# REVEALING THE DEPENDENCIES OF PARTITIONING AMERICIUM-241 AND URANIUM USING SORPTION TECHNOLOGY BASED ON SOLID-PHASE EXTRACTANT TODGA

ALEKSANDR SAVELEV

National Research Nuclear University MEPhI

Moscow, Russian Federation

Email: AASavelev@mephi.ru

NATALIA KLOCHKOVA

Leading Research Institute of Chemical Technology (VNIIKhT)

Moscow, Russian Federation

VALERIY RACHKOV

National Research Nuclear University MEPhI

Moscow, Russian Federation

**Abstract**

The objective of this work is to reveal the dependences of the separation of americium-241 and uranium using sorption technology based on the solid-phase extractant TODGA. In technologies for the purification of radioactive waste of low and medium activity levels with low contents of actinides, sorption and ion exchange methods are widely used due to their high selectivity. The required selectivity level, under extreme external conditions of the environment, is inherent in solid-phase extractants obtained using ligands. To extract americium-241 efficiently and separate from uranium, it is necessary to use solid-phase extractants based on N, N, N', N' - tetraoctyldiglycolamide (TODGA), which will allow the return of fissile materials to the nuclear fuel cycle and reduce the hazard class of the removed radioactive waste. For the effective use of experimental modified TODGA sample, it is necessary to identify the dependences of the extraction of americium-241 and its separation with uranium using model solutions that simulate real radioactive waste. Therefore, the determination of the kinetic parameters of the extraction of americium-241 and its separation with uranium in the process of sorption processing using experimental modified TODGA samples is necessary for the most efficient separation process. In this work, the mechanism of diffusion kinetics is determined. The film diffusion constants are found and the effective film diffusion coefficients of americium-241 and uranium during their sorption are determined for three prototypes of solid-phase extractants TODGA. The coefficients of their distribution are determined. The dependence of the kinetic parameters on the physical characteristics of solid-phase extractants TODGA has been established. An increased sorption rate of americium-241 compared to uranium for sample №2 was revealed.

## INTRODUCTION

To create nitride uranium-plutonium fuel, it is necessary to solve the problem of returning plutonium and uranium to the nuclear fuel cycle from irradiated fuel of thermal reactors, which is expected to be used in fast reactors in order to close the nuclear fuel cycle [1–2]. However, during the reprocessing of the irradiated fuel there is a decrease in its volume, but the radiation activity remains at the same level. For safe work with the obtained irradiated fuel, it is necessary to isolate the most highly active, dose-forming actinides. One of these actinides is americium-241. Americium-241 must be separated because of some reasons. The first cause is that the problem does not lay in its activity, but in the fact that during radioactive decay (432.8 years) americium-241 turns into neptunium-237, and this element already has a significant longer half-life 2.2·106 years, moreover this is the most dangerous alpha emitter. In addition, americium-241 makes a large contribution to the heat release of the nuclear fuel itself - if it is drawn back, the fuel will be hot enough, while having a high neutron radiation. The second problem is that americium-241 exhibits the same chemical properties as rare earth elements, which are quite abundant in the fuel: lanthanum, cerium, neodymium and others. However, the separation of americium-241 from rare earth elements is an expensive technology, since its content in a batch of irradiated fuel is about 1000 times less than the content of rare earth elements. As mentioned above, americium-241 is a fairly high-level radionuclide; with any methods used, the radiation load on the technological process will remain high.

Sorption and ion exchange methods are widely used in technologies for purification of liquid radioactive waste of low and medium level of activity. These methods are highly selective, which makes them possible to use in the tasks of isolating specified radionuclides [3]. Under extreme environmental conditions, in which trivalent actinide and lanthanide elements are selectively isolated from nitric acid solutions of spent nuclear fuel processing used for their extraction from raffinates of the PUREX process, solid-phase extractants obtained using ligands are considered to be promising. [4]. Among the ligands characterized by high efficiency and selectivity, the most effective ligands are diglycolamides, in particular N, N, N', N' – tetraoctyldiglycolamide (TODGA), the structure of which is shown in Fig. 1 [5–7].



*FIG. 1. Structure of N, N, N ', N' – tetraoctyldiglycolamide (TODGA).*

It has a high solubility in aliphatic hydrocarbons and is characterized by high distribution coefficients in the extraction of actinides (III) and lanthanides (III) from nitric acid solutions [7]. To fix the problem of selective separation of americium-241 and its separation with uranium, within the framework of the project «Proryv», modified samples of solid-phase extractants based on TODGA were synthesized at Leading Research Institute of Chemical Technology (VNIIKhT). Some characteristics are shown in table 1. The use of cation exchangers in combination with complexing elution processes has opened up new possibilities in the extraction and purification of actinides. Strongly acidic cation exchangers are most often used for the isolation and separation of actinides, which are practically not sorbed from nitric acid solutions by anion exchangers. The neutral functional was taken for comparison with cation exchangers. This article will consider only the separation of americium-241 and uranium from model nitric acid high-salt solutions to assess the kinetic parameters of the use of modified samples of solid-phase extractants based on TODGA necessary for the regeneration of uranium and the residual removal of minor actinides from the fuel cycle in order to close it.

TABLE 1. CHARACTERISTICS OF THE SOLID-PHASE EXTRACTANTS BASED ON TODGA SAMPLES UNDER STUDY

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Functional | Porosity, % | Specific grain area, m2/g | Average grain diameter, mm |
| 123 | cation exchangercation exchangerneutral | 33,857,754,3 | 87,011,883,2 | 1,01,30,7 |

To substantiate the use of domestic experimental modified on the solid-phase extractants based on TODGA samples, data on the course of sorption processing and the possibility of separating a pair of americium-241/uranium from model solutions of liquid radioactive solutions are required. Therefore, for the effective use of experimental modified on the solid-phase extractants based on TODGA samples, it is necessary to study the processes of mass transfer of americium-241 and uranium in sorption processing in order to determine the kinetic characteristics of the process. Determination of the kinetic parameters of sorption on prototypes with different characteristics will make it possible to identify the most promising on the solid-phase extractants based on TODGA sample for separating the americium-241/uranium pair.

Previously, a study of the sorption of americium-241 and uranium from model high-salt solutions of liquid radioactive waste was carried out using a solid-phase extractant based on N, N, N’, N’ – tetraoctyldiglycolamide. In the course of the study, the distribution coefficients of americium-241 and uranium were determined on experimental samples of the extractant and the separation coefficients of the americium-241/uranium pair were calculated [8]. This work continues the study of the dependences of the separation of americium-241 and uranium on their kinetic characteristics in order to identify the most efficient use of sorption technology based on the solid-phase extractant TODGA. The objective of this work is to reveal the dependences of the separation of americium-241 and uranium using sorption technology based on the solid-phase extractant TODGA.

## STATEMENT OF THE RESEARCH PROBLEM

To determine the dependences of the separation of americium-241 and uranium with their kinetic characteristics, it is necessary to consider the kinetics of the sorption process. The study of kinetics involves determining the rate of the sorption process, where it is necessary to highlight the optimal conditions for its implementation. Conventionally, the sorption mechanism consists of three stages:

* Transfer of substances contained in the solution to the surface of the adsorbent grains (to the external diffusion area);
* Sorption process;
* Transfer of substance inside sorbent grains.

The cumulative consideration of all stages is difficult to implement; therefore, they resort to the method of the limiting stage, which determines the overall rate of the process when using experimental modified solid-phase extractants based on TODGA samples. The sorption rate is determined either by the rate of diffusion directly in the grain (pore diffusion) or by the rate of diffusion in a stationary film (film diffusion). However, the following patterns can be used to estimate the mechanism of sorption:

* The film diffusion kinetics is characterized by the dependence of the sorption rate on the stirring rate;
* The pore diffusion kinetics is characterized by the independence of the kinetic curve from an increase in the stirring rate and an increase in the concentration of the solution. Also, the independence of the diffusion coefficient from the particle radius.

Thus, in order to determine the rate-limiting stage of the exchange and determine its characteristics, it is necessary to reduce the influence of one of these mechanisms on the sorption kinetics. Therefore, to estimate the reaction rate in a kinetic experiment, the method of limited volume was used − the exchange process occurs in a certain reactor at a constant volume of the stirred solution. Initial solution − 100 g/l NaNO3, 1235 mg/l uranium and 0,043 mg/l americium-241, pH 3,4.

To calculate the content of americium-241 and uranium on experimentally modified samples of solid-phase extractants TODGA in accordance with the material balance, the following formulas used:

 (1)

where *CMe-sample* – radionuclide concentration in the sample, mg/l; *Vsolution* – solution volume, ml; *CiniMe* – initial concentration of radionuclide in solution, mg/l; *CresMe* – residual concentration of radionuclide in solution, mg/l; *Vsample* – sample volume, ml.

The distribution coefficient was determined by the formula:

, (2)

where *CMe-solution* – radionuclide concentration in solution, mg/l.

The volume ratio of the model radioactive solution and TODGA was 50:1. This method assumes a rather high rate of transfer of a substance from solution to the sorbent surface and a weak effect of the diffusion boundary layer on diffusion. To accelerate the process associated with the transition of americium-241 and uranium from the volume of the solution into the surface liquid film covering the sorbent grain, the experiment was carried out with constant stirring of the solution and ambient temperature. It is assumed that, under the given experimental parameters, the concentration of americium-241 and uranium at all points in the volume of the model solution of radioactive waste and on the surface of solid-phase extractants TODGA is constant, i.e., diffusion from is considered to be a well-mixed solution. On the basis of the chosen method, which makes it possible to determine the limiting stage of the sorption process, the kinetics of the sorption of americium-241 and uranium on experimental modified samples of solid-phase extractants TODGA is considered. If the limiting stage in the experiment is described by pore diffusion, then to calculate the diffusion coefficients of the pore model, a model of substance transfer from a limited volume into a spherical body should be used, based on the dependence of the dynamics of fractional attainment of equilibrium with the sorbent on the sorption time.

To determine the diffusion coefficients for cases of limited intradiffusion kinetics, one can use the Boyd diffusion equation [9]:

 (3)

where *F* – fractional attainment of equilibrium of the substance, which is a function of the parameter; *t* – the time during which the given value of *F* is reached; *n* – the number of terms (1, 2, 3, ...). The ratio  is the rate constant of pore diffusion (s-1);  – effective pore diffusion coefficient, cm2/s.

Substituting *B* into equation (1), we get:

 (4)

where *Bt* is a dimensionless parameter that determines diffusion in a solid spherical body of radius *r0*.

If *F(t)* is linear, then the limiting stage is diffusion in the sorbent phase. If not, then the effect of external diffusion is noticeable and the Boyd equation can`t be used to calculate the diffusion coefficient. To describe the film diffusion of highly porous bodies, the Morris-Webber model equation [10] is used, which explains well the reaction rate at the initial time (*F≈1*) with a stirred solution

 (5)

where *kf* – diffusion film rate constant, mmol·g-1·min1/2; *С* – parameter related to the thickness of the boundary layer, mmol/g.

From the ratio of the diffusion film rate constant, the film diffusion coefficient can be determined:

 (6)

where  – effective film diffusion coefficient, cm2/s;  – effective thickness of the diffusion boundary layer, µm; *rsamples* – sample radius, mm.

The suitability of using kinetic models is determined by the linearization of data in the coordinates of their integral equations and statistical analysis with the determination of the coefficients of determination.

## THE DISCUSSION OF THE RESULTS

On the basis of the obtained experimental data on the sorption kinetics, the dependences of the share of achievement of the equilibrium capacity of the extractant on time for americium-241 (Fig. 2) and uranium (Fig. 3) were plotted for all samples. It follows from the constructed dependences that the time to reach equilibrium during the sorption of americium-241 is almost the same for samples №1 and №2 and is about 240 minutes, while samples №1 and №3 reached high equilibrium values after 60 minutes, the equilibrium concentration of uranium remained practically unchanged for 1 and 2 samples after 800 minutes, but for №3 sample a high equilibrium value of uranium was reached after 60 minutes. This dependence is evidenced by the continued saturation of solid-phase extractants based on TODGA with uranium upon reaching equilibrium with americium-241 for samples №1 and №2. For all samples, linearization of dependences is visible after 60 minutes for americium-241. For uranium, this is observed only for sample №3.

*FIG. 2. Dependence fractional attainment of equilibrium the extractant container with americium-241 with all samples on time.*

*FIG. 3. Dependence fractional attainment of equilibrium the extractant container with uranium with all samples on time.*

The non-linear form of the dependence indicates the mixed-diffusion mechanism of the kinetics of both radionuclides. At the beginning of the process, the effect of film diffusion is visible. This is especially noticeable for americium-241 (F≈1, 60 min). For uranium, the effect of film diffusion is much less than for americium-241. After saturation of the samples with americium-241 (240 min), with a strong effect of film diffusion, pore diffusion begins to predominate in the samples. In this region, it can be assumed that the dependence of pore kinetics is linear, but the capacitance of all samples is already close to 1, so consideration of pore diffusion is inappropriate and will contain large errors. The kinetic mechanism of americium-241 (Fig. 2) and uranium (Fig. 3) is in good agreement with the Morris-Weber model for a porous body and is described by dependence (5), which makes it possible to determine the film diffusion rate constant. Therefore, for americium-241 and uranium, it is possible to determine the diffusion rate constant for all samples by plotting the dependence of the kinetic characteristics in the coordinates of the Morris-Webber diffusion model (Fig. 4, 5).

*FIG. 4.* Dependence in coordinates *F – t 1/2* for americium-241 for all samples.

*FIG. 5.* Dependence in coordinates *F – t 1/2* for uranium for all samples.

Having determined the film diffusion rate constants, the effective film diffusion coefficient of americium-241 and uranium was estimated for all samples according to dependence (6). The distribution coefficients of americium-241 and uranium were also determined at the maximum achievement of the equilibrium of the samples. The results are presented in table 2.

TABLE 2. VALUES OF KINETIC CHARACTERISTICS FOR AMERICIUM-241 AND URANIUM

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | Distribution coefficient of americium-241 | Distribution coefficient of uranium | Diffusion film rate constant of americium-241, mmol·g-1·min1/2 | Diffusion film rate constant of uranium, mmol·g-1·min1/2 | Effective film diffusion coefficient of americium-241, n·10-5 cm2/s | Effective film diffusion coefficient of uranium, n·10-6 cm2/s |
| 123 | 26583045440 | 6287177 | 0,0090,0120,008 | 0,0080,0050,002 | 490,5 | 0,810,5 |

It can be seen from the analysis of the obtained results that the rate constant of the diffusion film and the effective film diffusion coefficient on solid-phase extractants of the TODGA samples are higher for americium-241 in sample №2. At the same time, the effective film diffusion coefficients are higher for americium-241 than for uranium for all samples. Based on the analysis of the obtained results, it can be stated that sample №2 has higher kinetic characteristics for the extraction of americium-241 than for uranium. This can be explained by the larger porosity and sample size. This dependence confirms that the obtained results on the assessment of the kinetics of the film diffusion kinetics of americium-241 and uranium for all solid-phase extractants of TODGA samples in the process of sorption from the model solution of LRW coincide with the separation coefficients for all samples. It is also seen that in samples №1 and №2, high distribution coefficients of americium-241 are achieved much more efficiently than uranium. The maximum distribution coefficient of uranium was determined for sample №3. At the same time, samples №1 and №2 confirmed the efficiency of using the cation exchanger functionality, while having different physical characteristics. Thus, the mechanism of sorption kinetics on TODGA solid-phase extractants is satisfactorily described by the film diffusion model, where the process rate is determined by the dependence on the physical characteristics of the samples. Using this dependence, it will eventually be possible to carry out a more efficient extraction of americium-241 and its separation with uranium during sorption processing using experimentally modified TODGA samples. For further study of the sorption of radionuclides from model solutions of liquid radioactive waste using prototypes of solid-phase extractants TODGA, the most promising sample №2 will be selected.

## CONCLUSION

The mechanism of diffusion kinetics has been established. The film diffusion constants have been found and the effective film diffusion coefficients of americium-241 and uranium during their sorption have been determined for three prototypes of solid-phase extractants TODGA. The distribution coefficients of americium-241 and uranium in all samples have been determined. From the analysis of the obtained results, an increased sorption rate of americium-241 compared to uranium for sample №2 has been revealed, which coincides with the distribution coefficients. The effective use of a functional cation exchanger has been confirmed. The dependence of the kinetic parameters on the physical characteristics of the samples has been established. The results of these studies will be used to continue work on the determination of desorption parameters on a modified solid-phase extractant TODGA sample №2 for the separation of americium-241/uranium.

References

1. ADAMOV E., ALEKSAKHIN R., BOLSHOV L., et. al. The Breakthrough Project – technological basement for large-scale nuclear energy, Izvestiya Rossiyskoy akademii nauk. Energetika, Title 1 (2015), 5–13.
2. ADAMOV E., RACHKOV V. A new technological platform for the formation of a national strategy for the development of nuclear energy, Izvestiya Rossiyskoy akademii nauk. Energetika, Title 2 (2017), 3–12.
3. MOKHODOEVA O., MYASOEDOVA G., ZAKHARCHENKO E. Solid phase extractants for the concentration and separation of radionuclides. New opportunities, Radiochemistry Title 53(1) (2011), 34–41.
4. BOLLESTEROS M.-J., CALOR J.-N., COSTENOBLE S., et. al. Implementation of Americium Separation from a PUREX Raffinate. Procedia Chemistry, Vol. 7 (2012), 178–183.
5. ANSARI S., PATHAK P., MOHAPATRA P. et. al. Chemistry of diglycolamides: promising extractants for actinide partitioning. − Chem. Rev., Title 112(3) (2012), 1751–1772.
6. ANSARI S., PATHAK P., MANCHANDA V. et. al. N, N, N’, N’ – tetraoctyl diglycilamide (TODGA): a promising extractant for actinide-partitioning from high-level waste (HLW). − Solv. Extr. Ion Exch., Title 23(4) (2005), 463–479.
7. SASAKI Y., TACHIMORI S. Extraction of actinides (III), (IV), (V), (VI), and lanthanides (III) by structurally tailored diamides. − Solv. Extr. Ion Exch., Title 20(1) (2002), 21–34.
8. KLOCHKOVA, N., SAVELEV, A., POZDNYAKOVA, N., et. al. Investigation of Americium Sorption from Model Liquid Radwaste Solutions Using TODGA-Based Solid-Phase Extractant, Atomic Energy, Title 127(1) (2019), 40–44.
9. BOYD G.E., ADAMSON A.W., MYERS L.S. J. Amer. Chem. Soc., 69, 2836, (1947).
10. WEBER W., MORRIS J. Kinetics of adsorption on carbon from solution, Journal of the Sanitary Engineering Division, Title 89 (1963), 31–60.