be close to calculated values and to be equal to 34, 51 and 71%, accordingly [16,17,19]. The transmutation rate, achieved in the reactor SM-3, permits to convert 50% of Tc into Ru during about 150 days. This transmutation rate meets the requirements for the industrial production of artificial ruthenium. Gamma-spectrometry measurements of the targets, made during some months after the unloading have shown the presence of some ^{103}Ru and also ^{59}Fe, ^{51}Cr, ^{54}Mn and other radionuclides. These element impurities could come to the targets during the Tc foil preparation by rolling and became radioactive during irradiation.

2.4. Isolation of ruthenium from irradiated technetium target

The isolation of tracer quantities of ruthenium from technetium targets has been made in Russia in JINR (Doubna) and IPC RAS in the experiments of ^{97}Ru ($T_{1/2}$ = 2.9 days) production via the reaction ^{99}Tc(p,3n)^{97}Ru. Technetium target, irradiated by 50-MeV protons and containing tracer quantities of ^{97}Ru has been dissolved in concentrated nitric acid in the presence of KIO_4. ^{97}RuO$_4$ was distilled from obtained solution with air stream at 90 °C. The decontamination factor of Ru from Tc has been determined to be higher than 1×10^4 for this process [20].

Technetium targets irradiated in the reactor SM-3 contained 20–70% of ruthenium and were much more resistant for their dissolution than technetium metal. The targets have been dissolved electrochemically in hydrochloric acid [16,17] or, without electrical current, in a potassium-hydroxide solution in the presence of KIO_4 at 70–80 °C [19]. The isolation of ruthenium from the obtained alkaline solution has been carried out by a two-step process. First, the ruthenium has been precipitated from KOH, KIO_4 solution by addition of ethanol. Technetium(VII) remained in the solution and the majority of gamma-emitting impurities have been co-precipitated with ruthenium(IV) hydroxide. The decontamination factor of Ru from Tc has been measured using addition of ^{99m}Tc and has been found to be about 10^4 for the precipitation of ruthenium hydroxide from KOH, KIO_4 solution, followed by three washings with hot water. For further isolation of Ru, the precipitate has been dissolved again in KOH, KIO_4 solution, sulphuric acid has been added up to pH 4–5 and the distillation of RuO_4 has been made with air stream at 60–80 °C. RuO_4 has been adsorbed with an ammonium hydroxide solution and ruthenium hydroxide has been precipitated by addition of ethanol. The decontamination factor of Ru from Tc has been measured during the distillation of RuO_4 using addition of ^{99m}Tc and has been found to be about 5×10^4. The precipitate of ruthenium hydroxide was washed with water, dried, calcined and reduced to the metal ruthenium in an hydrogen stream at 400 °C. The β,γ-measurements of the obtained ruthenium powder have shown the absence of radionuclides in the final product. The ruthenium yield during the isolation from the irradiated target has been determined using ^{103}Ru,

which appeared in the target during irradiation and has been found to be about 99%. The isotope composition of artificial ruthenium has been found as follows: ^{100}Ru 99.46%, ^{101}Ru 0.46% for Tc burn-up of 21% and ^{100}Ru 99.34%, ^{101}Ru 0.54% for Tc burn-up of 51%. The content of more heavy isotopes ^{102}Ru and ^{104}Ru was less than 0.01%. Our experimental data on isotope composition of obtained artificial ruthenium are in agreement with calculated data [7,8]. One can conclude that prepared artificial ruthenium has a quite another isotope composition than natural ruthenium has.

3. Prospects for the transmutation of technetium and for the production of artificial stable ruthenium

The cost of prepared artificial ruthenium includes the costs of Tc target, its irradiation, and reprocessing, including Ru isolation and Tc recycling. Evidently, artificial ruthenium is more expensive now than the natural one does, whose world production is about 8 tons per year and whose price is 30 $/g [21]. However, poor world resources of ruthenium in ores (3000–5000 tons only) will lead to its deficiency in the near future. Natural noble metal ruthenium is used in electro-technical industry as an additive to platinum to increase its hardness and wear-resistance. Another large application is the fabrication of titanium anodes covered with ruthenium dioxide for chlorine production from sodium chloride solution, for desalination of seawater by electrophoresis.

The transmutation of technetium will serve both for the elimination of this dangerous 'radioactive waste' and for the creation of a new and important source of stable ruthenium. The productivity of this new source and the price of artificial ruthenium depend first of all on the price of the thermal and resonance neutrons, whereas the radiochemical part of artificial ruthenium production can be more easily created at the plants. The first preparation of artificial stable ruthenium in RIAR Dimitrovgrad demonstrates that the transmutation of technetium and the production of artificial stable ruthenium will be efficient and real at the industrial scale in the near future.

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