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PURIFICATION OF THORIUM FROM URANIUM-233 PROCESS RESIDUE

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ABSTRACT

Thorium-229 can be used to produce ^{213}Bi. Researchers in phase I human trials are investigating the use of antibodies labeled with ^{213}Bi for selectively destroying leukemia cells. Other types of cancer may potentially be treated using similar approaches. Crude ^{229}Th was liberated from Rachig rings by sonication in 7.5 M HNO_3 followed by filtration. Contaminants included significant levels of uranium, a number of other metals, and radiolytic by-products of di-(2-butyl) phosphoric acid extractant (which was used in the original separation of ^{233}U from thorium). Thorium was selectively retained on Reillex HPQ anion-exchange resin from 7.5 M HNO_3 at 65°C, where U(VI), Ac(III), Fe(III), Al(III), Ra(II), and Pb(II) were eluted. Thorium and uranium isotherms on Reillex HPQ are reported. The thorium was then easily eluted from the bed with 0.1 M HNO_3. To overcome mass transfer limitations of the resin, the separation was conducted at 65°C. The resin stood up well to use over several campaigns. Other researchers have reported that HPQ has excellent radiological and chemical stability. The eluted thorium was further purified by hydroxide precipitation from the organic contaminants. This process yielded 65 mCi of ^{229}Th.

INTRODUCTION

Alpha particle emitters are of considerable interest for radioimmunotherapy applications. Due to their short range in tissue (a few cell diameters) and high linear-energy

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transfer, alpha particles may be especially suited for targeting micrometatases and single tumor cells such as leukemia, AIDS, and other bloodborne diseases.[1-3] Candidate radioisotopes include ^{212}Bi, ^{225}Ac, ^{211}At, ^{213}Bi, ^{256}Fm, ^{223}Ra, and ^{149}Tb. Among the list of potential radionuclides for these applications are alpha-emitting ^{212}Bi and ^{213}Bi. Bismuth-212 occurs in the natural decay series of ^{232}Th. The major drawback of using ^{212}Bi is the emission of a relatively intense and very high energy gamma ray (2.6 MeV, 38%). However, ^{213}Bi, a decay daughter of ^{229}Th, emits a 1.5-MeV gamma ray with an intensity of only 2%. Thus, ^{213}Bi, rather than ^{212}Bi, may be preferred for therapy. Bismuth-213 is currently being used as a substitute for ^{212}Bi in clinical studies conducted at Memorial Sloan-Kettering Cancer Center. Scheinberg (1997)[4] reported very high selectivity of ^{213}Bi-HuM195 in myeloid leukemia patients. He reported a target-to-background ratio of greater than 10,000 to 1.

Thorium-229 is the source radioisotope for both ^{213}Bi and ^{225}Ac. The isotopes ^{225}Ac and ^{213}Bi have half-lives on the order of days and minutes, respectively, whereas the half-life of ^{229}Th is 7340 y. Thus, ^{229}Th can be used to produce ^{225}Ac and ^{213}Bi for long periods of time. Thorium-229 is a decay daughter of ^{233}U but may also be produced by irradiation of ^{226}Ra; however, the ^{229}Th product from irradiation of ^{226}Ra would be very difficult to handle due to the radiation field produced from large quantities of ^{228}Th contaminant and its decay daughters.

This paper describes the separation and purification of thorium from a Raschig ring residue. We describe isotherm and mass transfer properties of the anion-exchange resin, Reillex HPQ, that was used to purify the thorium. The resin performed well over several campaigns and was contacted with over a hundred millicuries of ^{229}Th and associated decay products. This process is a pilot for separating ^{229}Th from ^{233}U materials stored at the National Repository for ^{233}U at Oak Ridge National Laboratory (ORNL). Future work will focus on the direct separation of ^{229}Th from ^{233}U. Essentially, the entire supply of ^{229}Th in the Western Hemisphere exists in ^{233}U stored at ORNL. Due to a number of factors, extraction of ^{229}Th from ^{233}U presently appears to be the most expeditious route available for producing research and medicinal quantities of ^{213}Bi and ^{225}Ac.

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METHOD AND MATERIALS

HPQ resin (30–60 mesh) was received from the manufacturer and extensively washed with distilled water in conical separators to remove fines. The resin was then stored in a dilute sodium chloride solution for at least 1 month with periodic washes to allow full hydration. Prior to use, the resin was converted to the nitrate form by washing with 10 *N* nitric acid until chloride could not be detected in the effluent using silver nitrate solution. Dry weights were measured by drying in an oven for 24 h at 65°C followed by evacuation over Drierite (EM Science, Gibbstown, NJ) until a constant weight was obtained.

Elements in the thorium residue were measured using inductively coupled plasma mass spectroscopy (Fisons Plasmaquad 2, Beverly, MA). A surrogate for the thorium residual used in initial tests consisted of Al (393 μg/mL), Ca (33 μg/mL), Na (740 μg/mL), Fe (364 μg/mL), Zn (45 μg/mL), ^{232}Th (2580 μg/mL), and ^{238}U (180 μg/mL) in 7.5 *M* HNO_3.

Distribution coefficients for the resin were measured by contacting the resin with thorium or uranium solution for 24 h in a temperature-controlled shaker bath. Mass transfer experiments were measured by contacting the resin with solution on a reciprocating, temperature-controlled shaker (AquaTherm, New Brunswick Scientific, New Brunswick, NJ).

Thorium was purified from the residue materials using anion exchange in 7.5 *M* HNO_3 at 65°C. An HPQ column (500-mL bed volume) was initially washed with three column volumes of 7.5 *M* HNO_3. After loading the thorium residue solution onto the column, uranium and other materials were removed with 8 column volumes of 7.5 *M* HNO_3. Passing 0.1 *M* HNO_3 solution through the column then eluted the thorium. Thorium and uranium were measured using inductively coupled plasma atomic emission spectroscopy (Perkin-Elmer Corp., ICP400, Norwalk, CT) or gamma counted using an EG&G Ortec gamma spectrometer.

The conditions chosen for the thorium separation were 7.5 *M* HNO_3, 65°C, and half-loading of the resin bed. A 2-cm-diameter glass column (500-mL bed volume) was filled with HPQ resin (30–60 mesh). This resin was converted to nitric acid and placed in a glove box. The load, wash, and elution solutions were pumped to the top of the column after being

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warmed to 65°C. The column sequence consisted of 5 L of load (10 column volumes), 4 L of 8 *M* HNO_3 wash (8 column volumes), and 1 L of 0.1 *M* HNO_3 (2 column volumes) for elution of thorium.

RESULTS AND DISCUSSION

Strong-acid anion exchange was selected because of its potential high selectivity for lower actinide elements.[5] In nitric acid, thorium forms a strong, negatively charged complex. Uranium forms a complex that is much weaker than that of thorium. In the present case, thorium was present at high concentration relative to that of uranium (Table 1). Buchanan and Faris reported that Th^{4+}, Np^{4+}, and Pu^{4+} bind strongly to Dowex-1 anion-exchange resin at high nitric acid concentration although UO_2^{2+} and Bi^{3+} bind less tightly.[6] Dowex-1 and other quaternary amine resins have demonstrated instability in strong nitric acid under conditions that include elevated temperature, column diameters exceeding 10 cm, and pressures above atmospheric. Incidents have resulted in accidents and fatalities.[7] Reillex HPQ [poly-4-vinylpyridine methylchloride quaternary salt, $(C_3H_{10}NCl)_n$] was selected as the anion-exchange resin for this work due to its safety and resistance to radiolysis as noted by Marsh, who reported that Reillex HPQ was more chemically stable than traditional quaternary amine resins.[8]

Figure 1 depicts distribution coefficients of thorium and uranium at different concentrations of nitric acid on the HPQ resin. The potential for separation of these metals is apparent, especially as the nitric acid concentration approaches 8 *M*. The nitric acid concentrations were varied and processed in duplicate. Samples were placed in a shaker/water bath for 24–48 h. Distribution coefficients were calculated using the following equation:

$$k_d = (C_i - C_f)\frac{V}{mC_f} \quad ,$$

where

C_f = *final liquid concentration* (mg/mL),

C_i = *initial liquid concentration* (mg/mL),

m = *dry weight of resin* (g),

V = *volume of liquid* (mL).

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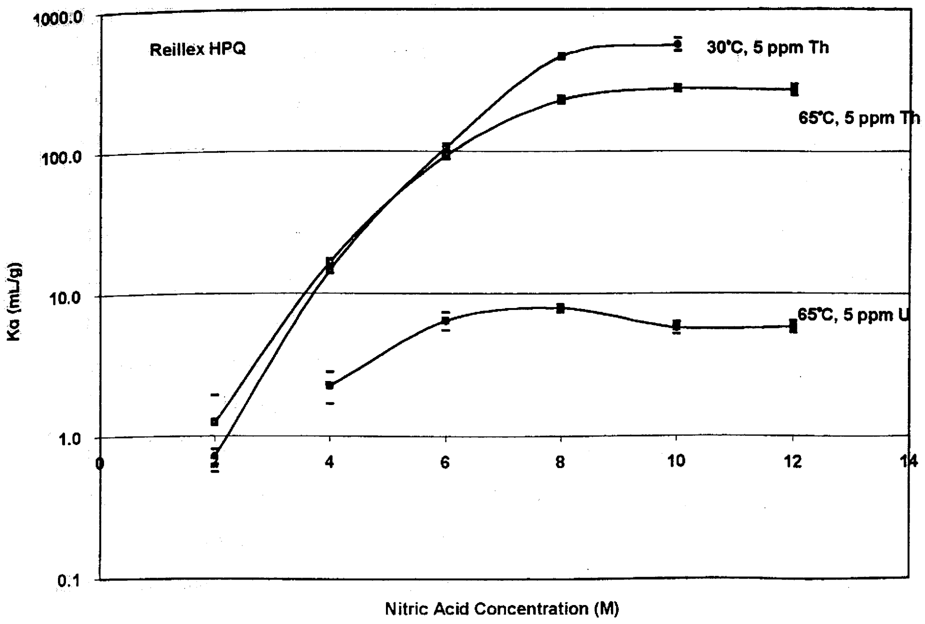

FIGURE 1. Distribution coefficients for thorium and uranium on Reillex HPQ resin as a function of nitric acid concentration.

This information provides insight into the complex formation of the Th^{4+} ion with the nitrate ion, which generally proceeds in successive steps: $Th(NO_3)^{3+}$, $Th(NO_3)_2^{2+}$, $Th(NO_3)_3^{+}$, $Th(NO_3)_4$, $Th(NO_3)_5^{-}$, $Th(NO_3)_6^{2-}$. When the species is complexed such that it forms a negative ion, the complex will be retained on the anion resin. Equilibrium values for the complexation of Th^{4+} or UO_2^{2+} with nitric ions indicate weak complex formation. Only a few of the successive equilibrium values (β) are published: $Th(NO_3)^{3+}$ $\log \beta_1 = 0.45$, $Th(NO_3)_2^{2+}$ $\log \beta_2 = 0.15$,[9] $Th(NO_3)^{3+}$ $\log \beta_1 = 0.78$, $Th(NO_3)_2^{2+}$ $\log \beta_2 = 1.89$, $Th(NO_3)_3^{+}$ $\log \beta_3 = 2.89$, and $Th(NO_3)_4$ $\log \beta_4 = 3.63$.[10] From the K_d values shown in Figure 1, it appears that the $Th(NO_3)_5^{-}$ and/or $Th(NO_3)_6^{2-}$ complexes form in 6 *M* HNO_3 or higher concentrations due to the retention of the thorium on the resin. If it is assumed that the $Th(NO_3)_5^{-}$ forms in 6 *M* HNO_3 such that the $[Th^{4+}] = [Th(NO_3)_5^{-}]$, the $\log k_{eq} = -3.9$ roughly agrees with the published data.

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A number of mechanisms were important for thorium purification and included temperature, particle size, and affinities of the resins for uranium and thorium solutes. The resin had a much stronger affinity for thorium than for uranium, and the affinities for both solutes were not significantly affected by changing the temperature from 30 to 65°C (Figure 2). Figure 3 illustrates that mass transfer is an important mechanism in thorium purification although the ion-exchange system approaches equilibrium much faster at 65 than at 30°C. The importance of mass transfer in this process is not unexpected due to the large size of the resin particles (300 to150 μm). For this range, resin diameter greatly affects mass transfer and results in less separation efficiency as the resin diameter increases.[11] The diffusion coefficient for the thorium nitrate complex is expected to be $<1.0 \times 10^{-5}$ cm/s. For molecules with high water-diffusion coefficients (typically 1.0 to 5.0×10^{-5} cm/s for small molecules), internal mass transfer is very important for particles in this diameter range. A lower diffusion coefficient could greatly increase the importance of mass transfer. Under some conditions, a large particle size is advantageous if a high flow rate is desired. Based on these experiments, column tests were conducted at 65°C.

The surrogate solution described previously was passed through a 10-mL column to determine breakthrough. Figure 4 depicts exit/feed concentration as a function of bed volume. Complete breakthrough occurred at 20 bed volumes. Figure 4 indicates that at 10 bed volumes (half-loading), the most effective separation of the uranium and thorium can be accomplished. Additional experiments revealed no significant effect of flow rate in the range of 0.7 to 3.0 L/min. Figure 5 illustrates a loading/wash/elution cycle resulting from half-loading the column with 10 bed volumes of the surrogate sample. The concentration of uranium contaminant in the thorium product has been significantly reduced.

To obtain small quantities of ^{229}Th for biological studies at ORNL, a residue from past ^{233}U processing was examined for purification. On examination, a mixture of ^{229}Th and natural thorium was present, adsorbed onto borosilicate Raschig rings (employed for criticality safety during ^{233}U operations). The residue was removed from the Raschig rings as a solution,[12] which contained a number of other metals as well as significant quantities of thorium and uranium. (See Table 1.) Figure 6 indicates that thorium was retained on the resin until elution with 0.1 M HNO_3. A small amount of breakthrough occurred as the resin

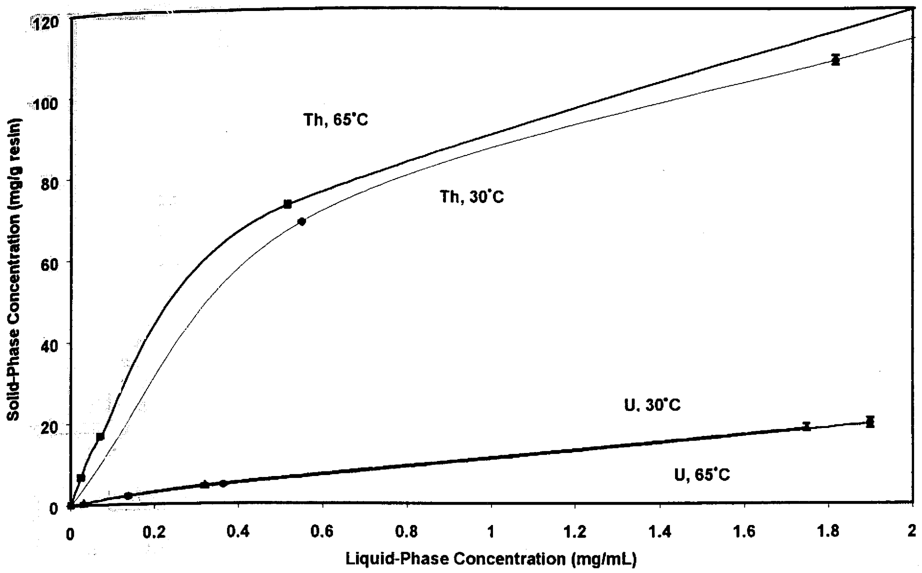

FIGURE 2. Uranium and thorium isotherms in 8 M HNO$_3$.

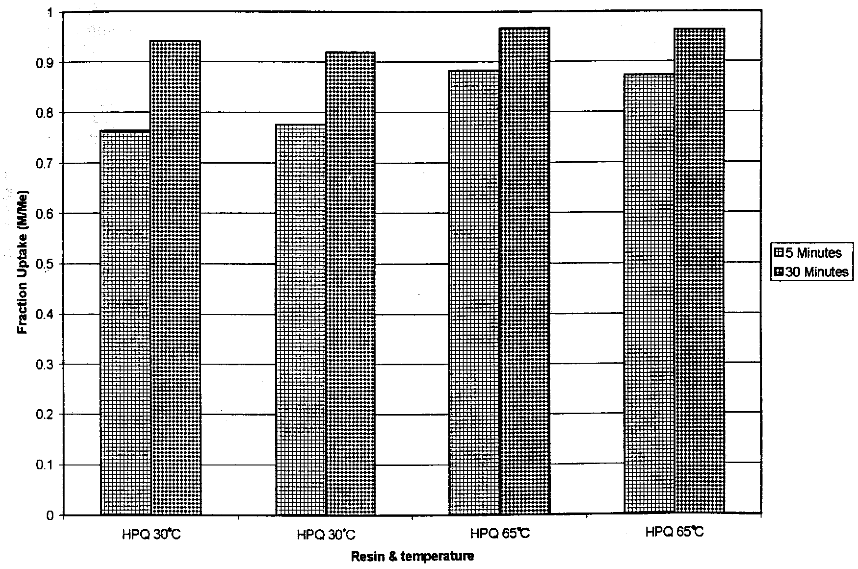

FIGURE 3. Effect of temperature on mass transfer of thorium into HPQ resin in 8 M HNO$_3$.

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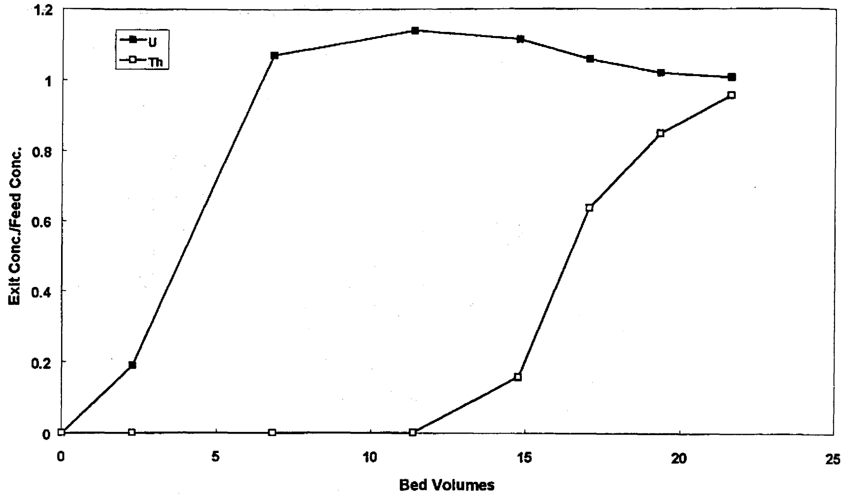

FIGURE 4. Loading of thorium and uranium surrogate solution onto 10-L column.

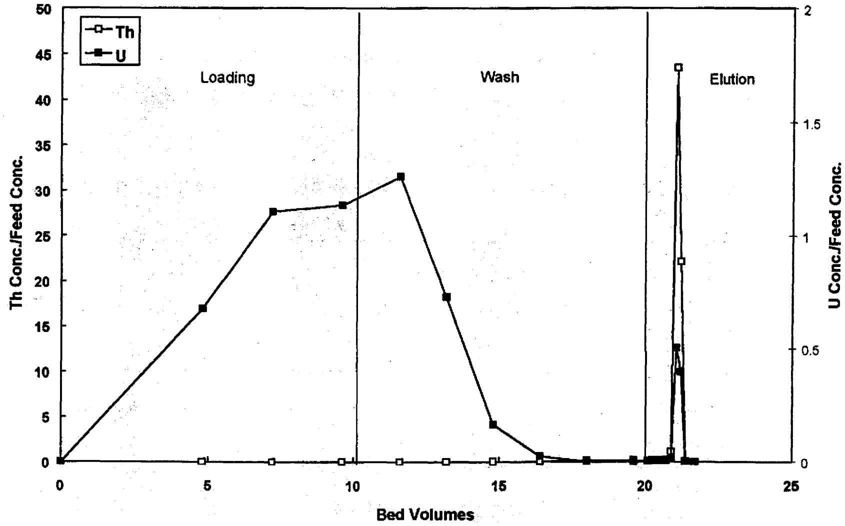

FIGURE 5. Separation of surrogate solution from half-loading the column.

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Table 1. Analysis results of the waste material rinsed from the Raschig rings prior to anion exchange and analysis results of the purified thorium sample

Element	Ring washes µg/mL (±)	Th product µg/mL (±)
Th-229	11.4 (0.1)	160 (10)
Th	2580 (2)	35300 (1530)
U	160 (2)	<0.02
Na	740 (2)	
Al	393 (10)	
Fe	364 (3)	
Zn	45 (0.2)	
Ca	33 (0.3)	
K	18 (0.6)	
Cr	4 (0.02)	<0.02
Mn	3 (0.02)	
Ni	3 (0.08)	0.14 (0.02)
Cu	2 (0.04)	0.03 (0.02)
V	0.32 (0.02)	<0.02
Ag	0.28 (0.06)	<0.02
Be	0.08	<0.02
Ba	<0.014	<0.02
Cd	<0.22	<0.02
Co	<0.144	<0.02
Mg	<0.197	
Sb	<2.2	<0.02
Pb		0.158 (0.01)
La-Lu		<0.02

was washed. This small fraction was recovered in subsequent purification efforts. A final analysis of the purified ^{229}Th solution is shown in Table 1. Approximately 15 mCi (about 15 g) of ^{229}Th (present at 0.4% in natural thorium) loaded successfully onto the 500-mL bed-volume column during each cycle. After each use, the HPQ resin was washed with distilled water and stored as nitrate form with water on the resin. There were no indications of resin instability or capacity losses after 10 batches of thorium were processed. Table 1 indicates that after purification most metals were present at below detection limits, except for lead, which is the stable decay daughter of ^{233}U and ^{229}Th.

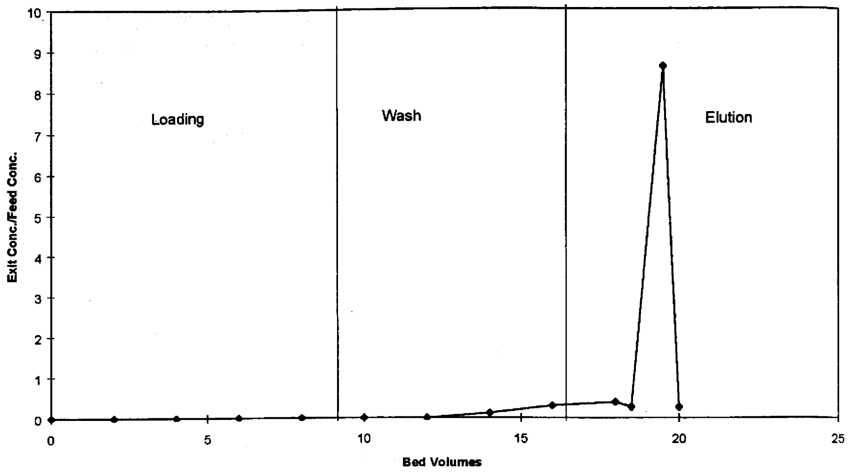

FIGURE 6. Loading, washing, and elution of ^{229}Th from waste solution on HPQ resin.

CONCLUSIONS AND FUTURE WORK

Thorium and uranium isotherms on Reillex HPQ are reported. Thorium-229 was successfully separated from ^{233}U process residuals using strong-acid ion exchange. Mass transfer limitations were overcome by increasing the temperature of the process to 65°C. There were no indications of resin instability, and the capacity remained constant after 10 separations. The results of this work indicate that strong-acid ion exchange with HPQ resin is a viable method for separating thorium from uranium. Use of HPQ, moderate temperatures, and gravity feed in a small column aided safe operation. Future experiments will focus on separating ^{229}Th from the stored ^{233}U, although the higher relative concentrations of uranium may challenge the present process. Ongoing investigations are also focused on separating ^{225}Ac and ^{213}Bi from thorium.

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