

Features of the isotopic distribution of uranium on the border of polar and non-polar environment

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Abstract: - The kinetics of the extraction process of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes has been studied in a heterogeneous system. In the process of adsorption, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes are formed at the vertical border of the 5.6 M HNO_3 polar solution and the solid surface of nonpolar polypropylene (C_3H_6)_n. Kinetics of the extraction process of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes is described by the pseudo-first-order Yerofeyev-Kholmogorov and pseudo-second-order Ho and McKay models.

Key-Words: - Uranium isotopes, extraction and adsorption processes, tributyl phosphate, X-ray fluorescence analysis, gamma spectroscopy

Received: April 23, 2024. Revised: September 15, 2024. Accepted: October 19, 2024. Published: November 7, 2024.

1 Introduction

The most effective methods of chemical enrichment of uranium are based on the reaction of isotope exchange between valence forms in different phases, for example, aqueous and organic. It has been established that if more than two isotopes of uranium are present in the solution, the isotopes with the highest atomic weight are predominantly in a lower valence state, and the rest in a higher one [1].

Ion exchange chromatographic systems are based on this principle, in which a layer of uranium is formed with reduction and oxidation zones at the upper and lower boundaries of the layer [2, 3]. As the layer moved along the column, the isotope ^{238}U accumulated at the reduction boundary, and the isotope ^{235}U accumulated at the oxidation boundary. Another example is the extraction of tributyl phosphate – nitric acid (TBP-HNO_3) in chromatographic system with isotope exchange between the valence forms of uranium U(IV) and U(VI) , which move in a band formed during countercurrent extraction [4]. The extraction system "50% solution of TBP in dodecane and 2M HCl" uses an isotope exchange reaction between forms U(III) and U(IV) to enrich uranium with the isotope ^{235}U [5].

In this work, we investigated the process of adsorption of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes in a heterogeneous system at the vertical border of a 5.6M HNO_3 polar solution and the surface of

nonpolar polypropylene (C_3H_6)_n. Extraction and adsorption systems with different concentrations of uranium in the aqueous phase and with different concentrations of TBP in the organic phase were studied.

Diphilic TBP molecules can spontaneously accumulate at the border between the polar and nonpolar phases [6]. In our case, this is the boundary between the solution and the wall of the polypropylene cup. In a heterogeneous system, the rate of adsorption at the solid–liquid border depends on the rate of molecular or convective diffusion of reacting substances and the rate of chemical reaction at the border, proceeding by the mechanism of physical or chemical adsorption. If the limiting stage of adsorption is diffusion, then the process is described by the pseudo-first-order Yerofeyev-Kholmogorov equation. If the limiting stage of adsorption is a chemical reaction, then the process proceeds according to the kinetic mechanism of Ho and McKay. If the rates of diffusion and chemical reaction are commensurate, then a mixed mechanism takes place.

2 Uranium-containing solutions

For the experiments, an initial solution (IS) of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ in 5.58 M HNO_3 was prepared. It contained uranium in the amount of 107.31 mg/ml. Isotopic composition of uranium in the initial solution: ^{234}U – 0.0016 ± 0.0003 at%; ^{235}U – 0.471 ± 0.007 at%; ^{238}U – 99.5 ± 0.3 at%.

2.1 Working solutions

Working solutions (WS) of extraction and adsorption systems $\text{HNO}_3\text{-TBP-(C}_3\text{H}_6)_n$ were prepared from the initial solution, Table.1. In the table, V_{IS} is the volume of the initial solution; V_{HNO_3} is the volume of working solution; C_{U} is the concentration of uranium in the aqueous phase; V_{TBP} and V_{GG} – volumes of TBP and galosha gasoline.

Table 1. The composition of working solutions of extraction and adsorption systems.

WS	Aqueous phase			Organic phase	
	V_{IS} , mL	V_{WS} , mL	C_{U} , mg/ mL	V_{TBP} , mL	V_{GG} , mL
WS1	4	24	17.885	1	0
WS1a	4	24	17.885	0.7	0.3
WS1b	4	24	17.885	0.9	0.1
WS2	8	24	35.770	1	0
WS4	2	24	8.943	0.7	0.3
WS6	3	24	13.414	0.7	0.3
WS7	5	24	22.356	0.7	0.3

2.1.1 Measurement of the uranium concentration distribution

The uranium content was measured on an X-ray fluorescence spectrometer with a radioisotope radiation source based on the radionuclide ^{109}Cd . Fig. 1 shows the distribution of uranium concentration by depth h at the solid-liquid border and in the center for different working solutions from Table. 1.

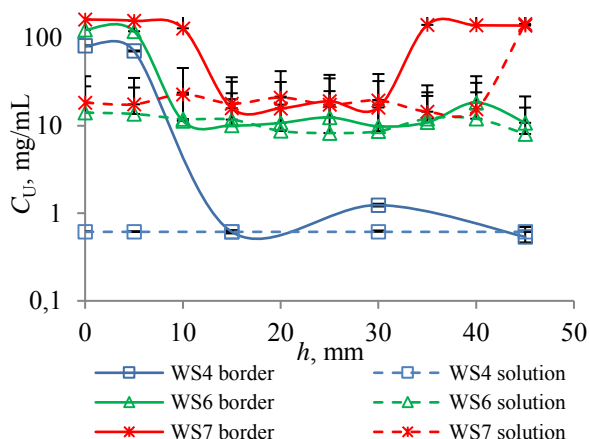


Fig.1 Distribution of uranium concentration in the heterogeneous system $(\text{C}_3\text{H}_6)_n\text{-TBP-HNO}_3$ by the depth of the solution h . Solid lines for the phase border, along the wall of the glass, dotted lines for a homogeneous phase, in the center of the glass.

An increase in the concentration of uranium near the surface ($h=0\text{mm}$) is due to the fact that, in

accordance with the extraction mechanism, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ molecules accumulate on the surface of polypropylene, and the density of TBP is less than the density of the aqueous phase. The accumulation of uranium at the bottom of the glass is due to the fact that with an excess of uranium in the aqueous phase and a small number of TBP molecules in the organic phase, almost all TBP molecules are bound into $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}_{\text{OP}}$ complexes, that with an increase in the phase contact time leads to an increase in the density of the organic phase. The concentration of uranium in the sample was calculated in a standard way based on the intensity of its characteristic radiation. The densities of the organic and aqueous phases were determined by the pycnometric method after establishing equilibrium in the system. For the WS6 working system, the density of the organic phase at the bottom of the glass was $1.26 \pm 0.02 \text{ g/ml}$, and the density of the aqueous phase in the center of the glass was $1.20 \pm 0.02 \text{ g/ml}$. For the WS1 system, the density of the organic phase at the bottom of the glass was $1.58 \pm 0.01 \text{ g/ml}$, and the density of the aqueous phase in the center of the glass was $1.16 \pm 0.02 \text{ g/ml}$. With a concentration of uranium in the aqueous phase of 8.94 mg/ml (WS4) and 13.41 mg/ml (WS6), the maximum values of uranium concentration at the solid-liquid border fall on a layer 5-10 mm wide at the surface of the solution. When the concentration of uranium in the aqueous phase is 17.88 mg/ml (WS1) and 22.36 mg/ml (WS7), the density of the organic phase at the solid-liquid border becomes higher than the density of the aqueous phase, and part of the organic phase shifts to the bottom.

2.1.2 The measurement of the isotopic composition of uranium

The isotopic composition (at.%) of uranium was determined by analytical lines of gamma radiation of radionuclides from the equilibrium decay chains of ^{234}U , ^{235}U and ^{238}U .

In the equilibrium decay chains of uranium, the radioactivity of any daughter nuclide is proportional to the radioactivity of the original parent uranium radionuclide.

When calculating the isotopic composition of uranium, it was assumed that the activities of all radionuclides correspond to the equilibrium state of decay chains.

As shown in Fig. 2, at the solid-liquid border, it is possible to form gradients of isotopic composition along the depth h .

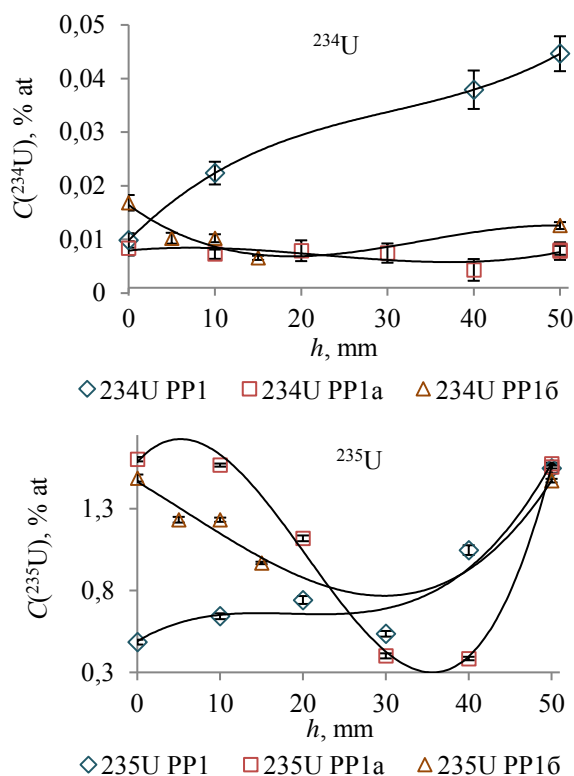


Fig. 2. Changes in the concentrations of isotopes ^{234}U (left) and ^{235}U (right) along the depth h at the solid–liquid boundary.

The results of measurements of the isotopic distribution of uranium in the WS1a system in the aqueous phase along the axis of symmetry of the glass in the direction from the surface of the liquid to the bottom of the glass are shown in Fig. 3. In the WS1 system at the bottom of the glass (organic phase – pure TBP), the concentration of ^{235}U was 1.55 ± 0.03 at%, and the ratio of $C_{235\text{U}}/C_{238\text{U}}$ concentrations of ^{235}U and ^{238}U was 0.016 ± 0.002 . In this system, the entire enriched ^{235}U organic phase accumulates at the bottom of the glass. In the WS1a system (the organic phase is TBP and gasoline in a ratio of 7:3) the concentration of ^{235}U at the bottom of the glass was 1.58 ± 0.01 at%, and the ratio of $C_{235\text{U}}/C_{238\text{U}} = 0.0160 \pm 0.0001$. At the solid–liquid border at the liquid surface, the concentration of ^{235}U was 1.60 ± 0.02 at %, and the ratio of $C_{235\text{U}}/C_{238\text{U}} = 0.0049 \pm 0.0006$. In the WS1b system (the organic phase is TBP and gasoline in a ratio of 9:1) at the solid–liquid border at the liquid surface, the concentration of ^{235}U is 1.49 ± 0.02 at%, and the ratio of $C_{235\text{U}}/C_{238\text{U}} = 0.015 \pm 0.001$.

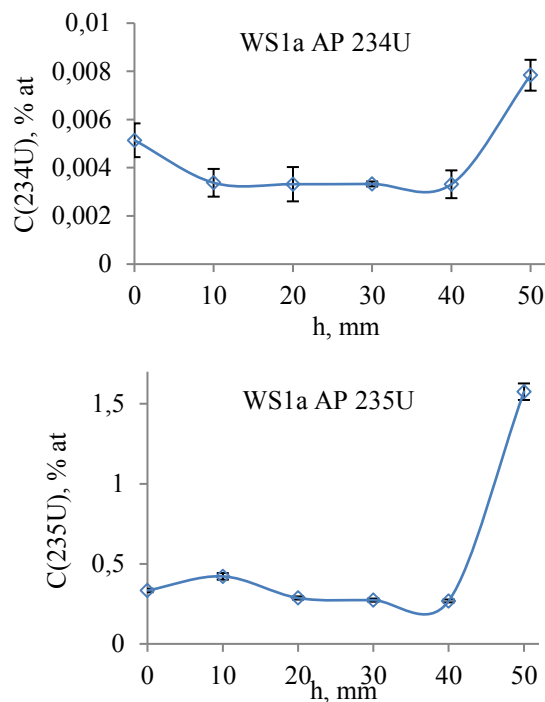


Fig. 3. Distribution of concentrations of ^{234}U (left) and ^{235}U (right) by depth h in the aqueous phase (PP1a system) along the axis of symmetry of the glass.

3 Adsorption kinetics

The kinetics of adsorption obeys the pseudo-first-order Yerofeyev–Kholmogorov equation [7, 8]. The greater the saturation of the surface, i.e. the smaller the difference $(a_\infty - a_t)$, the lower the rate of adsorption:

$$\frac{da}{dt} = k_1(a_e - a_t) \text{ or } \frac{dq}{dt} = k_1(q_e - q_t). \quad (1)$$

In equations (1) a_e and a_t are the adsorption values at the moment of equilibrium and at time t ; q_e and q_t are the amount of matter in the organic layer at the solid–liquid boundary at the moment of equilibrium and at time t ; k_1 is the adsorption rate constant. The degree of adsorption α at the solid–liquid border at the surface of the solution:

$$\alpha = \frac{a_0 - a_t}{a_0} = \frac{C_0^{\text{AP}} - C_t^{\text{AP}}}{C_0^{\text{AP}}} = \frac{q_0^{\text{AP}} - q_t^{\text{AP}}}{q_0^{\text{AP}}} = \frac{C_t^{\text{OP}} \cdot V^{\text{OP}}}{C_0^{\text{AP}} \cdot V^{\text{AP}}}, \quad (2)$$

where C is the concentration of adsorbate in the organic (OP) and aqueous (AP) phases, respectively. Solution of equation (1) describing the kinetics of adsorption in a heterogeneous system

$$\alpha = 1 - e^{-k_1 t^n} \quad (3)$$

or for concentration purposes

$$C_t^{\text{OP}} = C_0^{\text{AP}} \frac{V^{\text{AP}}}{V^{\text{OP}}} (1 - e^{-k_1 t^n}). \quad (4)$$

In the equations (2-4), the values q_0^{AP} и q_t^{AP} are the amount of adsorbate (uranium) in the aqueous phase at the initial moment of time and at time t ; q_t^{OP} is the amount of adsorbate (uranium) in the organic

phase at time t ; n is a constant that determines the nature of the adsorption process. At $n > 1.1$ the process is kinetic, at $n < 0.9$ the process is diffusive, at $0.9 \leq n \leq 1.1$ it is mixed (the rate of the chemical reaction is comparable to the rate of diffusion) [7, 8]. In the equations (3 – 4), k_1 is the effective process rate constant associated with the reaction rate constant K [9].

$$K = n \cdot k_1^{1/n}. \quad (5)$$

The values of K , k_1 and n were determined graphically.

$$\ln(-\ln(1 - \alpha)) = \ln\left(-\ln\left(1 - \frac{q_t^{OP}}{q_0^{OP}}\right)\right) = \ln(k_1) + n \cdot \ln(t). \quad (6)$$

In coordinates $\ln(-\ln(1-\alpha))$ from $\ln(t)$, the tangent of the slope angle of the line constructed according to experimental data is n ; the segment cut off by this line from the ordinate axis is $\ln(k_1)$.

To describe the kinetic laws of adsorption, the pseudo-second order equation of Ho and McKay is used [10]. It also serves to assess the effect of intermolecular interactions of adsorbed substances [11, 12] and to assess the overall speed of the process [13-15].

$$\frac{t}{a_t} = \frac{1}{k_2 a_e^2} + \frac{t}{a_e}. \quad (7)$$

In equation (7), k_2 is the pseudo-second order adsorption rate constant; $k_2 a_e^2$ is the initial adsorption rate [16]. The Ho and McKay model assumes that the rate of adsorption is limited by a chemical reaction occurring due to ion exchange or electron exchange between the adsorbent and the adsorbate. The values of a_e and k_2 are determined graphically by the linear dependence of t/a_t on t , based on experimental data. The tangent of the slope angle is $1/a_e$, the segment cut off by the graph from the ordinate axis is $1/(a_e \cdot k_2)$.

4 The speed of the process

Rate constants of isotope extraction ${}^i\text{U}$ ($i = 234, 235, 238$) from the aqueous phase during adsorption of the ${}^i\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes at the solid-liquid border, at the liquid surface ($h = 0$ mm) in a heterogeneous system of 7.53 M HNO_3 -TBP- $(\text{C}_3\text{H}_6)_n$ were determined by the kinetic curves of the process [17].

The kinetic curves of adsorption of uranium isotopes at the solid-liquid border in a heterogeneous WS2 system at the solution surface, experimentally measured and calculated using the Yerofeyev-Kholmogorov model, are shown in Fig. 4. These data are well described by a pseudo-first-order model.

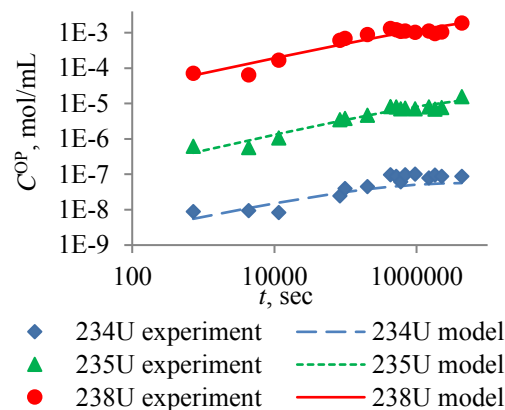


Fig. 4. Kinetic curves of accumulation of uranium isotopes at the solid-liquid border in the 7.53 M HNO_3 – TBP – $(\text{C}_3\text{H}_6)_n$ system at the surface of the aqueous phase in the PP2 sample.

The results of the graphical determination of the values of K , k_1 and n are given in Table 2.

Table 2. Kinetic parameters of the process of accumulation of isotopes ${}^{234,235,238}\text{U}$ at the solid-liquid border at the surface in the WS2 system

Isotope	k_1	n	K	R_2
${}^{234}\text{U}$	$6.33 \cdot 10^{-3}$	0.42	$2.48 \cdot 10^{-6}$	0.78
${}^{235}\text{U}$	$1.21 \cdot 10^{-3}$	0.45	$1.78 \cdot 10^{-7}$	0.91
${}^{238}\text{U}$	$1.03 \cdot 10^{-3}$	0.43	$4.92 \cdot 10^{-8}$	0.89

In a series of parallel measurements, it was found that the reproducibility of the measurement results for the value K is significantly better than for the value k_1 . Since $n < 0.9$, adsorption is limited by the process of diffusion of ${}^i\text{UO}_2(\text{NO}_3)_2$ molecules in the aqueous phase to the organic phase layer at the border near the solution surface. Values of the rate constants of adsorption of uranium isotopes in the form of complexes on the surface of polypropylene make up a series in which $K_{234\text{U}} > K_{235\text{U}} > K_{238\text{U}}$.

For the WS2 system, the values of a_e and k_2 were determined graphically from experimental data plotted in t/a_t coordinates from t [17]. Table 3 shows the kinetic parameters of adsorption of uranium isotopes determined by the Ho and McKay model at the solid-liquid border at the surface of the aqueous phase in the WS2 system, as well as experimental $a_{e \text{ exp}}$ and calculated $a_{e \text{ calc}}$ values of the equilibrium adsorption value.

The kinetic parameters of adsorption of uranium isotopes have the following units of measurement:

- $1/a_e$ [$\text{sm}^2 \cdot \text{mol}^{-1}$];
- $1/(k_2 \cdot a_e^2)$ [$\text{sm}^2 \cdot \text{sec} \cdot \text{mol}^{-1}$];
- $a_{e \text{ calc}}$ [$\text{mol} \cdot \text{sm}^{-2}$];
- $a_{e \text{ exp}}$ [$\text{mol} \cdot \text{sm}^{-2}$].

Table 3. Experimental and model-calculated adsorption parameters ^{234,235,238}U

Parameter	²³⁴ U	²³⁵ U	²³⁸ U
1/a _e	6.79·10 ⁷	7.97·10 ⁵	5.92·10 ³
1/(k ₂ ·a _{e2})	5.65·10 ¹²	4.66·10 ¹⁰	6.93·10 ⁷
a _{ecalc}	1.47·10 ⁻⁸	1.25·10 ⁻⁶	1.69·10 ⁻⁴
a _{eexp}	1.47·10 ⁻⁸	1.26·10 ⁻⁶	1.80·10 ⁻⁴

The rate of accumulation of adsorbate (uranium and its decay products) *V* at the solid–liquid border at the surface of the aqueous phase (0 mm < *h* < 10 mm) is equal to the value of the time derivative of the function *C_t^{OP}(t)*. To determine the value of *V*, the experimental data *C_t^{OP}* were approximated by a modified Langevin function

$$y = y_0 + L \cdot \left(\operatorname{cth} z - \frac{1}{z} \right), \quad (8)$$

where $z = \frac{t-x_c}{s}$; *t* is the phase contact time. The results of the approximation are presented in the table. 4.

Table 4. Parameters of approximation of experimental data

Isotope	²³⁴ U	²³⁵ U	²³⁸ U
y ₀	3.79·10 ⁻⁸	2.04·10 ⁻⁶	4.76·10 ⁻⁴
x _c	132042.78	46024.85	68165.53
L	5.49·10 ⁻⁸	5.86·10 ⁻⁶	6.39·10 ⁻⁴
s	69833.20	61724.51	27103.66
R ₂	0.91	0.96	0.95

The obtained form of the *V(t)* function for uranium isotopes, is shown in Fig. 5.

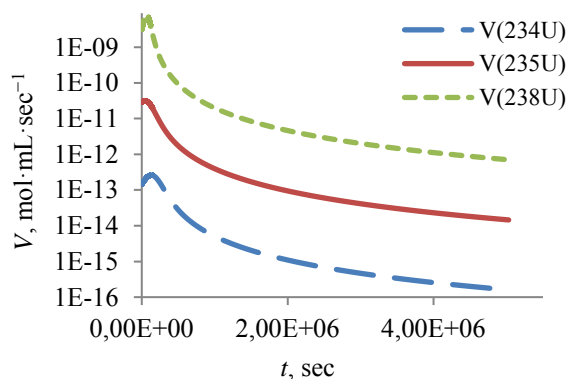


Fig. 5. Parameterization of experimental data by the Langevin function and the velocity *V(t)* for the adsorption of isotopes ^{234,235,238}U in the WS2 system.

This parameterization allows us to conclude that the rates of accumulation of ²³⁴U, ²³⁵U and ²³⁸U at the solid–liquid border at the surface of the aqueous phase obey the inequality *V*₂₃₄ > *V*₂₃₅ > *V*₂₃₈ or that the mobility of UO₂(NO₃)₂·2TBP complexes with light isotopes of uranium above.

5 Conclusion

In conclusion, we formulate the main results. The kinetics of the extraction process of UO₂(NO₃)₂·2TBP complexes has been studied in a heterogeneous system with a small amount of organic extractant TBP from a solution of nitric acid. In the process of adsorption of UO₂(NO₃)₂·2TBP complexes the isotopic distribution of uranium changes at the vertical border between the polar solution and the surface of nonpolar polypropylene. If the content of ²³⁴U in the initial solution was 0.0016 ± 0.0003 at%; ²³⁵U – 0.471 ± 0.007 at%; ²³⁸U – 99.5 ± 0.3 at%, then at the boundary the concentration of ²³⁴U increased to 0.045 ± 0.003 at%, ²³⁵U – to 1.55 ± 0.03 at% , and the content of ²³⁸U decreased to 98.4 ± 1.9 at%. A new method of chemical enrichment of uranium is based on this phenomenon [18].

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Contribution of individual authors to the creation of a scientific article (ghostwriting policy)

D. A. Rumyantseva and V. G. Zinoviev organized and conducted experiments.

D. A. Rumyantseva performed calculations of the elemental isotope concentration.

D. A. Rumyantseva and V. G. Zinoviev selected a kinetic model and performed calculations.

I. A. Mitropolsky was responsible for statistics, analyzed the results and edited the text of the article.

Sources of Funding for Research Presented in a Scientific Article or Scientific Article Itself

No funding was received for conducting this study.

Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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