# R&D ACTIVITIES ON PARTITIONING IN RUSSIA

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## Abstract

A concept of closed nuclear fuel cycle (NFC) accepted in Russia is presented. The Russian operating plant for spent nuclear fuel (SNF) reprocessing with the recovery of long-lived radionuclides is outlined. The results of the most promoted Russian developments on partitioning, including the sorption and extraction studies, are described. The results on operation of the world's first industrial extraction facility for the separation of long-lived radionuclides from high-level wastes (HLW) are given.

## Introduction

Russia has accepted the concept of closed NFC with allowance for SNF reprocessing [1]. It is known that the possibility to solve radically the problem on long-term safe management of long-lived radionuclides is one of the advantages of the closed NFC, because the reprocessing of SNF enables to recover these nuclides and to treat them as an individual fraction.

Transmutation is an efficient method for management of long-lived radionuclides. Another promising way is to create the extra strong matrices being disposed into geological formations. In particular, the technology for production of synthetic materials is now under development in Russia with the use of high-temperature synthesis of minerals of zircon group, garnet, cubic zirconium oxide a.o. [2]. The principal feature of these minerals consists of including into mineral matrix an individual element or at least chemical analogs, but not non-separated mixture of nuclides contained in SNF. Such compositions make these materials very close to natural minerals with stability tested during millions of years.

Hence, just as in the case of transmutation, so also in the synthesis of highly strong matrices for geological disposal, there is a need for selective recovery of long-lived radionuclides contained in SNF. This could be provided by the availability of reprocessing plants equipped with special facilities for recovery of long-lived radionuclides in the framework of NFC infrastructure.

In Russia there is now in operation the plant RT-1 for reprocessing of SNF, predominantly from WWER-440 reactors [2]. End product of the plant's uranium line is uranyl nitrate melt passed to fabrication of fuel elements for RBMK reactors; in such a manner the fuel cycle of WWER-440 becomes closed as applied to uranium even today. Next task is to return plutonium into the fuel cycle as MOX-fuel for thermal and fast reactors.

Management of long-lived radionuclides at the plant RT-1 is similar to other reprocessing plants functioning in the world: non-separated mixture of long-lived radionuclides is vitrified, and the resultant glass-blocks are directed to interim monitored storage in a special store facility. Thus, the efficient separation technologies for radical management of long-lived radionuclides are to be developed for the use in the future.

However it should be noted that even the present practice in management of radwastes requires selective recovery of long-lived radionuclides. This is caused by the fact that the accumulated and current high-level wastes have very complicated composition and contain, as a rule, great amounts of salts. In principle, such non-separated mixture of radwastes could be transferred to solidification without any preliminary treatment, but in this case the following drawbacks inevitably emerge:

- Large volumes of "ballast" material to be vitrified along with radionuclides increase expenses at the stage of glass boiling, as well as at the stage of glass-blocks monitored storage.
- Many macrocomponents of non-separated radwastes have harmful effect on glass boiling process, its safety and the quality of obtainable glass blocks.

Owing to this, there exists an alternative method for HLW management by solidification as follows:

- Long-lived radionuclides are separated from the HLW bulk and are concentrated in small volumes of solutions to be solidified, particularly by vitrification for interim monitored storage and subsequent disposal.

- Ballast mass of radwastes remained after recovery of radionuclides is sent to solidification, by means of cementing in particular, for subsequent near-surface storage as low-level waste (LLW).

The necessary recovery degree of long-lived radionuclides is specified by the limiting standards on their concentrations in LLW for near-surface storage.

The attained standard specifications provide a significant economic effect. For example, the calculations performed by the American specialists have shown that a variant with separation of radionuclides from Hanford HLW would require 12 000 containers for vitrified blocks instead of 40 000 ones needed for wastes without separation; in the case of separation, the saving of expenses would be around US$ 14 billion. The cost comparison of HLW and LLW management at different stages could offer another index of economic efficiency provided by separation of radionuclides from HLW. These data indicate that the production cost of waste in oxide form is equal to 2.126 US$/kg for HLW in comparison with 64 US$/kg for LLW.

Thus, summarising the urgency of efficient technologies for radwaste management, one can advance the following main arguments in favour of such approach:

- A radical promising technique for isolation of long-lived radionuclides from the biosphere by means of transmutation envisages their individual separation from the products of SNF reprocessing for subsequent burning in reactors or accelerators.
- The perspective extra-strong matrices for immobilisation of long-lived radionuclides for long-term safe storage and disposal require selective or fractional separation of the latter.
- The existing technologies for HLW management with vitrification and subsequent monitored storage of glass-blocks require the separation of radionuclides from the bulk of non-radioactive waste for higher glass quality, process safety and economy in operations of glass boiling and storage of solidified materials.

**Russian R&D on recovery of radionuclides**

In accordance with the foregoing, the systematic studies and developments of efficient methods for separation of long-lived radionuclides from HLW of spent fuel reprocessing have been conducted in Russia for the last 20 years.

These studies are carried out at several Russian Institutes (V.G. Khlopin Radium Institute, Institute of Chemical Technology, Institute of Physical Chemistry, Institute of Geochemistry and Analytical Chemistry a.o.) in collaboration with the radiochemical plants of the RF MinAtom.

Key operation of technologies for separation of long-lived radionuclides involves selective recovery of cesium, strontium, technetium, rare-earth and transplutonium elements, as well as residues of uranium, neptunium and plutonium from HLW remained after Purex-process. In the world's practice different processes (precipitation, sorption, extraction, chromatography a.o.) for recovery of these components are under development. The object of this communication is to consider those Russian developments which are now most feasible for application.

***Ferrocyanide Sorbents for Cesium Recovery***

As an example of successful use of sorption processes for recovery of radionuclides from HLW one could consider the method for sorption recovery of cesium by inorganic ferrocyanide-containing sorbents developed by Institute of Physical Chemistry in co-operation with "Mayak" PA. The chemical composition of these sorbents is described by the following bruto-formula [3]

$$K_{1.0}Me^{II}_{1.5}Fe^{II}(CN)_6 \cdot nSiO_2$$

where $Me^{II}$ – Ni, Cu or Zn.

Copper-potassium ferrocyanide was chosen for practical use due to its highest stability in the cycle of sorption – desorption – regeneration. The systematic studies on using this sorbent enabled to develop a technology for cesium recovery from HLW of SNF reprocessing [4]. A sorption column with volume 120 l was used in the technology tests at the "Mayak" PA. The recovery degree of cesium at the sorption stage was more than 98%, cesium yield into desorbate was 98-99%, concentrating degree attained 100. After 15 cycles of operation, the sorption properties of the sorbent remained unchanged. In the course of pilot-industrial tests there were recovered from HLW about 7 mln Ci of cesium.

***Crown-ethers for Recovery of Strontium and Cesium***

For recovery of strontium from HLW, a method with the use of macrocyclic polyethers (crown-ethers) is elaborated. In particular, the studies of the Institute of Chemical Technology with the use of dicyclohexyl-18-crown-6 (DCH-6) were also brought up to the level of pilot-industrial tests at the "Mayak" PA. As result of these tests there were reprocessed about 90 $m^3$ of HLW and were obtained more than 0.5 mln Ci of radiostrontium with 6-fold concentrating degree [3]. The recovery degree of strontium was 96%. The characteristic advantage of the DCH-method is the ease of strontium stripping operation being efficiently performed by water.

Investigations are also pursuing with the aim of using crown-ethers for efficient recovery of cesium from HLW [5]. In particular, dibenzo-21-crown-7 in polyfluorosubstituted alcohols extracts cesium in a wide range of acidity and provides rather low distribution coefficients in water stripping operation. 99% recovery of cesium with three-fold concentrating was achieved during the tests on HLW solutions performed at the Radium Institute.

***Monodentate organophosphorus reagents for recovery of actinides and technetium***

Deep recovery of actinides and lanthanides from HLW may be achieved by means of monodentate neutral organophosphorus extractants. Among them the phosphine oxides possess the most extraction ability; due to high solubility of these compounds in organic diluents, preference was given to different-radical phosphine oxide (POR), i.e. isoamyl dialkylphosphine oxide wherein alkyl radicals have normal structure with 7-9 carbon atoms [6,7].

The possibilities of this extractant were tested on real HLW, affording high recovery degree of actinides (up to 99,9%). Solid extractants wherein the macroporous polystyrol-divinylbenzene matrix contains up to 50% of phosphine oxide were synthesised on the base of POR. Trials of this sorption variant were conducted on industrial scale in 60 L-column. The obtained results have confirmed not only the high recovery degree of actinides, but also the efficient concentrating of them in desorbate. A distinguishing feature of the POR-based reactants is the possibility for recovery of technetium along with actinides. The recovery degree of technetium from actual HLW was about 70% [8].

***TRUEX-process for recovery of actinides and lanthanides***

In the modern world's practice the possibilities of the so-called TRUEX-process based on the use of bifunctional neutral organophosphorus compounds are studied thoroughly. An interesting modification of TRUEX-process was developed by the Radium Institute in collaboration with the Institute of Geochemistry and Analytical Chemistry [9]. In classical TRUEX-process phenyloctyl-isobutyl-carbamoylphosphine oxide is diluted by dodecane with addition of TBP as solubilizator. In the proposed modification diphenyldibutyl-carbamoylphosphine oxide diluted by a polar organofluoric compound (fluoropol) is used as extractant [10]. Elimination of solubilizator from the extractant composition allows to obviate thus the necessity for washing operation of extractant from TBP destruction products. The technology of the modified TRUEX-process was tested in the facility of centrifugal contactors to assess the possibility for deep recovery of actinides and lanthanides [11].

Feed solution contained 5 M/L $HNO_3$ and 13 g/L of lanthanides and actinides. Fe(II), Zr(IV) and Mo(VI) were stripped by acetohydroxamic acid; TPE and lanthanides were stripped by 0.01 M $HNO_3$. The recovery degree of actinides and lanthanides was more than 99.5% at concentrating factor of 4-6 and at purification coefficients from iron, zirconium and molybdenum above 50. These results were confirmed by the tests under static conditions, but on actual industrial HLW [12].

***Chlorinated cobalt dicarbollyde in HLW reprocessing***

The extraction technology with the use of chlorinated cobalt dicarbollyde (ChCoDiC) in a polar diluent is now the most promoted technology for recovery of radionuclides from HLW. Fundamentals of the extraction process on the basis of ChCoDiC were developed by the specialists of the Radium Institute and the Institute of Nuclear Research (Czech Republic) [13], whereupon the RI in collaboration with the "Mayak" PA brought this development up to the level of industrial use at the radiochemical plant RT-1 [14].

ChCoDiC in polar diluent extracts efficiently cesium from aqueous solutions; addition of polyethylene glycol (PEG) to the extractant makes it possible to extract strontium, as well as TPE and RE. Selective recovery of cesium was tested on actual HLW [6,7], the recovery degree therewith was 99.998%. Different variants of the flowsheets with combined and separate recovery of cesium, strontium, TPE and RE were put through a series of tests from laboratory to pilot-industrial scale [15,16]. The developed and tested pseudomembrane method which enables to increase the recovery degree of trivalent elements from HLW by a factor of tens should be considered as an original modification of the extraction process with the use of ChCoDiC. This is achieved by changing the topology of connections between apparati in the membrane variant as compared to a linear one, providing therewith the increase in efficient capacity of extractant [17,18].

The universal flowsheet for recovery of cesium, strontium, TPE and RE was tested in a test facility in hot cells of the RI with the use of 24 l of actual raffinate from reprocessing of WWER-1000 spent fuel. The tests results on recovery degrees into extract were as follows: Cs – more than 99.999%, Sr – 99.998%, An – over 99.992%. Concentrating degree of recovered radionuclides was equal to six.

The pilot-industrial tests of ChCoDiC-process at the "Mayak" PA confirmed high efficiency in recovery of long-lived radionuclides from HLW. As a result of these tests, the megacurie quantities of cesium and strontium were recovered, the TPE concentrate containing 240 g of americium-241 and 21 g of curium-244 was obtained as well [16].

***Industrial Facility for HLW Partitioning at the "Mayak" PA***

The most achievement in the use of ChCoDiC-process in Russia is now the introduction of partitioning technology for HLW with different composition at the "Mayak" PA. By means of this technology, the first in the world commercial facility UE-35 for recovery of radionuclides was put into operation in August 1996. The first line of this facility envisages selective recovery of cesium and strontium from HLW. The facility was successfully functioning for three months, then it was stopped because of financial difficulties. However in September of this year the facility was restored to operation and is now in service at present.

During its operation there were reprocessed approximately 400 $m^3$ of HLW; the concentrates of cesium and strontium with total activity of about 15 mln Ci were produced. The average indices on the recovery degree of cesium and strontium were at a level of 98.5%. The cesium and strontium concentrates were passed to vitrification; this enabled to increase the specific activity of glass blocks up to 550 Ci/kg. Thus, the increase of expenses for the partitioning facility by 5% led to the decrease of the production cost of high-level active glass by 60%.

The second line of the UE-35 facility at the "Mayak" PA was intended for deep recovery of actinides and technetium, along with cesium and strontium from HLW. Three feasible extraction processes are now under investigation for these purposes.

The first process involves the recovery of actinides, RE and technetium by POR from raffinates arising upon the recovery of cesium and strontium by ChCoDiC. This process was successfully tested by joint efforts of the specialists of the Radium Institute and the Idaho National Laboratory at a set-up of centrifugal contactors with the use of actual acidic Idaho HLW [6,8].

The second variant for separation of An and RE from HLW at the "Mayak" PA is based on the Russian TRUEX-process described above. The results of dynamic tests on simulated HLW of the "Mayak" PA were confirmed by static tests on actual raffinates arising from recovery of cesium and strontium at the UE-35 facility. The 99.7% recovery degree of alpha-nuclides was achieved in 4 contacts in the course of these tests.

The third alternative variant of the second line of the UE-35 facility at the "Mayak" PA envisages the use of an unified process for recovery of cesium, strontium, actinides and RE. The fundamentals of this process were elaborated by the specialists of the Radium Institute and the Idaho National Laboratory and were brought up to the level of dynamic tests in multi-stage centrifugal contactors on actual acidic HLW of the Idaho Center [19,20].

*Universal Extractant for Separation of Cesium, Strontium, Actinides and Rare-earth Elements from HLW*

The universal extractant (UE) is a mixture containing chlorinated cobalt dicarbollyde, diphenyl-dibutyl-carbamoyl phosphine oxide with addition of polyethylene glycol and specific diluent. This solvent extracts effectively from acidic HLW cesium, strontium, uranium, neptunium, plutonium, americium, curium and RE.

The flowsheet of this process was tested on actual HLW of the Idaho Center with the use of 24-stage cascade of centrifugal contactors including 8 extraction stages, 2 stages for extract scrubbing, 6 stages for cesium and strontium stripping, 3 stages for An and RE stripping, 5 stages for extractant regeneration.

In the tests conducted in June of this year the recovery degrees were as follows: Cs – 99.95%, Sr – 99.985%, gross alpha-activity – 95.2%.

In view of potential prospects for introducing the universal extractant at the “Mayak” PA in Russia and the Idaho National Laboratory, efforts are now made to optimise this process. Problems on operational safety, i.e. explosion and fire-safety of the process, toxicity and corrosion agressivity, are also under study. It should be noted in this connection that these problems are elaborated in detail, as applied to the ChCoDiC-process with the aim of cesium and strontium recovery.

**Conclusion**

The concept of closed nuclear fuel cycle is accepted in Russia; this enables to solve radically the problem of long-term safe management of long-lived radionuclides. In accordance with this concept, there is created the appropriate infrastructure including spent nuclear fuel reprocessing and management of radwastes in the nuclear industry of the Russian Federation.

To reduce the volumes of HLW being vitrified, a facility for recovery of long-lived radionuclides has been constructed at the reprocessing plant of the “Mayak” PA. The efficient separation technologies are under development not only for reduction of HLW volumes, but also for obtaining of the fractions of individual radionuclides. This creates prerequisites for the future use of radical methods for management of the most hazardous radionuclides by transmutation techniques or by final disposal in the form of very strong matrices of Synrock type.

Several Russian institutes are developing the sorption and extraction processes which provide the deep recovery of radionuclides. Among the methods under development, the most progress has been made in using the ferrocyanide sorbents, mono- and bidentate organophosphorus compounds and crown-ethers.

The most advanced method for HLW reprocessing is now the extraction by chlorinated cobalt dicarbollyde. This method which affords deep recovery of cesium and strontium has been introduced on industrial scale at the “Mayak” PA (UE-35 facility). The introduction of the first partitioning stage has already given an economic effect due to reduced volumes of HLW being vitrified.

Three process variants for the second line of the UE-35 facility are now under development for recovery of actinides, RE and technetium. The first variant is based on POR, the second – on the Russian modification of TRUEX-process, the third – on the use of the so-called universal extractant (mixture of ChCoDiC, CMPO and PEG in special diluent).

Further efforts of the Russian specialists in separation technologies are aimed at obtaining the individual fractions of long-lived radionuclides, as well as at affording the safety of processes and equipment being in service.

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