

Scientific Session of the General Meeting of RAS Members “75 Years of the Nuclear Industry: the Contribution of the Academy of Sciences”

Chemical Technologies for Closing the Nuclear Fuel Cycle

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Received February 1, 2021; revised March 8, 2021; accepted March 11, 2021

Abstract—Nuclear power is a highly concentrated energy source that does not emit greenhouse gases and does not affect the climate. In the future, it should hold a significant share in the world energy balance, but this possibility is realized only if the technological problems of closing the nuclear fuel cycle like minimizing the radioactive waste generated and multi-recycling of fissile isotopes are solved. This will make it possible to solve both ecological and economic problems, moving away from deep disposal of long-lived radionuclides to their transmutation, followed by near-surface disposal of short-lived radionuclides.

Keywords: nuclear fuel cycle, minor actinides, purex process.

DOI: 10.1134/S1019331621030114

FORMATION AND STAGES OF DEVELOPMENT OF RADIOCHEMISTRY

The birthday of radiochemistry as an independent science can rightfully be considered March 2, 1896, when A. Becquerel, at a meeting of the Paris Academy of Sciences, reported on his experiments with crystals of double potassium sulfate and uranyl [1]. The radiation observed by the scientist in these experiments was later called (at the suggestion of M. Sklodowska-Curie) radioactive, and the phenomenon itself was called radioactivity. In 1898, the Curies announced the discovery of a new radioactive element, polonium [2], named by M. Sklodowska-Curie in honor of the country where she was born and raised, and in December of the same year, they announced another radioactive element, radium [3]. For these works P. Curie, M. Sklodowska-Curie, and A. Becquerel were awarded the Nobel Prize in Physics in 1903. Soon after the discovery of radium, thorium radioactivity was discovered, and actinium was isolated from uranium ore [4]. In 1900, E. Rutherford discovered

thorium emanation (radon-220) [5] and E. Dorn, radium emanation (radon-222) [6]. In 1903, E. Rutherford and F. Soddy came to the conclusion that the atoms of radioactive elements undergo spontaneous transformations: some elements along the decay chain transform into others, and this transformation is accompanied by radioactive radiation. By the end of the first decade of the 20th century, researchers managed to identify many other radioactive elements, and the question arose about their placement in the periodic table. In 1910, at the suggestion of Soddy, the term isotope was introduced, a type of atoms of any chemical element with the same atomic number (which, respectively, are located in the same cell of the periodic table), but at the same time having different mass numbers.

These discoveries largely determined not only the paths of further development of natural science, but also human civilization as a whole. One of the first to appreciate the significance of the discovery of radioactivity was Academician V.I. Vernadsky. In his speech at a meeting of the Imperial St. Petersburg Academy of Sciences on December 29, 1910, he prophetically noted: “... now, in the phenomena of radioactivity, sources of atomic energy are opening up before us, millions of times exceeding the sources of power that the human imagination has dreamed of” [7].

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Russian scientists have made a significant contribution to the study of radioactivity [8]. Thus, Professor of Moscow University A.P. Sokolov developed a method for determining radium from the emitted radon, which is still used in our time. G.N. Antonov was honored for his discovery of thorium-231 in 1911, a decay product in the natural radioactive family of uranium-235. On the territory of Russia, the radioactivity of minerals, mineral waters, and muds has been studied intensively (I.A. Antipov, E.S. Bursker, A.P. Gruzintsev, P.P. Orlov, A.P. Sokolov, N.A. Umov, and others). In parallel, the study of chemistry and the transformation of radioactive chemical elements continued. In 1897–1907, P.G. Melikov and L.V. Pisarzhevskii discovered naduranic acid; S. Lordkipanidze, fluoronaduranic acid; L.A. Chugaev and N.A. Orlov, halides, sulfates, and oxalates of tetravalent uranium; and A.M. Vasil'ev synthesized uranyl nitrate hydrate.

Undoubtedly, the greatest merit in the development of complex studies of radioactivity in Russia belongs to Academician V.I. Vernadsky. Through his efforts in 1915, the Radium Laboratory was organized at the Academy of Sciences, and in 1922 the Radium Institute was created, of which Vernadsky became the first director, and V.G. Khlopin, the founder of domestic radiochemistry and the creator of the main technological processes for extracting radium from natural ores, became his deputy and head of the chemical department. Under the leadership of Khlopin, a technological process for the processing of radioactive ores was organized, and by December 1, 1921, the first domestic preparations of radium were obtained.

A new stage in the development of radiochemistry was due to the discovery of artificial radioactivity (I. and F. Joliot-Curie, 1934). It was preceded by the discovery of the neutron (J. Chadwick, 1932), thanks to which a new instrument appeared in the hands of experimenters: now they could conduct numerous experiments on irradiation of various substances, including uranium, with neutrons in order to obtain new transuranic elements (E. Fermi). However, the results of experiments on irradiation of uranium with neutrons at that time could not be explained, only in 1938 did O. Hahn and F. Strassmann discover the process of nuclear fission, and only then did O. Frisch and L. Meitner give its physical explanation. In fact, this discovery began a new stage in the development of “nuclear” sciences associated with the creation of nuclear weapons.

In 1940, by irradiating uranium with neutrons, neptunium, the first transuranic element, was obtained, and in 1941, by irradiating uranium with deuterons at a cyclotron, ^{238}Np , which was converted into plutonium-238 by beta-minus decay. During this period, radiochemists solved the most important problems associated with the study of the chemical properties of artificially obtained elements, the cre-

ation of technological methods for processing irradiated uranium, and deep purification of fissile isotopes.

A significant result in the study of the chemical properties of actinides was the discovery by N.N. Krot of the seven-valent state in plutonium, neptunium [9], the development of methods for stabilizing the tetravalent oxidation state of americium [10], and the identification of the possibility of the existence of some of the transuranic elements in lower oxidation states than trivalent [11].

In the study of the redox reactions of actinides, domestic radiochemistry takes a leading place in the world. A great contribution to the study of such reactions with the participation of uranium, neptunium, and plutonium ions, as well as some fission products (technetium, rhodium, ruthenium, and palladium), in various aqueous solutions was made by V.S. Koltunov. Together with his students, he clarified the mechanism of more than 70 redox reactions, in particular, the reduction of plutonium and neptunium ions with iron(II), uranium(IV), vanadium(IV), hydrogen peroxide, hydrazine, hydroxylamine, and ascorbic, sulfurous, and nitrous acids; oxidation of uranium(IV), neptunium, and plutonium ions with iron(III), vanadium(V), manganese ions, and nitric and nitrous acids; and disproportionation reactions of plutonium(V) and neptunium(V) ions [12]. A new direction was formed, the study of redox reactions of neptunium and plutonium in solutions of tri-n-butyl phosphate. The results obtained have found application in the purex process (from Plutonium Uranium Extraction), a technological method for the separation of uranium and plutonium from uranium irradiated in a reactor [13]. The process is based on liquid extraction of uranium(VI) and plutonium(IV) from aqueous solutions with tri-n-butyl phosphate in aliphatic solvents. The separation of plutonium from uranium is achieved by reduction of plutonium(IV) (usually using U(IV), Fe(III), or electrochemically) to plutonium(III), which is not extracted with the tri-n-butyl phosphate solution. The purex process remains the world's main method for reprocessing spent nuclear fuel (SNF).

The creation of the domestic nuclear industry began in the mid-1940s under the leadership of I.V. Kurchatov. The country's radiochemists were assigned two main tasks: the development of a hydrometallurgical technology for the separation, concentration, and refining of uranium extracted from domestic ores, and a technology for the separation of plutonium-239 from irradiated uranium to create atomic weapons. The solution of the first of these problems in 1950 was entrusted to the All-Union Scientific Research Institute of Chemical Technology (VNIKhT).

At first, they tried to obtain plutonium using the precipitation method developed by scientists of the Radium Institute of the USSR Academy of Sciences under the leadership of Academician V.G. Khlopin.

To check the technological parameters of the method and the production of weighed amounts of plutonium at the All-Union Scientific Research Institute of Inorganic Materials (VNIINM), a U-5 semi-industrial installation was created, on which the first plutonium concentrate in the Soviet Union and Europe was isolated from irradiated uranium in mid-1945, and at the end of 1948, weighed amounts (300 mg) of plutonium of the required quality were obtained. It should be noted that many radiochemists from various research institutes and Combine No. 817 worked at the U-5, where they underwent training and study. In 1949, in Ozersk (Chelyabinsk-40), at this Combine, which was later transformed into PA Mayak, the first radiochemical plant was launched, operating on the basis of precipitation technology.

Beginning in the mid-1950s, in close cooperation with specialists from VNIINM, VNIKKhT, the Radium Institute, and PA Mayak, an extraction method for processing irradiated uranium blocks using tri-*n*-butyl phosphate and new sorbents was developed. The result was an original extraction and sorption technology that was successfully introduced at the Mayak plant in 1976.

The problem of providing reliable analytical control of new technologies for the production of ultrapure uranium and plutonium was solved under the leadership of the close associate of I.V. Kurchatov, Academician A.P. Vinogradov. Radiochemists—analysts of the Institute of Geochemistry and Analytical Chemistry (GEOKHI) of the USSR Academy of Sciences, VNIINM, PA Mayak, and the Radium Institute studied the chemical properties of neptunium and plutonium, then little-known, and developed effective methods for their isolation and deep purification from fission-product elements. Highly sensitive methods were created for determining the presence of neptunium and plutonium in solutions of complex composition: radiometric, spectral, electrochemical, luminescent, and others. No less attention was paid to the problem of control over the content of trace impurities in metallic uranium at a level not exceeding 10^{-5} – $10^{-4}\%$. For this purpose, the sensitivity of direct (mainly spectral and electrochemical) methods for the determination of impurities was increased, while the search for extraction sorption methods of concentration was under way. The results of this work were summarized by A.P. Vinogradov in his report “Physicochemical Methods of Controlling Uranium Production” at the First International Conference on the Peaceful Uses of Atomic Energy in 1955 in Geneva [14, pp. 72–89].

Technological and engineering solutions that were used in the weapons projects of the Soviet Union and the United States were used practically simultaneously in the peaceful atom, that is, in nuclear power engineering. The industrial development of nuclear energy began with the launch in 1954 in the Soviet Union of

the first nuclear power plant with a capacity of 5 MW. In 2019, there were 449 operating nuclear power reactors in 34 countries of the world; as of mid-2019, 54 reactors were under construction [15]. According to IAEA forecasts, by 2030 growth in the nuclear power sector will range from 17% under the pessimistic scenario to 94% under the optimistic scenario. There are 11 nuclear power plants (38 power units) operating in Russia with a total capacity of about 31 GW, they produce about 13% of all electricity in the country.

THE PROBLEM OF HANDLING RADIOACTIVE WASTE

The problem of handling radioactive waste (RW) generated at all stages of the nuclear fuel cycle (NFC) is one of the factors that negatively affect the further development of nuclear power. There are two fundamentally different strategies—open and closed NFC.

According to the first of them (it is adopted in the United States, Sweden, Finland, and Switzerland), spent nuclear fuel (SNF) is not reprocessed, but stored in special storage facilities with the possibility of reprocessing or final geological disposal in the future. More than 200000 tons of spent nuclear fuel has already been accumulated in the world, and although currently there is not a single licensed deep geological storage facility for spent nuclear fuel on the planet, it is being stored until the final decision on its fate is made, while the volume of spent nuclear fuel annually increases by about 8000–10000 tons [16].

In a number of countries with developed nuclear power engineering (France, Great Britain, Japan, and Russia), spent nuclear fuel is reprocessed with the extraction separation of uranium and plutonium in the purex process and subsequent solidification of the liquid radioactive waste (pilot plants with this technology exist in China and India). Deep geological disposal of solidified radioactive waste is carried out at the final stage of the closed nuclear fuel cycle. High-level radioactive waste (HLW) after reprocessing spent nuclear fuel, as a rule, contains solutions and pulps with fission products—radionuclides of Cs, Sr, Zr, Tc, Mo, Ru, I, rare-earth elements, and activation products and the corrosion of these fission products (radionuclides of Cr, Mn, Fe, Co, Ni, and Zr), minor actinides (Np, Am, and Cm), and residual amounts of U and Pu.

As in the case of spent nuclear fuel, there is not a single licensed deep storage facility for high-level radioactive waste in the world. The reason is the need to justify the safety of such storage facilities for a period of up to 1 million years. Calculated data on the reduction of the potential long-term impact on the environment during disposal of, on the one hand, spent nuclear fuel, and, on the other hand, radioactive waste generated during a closed nuclear fuel cycle with

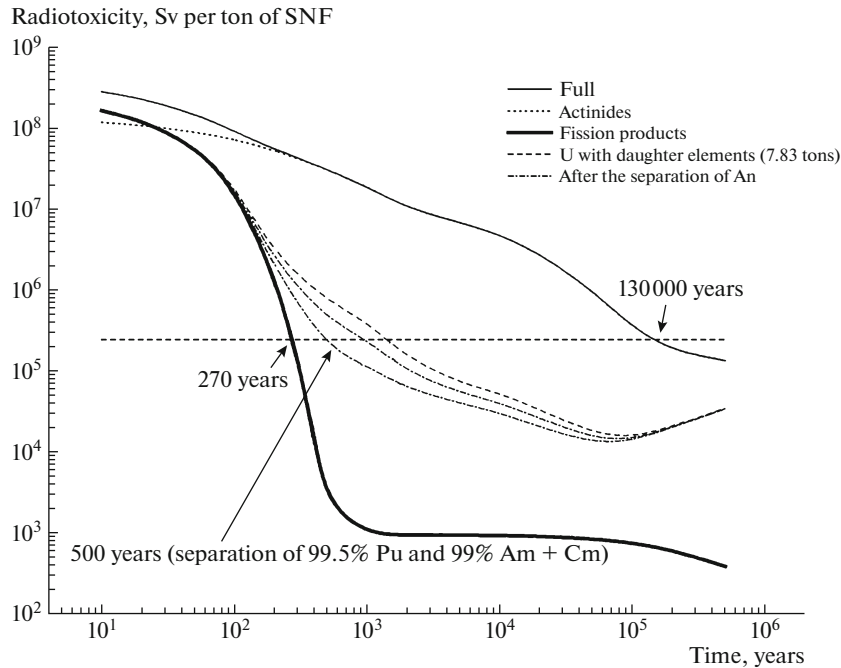


Fig. 1. Time evolution of radioactive waste radiotoxicity. Source: [17].

the release of fissile actinides (^{239}Pu and ^{235}U) for reuse in nuclear power and minor actinides (^{237}Np , ^{241}Am , ^{244}Cm) for the purpose of their transmutation in fast reactors are shown in Fig. 1 [17]. Thus, the radiotoxicity of radioactive waste over time, after the isolation of long-lived actinides from spent nuclear fuel, decreases by many orders of magnitude in comparison with the radiotoxicity of the initial spent nuclear fuel. Thus, the closure of the nuclear fuel cycle with multi-recycling of fissile components, fractionation of radioactive waste to isolate the most environmentally hazardous long-lived isotopes (such as americium-241, 243) for their subsequent transmutation, and a significant reduction in the volume of radioactive waste is a strategic scientific and technological task facing the country's nuclear industry.

STRATEGY OF CLOSING THE NUCLEAR FUEL CYCLE

The strategy of closing the nuclear fuel cycle in a two-component nuclear power system with thermal and fast neutron reactors involves recycling fissile materials, minimizing or completely abandoning the deep burial of highly radioactive waste by separating the actinide–lanthanide fraction with the subsequent separation of americium and curium for the transmutation of americium and storage of curium, fractionation of radioactive waste in order to isolate the short-lived fraction (Cs, Sr), platinum group metals, as well as technetium and other elements, and minimization of the volume of radioactive waste. Thus, the

implementation of this concept [18–21] will allow the following:

- solving the pending problems of spent nuclear fuel and radioactive waste handling, consistently reducing the volume of accumulated spent nuclear fuel and prevent its further accumulation;
- involving plutonium in the nuclear fuel cycle as a reprocessing product of spent nuclear fuel from thermal reactors (VVER) for the manufacture of fuel for fast reactors and full use of the energy potential of natural uranium (^{238}U) through multiple recycling of fuel materials;
- fractionating radioactive waste, extracting long-lived minor actinides for afterburning or transmutation in nuclear reactors, which, together with multiple recycling of plutonium, will significantly reduce the environmental hazard of radioactive waste;
- technologically supporting the regime of non-proliferation of fissile materials by gradually eliminating the circulation of enriched uranium and separating pure plutonium.

One of the essential grounds for the transition to a closed nuclear fuel cycle with the use of “fast” reactors is the successful and unparalleled operation of the industrial BN-600 “fast” reactor at the Beloyarsk NPP. In 2016, the 4th power unit with BN-800 was put into operation, initially focused on the development of technologies for closing the nuclear fuel cycle [18, 22, 23].

The modern closed fuel cycle infrastructure in our country is represented by several enterprises. Since

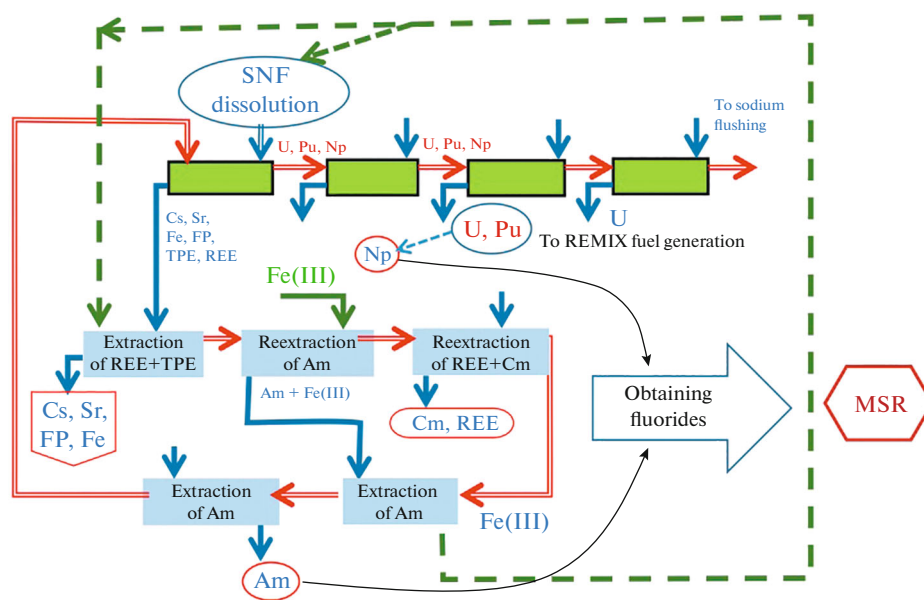


Fig. 2. Schematic diagram of the “iron” extraction purex process. REE, rare-earth elements; TPE, transplutonium elements; MSR, molten salt nuclear reactor.

1977, the RT-1 plant of the PO Mayak has been operating. Modernization of RT-1 will allow it to operate until 2035 with the possibility of extending this period. The plant can process up to 400 tons of spent nuclear fuel per year from the VVER-440, VVER-1000, BN-600, and RBMK-1000 power reactors and transport and research reactors. During its operation at the RT-1 plant, more than 6000 tons of spent nuclear fuel have been reprocessed. Reprocessing spent nuclear fuel from BN-800 fast reactors has not yet been carried out. In 2012 and 2014, the plant successfully reprocessed eight fuel assemblies with mixed uranium–plutonium oxide (MOX) spent fuel of BN-600 with a burnup of 73–89 GW day/t and a cooling time of about 20 years. At the same time, no significant losses of plutonium to waste were recorded, the plutonium content in the raffinate was less than 0.1 mg/L, and no plutonium was found in the insoluble residues [20, 24].

At the Mining Chemical Combine of the Rosatom State Corporation, a plant for the production of mixed oxide uranium–plutonium (MOX) fuel for BN-800 and the first stage (research hot chambers) of the Experimental Demonstration Center for reprocessing VVER-1000 spent nuclear fuel were put into operation. The second stage of this center, with the production of initial oxides suitable for the manufacture of MOX and/or fuel based on an unseparated and unenriched mixture of reprocessed uranium and plutonium doped with enriched uranium, is planned to be commissioned in 2021 [18, 19].

A development of the technologies of the Experimental Demonstration Center could be the extraction purex process (Fig. 2). It involves the use of tributyl phosphate as an extractant; separation and recycling

of uranium, plutonium, and neptunium; fabrication of fuel from recovered fissile materials; isolation of the actinide–lanthanide fraction from the raffinate, followed by the extraction of americium by the extraction or precipitation method for its afterburning; handling of 1 class radioactive waste containing cesium, strontium, and other fission products; controlled storage of conditioned radioactive waste with curium and lanthanides until decay with subsequent reprocessing to recover plutonium accumulated during decay.

At the Siberian Chemical Combine of the Rosatom State Corporation, a Pilot Demonstration Power Complex (PDEC) is being created as part of a power unit with a BREST-OD-300 reactor and on-site production closing the nuclear fuel cycle, which includes modules for reprocessing irradiated mixed nitride uranium–plutonium fuel (MNUP) and fabrication/refabrication for the manufacturing of starting fuel elements from imported materials and fuel elements from recycled materials. Currently, the construction of the PDEC fabrication/refabrication module for the production of MNUP fuel is being completed, which is planned to be commissioned in 2022. In 2024, it is planned to begin construction of the spent nuclear fuel reprocessing module. In the first of these modules, the technology of carbothermal synthesis will be implemented; at the second one, it is planned to implement the technology of combined pyrochemical and hydrometallurgical processing of MNUP spent nuclear fuel, which is also suitable for reprocessing MOX spent nuclear fuel from fast reactors [23]. For reprocessing MNUP and MOX spent nuclear fuel from fast neutron reactors with a short cooling time, a combined technology has been devel-

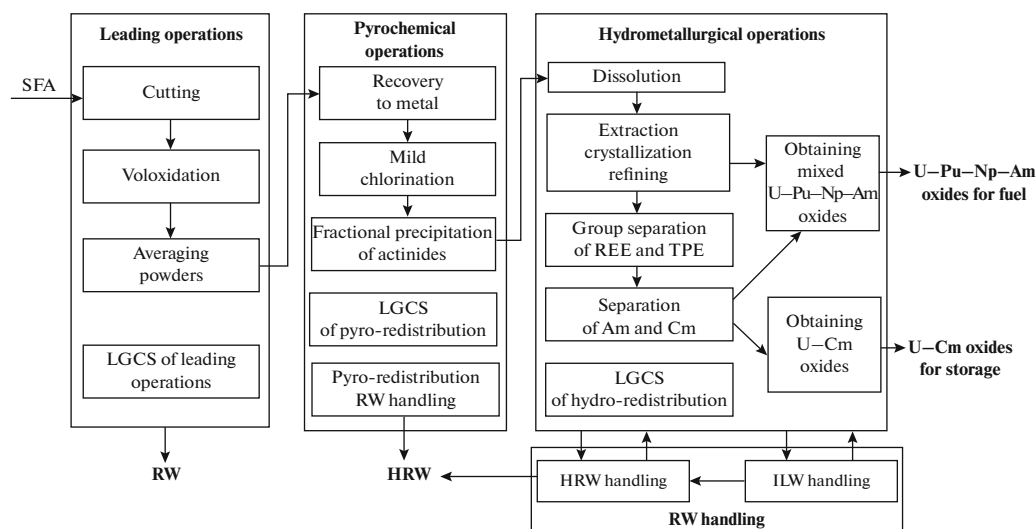


Fig. 3. Schematic flow diagram of a combined technology for reprocessing mixed uranium–plutonium nitride (MNUP) and mixed uranium–plutonium oxide (MOX) spent nuclear fuel (RN-process). SFA, spent fuel assembly; LGCS, local gas cleaning system; RW, radioactive waste.

oped [25], which involves the joint separation of uranium and plutonium, as well as its purely hydrometallurgical version. Both options provide for the isolation and separation of americium and curium, obtaining a mixture of uranium, plutonium and, neptunium oxides, mixtures of uranium and americium oxides, and uranium and curium oxides as the target product. Alternatively, it is possible to obtain mixed oxides of uranium, plutonium, neptunium, and americium. The pyrochemical redistribution of the combined technology is currently under development, and the research on the hydrometallurgical redistribution of the combined technology (Fig. 3) is at the final stage.

As a backup option, the development of a purely hydrometallurgical technology for reprocessing spent nuclear fuel from fast reactors is being completed. For the first time in the world, the PDEC must demonstrate the stable operation of a complete complex of facilities that ensure the closure of the nuclear fuel cycle. The on-site version of the fuel cycle organization makes it possible to work out the technologies of a closed nuclear fuel cycle with a short external fuel cycle time in the shortest possible time within one site. The introduction of competitive fast reactors and the transition to a two-component structure of nuclear power and a closed nuclear fuel cycle is expected from the mid-2030s (see Fig. 3).

Closing the nuclear fuel cycle sets the task of multiple recycling of plutonium, and hence the development of new technologies for the production of mixed uranium–plutonium fuel. The use of microwave radiation for the preparation of uranium dioxide powder [26] as a basis for nuclear fuel from its nitric acid solutions and uranium compounds (trioxide, peroxide, U_3O_8 , etc.), including in the presence of organic

reducing agents (carbohydrazide, acetohydroxamic, and aminoacetic acid), as well as in a reducing, inert atmosphere and in air, opens up wide possibilities. The results of studying the granulometric composition, morphology of particles, physicochemical and technological properties of the obtained samples, determination of the bulk density, specific surface area, and the mass fraction of moisture show that the obtained uranium dioxide powders meet the regulatory requirements. When sintering pellets of compressed uranium dioxide under the action of microwave radiation with a power of 2.1 kW at 1650°C for 2 h, ceramic fuel pellets with a density of about 10.40 g/cm³ and an open porosity of about 0.25 vol % were prepared, which also meets the requirements.

A method has been developed for obtaining powders of solid solutions of uranium and cerium dioxides (simulator of americium) with a content of the latter of 3 and 10 wt %, based on reductive thermochemical denitration of their nitric acid solutions using microwave radiation [27]. It was shown that Ce(IV) forms a solid solution of its dioxide in a UO_2 matrix with a fluorite structure. The resulting powders consist of particles (granules) forming fractions with a dimension of not more than 400 μm , and a fraction of particles with a dimension less than 25 μm of not more than 1 wt %. Their bulk density and bulk weight with tapping are 1.8–2.5 g/cm³, and their total specific surface area is not less than 2 m²/g. In connection with the planned variant of afterburning americium in the BREST-OD-300 reactor, a method can be recommended for use as the main method for producing mixed uranium and americium oxides at the spent nuclear fuel reprocessing module of the experimental demonstration power complex of the Siberian Chemical Combine.

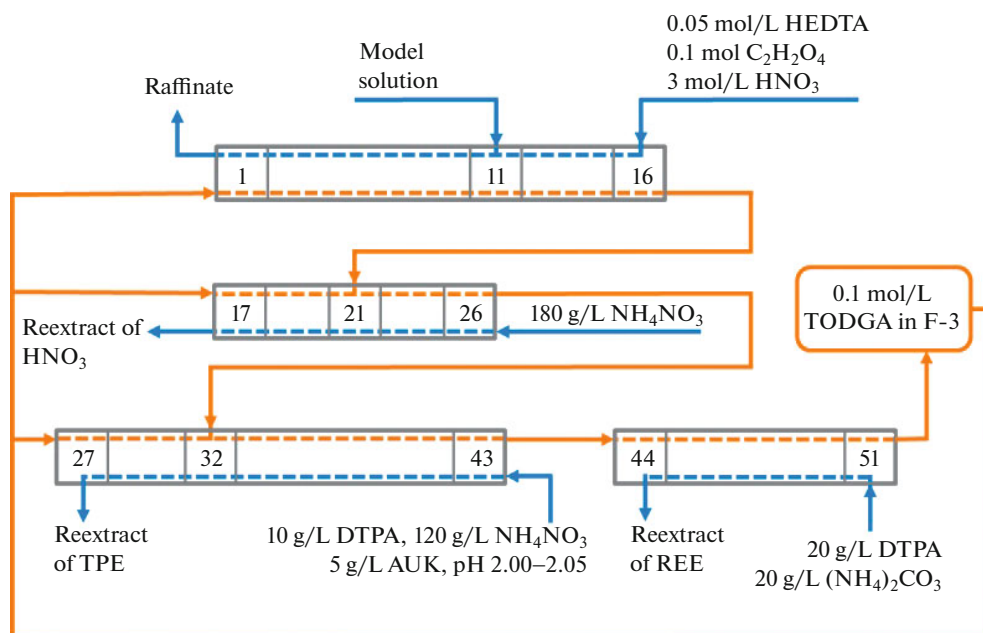


Fig. 4. Principal technological scheme for the isolation of the concentrate of transplutonium elements in the TODGA extraction system—F-3.

SEPARATION METHODS FOR Am(III) AND Cm(III)

The most important scientific and technological problem that requires a solution in the implementation of a closed nuclear fuel cycle and minimization of deep disposal of long-lived radioactive waste is the group separation of isotopes of rare-earth elements and minor actinides (americium and curium), as well as their separation among themselves. The complexity of the problem is determined by the closeness of the chemical properties of these elements.

Regardless of the strategy for implementing closure of the nuclear fuel cycle based on the purex process or a combined pyrochemical and hydrometallurgical technology, in nitric acid raffinates, which represent the bulk of highly radioactive waste, fission products and isotopes of transuranic elements (minor actinides) remain: neptunium, americium, and curium. The content of minor actinides by weight does not exceed 0.1% of highly radioactive waste, but it is they (primarily americium) that pose the greatest danger during further geological disposal, since they are long-lived and have high heat release. Therefore, a closed nuclear fuel cycle should include, as an obligatory step, the separation of lanthanides and actinides that are extremely close in chemical properties, as well as the separation of americium and curium. The americium separated from highly radioactive waste can be further transmuted in fast reactors. Curium is the starting nuclide for the production of californium-252, which is used in neutron sources in nuclear medicine, basic research, and the nuclear industry.

Today, the technology of separation of actinides and lanthanides on the basis of countercurrent extraction in a two-phase system “aqueous solution/organic solvent” using selective organic ligands is generally accepted. To isolate minor actinides efficiently for the purpose of afterburning and reduce the radioecological hazard of buried highly radioactive waste, technologies for group separation of transuranic and transplutonium elements have been developed using the extraction system N,N,N',N'-tetraoctyldiglycolamide (TODGA)—methanitrobenzotrifluoride (F-3) (Fig. 4). In 2017–2018 at PA Mayak, the first “hot” dynamic tests of the extraction technology for the separation of americium and curium from real highly radioactive waste—raffinates from reprocessing spent nuclear fuel from the BN-600 and VVER-440 reactors—were carried out. As a result, the extraction of 99.9% americium was achieved [25].

For the separation of americium and curium in the fractionation of highly radioactive waste, specialists from VNIINM and Moscow State University proposed a new extraction system based on asymmetric diglycolamides (C8–C12 N,N-dioctyl-N',N'-didodecyldiglycolamide and C10–C12 N,N-didodecyl-N',N'-didodecyldiglycolamide) with non-flammable diluents not containing fluorine or chlorine.

In the course of studying the extraction properties of the obtained ligands, it was shown that the stoichiometric amount of nitric acid is extracted in all systems at an equilibrium nitric acid content of 3 mol/L. The type of solvent (tridecane or “Isopar-M”) does not affect the extraction characteristics. For all extraction systems, a phase stability of up to 50 g/L for neodym-

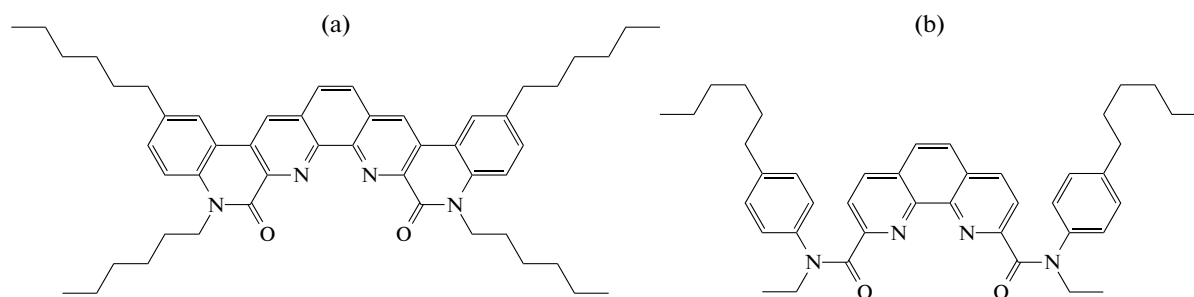


Fig. 5. Basic structures of phenanthralinedicarboxylic acid diamides studied for the separation of rare-earth elements and minor actinides, as well as americium and curium.

(a) With a pre-organized structure; (b) with a movable structure.

ium in the aqueous phase is shown. The formation of third phases is observed upon contact of organic solutions with solutions of highly radioactive waste imitators containing palladium(II) and zirconium(VI) above 0.6 g/L and 0.7 g/L (for organic phases based on C8–C12). The formation of third phases at higher concentrations of these elements can be suppressed by introducing water-soluble complexones or octanol-1 into the organic phase. With an increase in temperature from 10 to 50°C, the distribution coefficients fall by ten times. Washing from the fission products, palladium(II) and zirconium(IV), can be carried out by introducing the HEDTA complexone and oxalic acid, respectively.

Quantitative reextraction of americium and curium can be carried out with a solution of diethylenetriaminepentaacetic acid 10 g/L at pH 2 in the presence of 0.5 mol/L sodium nitrate.

VNIINM and the Frumkin Institute of Physical Chemistry and Electrochemistry (IPCE) of the Russian Academy of Sciences are jointly developing sorption-chromatographic technology for the separation of Am and Cm. As a result, a mathematical model of the separation process has been developed and options for handling the spent sorbent have been proposed.

In 2015, pilot tests of the sorption-chromatographic technology for separating americium and curium using a sulfonic cation exchanger were carried out at the pilot plant of the PA Mayak with the participation of the IPCE RAS. A concentrate of rare-earth and transplutonium elements obtained from the raffinate of the extraction processing of VVER-440 spent nuclear fuel was used as the initial solution. During the tests, the pressure in the system did not exceed 3 atm. As a result of the refining process, about 9 g of pure Cm and about 65 g of pure Am (56% of the initial) were isolated with a curium content of less than 0.8% by mass and $^{154,155}\text{Eu}$ of less than 0.1% in terms of activity.

On the basis of VNIINM, using a concentrate of rare-earth and transplutonium elements obtained as a result of reprocessing VVER-440 spent nuclear fuel,

the separation of Am and Cm was verified by high-performance liquid chromatography. As a result, 1.39 g of Am was obtained with a purity of more than 99.9% (96% of the initial amount). The combined Cm fraction contained 36.4 mg Am (about 2.6% of the initial amount). The Am amount in the Am–Eu and Am–Cm fractions did not exceed 4% of its initial amount. The use of the monodisperse sulfonic cation exchanger produced by OOO Tekhnosorbent made it possible to achieve a high yield and purity of the Am fraction, while the mixing zones of Am–Cm and Am–Eu were insignificant in volume.

Within the framework of cooperation, the Rosatom State Atomic Energy Corporation, the Innopraktika company, Moscow State University, and the Russian Academy of Sciences studied various highly selective extraction systems for the separation of both rare-earth elements and minor actinides, and americium and curium. Based on the results of supercomputer modeling and subsequent studies, extractants (diamides of phenanthralinedicarboxylic acid, Fig. 5) were identified, which, according to theoretical predictions, should have high selectivity in the processes of extraction separation of trivalent f-elements. A large series of compounds of these types was developed and synthesized; selectivity factors were obtained for the separation of the standard americium/europium pair $\text{SFAm}/\text{Eu} \geq 150$ and for the separation of the americium/curium pair $\text{SFAm}/\text{Cm} \geq 7$, which is close to the record values achieved in the world to date. A new approach to the creation of extraction systems for the separation of actinides and lanthanides was developed and successfully tested, based on the use of hydrophilic and hydrophobic ligands in the aqueous and organic phases, respectively (the strategy of a hydrophilic–hydrophobic pair), which makes it possible to improve significantly the selectivity of the separation of target metals.

It is important that the proposed ligands have high radiation and hydrolytic stability, do not lose their extraction properties under γ -irradiation up to doses of 500 kGy, and with alpha-irradiation up to doses of the order of 200–300 kGy, the extraction process is fast

and completely reversible. In addition, the developed extraction system is fire and explosion safe.

During tests on centrifugal extractors (Khlopin Radium Institute), from nitric acid solutions containing a mixture of americium and curium (total concentration 0.11 g/L), it was possible to isolate into a separate fraction at least 99% americium with a purity of at least 99.9% (by curium). Moreover, the initial solution contained interfering components such as ammonium nitrate (570 g/L), diethylenetriaminepentaacetic acid (10 g/L), aminoacetic acid (5 g/L), and an admixture of plutonium. This did not prevent the separation of the target components.

NEW SAFE MATRICES FOR RADIOACTIVE WASTE IMMOBILIZATION

Due to the high radiation hazard and chemical toxicity of highly radioactive waste, it is necessary to convert it into a safer form for subsequent storage. To date, only one technology has been brought to the stage of industrial application—vitrification of highly radioactive waste. It includes the processes of drying, calcination, fusion with glass-forming additives in special furnaces (melters), and filling into canisters for long-term storage. The vitrification technology is used for curing unfractionated highly radioactive waste in France, Russia, Great Britain, the United States, and other countries. Borosilicate-based glass is most often used, while in Russia, alumophosphate-based glass is used [28].

The choice of the composition of the matrix material for immobilization of highly radioactive waste depends primarily on the chemical composition of these wastes themselves, as well as on the type of melter and other equipment used, the geological conditions for further storage, etc. Most often, borosilicate glasses are used for these purposes, which are obtained at temperatures of 1050–1200°C. They have high chemical and radiation resistance, good mechanical strength, thermal conductivity, and toughness. At the same time, they are characterized by low solubility in relation to actinides, rare-earth elements, and a number of transition elements. Alumophosphate glasses obtained at lower temperatures (800–1000°C) are capable of dissolving larger amounts of these highly radioactive waste components than borosilicate glasses; however, they are characterized by a sharper change in viscosity with temperature and have a lower crystallization stability, and they have fewer regions of glass compositions with a high chemical stability.

High physicochemical stability in the geological environment of natural phosphate minerals (monazite, apatite) containing natural uranium and thorium in concentrations reaching tens of mass percent is known. This indicates that the use of synthetic analogs of minerals as matrices for immobilization of radioactive waste is promising. Breakthrough results in

recent years [29–31] were obtained in the study of the possibility of using crystalline double orthophosphate of magnesium and potassium (MPP) as synthetic matrices for long-term and environmentally safe storage (or disposal) of liquid radioactive waste, including actinide-containing waste. The synthesis of the MPP matrix occurs in an aqueous solution according to the reaction



The nonthermal process (room temperature, atmospheric pressure) of obtaining MPP matrices is similar to cementing and is characterized by low energy consumption, ease of implementation, and mobility of the curing process, and the simplicity of the hardware design of the method leads to minimization of “secondary” radioactive waste. The use of MPP provides a number of tangible advantages: the possibility of solidification of waste in a wide range of their pH, a high degree of filling of the resulting matrices with radioactive waste components, high chemical and radiation resistance, and resistance to low temperatures.

* * *

Nuclear power is the only highly concentrated “green” source of electricity, the share of which in global production is likely to increase. According to the decarbonization scenario (production of no more than 50 g of CO₂ per kW of electricity generated), by 2040 the share of nuclear power is expected to increase by 55% to 4320 TW h of generated electricity. However, the implementation of a new generation nuclear fuel cycle should include solving the problems of accumulating radioactive waste, minimizing them while maximizing the use of the potential of fissile materials by means of their multi-recycling. This strategy is based on two-component nuclear power—thermal reactors with a low reproduction factor produce cheap electricity, and fast neutron reactors with a reproduction factor greater than 1 provide the fuel base for the entire system and dispose of spent nuclear fuel from thermal reactors.

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Translated by S. Avodkova