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Fluid dynamics simulation of highly loaded anion-exchange chromatography of Np(IV) based on adsorption isotherm determined by $^{237+239}$Np

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Abstract

In order to investigate the optimum condition for anion-exchange chromatography for purification and recovery of actinide(IV) constituting transuranium elements, a convective-diffusion equation model treating mass balance and Langmuir-type kinetics in porous system, which was developed for thorium(IV) by us, was applied to neptunium(IV). Absorption isotherm of neptunium(IV) to anion-exchange (MSA-1) resin was carried out by using $^{237+239}$Np in 6N HNO_3 media and hereby parameters of the Langmuir-type kinetics were determined as $k_0 = 2.5 \times 10^3$ and $s_{max} = 1.0$. Accompanied with the fluid dynamics parameters already determined for the column system used for $^{227+232}$Th, elution curves of neptunium(IV) at highly loaded condition were estimated by the numerical calculation. According to the result, the loading of more than 10% of resin capacity leads to rapid breakthrough and severe tailing of neptunium which lowers purity and yield in the purification procedure. This numerical calculation will serve as a valuable measure to figure out column operation conditions for purification and recovery of transuranium elements.

Keywords: Neptunium; Preparatory chromatography; Highly loaded condition; Elusion curve; Fluid dynamic simulation

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1. Introduction

Metals of transuranium elements with very high purity are essential for reliable studies of the solid-state physics of transuranium compounds, especially of physical phenomena properties such as the de Haas–van Alphen effect where the infinitesimal quantity of impurities interfere the observation of the signal [1–3]. For neptunium compounds, the purity of prepared compounds is governed by the purity of the starting metal which is produced from the supplied neptunium oxide whose purity is as low as 99.9%. In order to prepare gram-amount neptunium metals, our research group developed a new method which only requires an aqueous acidic solution of the starting metal ion [4,5]. This method is especially suitable for preparation of highly radioactive neptunium metal at high purity. Due to the cost of man-made element and the strict management under the nonproliferation policy, there is an increased need for purification, reuse and recovery of the neptunium element from used compounds or residues. The most suitable method for the extensive purification prior to the metal preparation is the anion-exchange chromatography because the stable formation of hexanitrate anion $An(NO_3)_6^{2-}$ is characteristic to the actinide (An) chemistry [6].

The distribution constants K_D of Np(IV) to anion-exchange resin in nitric acid was determined to show the maximum value of $K_D > 10^3$ at the nitric acid concentration of 5–10N [7]. At tracer scale the large value of K_D enables us to purify neptunium(IV) easily due to its exclusively large distribution to resin in nitric acid. However, with increasing amount of loading the value of K_D decreases and the purification becomes difficult. For example of thorium(IV) chromatography, when the amount of thorium loaded onto the column is increased, peak position moved forward and distribution coefficient decreased substantially [8]. Simultaneously, the elution curves changed from Gaussian-type curves to frontal peaks with tailings.

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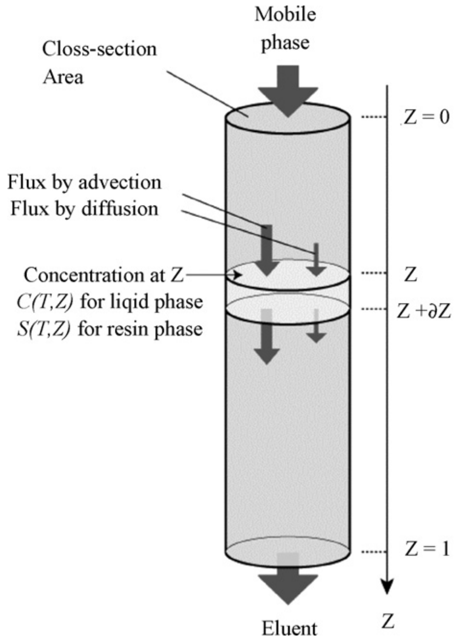

Scheme 1. Model of mass balance in minute region considering adsorption for solid phase.

In preparatory chromatography, it is essential to figure out column operation condition by which all of high throughput, high purity and high yield are achieved [9]. Experimental optimization of the column operation condition for neptunium, however, is prohibitedly difficult due to long retention time and large cost due to large amount (150–200 times of column volume) of radioactive effluent. Therefore, it is great helpful to use numerical calculation of elution curves for the determination of the column operation condition of the preparatory anion-exchange chromatography. For organic compounds such as medicinal compounds, the numerical calculation of elution curves for the estimation of the column operation condition is widely used for purification [10]. Therefore, large efforts have been devoted to study of the numerical calculation based on adsorption isotherm for non-linear chromatography at highly loaded state [9,11,12]. However, to the best of our knowledge, no theoretical study on the preparatory ion-exchange chromatography of inorganic compounds has been reported.

Recently, we have developed a theory and a numerical calculation method of preparatory anion-exchange chromatography of thorium(IV) hexanitrate anion [13], which are based on fluid dynamics in porous systems [14,15] (Scheme 1). The dimensionless and normalized form of the advection-diffusion equation is given by

$$\frac{\partial C}{\partial T} + \frac{1-\varepsilon}{\varepsilon}\frac{\partial S}{\partial T} = \frac{F_0}{\varepsilon}\frac{\partial^2 C}{\partial Z^2} - \frac{U}{\varepsilon}\frac{\partial C}{\partial Z} \tag{1}$$

where F_0 is the Fourier number and T, Z, U, C and S are the dimensionless parameters of time, axis along column, flow rate, concentrations in mobile and in stationary phases, respectively. The mathematical model of adsorption equilibrium and kinetics proposed by James [16] was modified by Bain [17]. The adsorption site consisting of cation exchange site (R^+) is treated not as two molecules ($R^+ + R^+$) but as a single molecule (R_2^{2+}) which react with the hexanitrate anion of thorium(IV) [6] to produce the adsorbed product $[Th(NO_3)_6]R_2$. The adsorption kinetics is thus assumed to be the first order and adsorption (k_s) and desorption (k_d) rate constants can be defined and the Langmuir-type isotherm is obtained as [17–19]:

$$\frac{1}{s} = \frac{1}{s_{\max}}\left(\frac{1}{k_0 c} + 1\right) \tag{2}$$

was combined with Eq. (1), where $k_0 = k_s/k_d$ is the distribution coefficient, $s_{\max}$ is the maximum adsorption concentration. In order to apply this numerical model to preparatory chromatography of neptunium(IV), the parameters of the Langmuir-type isotherm (k_0 and $s_{\max}$) for neptunium(IV) are required to be determined corresponding to a combination of specific resin and specific nitric acid concentration and fine tuning of the parameters of D and k_s for neptunium(IV) in specific column with specific mobile phase are required. Considering the similarity among actinide(IV), the values of D and k_s for the neptunium(IV) system can be assumed to be identical to those for the thorium(IV) system used in the previous study[13].

In the present study, adsorption isotherm of neptunium(IV) to anion-exchange resin in highly loaded conditions was determined in a distribution experiment carried out by using $^{237+239}Np$ in 6N HNO_3 media and parameters of the Langmuir-type kinetics were determined as $k_0 = 2.5 \times 10^3$ and $s_{\max} = 0.5$. Numerical calculations of elusion curves of neptunium(IV) were carried out on the basis of this adsorption isotherm, as well as fluid dynamics parameters already determined for the column system used for $^{227+232}Th$. Finally, elution curves of anion-exchange chromatography at heavily loaded conditions of neptunium(IV) were calculated numerically and discussed.

2. Experimental

2.1. Preparation of $^{237}Np(IV)$ stock solution in 6 M HNO_3

In a glove box with subatmospheric pressure, neptunium dioxide ($^{237}NpO_2$) 8.3558 g was dissolved in 6 mol dm^{-3} nitric acid and the solution volume was 57 mL. A portion of the neptunium(V) solution (0.750 mL; 4.1×10^{-4} mol) was transferred to a vial container. The ^{237}Np solution was heated and its volume was reduced to 20 mL. Addition of aqueous ammonia leaded to formation of hydroxide precipitation of neptunium(V) (brownish-red, soggy precipitate). After matured for 30 min, the precipitation was separated by centrifuge. The precipitation was washed with 1/100-diluted aqueous ammonia and separated by centrifugation and this process was repeated again to remove a trace residue of nitrate anion. The precipitation was dissolved by an addition of 10 mL of 2 mol dm^{-3} HCl. By adding 1 mL of 10% hydroxylamine $NH_2OH{\cdot}HCl$ aqueous solution and heating the solution for 5 min, a change in solution color from brownish yellow-green to emerald green was observed, which is indicative of Np(IV). By an addition of aqueous ammonia a greenish-brown precipitate of hydroxide of Np(IV) was prepared. The precipitation was washed with 1/100-diluted aqueous ammonia and separated by centrifugation and this process was repeated again to remove remaining impurities. The precipitate was dissolved in 8 mL of 6 M HNO_3 with 1% H_2O_2. The color of the solution is greenish-yellow.

Concentration of ^{237}Np in the stock solution was determined by the α-spectrometry. The solution was diluted by 1/100 and an aliquot (10 μL) of the diluted solution was sampled onto niobium plate and after the solution was dried up, the plate was set into the α-spectrometer (detector efficiency: 1.07%) and the α-spectrum was accumulated for 40,000 s. On basis of a peak at around 4760 keV, the concentration of the solution was determined as 3.76×10^{-2} mol dm^{-3}.

2.2. Preparation of stock solution of ^{239}Np(IV) tracer in 6 M HNO_3

By addition of Fe(III) and then aqueous ammonia to ^{243}Am stock solution, ^{243}Am and ^{239}Np were coprecipitated with $Fe(OH)_3$. The precipitation was separated by centrifugation and washed with purified water and separated again by centrifugation in order to remove trace contamination of ammonium anion. The precipitation was dissolved in 9 M HCl and loaded onto anion-exchange resin to remove Fe(III) by its adsorption onto the column. By washing with 9 M HCl aqueous solution, only ^{243}Am and ^{239}Np were eluted. After the volume was reduced to 10 mL, 1 mL of 10% hydroxylamine $NH_2OH{\cdot}HCl$ was added and heated for 5 min in order to reduce the neptunium to IV valence. After the acidity of the solution was adjusted to 9 M HCl, the solution was loaded onto anion-exchange column conditioned and the column was washed with 25 mL of 9 M HCl. Then ^{239}Np(IV) was eluted by washing with 20 mL of 0.1 M HCl. After the HCl solution was evaporated by heating the residue was dissolved in 10 mL of 6 M HNO_3 with 1% H_2O_2.

2.3. Determination of adsorption isotherm

Strongly basic anion-exchange resin, Dowex MSA-1 (macroporous-type, 200–400 mesh; Dow Chemical Company, USA), sieved by Muromachi Chemicals Inc. (Japan) was used after repeated stirring and decantation processes in order to achieve homogeneity of particles. In order to adjust loading to column m_{Np}/m_c, where m_c is the exchange capacity of column for dipositive cation (mol), m_{Np} the quantity of neptunium (mol). A fixed quantity of resin, ^{239}Np tracer solution and ^{237}Np solution for adjusting loading quantity were collected in polypropylene tube. On basis of the γ-ray spectrometry using a Ge semiconductor detector, concentration of ^{239}Np in the solution was determined on basis of the peak area at 277.60 keV. Also, the concentration of ^{237}Np was determined from the peak area at 86.49 keV by subtracting the contribution of ^{233}Pa (86.61 keV) which can be deduced by the peak area at 311.90 keV. The samples in polypropylene tubes were shaken in a constant-temperature bath of $30 \pm 1\,^\circ$C up to 1 day, and the supernatant was sampled after centrifuge. The γ-ray spectrometry of the supernatant samples gave concentration of liquid phase c (mol cm^{-3}). Then the concentration of resin phase s (mol cm^{-3}) was determined as $s = (c_0 V_l - c V_l)/V_s$, where V_l (cm^3) is the volume of liquid phase, V_s (cm^3) that of resin phase, and this yields the distribution coefficient $K_D = s/c$.

3. Results and discussion

3.1. Adsorption isotherm

This is the first determination on the distribution to the MSA-1 macroporous resin. Distribution coefficients (K_D) determined along with elapsed time are shown in Table 1. The value of K_D at tracer scale is 2.5×10^3, which can be compared with the value of other anion-exchange resin of $>10^3$ to Dowex 1×4 resin at 5–10N of nitric acid concentration [7]. This value of K_D is stable up to 0.47 day but decreases to 2.0 up to 0.91 day. This decrease in the distribution constants may be attributed to decrease in Np(IV) concentration accompanied with oxidation to Np(V) in 6 M nitric acid. The dependence of K_D on elapsed time indicates that the adsorption equilibrium is apparently achieved within half a day. Thus the values at 0.16 day were adopted in the present study. The distribution coefficient decreases with increasing the loading quantity of neptunium from $K_D = 2.5 \times 10^3$ ($m_{Np}/m_c = 1.4 \times 10^{-15}$; tracer scale) to $K_D = 5.1 \times 10^2$ ($m_{Np}/m_c = 0.29$).

The K_D values are plotted in a form of the adsorption isotherm (Fig. 1a). The dashed-dotted line assumes the linear equilibrium without dependence on the solution concentration. This plot supports the non-linear isotherm for Np(IV). The concentration range for the isotherm is extraordinarily large so that

Table 1
Distribution coefficients K_D of neptunium(IV) to anion-exchange resin MSA-1 in 6 M HNO_3

Sample	m_{Np}/m_C	$K_D/10^3$		
		0.16[a]	0.47[a]	0.91[a]
1	1.4×10^{-15}	2.5	2.5	2
2	1.6×10^{-3}	2.3	2.1	1.9
3	2.9×10^{-2}	0.53	0.55	0.53
4	2.9×10^{-1}	0.51	0.52	0.52
k_0		2.5×10^3	2.5×10^3	2.0×10^3
s_{max}		1.0	1.0	1.0

Parameters k_0 and s_{max} are determined in Fig. 1b according to Langmuir adsorption isotherm equation.

[a] Elapsed time/day.

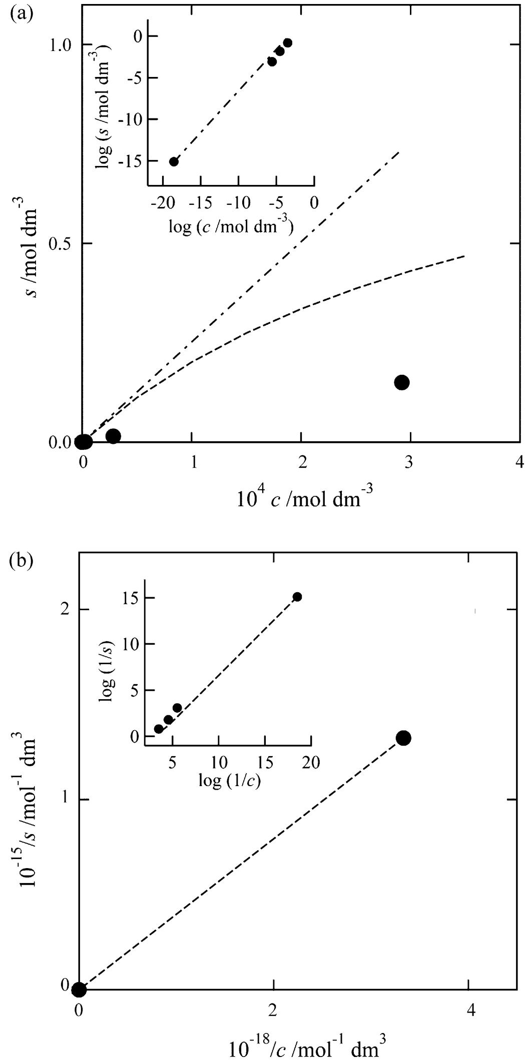

Fig. 1. Result of equilibrium measurement of neptunium(IV) with anion-exchange resin MSA-1 in 6 M HNO_3. Elapsed period: 0.16 day. Dashed-dotted line indicates $s = k_0 c$ where $k_0 = 2.52 \times 10^3$ is determined at tracer scale. Dashed curve indicates Langmuir-type isotherm with $k_0 = 2.52 \times 10^3$ and $s_{max} = 1.0$. Since the concentration range is extraordinarily large due to inclusion of tracer scale, log-scaled plot is also shown (inset): (a) adsorption isotherm; (b) Langmuir-type plot.

the double logarithm plot (Fig. 1a, inset) of the isotherm is also required, since the isotherm is to be incorporated into estimation of equilibrium at each stage of chromatography.

3.2. Numerical calculation of elution curve of anion-exchange chromatography at highly loaded state

Guiochon et al. [11] reported numerical calculations on elution curves of highly loaded conditions, and summarized effects of various parameters to elution curves. On basis of our theoretical study *n* on elusion process of thorium(IV) [13], two main equations governing the chromatography are the solution of advective-diffusion equation as

$$C_j^{n+1} = B_1 C_{j-1}^n + B_2 C_j^n + B_3 C_{j+1}^n + B_4 \left(\frac{\partial S}{\partial T}\right)^{n+1} \tag{3}$$

where $B_1 = \frac{F_0}{\varepsilon}\frac{\Delta T}{(\Delta Z)^2} + \frac{U}{\varepsilon}\frac{\Delta T}{\Delta Z}$, $B_3 = \frac{F_0}{\varepsilon}\frac{\Delta T}{\mathrm{Pe}(\Delta Z)^2}$, $B_2 = 1 - B_1 - B_3$, $B_4 = \frac{\varepsilon - 1}{\varepsilon}$,$\varepsilon$ is void ratio, Pe is the Peclet number. The differential form of the Langmuir-type kinetics is

$$\left(\frac{\partial S}{\partial T}\right)^{n+1} = k_\mathrm{s}\left(1 - \frac{c_0 S_j^n}{s_\mathrm{max}}\right) C_j^n - k_\mathrm{d} c_0 S_j^n \tag{4}$$

where S_j^n is given by

$$S_j^n = S_j^{n-1} + \left(\frac{\partial S}{\partial T}\right)^n \Delta t \tag{5}$$

In the calculation procedure, $(\partial S/\partial T)^{n+1}$ is determined using S_j^n and C_j^n at the previous time step according to Eq. (4). S_j^{n+1} and C_j^{n+1} are successively calculated at the next time step according to Eqs. (3) and (5). Typical conditions used in the calculation are: column of Ø1.0 cm × 3.7 cm, void ratio of 0.65, flow rate of 0.637 cm/min, $D = 6 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, $k_0 = 2.5 \times 10^3$, $k_\mathrm{s} = 1.3\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, time required for injection is 382 s, Resin is MSA-1 (200–400 mesh), column temperature is 30 °C.

Fig. 2(left) shows the elusion curves of neptunium(IV) compared with these of thorium(IV) (right) depending on loading $m_\mathrm{M}/m_\mathrm{c}$ (M = Np, Th). As shown in the result of thorium(IV), there is an excellent agreement of calculation based on this model with the experimental result [13]. In the result of neptunium(IV), the shape of the elusion curve changes from symmetric Gaussian-type curve (Np-1; tracer scale) to asymmetric curve of "tailing-type" or "frontal-type" (Np-5). This is the behavior of the non-linearity of adsorption isotherm shown in Fig. 1a.

Fig. 3 shows the elusion curves calculated for more highly loaded conditions. As shown in the figure, loading more than 10% leads to rapid breakthrough and severe tailing of neptunium which lowers purity and yield in purification procedures. If one may have a need to purify neptunium from thorium impurity, the column operation condition can be discussed in Figs. 2 and 3. Comparing the elusion curve of Np-5 (the loading is 5% to the resin capacity) with experimental curve of Th-1 (tracer scale) in Fig. 2, the tailing of thorium(IV) finished at 5×10^4 s and just after that the elusion of neptunium(IV) begins. The loading of more than 15% (Fig. 3) no longer results in contamination of

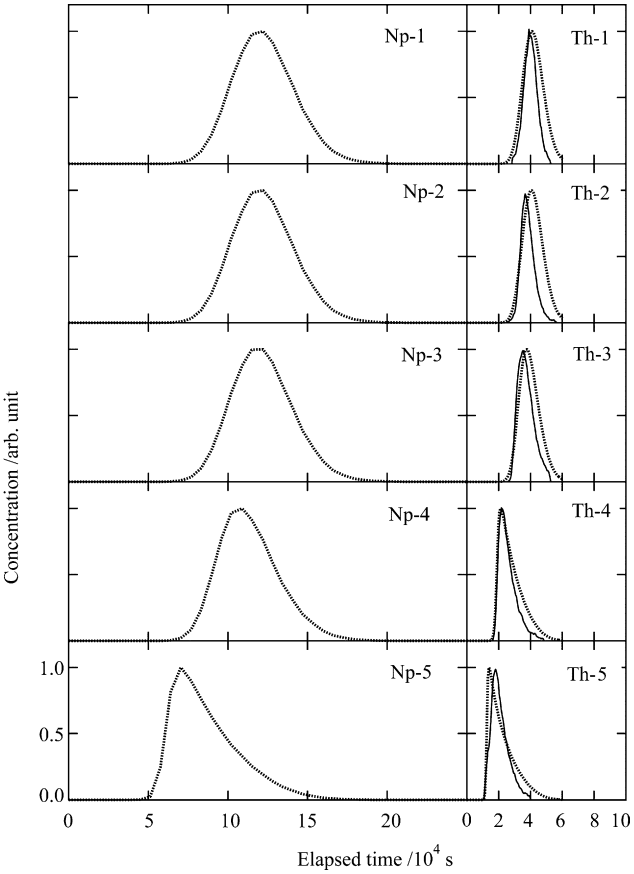

Fig. 2. Calculated elusion curves for neptunium(IV) at various loading quantity as $m_\mathrm{Np}/m_\mathrm{c} = 1 \times 10^{-10}$ (tracer scale; Np-1), 1×10^{-4} (Np-2), 1×10^{-3} (Np-3), 1×10^{-2} (Np-4) and 5×10^{-2} (Np-5). Parameters in calculation—column size: Ø10 mm × 37 mm, flow rate: $1.9\,\mathrm{mL\,min^{-1}\,cm^{-2}}$, $k_0 = 2.52 \times 10^3$ and $s_\mathrm{max} = 1.0$. The calculated elusion curves of Np(IV) are compared with the elusion curves experimentally obtained (Th-1–5; solid curves) and calculated elusion curves (Th-1–5; dotted curves). Parameters for thorium are same with the exception of kinetic parameters.

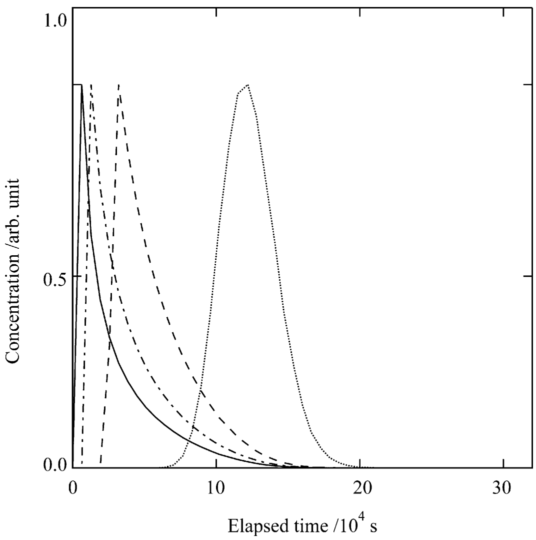

Fig. 3. Calculated elusion curves for neptunium(IV) at various loading quantity as $m_\mathrm{Np}/m_\mathrm{c} = 0.5$ (solid curve), 0.25 (dashed-dotted curve) and 0.15 (dashed curve) compared with 1×10^{-10} (dotted curve). Used parameters are identical to these shown in Fig. 2.

neptunium(IV) by thorium(IV), in spite of the large difference between $K_D = 2.5 \times 10^3$ for neptunium(IV) and $K_D = 2.2 \times 10^2$ [7] or 2.5×10^2 for thorium(IV) [13].

Conclusively, this is the first study of adsorption isotherm of neptunium(IV) in nitric acid to anion-exchange resin. The value of K_D at tracer scale is 2.5×10^3, which can be compared with the value of other anion-exchange resin of $>10^3$ to Dowex 1 × 4 resin at 5–10N of nitric acid concentration [7]. The elusion curve of neptunium(IV) from MSA-1 anion-exchange resin was successfully calculated at wide range of the loading from tracer to 50% of resin capacity. According to the result, more than 15% of the loading may cause contamination of e.g. thorium(IV) in spite of one order of difference in the distribution constants at the tracer scale.

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