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SAFE HANDLING OF NUCLEAR MATERIALS

Salting Out of Americium-241 during Sorption Using a Solid-Phase Extractant Based on TODGA

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Abstract—The Proryv project is developing effective ways of reprocessing irradiated nuclear fuel (SNF) to return long- lived radionuclides to the fuel cycle and close it. One of the challenges of closed fuel cycle development is the reprocessing of highly active nitric acid raffinates from the PUREX process. To do so, americium-241 must be separated from liquid radioactive waste. Technologies for the extraction, sorption, purification, and concentrating of radionuclides are widely used when processing and fractionating liquid radioactive waste. The highest efficiency and selectivity in the extraction of actinoids (III) and lanthanides (III) with rare earth elements (REE) and transplutonium elements (TPE) from nitric acid solutions of spent nuclear material reprocessing are shown by extractants based on *N*, *N*, *N*', *N*'-tetraoctyldiglycolamide (TODGA). Before using a solid-phase extractant based on TODGA, ions of the substance in the solution must be converted to neutral complexes or other nondissociated compounds. This can be done by adding neutral salts to the solution that reduce the solubility of the elements to be separated, shift the distribution of extraction, and greatly improve the efficiency of extraction. The extracted substance is taken in the form of a new phase: a solid precipitate, or a liquid or a gas phase. (With liquid extraction, there is an increase in the capacity of the extractant for the target component). Adding salts or salting agents to an aqueous phase to improve the ionic strength of a solution raises the coefficients of distribution of extracted substances, which in turn increases the capacity of sorbents. The aim of this work is to study the salting out of americium-241 during sorption using an experimental modified sample of solid-phase extractant based on TODGA and model solutions of liquid radioactive waste with a uranium macrocomponent for different contents of $NaNO_3$. It is found that the highest coefficients of distribution for the sorption of americium-241 and uranium are obtained in a solution containing 100 gL of $NaNO_3$, but this effect is much less pronounced for uranium than for americium-241. Studying the sorption kinetics of americium-241 and uranium reveals the salting effect, which is confirmed by the equilibrium concentrations of americium-241 and uranium in the solution at the same time but with different concentrations of $NaNO_3$. The difference between the equilibrium concentrations for americium-241 is an order of magnitude, in favor of a drop when the concentration of $NaNO_3$ is raised to 100 gL. The use of this effect allows the maximum capacity for americium-241 to be obtained in a system with uranium macrocomponents.

Keywords: americium-241, salting out, sorption, TODGA

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INTRODUCTION

The Proryv project is developing effective ways of reprocessing spent nuclear fuel (SNF) to return long-lived radionuclides to the fuel cycle and close it [1–3]. One task in developing a closed fuel cycle is the processing of highly active nitric acid refineries of the PUREX process [4–6]. To do so, we must isolate the most radioactive minor actinides (americium-241 and curium-244) that form during reactor operation and are in the irradiated fuel [5, 7]. The main isotopes of curium have short half-lives and high radioactivity (e.g., neutron). This greatly increases the radioactivity of nuclear fuel when it is returned to the reactor for transmutation, making it difficult to produce and recycle. It is therefore desirable to extract curium from irradiated fuel during reprocessing and store it for 50–100 years and returning its products of decay (isotopes of plutonium and long-lived curium) to the reactor. Americium-241 must be isolated from SNF for several reasons. First, it is a highly toxic and long-lived element with a half-life of 432.6 years (it decays into neptunium-237, which has a half-life of more than 2.2 million years). Second, its alpha activity grows when storing SNF with americium-241, due to the decay of plutonium-241, which has a half-life of about 14 years. It should therefore be noted that americium-241 exhibits such chemical properties as rare-earth elements (REE), of which there are many in irradiated fuel (eg., lanthanum, cerium, and neodymium). Isolating minor actinides will allow transmutation in gen-

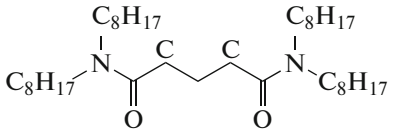

Fig. 1. Structure of *N*, *N*, *N*', *N*'-tetraoctyldiglycolamide (TODGA).

eration IV reactors to produce short-lived radionuclides or stable elements [8]. The concept of isolating minor actinides will greatly reduce the total SNF activity in the long term. However, it is difficult to separate americium, curium, and lanthanides, since the chemical properties of these elements are very similar [9].

The Proryv project employs an integrated approach to processing high–level waste: fractionation, the separating of several groups of similar chemical and identical/homogeneous physical properties of radionuclides in one processing cycle. Technologies for the extraction, sorption, purification, and concentrating of radionuclides are widely used in the processing and fractionation of liquid radioactive waste (LRW) [10–13]. Extractants based on *N*, *N*, *N*', *N*'-tetraoctyl diglycolamide (TODGA) have shown the greatest efficiency and selectivity in extracting actinoids (III) and lanthanides (III) with rare earth elements (REEs) and transplutonium elements (TPEs) from nitric acid solutions for processing spent nuclear material [14–18]. The structure of TODGA is shown in Fig. 1.

Nevertheless, extractants have a major drawback: low capacity, due to the formation of a third phase in the solution and physical entrainment of the extractant. One way of eliminating these disadvantages is to immobilize the extractant on a porous solid carrier (granule), which also simplifies the design of the hardware and greatly reduces consumption of the extractant. However, the rate of metal extraction slows somewhat as a result of stabilizing the interface in the granules of the porous material and an increase in diffusion difficulties. In many cases, so-called granular extraction proves effective in extracting metals from complex solutions due to the wide variety of matrices, the composition of the extractant in granules, and the way of introducing it into a solid carrier. These parameters allow us to select favorable conditions for metal extraction. Results from studying the use of TODGA led to the creation of solid-phase extractants (SPEXTs) obtained through the polymerization of monomers using an extractant. In manufacturing SPEXTs, the type of monomer and the content of the extractant strongly influence the size, quantity, and locations of microcells containing the extractant, the degree of their interconnection with one another, and with the outer surface of the granules, which ultimately determines both the mechanical and extractive properties of the SPEXT [19].

The capacity in this case depends on both the amount of impregnated extractant and the composition of the aqueous phase in which the substances are in the form of ions weakly transitioning into the SPEXT phase. The ions of the substance in the solution must therefore be converted into neutral complexes or other nondissociated compounds before using SPEXT TODGA. This can be done by adding neutral salts to the solution that reduce the solubility of the separated elements, shift the distribution of extraction, and greatly improve the efficiency of extraction. This effect is referred to as salting out and is often encountered during extraction in high-salt test media. Extraction is the act of separating a substance from a solution by adding another substance that is highly soluble in it: the salivate. The salted substance is extracted in the form of a new phase: a solid precipitate, or a liquid or gas phase. In liquid extraction, the extractant's capacity grows according to the target compound. Salting occurs as a result of an increase in the thermodynamic activity of the salted substance when a salting agent is added, regardless of whether a new phase is formed during the process [20]. Adding salting salts to an aqueous phase in order to raise the ionic strength of the solution therefore elevates the coefficient of distribution of the extracted substances, which in turn increases the capacity of the sorbents. The sorption of americium-241 and uranium was studied earlier using a solid-phase extractant based on *N*, *N*, *N*', *N*'-tetraoctyl diglycolamide (SPEXT TODGA) [21, 22]. However, those works did not consider in detail the kinetics of americium-241 and uranium during their sorption using an experimental modified sample of SPEXT TODGA with a different content of $NaNO_3$ in the studied solutions. This work was devoted to studying the desalination of americium-241 and uranium during their sorption in order to improve the capacity of SPEXT TODGA in model solutions of LRW with different contents of salt.

STATEMENT OF THE PROBLEM

The desalination of americium-241 and uranium during their sorption using SPEXT was studied for the most promising experimental modified sample of SPEXT TODGA [19, 20]. The composition of the base matrix of the sample was highly porous polystyrene. The crosslinking of divinylbenzene, the content of styrene, ethyl styrene, and other components of the polymerization mixture correspond to industrial SPEXT–TBF and SPEXT–FOR. A modification of the basic polystyrene matrix with polyacrylonitrile was used in the sample, allowing us to fix the TODGA in the matrix via physical adsorption in micropores on polystyrene and covalent or coordination bonds with the functional groups of the matrix. Additional fixing of TODGA in the matrix can reduce extractant washout and improve the operational characteristics of the synthesized solid-phase extractant. Modification of

the matrix composition and its intermediate processing can also affect the rate of diffusion of the target components, and thus the kinetics of ion exchange. An experimentally modified sample is shown in Fig. 2, and its composition is described in Table 1.

$NaNO_3$ was used as the salting salt in this work. The experiment used limited volume to study extraction in an americium-241 and uranium system during sorption; i.e., exchange occurs in a reactor with a constant volume of the solution being stirred. The volumetric activity of americium-241 (59.54 keV) was controlled analytically using a gamma-spectrometric automated spectrometer. The error of each measurement was no more than 12–13%. The volumetric activity of americium-241 measured via gamma spectrometry in a solution was then recalculated to the mgL dimension. The content of uranium in model solutions containing americium-241 was determined via ICP-MS (inductively coupled plasma mass spectrometry). The measuring error was 5% [23].

To calculate the content of americium-241 and uranium in the SPEXT TODGA in accordance with the material balance, we used the formula

$$C_{\text{MeSPEXT}} = V_{\text{sol}}(C_{\text{initMe}} - C_{\text{resMe}})/V_{\text{SPEXT}}, \quad (1)$$

where V_{sol} is the volume of the solution, mL; C_{initMe} is initial radionuclide concentration in solution, mgL; C_{resMe} is residual concentration of radionuclide in solution, mgL; V_{SPEXT} is the volume of SPEXT, mL; C_{MeSPEXT} is the concentration of radionuclide in SPEXT, mgL.

The coefficient of distribution is determined by the formula

$$K_d = C_{\text{MeSPEXT}}/C_{\text{Me sol}}, \quad (2)$$

where $C_{\text{Me sol}}$ is the concentration of the radionuclide in the solution, mgL.

EXPERIMENTAL

Using the analytical controls described above and formulas for calculating the content of americium-241 and uranium with allowance for the material balance (1–2), their kinetics was studied from model high-salt solutions of LRW with different contents of $NaNO_3$.

Three model low-acid (pH 3.4) solutions were prepared for this purpose:

1. $NaNO_3$—10 g/L: americium-241—0.044 mg/L; uranium—1452 mgL;

2. $NaNO_3$—50 g/L: americium-241—0.031 mg/L; uranium—1014 mgL;

3. $NaNO_3$—100 g/L: americium-241 to 0.040 mgL; uranium—1000 mgL.

These investigated model solutions of LRW were characterized by the high-salt composition and relatively low acidity of the medium. The volume ratio of solutions and SPEXT was 50:1 (mL). The studies were performed at room temperature with continuous stirring by mechanical agitators. Samples were in contact with the solutions for 300 min. Our data were used to construct curves of kinetic sorption for americium-

Fig. 2. Experimental modified sample of solid-phase extractant based on TODGA.

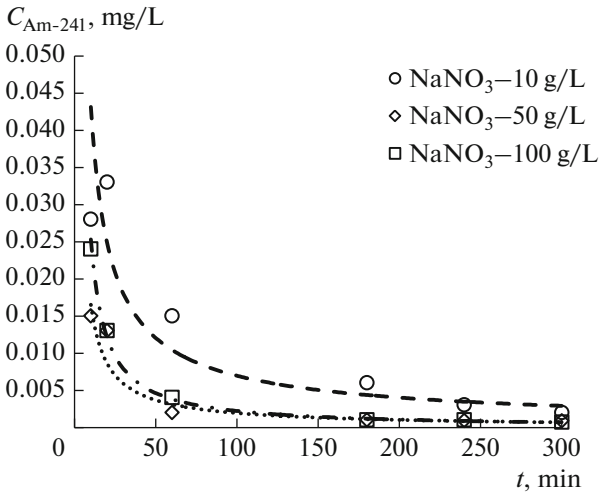

Fig. 3. Kinetics of americium-241 sorption in model solutions of LRW with different contents of $NaNO_3$.

Table 1. Composition of an experimental modified sample of solid-phase extractant based on TODGA

Modifying monomer (content 40% by weight)	Nitrile acrylic acid
TODGA content, % by weight	40
Type of functionality	cationite
Total volume capacity of the matrix, mg- eq/g	0.72
Conversion of NAA, %	25
NAA polymer content, % by weight	30
Hydrolysis temperature, °C	70
Porosity of the matrix, %	57.7
Specific surface area of the matrix, m^2/g	11.8

Table 2. Comparison of coefficients of distribution for americium-241 and uranium from model LRW solutions containing 10–50–100 gL of $NaNO_3$

Period of contact, min	Kd_U for 10 gL of $NaNO_3$	Kd_U for 50 gL of $NaNO_3$	Kd_U for 100 gL of $NaNO_3$	$Kd_{Am\text{-}241}$ for 10 gL of $NaNO_3$	$Kd_{Am\text{-}241}$ for 50 gL of $NaNO_3$	$Kd_{Am\text{-}241}$ for 100 gL of $NaNO_3$
10	12	31	40	29	0.018	0.025
20	27	16	47	17	66	113
60	29	18	42	102	806	506
180	32	31	39	334	1663	1920
240	38	30	40	752	1663	2117
300	—[a]	27	59	931	1743	3045

[a] No result.

241 (Fig. 3) and uranium (Fig. 4), depending on the content of $NaNO_3$ in solution.

RESULTS AND DISCUSSION

Analysis of the kinetics of americium-241 sorption presented in Fig. 3 shows that if we compare the equilibrium concentrations of americium-241 in solution at the same point (300 min) in the order 10–50–100 gL $NaNO_3$, they will have values of 0.002–0.001–0.0007 mgL. We can therefore say there is a weak salting effect in this system. When analyzing the dependence shown in Fig. 4, we may conclude that at contents of 100 and 50 gL of $NaNO_3$, the kinetics of uranium sorption virtually coincide. The data presented in Table 2 confirm this assumption when comparing the coefficients of distribution of americium-241 and uranium with a different salt background of the solution.

Analysis of the data presented in Table 2 shows that the highest coefficients of distribution for the sorption of americium-241 and uranium were obtained in a solution with a $NaNO_3$ content of 100 gL, but this effect is much less pronounced for uranium than for americium-241. In studying the kinetics of sorption of americium-241 and uranium, a salting effect was revealed and confirmed by the equilibrium concentrations of americium-241 and uranium in solution at the same point in time, but with different concentrations of $NaNO_3$. For ameretium-241, the difference between equilibrium concentrations was an order of magnitude in the direction of a drop with the concentration of $NaNO_3$ rising to 100 gL. This effect allowed us to obtain the maximum capacity of americium-241 in a system with uranium macro components.

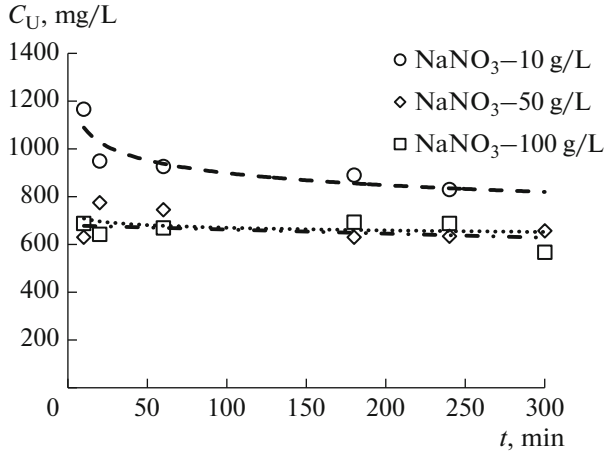

Fig. 4. Kinetics of uranium sorption in model solutions of LRW with different contents of $NaNO_3$.

CONCLUSIONS

We studied the desalination of americium-241 and uranium during their sorption using an experimental modified SPEXT TODGA sample with different contents of $NaNO_3$ in high-salt LRW solutions with a uranium macro component. The highest coefficients of distribution for the sorption of americium-241 and uranium were obtained in a solution with a $NaNO_3$ content of 100 gL, but this effect was much less pronounced for uranium than for americium-241. In studying the kinetics of sorption of americium-241 and uranium, the effect of desalination was revealed and confirmed by the equal concentrations of americium-241 and uranium in the solution at the same point in time, but with different concentrations of $NaNO_3$. For americium-241, the difference between equal-weight concentrations was an order of magnitude in the direction of a drop and the concentration of $NaNO_3$ rising to 100 gL. Using this effect allowed us to obtain the maximum capacity of americium-241 in a system with uranium macro components.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest.

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