

THE COMPARATIVE CHARACTERISTIC OF METHODS PARTITIONING HLW IN RUSSIA FOR  
TRANSMUTATION OF RADIONUCLIDES.

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Methods of recovery long-lived radionuclides from HLLW with the purpose more safe isolation from environment and transmutation the most toxic radionuclides, are considered.

For separation of minor actinoids and fission products are offered extraction, membrane extraction, ion-exchange chromatographic, precipitation and pyrometallurgical methods with use neutral monodentate and polydentate compounds including carbonyl, amide and phosphoryl groups, phosphorus-organic acids and their salts, cobalt chlorinated dicarbollyde.

The basic problems, arising by use of phosphorus-organic acids (POA) for isolate of pure fractions of minor actinoids from HLW, are discussed.

Opportunity of use new extractant on a basis of acid zirconium compounds salts (ZCS) of POA for partitioning HLW is shown.

Acid zirconium compounds salts (ZCS) of HDEHP and n-alkil( $C_8C_{10}$ ) phenyl-phosphonic acid may be used for deep extraction of TPE and other  $\alpha$ -nuclides from HLW with concentration up to 2 mol/l  $HNO_3$ . The extraction process of long-lived radionuclides from the solutions, characterized by complex salt composition and high radioactivity level, can be fulfilled by two successive stages. In case ZCS of HDEHP on first stages we separated light REE and TPE, on the two stages REE yttrium group. Scheme of TPE, Ln and  $^{90}Sr$  extraction with simultaneous removal of other  $\alpha$ -nuclides from HLW includes TPE and Ln extraction with 0,9 mol/l n-alkil( $C_8-C_{10}$ )phenylphosphonic acid solution in n-paraffin dissolvent and  $^{90}Sr$  extraction with 0,15 mol/l solution of zirconium salt of the indicated acid.

The perspective approach by choice of technology partitioning consists in combined extraction, sorbtion and precipitation methods for preparation radionuclides to transmutation. The minimization of secondary waste of partitioning is connected with development of new selective reagents, methods of multistage processes organization and also physical methods separation.

Partitioning HLW - the separation long-lived radionuclides from salts, is expedient for reduction of volume the most toxic wastes and for recovery of fractions radionuclides with the purpose transmutation [1]. Both purposes assume deep removal long-lived radionuclides from HLW, and recovery of fractions radionuclides in the form, necessary for inclusion in a matrix with the purpose of reliable disposal or transmutation.

In Russia a number of technologies on partitioning HLW of a working radiochemical plant RT-1 (Mayak) is developed. First of all it concerns to technology partitioning HLW, developed in ARSRIIM after A. A. Bochvar (Moscow) as the part of complex technology of reprocessing spent fuel VVER, based on use HDEHP for extraction of transplutonium (TPE), rare earths elements (REE) and strontium-90 [2]; technologies of removal cesium-137 and strontium-90 extraction CCD, developed in Khlopin Radium institute (St. Peterburg) [3] and soption cesium -137 on ferrocyanide FC-10, developed in the Institute of Physical chemistry (Moscow) [4].

To new development on partitioning HLW use bidentate extractants for removal  $\alpha$ -nuclides from HLW (ARSRIIM, Khlopin Radium Institute, Vernadsky Institute of Geochemistry and Analytical chemistry of RAS) [5-9], use of acidic zirconium compounds salts of phosphorus-organic acids (ZCS POA) for extraction  $\alpha$ -nuclides and strontium-90 from nitric acid solutions (ARSRIIM) [10]; of extraction system on basis of crown-ethers for extraction strontium-90 and cesium-137 (ARSRI Chemical Tecknology) [1, 11];

A number of processes of separation radionuclides: use cationic chromatography for separation TPE and REE [12,13], extraction and precipitation TPE [14, 15], can be directly used in technology partitioning HLW, in particular for partition more short lived curium. Methods partitioning HLW by use of heavy water blanket [16] and molten fuel [17,18] for transmutation radionuclides are developed.

At the moment on a plant on reprocessing spent fuel RT-1 total losses U, Pu and Np with raffinate of the first and second cycle make accordingly 0,01; 0,025 and 0,5 %. Practically whole Pu and Np through oxalic precipitation are transformed in dioxides and are directed on storage ( part Np is used for reception  $^{238}\text{Pu}$  ) [19]. Work on partition Tc will be carried out at processing spent fuel, thus more than 95 % the localization Tc [20] is expected. Generation of Ru from Tc will potentially allow to pay back a part of expenses on transmutation[21].

HLW concentrate by evaporation and direct on temporary storage and solidification [22]. At evaporation of acidic HLW it is possible remove practically the whole nitric acid, thus rate of evaporation is determined solubility of nitrate HLW [23]. At the given stage there is the basic opportunity of physical partition of HLW in view of various solubility of nitrate radionuclides .

The flow sheet of complex reprocessing spent fuel VVER, developed in ARSRIIM included operations evaporation raffinate after extraction U, Pu and Np for removal of a nitric acid (final acidity - 0,2 - 0,3 mol/l establishments pH 4-4,5 for maintenance of conditions extraction strontium-90 by introduction sodium acetate and citric-ion in quantit 120 % from stoichiometry for linkage Fe, Cr and Ni; joint extraction REE, TPE and strontium-90 by a solution 0.6 mol/l HDEHP in paraffine diluent; stripping strontium-90 0,1 mol/l by a solution of a nitric acid; selective stripping TPE by a solution, containing 0,8 mol/l of lactic acid and 0,05 mol/l of DTPA; stripping REE 3 mol/l by a nitric acid; carbonate regeneration of extractant [2].

By extraction of  $\alpha$ -nuclides the aforesaid complexone it is not required. In such variant the process ARSRIIM can be used for partitioning evaporated raffinate of Purex-process at concentration  $\text{HNO}_3$  0,2 - 0,3 mol/l.

In spite of the fact that the purposes of reprocessing HLW and the requirements to parameters of process of separation long-lived radionuclides have at the moment changed, extractants on a basis of phosphorus-organic acids remain the most effective for group separation of transplutonium and rare earth elements.

For deep extraction TPE and other  $\alpha$ -nuclides from HLW with concentration up to 2 mol/l  $\text{HNO}_3$  can be used of ZCD HDEHP and of a n-alkyl( $\text{C}_8\text{C}_{10}$ )phenylphosphonic acid (n-APPhonK).

By use ZCD HDEHP the technological flow sheet includes [10]: evaporation HLW up to final concentration [ $\text{HNO}_3$ ] 1,5 - 2 mol/l; extraction of a sum  $\alpha$ -nuclides and REE from HLW; stripping of a sum REE and TPE 6 mol/l  $\text{HNO}_3$ ; regeneration extractant with removal of the rests  $\alpha$ -nuclides.

The flow sheet of separation TPE, REE,  $^{90}\text{Sr}$  by simultaneous removal from HLW other  $\alpha$ -nuclides includes extraction REE and TPE 0,9 mol/l; by a n-APPhonK in n-paraffine diluent and extraction  $^{90}\text{Sr}$  0,15 mol/l by a solution ZCD of the specified acid [24].

The salts of POA with polyvalent cations as Zr and Hf are effective extractants for alkaline earth elements (AEE), REE and TPE from nitric acid solutions. In a complex  $H_2ZrA_6$ , where A - anion POA, under influence central cation there is the strengthening of extraction properties of coordinated molecules HA in relation to one elements and suppression extraction of other elements. Extraction of metals proceeds on the cation exchange mechanism. The solutions ZCS POA in n-paraffine diluents are characterized by significant radiating and chemical stability, keep high extraction ability and capacity on taken metals after boiling (5-6 hours) with 3 mol/l nitric acid and practically do not change of extraction properties up to a dose of absorbed energy  $4 \cdot 10^5$  Gr. The water solutions for reprocessing spent fuel have complex radiochemical and chemical composition. At transition from POA to ZCS POA there is the suppression extraction number salt cations HLW in particular of products of corrosion (Ni, Cr) and some radionuclides, that increases selectivity of separation TPE and  $^{90}Sr$  from HLW. The essential increase of extraction properties POA by linkage them in the form of zirconium salts at simultaneous increase of selectivity of partitioning long-lived radionuclides from HLW opens prospect of wider use extractants of the given class in practice of reprocessing HLW [25].

For removal  $\alpha$ -nuclides from HLW are offered extractants on a basis carbamoylphosphine oxides and diphosphine dioxides [5-6]. The effect anomalous aryl strengthening of the complexes of actinides provides high extraction ability diphosphine dioxides at clearing HLW from actinides [6].

On experienced laboratory plants an opportunity of deep removal (factor of distribution on one step membrane extraction is 10-20) and concentration actinides membrane extraction ditolyldibutylcarbamoylphosphine oxide the house is shown: from 0,01 mg/l up to 80 mg/l on Pu [7].

With the purpose of minimization secondary wastes, formed at partitioning HLW, exchanged explosion- and fire-safety of process in Khlopin Radium institute in quality diluents of neutral bidentate pyosphororganic compounds are offered fluorcontained ethers. At partitioning offered extractants 3-8-divisible reduction of volume HLW is received at a degree of clearing from  $\alpha$ -nuclides -  $10^4$  [8].

Essential lack bidentate extractants, offered for partitioning  $\alpha$ -nuclides from HLW, is low selectivity. For separation REE and partition actinides on a fraction search selective reactants and new ways of realization of multistep processes will be carried out. It is shown, that by use 1,2,4,- tris-(diphenylphosphinmetyl)benzene at extraction from 3 mol/l of a nitric acid factor of separation Am/Eu is equal 7 [9]. The selectivity extractants of the given class is determined by a mutual stereosequence of diphosphine groups. For selective separation radionuclides bidentate extractants engineering extraction chromatography with the purpose of increase of steps of separation can be used, however is more perspective, in our opinion, development of engineering liquid chromatography with a free liquid phase [26].

In Khlopin Radium institute partitioning of HLW is developed by use a solution chlorinated cobalt dicarbollide (CCD):  $H^+ \{ [p-(3)-1,2-B_9C_2H_{11}C_{12}]_2 Co \}$  and polyethylene glycol in a mix polar nitroorganic and nonpolar solvents [3, 27 - 29]. The most effective extractant can be used for removal Cs and Sr. At extraction directly from raffinate of Purex-process removal Cs and Sr is achieved more than 99 % with a degree of clearing from impurity  $10^3 - 10^4$ . With increase of cation charge the efficiency extraction falls, therefore a sum TPE and REE CCD takes from solutions with  $[HNO_3]$  no more than 0,5 mol/l, and the extraction actinides with higher charge is problematic.

The complex flow sheet partitioning HLW of extraction CCD includes operation evaporation HLW, decrease of concentration nitric acid (no more than 0,5 mol/l) with subsequent extraction and fraction stripping REE, TPE,  $^{90}Sr$  and  $^{137}Cs$ .

The Institute of Physical chemistry (Moscow) has developed the sorption partitioning of  $^{137}Cs$  from spent fuel solutions. Copper ferrocyanide-based sorbent (FC-10) used is delivered by the Perm State University manufacturing department.

When sorbing from the PUREX raffinate, the FC-10 capacity is  $100 \pm 5$  mg/g at 0.3 mole/l  $HNO_3$  and  $5 \pm 0.5$  mg/g at 3 mole/l  $HNO_3$ . With hydrazine addend for combining with nitrous acid, the sorbent capacity is much higher in acidic solutions. Table 1 lists data on the Cs sorption from imitated solutions having 0.05  $N_2H_4$  as a function of the  $HNO_3$  concentration.

Table 1  
Capacity FC-10 on Cs by sorption from imitation solution contained 0,05 mole/l  $N_2H_4 \cdot HNO_3$

[HNO <sub>3</sub> ], mole/l	Dynamic capacity FC-10, mg/g	
	before detection	entire
2.0	83±4	160±8
3.0	78±4	155±8
4.0	55±3	145±7

As can be seen, the gtllds good results at 4 mole/l HNO<sub>3</sub>. When desorbing <sup>137</sup>Cs by 6-10 mole/l, no less than 95 % of sorbed is are washed out with the first fire column volumes of eluate.

The sorbent can be regenerated (to convert Fe(III) to Fe(II)) by the following solution, g/l: sodium nitrite, 18; potassium nitrate, 40; (pH 6-8).

Average sorbent losses during 20 successive sorption - desorption - regeneration cycles amount 0.3-0.5 % per cycle.

Major stages of the <sup>137</sup>Cs recovery are: pH adjustment; hydrazine addition; <sup>137</sup>Cs sorption by FC-10; <sup>137</sup>Cs desorption by HNO<sub>3</sub>; sorbent regeneration; <sup>137</sup>Cs desorbate evaporation to cerium nitrate.

Within 1988-93 about 8·10<sup>6</sup> m<sup>3</sup> of diverse process solutions was reprocessed to yield 4·10<sup>6</sup> <sup>137</sup>Cs.

In ScientificResearch Institute Nuclear Reactors (SRINR) extraction HDEHP is used for separation individual TPE from irradiated targets [13]

The clearing TPE from Al, Fe, Zr will be carried out extraction 0,5 mole/l HDEHP in n-paraffine diluent from citric solutions. For separation TPE and REE is used similar extraction system, but in addition in 0,3 мгь/л citric solution (pH 3-3,5) is entered 0,015 mole/l DTPA. The separation Bk, Cf and Es will be also carried out extraction 0,5 mole/l by a solution HDEHP, and separation Am and Cm precipitation double carbonate K and Am after oxidation Am of amonium persulfate. The basic characteristics of separation TPE and REE are resulted in tab. 2.

Table 2  
Parameters of separation TPE and REE at processing irradiated targets

Element	D	Factor of separation		
		Ce/TPE	Pm/TPE	Eu/TPE
Cm	0,05	120	40	70
Cf	0.20	30	10	7

For separation Am and Cm in SRINR is investigated a carbonate method. Process of preparations of fractions Am and Cm with the contents Cm in a fraction of Am up to 0,1 % and Am in a preparation of Cm up to 0,3 - 0,5 % is developed [15].

For recovery individual radionuclides are offered of extraction system on a basis dicyclohexane-18-crown-6 for <sup>90</sup>Sr and dibenzo-21-crown-7 for <sup>137</sup>Cs [30]. The technological flow sheet with use of crown-ethers differ by simplicity; from concentrate Sr and Cs desired products can be received by precipitation radionuclides or evaporation of solutions.

Pyrometallurgical (dry) methods of the reprocessing HLW for transmutation radionuclides in blanket molten fluoric salts are developed at the moment in SRINR [18]. The basic flow sheet provides removal »of noble fission products from a flow and plant of electrochemical processing of molten fuel. The electrochemical processing of molten fuel includes electrolyzer for separation Zr and minor actinides, electrolyzer for clearing fuel salt from REE and unit of updating of composition of fuel salt.

From considered methods of recovery and the separations long-lived radionuclides at the moment for practical application in Russia are the most fulfilled water extraction and sorption processes. For reprocessing HLW, formed on working radiochemical plants RT-1, in Russia three methods with use POA, CCD and bidentate extractants for removal α-nuclides are offered. Use POA allows thus also to take and <sup>90</sup>Sr, and in a case CCD to them radionuclides is added and цезий-137.

Despite essential advantages bidentate extractants, first of all an opportunity of removal  $\alpha$ -nuclides directly from raffinate Purex-process and simplicity stripping, POA, in our opinion can quite compete at economic comparison of the given technologies. It is connected to expediency evaporation HLW for reduction of their volume. In process evaporation acidity HLW can be lowered up to value, at which can be used POA or them zirconium compounds. The important advantage POA in comparison with bidentate extractants is high selectivity  $\Phi_{\alpha}$  at group separation TPE and REE. For regeneration POA - strong extractants heavy REE, Fe, Zr and similar cations, phosphoric acid by analogy to processes in a uranium industry [30] can be used. The formed product can be directed on vitrification.

Use CCD as universal extractants for partitioning HLW is limited first of all by its difficulty extraction fourthvalent actinides.

For recovery from raffinate of Purex-process Sr and Cs crown-ethers, however the published losses given not enough for an estimation extractants can be used at processing HLW.

For recovery Cs is well fulfilled copper ferrocyanide-based sorbent (FC-10). Essential advantage given sorbent is an opportunity of its long-duration use in cycles sorption-desorption, that allows to minimize accumulation ferrocyanide waste at partitioning HLW.

For separation TPE and REE are used Talspeak-process and its updatings. But the capacitance of extractants used to REE and supplementary recovery of TRE from complexing agent-bearing solutions set a limit on the process. The TPE recovery could be excluded by allowing the TRE concentrate to stand until organic constituents are completely decomposed.

The basic diagram of the Talspeak-process is unaffected by one or other type of POA.

Extraction chromatography and TVEX processes are useful for selective partitioning of TPE and REE but extractant capacity limitations are much more dramatic in this case.

The solvent chromatography involving a free liquid phase has the advantage of combining a complete exhaustion of extractants with efficient chromatographic partition.

Cation chromatography has its greatest impact in partitioning individual constituents

Use of dry methods partitioning HLW is of interest for use of physical methods separation - electrolysis, distillation, not requiring introduction chemical reactants. In too time at the stage of gas cleaning there is the essential accumulation secondary waste of processing. An opportunity of use of physical methods partitioning HLW is insufficiently investigated at processing raffinate of Purex-process. First of all it concerns to an opportunity fractional crystallization in process evaporation HLW at modify of concentration of a nitric acid and salts.

The inclusion of processes partitioning HLW and transmutation actinides and fission products in the nuclear fuel cycle requires accent on problems of safety, protection of an environment and non-distribution [32]. Processing the most active products (up to 1000 Ku/l), containing extremely toxic radionuclides, requires as much as possible reliable technology.

The perfection of processes partitioning HLW is connected to development new selective reactants and methods of organization of multistep processes:

· Perfection of existing processes with the purpose of minimization secondary waste and increase of safety of processing HLW;

· seeking for stereoselective polydentate compounds containing carbonyl, amid and phosphoryl groups for selective partitioning of TPE and REE;

· development of the equipment for realization of multistep processes of separation radionuclides, in particular liquid chromatography with a free liquid phase.

· Use of physical methods of recovery and separation radionuclides for minimization total accumulation HLW.

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