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Methods of separation of actinide elements based on complex formation in extraction and sorption systems

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Abstract

In the frame of development of improvements of current liquid–liquid extraction technologies for reprocessing spent nuclear fuel, and for development of effective schemes of HLW treatment, novel methods of recovery and separation of uranium, transuranium and rare-earth elements have been proposed. The methods of solvent-free extraction in supercritical CO_2, countercurrent chromatography, and sorption by fibrous "filled" sorbents are discussed.

Keywords: Actinides; Lanthanides; Extraction; Sorption; Separation

1. Introduction

The problem of spent nuclear fuel reprocessing, high radioactive waste (HLW) treatment and storage is at present one of the most important ecological problems in Russia and in the U.S.A. Solutions to this problem have two general aspects: (1) development of effective methods of HLW partitioning and disposal and (2) recognition, isolation and determination of hazardous radionuclides. In practice, for these purposes an extraction and sorption methods are used. In our opinion the following directions in the frame of development of fundamental knowledge of the processes of separation in nuclear technology will predominate in the 21st century: (1) practical realization of supercritical fluid extraction (SFE) method based on quantitatively dissolution of UO_2 in some organic reagents, saturated with nitric acid in supercritical CO_2 as a solvent and separation of actinides by liquid–liquid extraction, and countercurrent chromatography (CCC) from different media; (2) the directed design and study of selective macrocyclic ionophores and another ligands with high chemical and radiolytic stability for isolation of a long-live radionuclides; (3) development of effective sorption methods of recovery of Pu and other TRU elements from different technological and environment solutions using a fibrous "filled" sorbents. The results of a systematic study on realization of these three directions are summarized in our paper.

2. Results and discussion

2.1. The use of solvent-free extractants for recovery of the actinides from dioxides and aqueous solutions and countercurrent chromatography for their separation

Spent nuclear fuel reprocessing and partitioning of actinides from acid waste solutions are performed with the use of various extraction systems. As a rule, solutions of extractants in organic solvents are used for extraction and separation of actinides. On solving the main problem, namely extraction of radionuclides, there arises the second problem connected with generation of great additional volumes of aqueous and water–organic toxic waste solutions containing mainly high-level fission products and remains of unextracted actinides. Moreover, there exist the problems connected with selection of organic solvents for extracting reagents. Therefore, the most effective approach is

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Table 1
Extraction of actinides from nitric acid solutions (4 M) using the adduct of Ph_2Bu_2–HNO_3 and the solution of Ph_2Bu_2 in dichloroethane at ambient conditions

Nuclides	Mode of extraction performance	Extraction (%)
Pu(III)	Adduct	98.5
Pu(IV)		99.7
Pu(VI)		97.1
U(VI)		98.8
Am(III)		98.2
Np(IV)	Adduct	99.6
	Ph_2Bu_2 in dichloroethane	95.2
Np(VI)	Adduct	98.8
	Ph_2Bu_2 in dichloroethane	88.4

Initial amount of Ph_2Bu_2 for Pu and Am 30 mg per volume stock solutions 1.5 and 1.2 mL, respectively, for U(VI)—37 mg and 1.0 mL. In experiments with Np(IV) and Np(VI)—16.3 mg. The volume of Np stock solutions is 1.2 mL. The volume of adduct of Ph_2Bu_2–HNO_3 for Pu and Am is 0.033 mL, Np(IV) and Np(VI)—0.018 mL, U(VI)—0.05 mL. The mixing time of the aqueous and organic phases was 3 min. Extraction efficiency (E) were calculated according to the formulas: $E = [D/(D + V_{aq.}/V_{org.})]100$.

the use of extracting reagents without application of organic solvents.

2.1.1. The adduct of diphenyldibutylcarbamoylmethylphosphine oxide with HNO_3

It was found that solution of diphenyldibutylcarbamoylmethylphosphine oxide (Ph_2Bu_2) in meta-nitrobenzofluoride is the most effective extractant of a type of bidentate neutral organophosphorus reagents, and it is used in the technology of isolation of actinides and lanthanides from strongly acidic solutions [1–3]. The study of properties of Ph_2Bu_2 (a powdery solid) has shown that on contact with acid solutions it turns into a water-immiscible liquid. Compositions of the compounds being formed as a result of such interaction of Ph_2Bu_2 with mineral acids correspond to the general formula: $n Ph_2Bu_2 \cdot m HAn$, where $m = n = 1$ for HNO_3 and $m = 2$ and $n = 1$ for $HClO_4$ and HCl. It turned out that the Ph_2Bu_2–HNO_3 adduct is more effective extractant for tetra-, hexa- and trivalent actinides as well as for trivalent lanthanides than the Ph_2Bu_2 solutions in dichloroethane (DCE) (Table 1). The extraction efficiency of metal cations into organic phase of Ph_2Bu_2 in DCE decreases as a result of the lower activity of the extractant when it is diluted in DCE because in the presence of dichloroethane part of reacting sites of the extractant is occupied owing to salvation.

Table 2
Extraction of actinides from their compounds using the TBP–HNO_3 adduct ($V_{adduct} = 1$ mL, $t = 60°C$, $\tau \sim 1.5$ h)

Compound		Actinide (mg)	Extraction (%)
Individual	UO_2	9.6	98.4
	NpO_2	6.4	<0.01
	PuO_2	1.5	<0.01
Mechanical mixture	UO_2	5.6	98.9
	PuO_2	3.7	<0.01
	UO_2	6.6	96.9
	NpO_2	5.7	<0.1

2.1.2. Extraction of actinides from their dioxides by adducts of organic reagents with HNO_3

For direct extraction of actinides from their solid dioxides excluding a stage of dissolution of the dioxides in acid solutions the following adducts with HNO_3 were used: tri-*n*-butylphosphate (TBP—$(C_4H_9O)_3PO$); methyl isobutyl ketone (MIBK—$(CH_3)(C_4H_9)CO$); *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA—$[CH_3C_8H_{17}N{-}C(O)]_2{-}CH(C_2H_2{-}O{-}C_6H_{13})$). As evident from Tables 2 and 3 uranium is quantitatively extracted by all adducts under study from all solid actinide compounds involved (individual dioxides, mechanical mixtures and solid solutions of those). At the same time, Np and Pu are not extracted both from their individual dioxides and from mechanical mixtures of those. In the case of the solid solutions of Np and Pu dioxides with UO_2, neptunium and plutonium are extracted together with uranium by the TBP–HNO_3 and DMDOHEMA–HNO_3 adducts practically quantitatively. Difference in actinides behavior in the process of extraction from the solid solutions of their dioxides consists in the fact that on a contact with adducts U(IV) is readily oxidized to U(VI). In this case a destruction of the crystal lattice of UO_2 occurs initiating the formation of the complexes of Np(IV) and Pu(IV) with the adducts of TBP and malonamide. At the same time MIBK extracts U(VI) only, and plutonium remains in the residue. Thus, uranium can be selectively extracted from the solid solution of UO_2 with PuO_2 and separated from plutonium using the MIBK–HNO_3 adduct [4].

2.1.3. Extraction of actinides from their dioxides by supercritical CO_2 containing the TBP–HNO_3 adduct

For the following separation of actinides after dissolution of dioxides we have suggested the use of supercritical carbon diox-

Table 3
Extraction of actinides from the solid solutions of actinide dioxides using the adducts of various extractants with nitric acid ($V_{adduct} = 3$ mL, $t = 60$ °C, $\tau \sim 1.5$ h)

Adduct	Actinide (mg)			Actinide found (mg)					
	U	Pu	Np	In adduct			In residue		
				U	Pu	Np	U	Pu	Np
TBP–HNO_3	14.6	0.6	0.8	13.6	0.6	0.8	–	–	–
MIBK–HNO_3	40.9	4.7	–	39.2	0.2	–	–	4.5	–
DMDOHEMA–HNO_3	25.6	2.1	–	24.6	2.1	–	–	–	–

ide, in which complexes of actinides with the above adducts are well soluble. Supercritical carbon dioxide (SC-CO_2) has penetrating power of gases and solvating capability of liquids. It is nontoxic, environmentally benign, cheap, readily available in a pure form and has moderate critical parameters ($t = 31.3°C$, $P = 72.8$ atm). Upon using, it can be readily removed from the system as a gas and, if it is necessary, it can be recycled. The data on extraction of actinides from the mechanical mixtures and solid solutions of their oxides with the use of SC-CO_2 show that under equal conditions (temperature and time) extraction efficiencies of actinides from their solid compounds under study by the adducts dissolved in SC-CO_2 remain the same as those found for the adduct without a solvent (Table 4). At that, uranium is quantitatively extracted from all studied oxides, and other actinides are extracted together with uranium only from the solid solutions of their dioxides in UO_2. Therefore, SC-CO_2 plays a part of solvent, and after transport of the extracted actinides it may be removed from the system or recycled. Thus, extraction of actinides from aqueous solutions and their solid oxides using adducts of organic reagents with acids or SC-CO_2 containing these adducts may be an alternative approach to isolation of these radionuclides for their subsequent use or incorporation in suitable matrices for a long-term environmentally appropriate disposal. This approach may avoid or minimize generating volumes of highly toxic aqueous and organic radioactive wastes associated with currently used technologies of spent nuclear fuel reprocessing.

Table 4
Extraction of actinides from their solid compounds using SC-CO_2 containing the TBP–HNO_3 adduct ($t = 60°C$, $P = 250$ atm, $\tau \sim 1.5$ h)

Compound under study	Actinide (mg)	Molar ratio in adduct	Extraction (%)
Oxide			
UO_2	61.5	1:50	>99
	334.4	1:10	90
UO_3	175.1	1:20	92
U_3O_8	177.3	1:20	85
PuO_2	8.1	1:250	<0.1
	50.1	1:50	<0.1
NpO_2	5.6	1:250	<0.1
	55.0	1:50	<0.1
Mechanical mixture of dioxides			
UO_2	150.5	1:20	87
PuO_2	37.4		<0.1
UO_2	120.6	1:20	91
NpO_2	11.5		<0.1
UO_2	133.5	1:20	89
ThO_2	58.5		<0.1
Solid solution of dioxide			
UO_2	4.70	1:20	94
NpO_2	0.25		90
UO_2	6.14	1:20	89.6
PuO_2	2.15		93.1
Eu_2O_3	0.43		91
AmO_2	0.004		88

2.1.4. *Separation of uranium, plutonium and americium by the method of countercurrent chromatography*

Further reprocessing of TBP–HNO_3–U(Pu) complexes for separation of uranium and plutonium may be performed by the method of countercurrent chromatography (CCC) under dynamic conditions after transport of TBP–HNO_3–U(Pu) complexes using environmentally appropriate supercritical (liquid) CO_2 into a collection vessel in front of the planetary centrifuge and removal CO_2 as gas [5,6]. The possibility of U and Pu separation by the CCC method in the system “30% TBP–Wight Spirit (WS)–0.5 M HNO_3” is demonstrated. The following working characteristics of the process were used for separation of U and Pu: $F = 0.7$ mL/min; $\omega = 660$ rpm. The system “30% TBP–WS–0.5 M HNO_3” allowed the concentration of uranium in the stationary phase, while plutonium was eluted with a flow of the mobile phase. The step elution permitted practically complete separation of uranium and plutonium. In this case first plutonium fraction (10 mL of 0.3 M HNO_3 solution) contained 98.9% of all Pu and 0.07% of U, and the second uranium fraction (18 mL of 0.1 M HNO_3) contained 99.93% of all U and 1.1% of Pu [7].

It has been shown also that efficient separation of Am, U and Pu can be achieved by both isocratic and step elution if DMDOHEMA solutions in dodecane was used as a stationary phase.

At that application of step elution mode provides higher purity of the separation fractions: the first fraction contains pure Am, the second uranium fraction—100% of U, and 0.7% of plutonium and final Pu fraction—99.3% of plutonium (Fig. 1). It should be noted that uranium and plutonium are also separated from trivalent rare-earth elements because elution curves of americium coincide completely with elution curves of Eu(III).

Thus, it is seen from the data obtained that efficient separation of Pu, U and Am and may be achieved by both isocratic and step elution on using both aqueous and organic test samples to be analyzed.

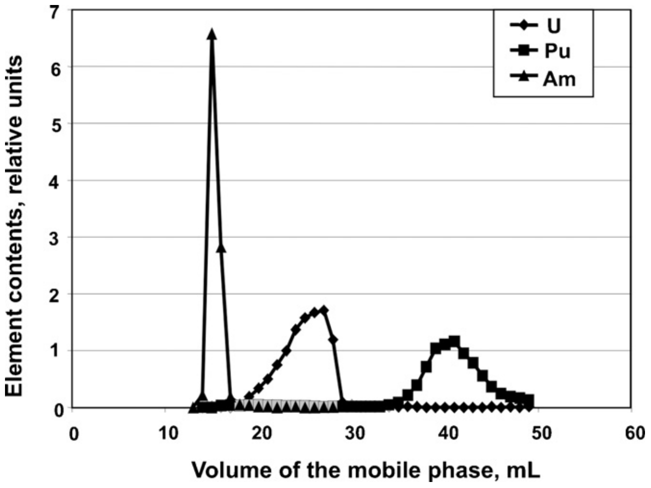

Fig. 1. Isocratic separation of ^{239}Pu, ^{233}U and ^{241}Am in the system “0.05 M DMDBDDEMA solution in dodecane—2 M HNO_3”. Parameters of the column: $L = 15.6$ m, $S_f = 0.49$, $V_{column} = 30.5$ mL. Working characteristics of the process: $\omega = 660$ rpm, $F = 0.6$ mL/min. Test sample: 0.1 mL of 2 M HNO_3 solution containing Pu, U and Am.

2.2. Extraction separation of actinide and rare-earth elements by crown-ethers

During the last two decades crown-ethers have attracted a great deal of interest for the molecular design of preorganized three-dimensional receptors for different ionic species, including radionuclides. Presently, some information is available about the thermodynamics and control/design of radionuclide recognition by macrocycles, but a detailed mechanistic and structural understanding remains elusive.

Extraction of U and TRU from nitric acidic media by (4,4′(5′)) bis(dialkylphosphoryl)-, bis(diphenylphosphoryl)-, bis(*O*-alkyl)phosphoryl)-dibenzo-*n*-crown-*m* ethers ($n = 18$ and $m = 6$; $n = 21$ and $m = 7$; $n = 24$ and $m = 8$, respectively) (Fig. 2) solutions in 1,2-dichloroethane and chloroform has been studied. These reagents were synthesized by Professor Vitaly Kalchenko from the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. It has been demonstrated that, during extraction, distribution coefficients (D_M) of Pu(IV), U(VI), Am(III), Eu(III) depend upon experimental conditions as well as upon structural features of the molecular complexes used. It is important that, within the range of $[HNO_3] = 0.02–1.0$ M, the D_M values for metals depend on stereochemical orientation of phosphoryl-groups. It was found out that the extraction ability of *cis*(4,4′-) isomers is higher than for *trans*(4,5′-) isomers and for their mixtures (Table 5) [8]. Using compound that has *cis*-oriented $(n\text{BuO})_2P(O)$-groups as an example, it was observed that the highest $D_U = 0.98$ in 3 M HNO_3; $D_{Pu} = 5.1$ in 0.5–3 M HNO_3; $D_{Am} = 0.007$ at pH 2 (Fig. 3). For *trans*-conformer under the same conditions D_M for U(VI), Pu(IV) and Am(III) are 0.091, 1.8, 0.003, respectively. Under the same other conditions, the influence of the dimensions of the macrocycle (C_n) upon extraction is essential. Using extraction of Am(III) from 0.01 to 3 M HNO_3 as an example, it has been demonstrated that for all molecules investigated, the most effective extragents are crown-ethers with $C_n = 21$. The shift of the D^{max}_{Am} to the higher [HNO_3] was observed with the increase of *n*. The sequence of the coordination properties of phosphoryl-containing ligands based upon functionalized benzo-21-crown-7 under extraction of Am(III) from 0.01 to 3 M HNO_3 is as follows: $(n\text{BuO})(OH)P(O){-} \gg (n\text{BuO})_2P(O){-} > Ph_2P(O){-}$. Extraction properties of di(nBuO)(OH)P(O)-dibenzo-21-crown-7 ($D_{Am} = 814$ in 0.1 M HNO_3) are $>10^2$ higher for all compounds studied. The conditions of selective separation of Am(III)/Eu(III) by means of bis(*O*-alkyl)(OH)phosphoryl)-dibenzo-21-crown-7 have been determined with separation factor of >90 at 0.01 M HNO_3 (Table 6) [9].

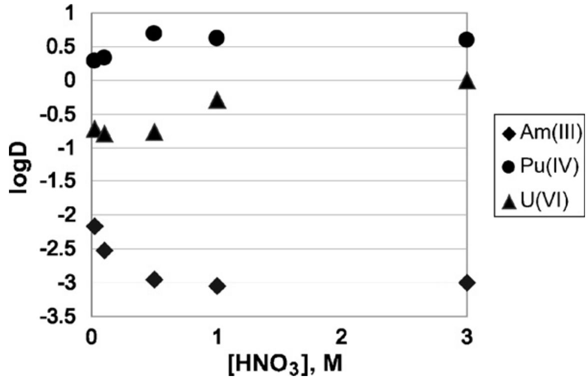

Fig. 3. The dependence of extraction of Pu(IV), U(VI), Am(III) 0.05 M solutions of the reagent with *cis*-isomer of $(n\text{BuO})_2P(O)$-groups in dichlorethane on HNO_3 concentration.

Table 5
Coefficients of distributions of actinides, extracted by 0.05 M solutions *cis*- and *trans*-isomers of bis(di-*n*-butyl phosphoryl)dibenzo-18-crown-6 in dichorethane from nitric acid solutions

[HNO_3] (M)	D_{Am}		D_{Pu}		D_U	
	Cis	*Trans*	*Cis*	*Trans*	*Cis*	*Trans*
0.02	0.007	0.003	1.95	1.49	0.18	0.18
1.0	0.003	0.002	4.15	1.72	0.50	0.31

2.3. Application of fibrous "filled" sorbents POLYORGS for concentration of Pu and other radionuclides

Determination of radionuclides in different technological solutions and natural waters demands their preliminary concentration. The most effective methods are sortion methods using complexing sorbents which provide a high selectivity of radionuclide extraction from complex solutions. The selectivity complexing sorbents is caused by ability actinides to coordinate with functional groups of sorbents. Recently, the fibrous sorbents are widely used for extraction radionuclides from saline solutions [10]. These sorbents possess better kinetic properties in comparison with traditional granule sorbents. The fibrous sorbents are more convenient for practical application also. The

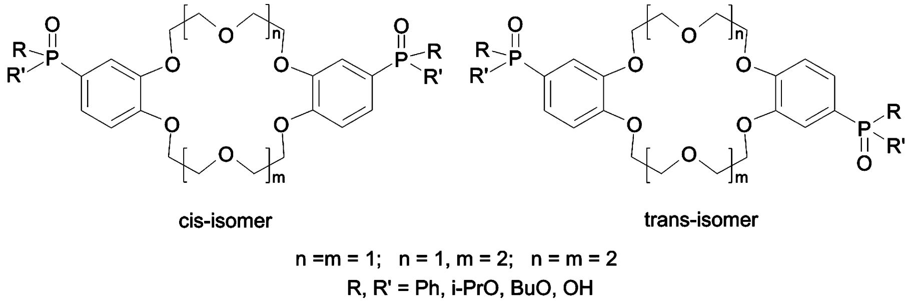

Fig. 2. Structures of the investigated diphosphoryldibenzocrown-ethers.

Table 6
Values of distribution coefficients of Am(III) and Eu(III), extracted by 0.05 M chloroform solutions of reagent with the chelate group (BuO)(OH)P(O)— $(n=21)$ in dependence on HNO_3 concentration

[HNO_3] (M)	D_{Am}	D_{Eu}	$f_{\mathrm{Am/Eu}}$
0.01	814	8.8	92.5
0.1	5.7	2.8	2.0
0.5	0.1	0.1	1.0
1.0	0.01	0.01	1.0
3.0	<0.01	<0.01	–

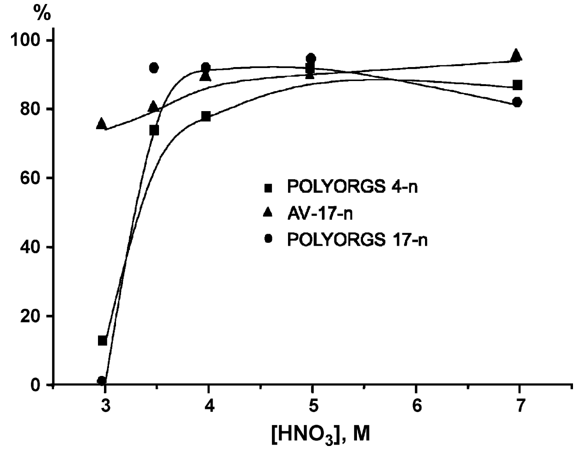

Fig. 4. Sorption of Pu(IV) by fibrous “filled” sorbents from HNO_3 solutions.

new type of fibrous sorbents—the fibrous “filled” materials were proposed for extraction and separation of radionuclides from solutions. These sorbents are characterized by good hydrofilling and filtering properties and are produced in form of nonwoven fibrous material which is convenient for practical using. These materials consisting of two polymers: polyacrilonitrile fibre and filler. In quality of filler can be used complexing sorbents and others sorption materials: polymeric and mineral ion exchangers and others. The small size of filler particles (10–30 µm) and fibre diameter (30–100 µm) and the big surface of fibrous material provide the good kinetic properties of these sorbents. This allows the effective extraction of targeted elements in shorter time. The fibrous “filled” sorbents are stable in water solutions, including acid and alkaline solutions and with heating. The filler adheres strongly to the fibre and these sorbents can be used repeatedly. The some fibrous “filled” sorbents with different filler (complexing and ion exchangers sorbent) were synthesized in Vernadsky Institute of Russian Academy of Science. There sorbents intend for extraction of radionuclides from different solutions and waters: natural waters, alkaline, acid and some technological media. These sorbents were applied for extraction of Pu, U, Th, Np, Am, Tc and Pa from model solutions. For example the extraction of different radionuclides from natural water and alkaline solutions can be used comlexing sorbents POLYORGS 33-*n* and 34-*n* with amidoxime and hydrazidine groups (Table 7). For extraction of Pu and separation from other radionuclides can be used the fibrous “filled”sorbents with complexing and ion exchanger groups (Fig. 4). These sorbents are demonstrated the high distribution coefficients and coefficients separation Pu from other radionuclides (Table 8). The sorption of Pu is realized very fast. These fibrous “filled” sorbents can be used for extraction radionuclides in static and dynamic mode from big volume of solutions [11].

2.4. Future work

Further research will be directed to the study of kinetics of extraction of U, Pu and other actinides from simulated ^{238,235}U–^{239}Pu MOX fuel using adducts of organic reagents with nitric acid. Separation of the above actinides as well as isolation of those from ^{37}Cs, ^{90}Sr, ^{140}Ba, ^{140}La, $^{141-144}$Ce, ^{147}Nd, ^{95}Nb, ^{95}Zr, ^{103}Ru, ^{131}I, ^{99}Tc will be also investigated. The study of peculiarities of redox behavior of actinides in various media, including supercritical CO_2, are planned for the enhancement

Table 7
The fibrous “filled” sorbents using for radionuclide separation

Application	Filler	Sorbents
Extraction and separation of Pu from nitric acid solutions	Complexing sorbents with 3(5)-methylpyrazole Complexing sorbents with 1,3(5)-dimethylpyrazole groups Strongly basis anion exchanger	POLYORGS 4-*n* POLYORGS 17-*n* AV-17-*n*
Extraction Pu, U, Th, Np, Am, Pa from natural waters	Complexing sorbents with amidoxime and hydrazidine groups Complexing sorbents with amidoxime and amine groups	POLYORGS 33-*n* POLYORGS 34-*n*
Extration of Tc from technological solutions and natural waters	Complexing sorbents with 1,3(5)-dimethylpyrazole groups Strongly basis anion exchanger	POLYORGS 17-*n* AV-17-*n*

Table 8
The distribution coefficients and separation coefficients of Pu(IV) from others elements by POLYORGS sorbents

Sorbents	Distribution coefficients (cm^3/g)	Separation factors from:	
		Am(III), Eu(III), U(VI), Cs(I)	Np(V), Tc(VII)
POLYORGS 17-*n*	1.5×10^3	–	–
POLYORGS 4-*n*	1.0×10^3	10^5–10^6	$(0.6/0.9) \times 10^2$
AV-17-*n*	9.0×10^2	–	–

of efficiency of separation of actinides and isolation of those from fission products, especially with the use of planetary centrifuge which allow the process of multistage extraction to be realized in dynamic mode.

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