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
INTRODUCTION

Objective

To reveal the dependences of the separation of americium-241 and uranium using sorption technology based on the solid-phase extractant TODGA.

Sorption and ion exchange methods

- widely used in technologies for purification of liquid radioactive waste of low and medium level of activity
- highly selective, which makes them possible to use in the tasks of isolating specified radionuclides

Under extreme external conditions of the environment, in which there is a selective release of trivalent actinide and lanthanide elements from nitric acid solutions of processing spent nuclear materials, solid-phase extractants obtained using ligands are considered promising.

Among the ligands characterized by high efficiency and selectivity, the most effective ligands are diglycolamides, in particular N, N, N’, N’ – tetraoctyldiglycolamide (TODGA), Fig. 1.

Advantages of TODGA

- a high solubility in aliphatic hydrocarbons
- characterized by high distribution coefficients in the extraction of actinides (III) and lanthanides (III) from nitric acid solutions

FIG. 1. Structure of N, N, N’, N’ – tetraoctyldiglycolamide (TODGA)
INTRODUCTION

To fix the problem of selective separation of Am-241 and its separation with U, 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 – VNIKhiT. (some characteristics are shown in table 1)

To do

• To substantiate the use of domestic experimental modified on the solid-phase extractants based on TODGA samples

• Therefore, for the effective use of experimental modified on the solid-phase extractants based on TODGA samples,

It is necessary

○ Data on the course of sorption processing and the possibility of separating a pair of americium-241/uranium from model solutions of liquid radioactive solution

○ 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.

Table 1. Characteristics of the solid-phase extractants based on todga samples under study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Functional</th>
<th>Porosity, %</th>
<th>Specific grain area, m²/g</th>
<th>Average grain diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cation exchanger</td>
<td>33,8</td>
<td>87,0</td>
<td>1,0</td>
</tr>
<tr>
<td>2</td>
<td>cation exchanger</td>
<td>57,7</td>
<td>11,8</td>
<td>1,25</td>
</tr>
<tr>
<td>3</td>
<td>neutral</td>
<td>54,3</td>
<td>83,2</td>
<td>0,7</td>
</tr>
</tbody>
</table>
To determine the dependences of the separation of Am-241 and U 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.

**The sorption mechanism**

- Transfer of substances contained in the solution to the surface of the adsorbent grains
- Sorption process
- Transfer of substance inside sorbent grains

- The cumulative consideration of all stages is difficult to implement
- **We should use**

  the method of the limiting stage to determine the rate of diffusion directly in the grain (gel diffusion)
To determine the diffusion coefficients for cases of limited interdiffusion kinetics, the Boyd diffusion equation was used:

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t / r_0^2),
\]

where \(F\) – the fraction of the conversion of the substance, which is a function of the parameter \(\bar{D} t / r_0^2\); 
\(t\) – the time during which the given value of \(F\) is reached; 
\(n\) – the number of terms (1, 2, 3, ...).

The ratio \(B = \bar{D} \pi^2 / r_0^2\) is the rate constant of gel diffusion (s\(^{-1}\));
\(\bar{D}\) – coefficient of gel diffusion, cm\(^2\)/s.

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \exp(-Bt n^2),
\]

where \(Bt\) – dimensionless parameter that determines diffusion in a solid spherical body of radius \(r_0\).

The calculation of the diffusion coefficients of Am-241 and U, depending on the characteristics of the prototypes of TVEX TODGA, was carried out for the experimental data on the kinetics of sorption of Am-241 and U.
THE DISCUSSION OF THE RESULTS

FIG. 2. Dependence of filling the extractant container with americium-241 with samples 1 (○), 2 (◊), 3 (□) on time

FIG. 3. Dependence of the filling of the extractant container with uranium with samples 1 (○), 2 (◊), 3 (□) on time

- the time of reaching equilibrium upon sorption of Am-241 ≈ 240 min \(^1\),
- the equilibrium uranium concentration ≈ 800 min

\(^1\) The time of reaching equilibrium upon sorption of Am-241 is almost the same for all studied samples

These dependences are evidenced by the continuing saturation of solid-phase extractants based on TODGA with U upon reaching equilibrium with respect to Am-241.
THE DISCUSSION OF THE RESULTS

Based on the obtained values of the gel diffusion constant, the diffusion coefficients were calculated for three samples of solid-phased extractants TODGA from a model solution (table 2).

Table 2. Calculated values of the coefficients of gel diffusion on the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffusion coefficient of Am-241, n·10^{-8} cm^2/c</th>
<th>Diffusion coefficient of U, n·10^{-9} cm^2/c</th>
<th>Partition ratio Am-241/U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3</td>
<td>1.3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>1.2</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.2</td>
<td>15</td>
</tr>
</tbody>
</table>

- The diffusion coefficients of Am-241 and U on the solid-phased extractants TODGA samples are higher for sample № 2 with a large average diameter and a higher porosity of the extractant.
- The values of the diffusion coefficient for Am-241 are an order of magnitude higher than for U in all samples of the samples.

It consists with the data on the faster filling of the sample container with Am-241 in the system and higher values of the diffusion coefficients for it.

This dependence (FIG. 4) confirms that the obtained results of calculating the coefficients of gel diffusion of Am-241 and U for all solid-phased extractants TODGA samples in the process of sorption from a model solution of liquid radioactive waste coincide with the value of the separation coefficients.

Using this dependence, it will be possible to carry out more efficient extraction of Am-241 and its separation with uranium during sorption processing using experimentally modified TODGA samples.

After analyzing the results of calculating the diffusion coefficients for sorption of Am-241 and U from a model solution of liquid radioactive waste using experimental solid-phased extractants TODGA samples, a sample with the highest extraction rate for both radionuclides, № 2, was determined, which is fully consistent with the results of the kinetic experiment.

FIG. 4. The dependence of the relative diffusion coefficients of Am-241 and U on their separation coefficients
CONCLUSION

1. The diffusion coefficients of Am-241 and U in the process of their sorption were calculated for three prototypes of solid-phased extractants TODGA.

2. The dependence of the reaction rate on the value of the diffusion coefficients was estimated.

3. Based on the dependence of the diffusion coefficients on the characteristics of the solid-phased extractants TODGA prototypes, the increased rate of sorption for Am-241 in comparison with U was determined by calculation.

4. Based on the calculation of the diffusion coefficients of Am-241 and U, a prototype of solid-phased extractant TODGA with the highest kinetic characteristics, № 2, was determined.

These research results will be used to continue work to determine the desorption parameters on this modified solid-phased extractant TODGA sample № 2 for the separation of the Am-241/U pair, which should be the ultimate goal of this study.