

Adsorption of Uranium (VI) Ion on 1-Aza-12-Crown-4 Synthetic Resin with Styrene Hazardous Material

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Abstract

1-Aza-12-crown-4 macrocyclic ligand was combined with styrene (2th petroleum in 4th class hazardous materials) divinylbenzene copolymer having 1%, 2%, 3%, and 6% crosslinks by a substitution reaction, in order to synthesize resin. These synthetic resins were confirmed by chlorine content, elementary analysis and IR-spectrum. As the results of the effects of pH, equilibrium arrival time, crosslink of synthetic resin, and dielectric constant of a solvent on uranium ion adsorption for resin adsorbent, the uranium ion showed high adsorption at pH 3 or over and adsorption equilibrium of uranium ion was about 2 hours. In addition, adsorption selectivity for the resin in methanol solvent was the order of uranium (UO_2^{2+}) > iron (Fe^{3+}) > lutetium (Lu^{3+}) ions, adsorbability of the uranium ion was in the crosslinks order of 1%, 2%, 3%, and 6% was increased with the lower dielectric constant.

Key words: 1-Aza-12-crown-4, Macrocyclic Ligand, Styrene, Crosslink, Divinylbenzene

1. Introduction

Every country in the world caused exorbitant environment destruction during the courses of indiscreet energy development to secure energy sources. Some countries with insufficient natural resources strove to solve their energy-short problem through the undeveloped countries. Korea also has nearly empty natural resources, and maybe reaches a big deadlock in providing the energy in future if there is no epochal alternative plan. On account of this, one of perpetual solutions to preserve the environment as best as possible and to secure the production of energy is the advent of atomic energy industry using uranium. Korea holds 0.42-1.2%^[1] of uranium within coal of low quality in Goisan, waste of phosphatic fertilizer and so on, according to producing districts. Consequently, effective separation and withdrawal must be guaranteed without delay in respect of disposal of radioactive waste matter and natural resource preservation.

Macrocyclic compounds comprise alkali, alkaline earth metal, transition metal, heavy metal ions and sta-

ble complexes^[2] by the properties of donor atom forming a ring. A method for separating metal ions from these kinds of complexes was initiated from the studies on the equilibrium of a solvent extraction system^[3].

Grimsley et al.^[4] synthesized a chain of nitrogen-oxygen donor (cryptand) macrocyclic ligands, and examined complex formation of the ligands, transition metal ions and post-transition metal ions for finding the macrocyclic ligands to select specific metal ions and for verifying the causes to exist the selectivity.

Moreover, whereas a method to separate metal ions by using neutralization or precipitation gives a low separating effect due to high solubility of the metal ions and has some technical difficulties, another method to adsorb and separate the metal ions by using minerals is being used as a variety of forms because of easy application without requiring high technology or complicated equipment^[5].

Bombieri et al.^[6] identified the structure of lanthanoid and uranium complexes through X-ray analysis, and verified that all oxygen atoms on a same plane are combined with uranium ions. Meanwhile, studies have been actively under way for preventing environmental contamination due to the loss of toxicant macrocyclic compounds possibly produced in the chromatography moving the solvent extraction or the macrocyclic compounds into a fixed phase or a mobile phase^[7], and for

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developing a separation method with an excellent separating effect. Blausius et al.^[8] synthesized resins by condensing various macrocyclic compounds and formaldehyde, or copolymerizing divinylbenzene and macrocyclic compounds containing vinyl radicals. They also substituted cryptand series for styrene-1,4-divinylbenzene (styrene-DVB), and studied the separation of metal ions by using these resins. And, cryptand series resin and metal ion adsorption are dependent on the characteristics of ion diameter-cavity radius.

Styrene^[9] is 2th petroleum in 4th class hazardous materials, as a colorless and toxic benzene derivatives, it has a distinctive smell. It dissolves in alcohol, ether and carbon disulfide is insoluble in water. It forms a colorless solid matter by polymerization.

On the other hand, the analysis of micro impurities in uranium dioxide is recognized as very important in the production and quality control of nuclear fuel appropriate to the atomic power generation. Especially, in senses of the lanthanoid elements having a large cross-sectional area absorbing neutrons and the resource collection, the separation and condensation of a very small amount of uranium should be necessarily studied in the field of separating nuclear fuel and nuclear substances.

Therefore, this study synthesized^[10] and chloromethylated the styrene-DVB copolymer available to selectively separate and collect uranium from transition metals. Hereupon, the chloromethylated copolymers were chemically combined with 1-aza-12-crown-4 (1-aza-12-C-4) macrocyclic ligand to produce a new functional resin, and then, the adsorption^[11-14] of uranium (UO_2^{2+}), iron (Fe^{3+}), and lutetium (Lu^{3+}) ions was examined.

2. Experimental Section

2.1. Materials

1-Aza-12-crown-4, uranium nitrate, lutetium nitrate and styrene were purchased from Aldrich Co., special grade 1,4-divinylbenzene (55%), 1,4-dioxane and benzoyl peroxide were bought from Donggyeong Hwa-seong, and iron nitrate, benzene, toluene, potassium iodide, etc. were used with general reagents.

An infrared ray spectrum was analyzed through Shimadzu IDP-440 A, and element analysis were performed using Model 1108 of Carlo-Erba Co. pH was measured through a calomel glass electrode of Corning

pH meter 320, and a quantitative analysis of Cl^- was conducted by Orion chloride ion-selective electrode. The uranium (UO_2^{2+}), iron (Fe^{3+}), and lutetium (Lu^{3+}) ions were measured through ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) Lab-test 710 type and Coleman spectrophotometer (350~750 nm).

2.2. Synthesis of Styrene-DVB Copolymer

For the synthesis^[10] of styrene-DVB copolymer, a 500 mL triple mouth flask equipped with a reflux condenser and a thermometer was connected with a nitrogen gas injection tube, and was installed with an apparatus to confirm the stirring speed. Distilled water 250 mL was added into the triple mouth flask. The added amount of resin was varied according to the crosslinks such as follows : styrene 99 mL/DVB 1.8 mL for 1% of the crosslink, styrene 98 mL/DVB 3.6 mL for 2%, styrene 97 mL/DVB 5.40 mL for 3%, and styrene 94 mL/DVB 10.8 mL for 6%. Benzoyl peroxide 1 g as an initiation reagent, NaCl 10 g as stabilizer, gelatin 0.5 g and Arabic rubber 1.5 g were added and stirred at 1,200 rpm with being reacted at 90°C for 6 hours, and then cooled. Supernatant was removed, and the copolymer was washed with methanol, distilled water and methanol in order.

2.3. Chlorination of Copolymer

Styrene-DVB copolymer was dried at 110°C for more than 12 hours, and 5 g of which and 100 mL of chloroether were swollen at room temperature for 2 hours in a 250 mL flask. Zinc chloride 2 g was dissolved in chloroether 25 mL, which was added to and placed in the flask. The supernatant was removed, and 100 mL of dioxan-distilled water mixture (70:30) was added to the flask and stirred for an hour for washing the copolymers during the stirring process. Then, the washed copolymers were dried at 50°C for 4 days.

2.4. Function Reaction of Copolymer

Each 2.83 g of chloromethylated 1%, 2%, 3%, and 6% styrene-DVB copolymers was mixed with 50 mL of benzene, and then stirred, refluxed and swollen at boiling temperature for 2 hours. After remaining benzene was removed, 50 mL of toluene, 0.75 g of KI and 1.76 g of 1-aza-12-C-4 macrocyclic ligand were added, stirred and refluxed at 55°C for 30 hours under nitrogen con-

dition, which was cooled at room temperature and filtered. The washing process was conducted with 2 M hydrochloric acid, distilled water, 1 M sodium hydroxide and distilled water in order. Finally, the copolymer was washed several times with methanol and then dried in the air, to get 1-aza-12-C-4-styrene-DVB resin (called resin or cryptand ion exchange resin) having 1%, 2%, 3%, and 6% crosslinks. The size of resin cavity was 300-400 mesh.

2.5. Experimental Method

It was measured to take the content of chloro according to crosslink in the process of synthesizing the resin using chloride ion-selective electrode. It was confirmed that the synthesis of resins is a IR-spectrum due to KBr disc method and the ultimate resins that each is composed of 1%, 2%, 3%, and 6% crosslinks analyzed the content of elements like C, H, N, O using elementary analysis. Also, $\text{UO}_2(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, and $\text{Lu}(\text{NO}_3)_3$ solutions of 3.0 mM were controled the pH by dilute nitric acid or sodium hydroxide to investigate the adsorption character of metallic ion according to pH, equilibrium arrival time, crosslink, and dielectric constant of solvent.

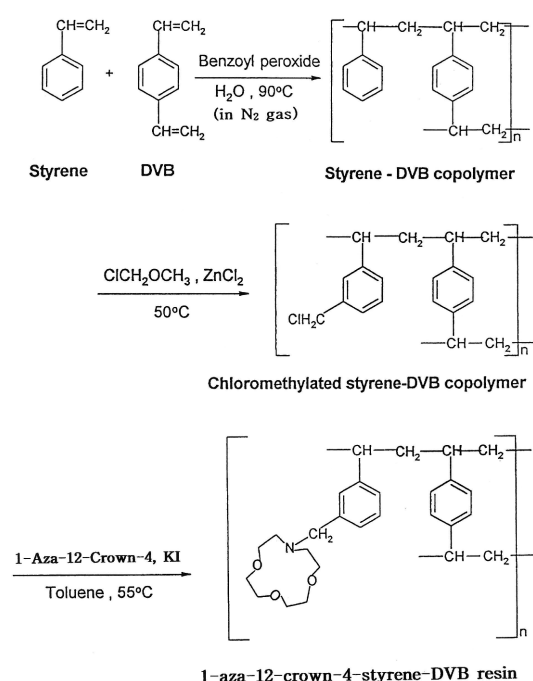
The resin having 1% crosslink was added 1 g to each solution, and solutions were filtered after being stirred for two hours in room temperature. Each ion of uranium, iron, lutetium was quantitatively analyzed using ICP-AES under the circumstances of dilute nitric acid.

3. Results and Discussion

3.1. Confirmation of Resin

Styrene-DVB copolymer was synthesized^[10] as shown in Scheme 1 through suspension polymerization in an aqueous solution with benzoyl peroxide as an initiation reagent that is commonly used to synthesize conventional polymerized-type ion exchange resin.

To measure the content of chlorine according to crosslinks during the copolymerization, HCl produced through heat hydrolysis was absorbed into distilled water, and the chlorine content was measured using chlorine ion-selective electrode as shown in Table 1. With the increase of the crosslink, the chlorine content was decreased. This can be understood by the fact that the increase of the crosslink increased the DVB content and consequently increased the crosslink density, and



Scheme 1. Synthesis of 1-aza-12-crown-4-styrene-DVB resin

Table 1. Chlorine contents in copolymer (3-chloromethyl styrene-DVB)

Degree of crosslinking (%)	Percent of chlorine
1	12.35
2	11.86
3	10.75
6	10.18

also the porosity according to the increase of the crosslink density of copolymers became lower and reduced the chlorine content during the substitution reaction.

Table 2 is an IR-spectrum obtained through KBr disc method. As a result that the chloromethylated styrene-DVB copolymer was combined with 1-aza-12-C-4, the 1-aza-12-C-4 was maybe displaced because there were no N-H peak near 3400 cm^{-1} and C-Cl absorption peak around 650 cm^{-1} . Moreover, the induction of the macrocyclic ligand brought stretching vibration peaks of strong and wide C-O-C and C-N-C in 1265 cm^{-1} , and a new stretching vibration peak of sharp C-N.

Chloroether acts as chloromethylation agent and solvent in a chloromethylation process. Because the copol-

Table 2. IR-spectrum of 1%, 2%, 3%, and 6% crosslinked styrene-DVB copolymer (A), 1-aza-12-C-4 (B), and 1% crosslinked 1-aza-12-C-4- styrene-DVB resin (C)

Kinds of resin function group	Frequency (cm ⁻¹)		
	(A)	(B)	(C)
N-H	---	3400	---
Aromatic (C-H)	3100-3200	---	3100-3200
Aliphatic (C-H)	2900-2950	2800-2950	2850-2950
Benzene ring (C=C)	1460-1510	---	1460-1510
C-O-C C-N-C	---	1100-1200	1265
Mono Substitution (4 peaks)	1800-1960	---	1800-1960
C-Cl	650	---	---
C-N	---	---	1024

ymers having 1% and 2% crosslinks were greatly swollen by chloroether, the copolymers lost a round shape and turned into a distorted shape due to the gelation during the reaction. The chloromethylated copolymers express a light yellowish white color when the crosslink is low, but the copolymers of 3% and 6% crosslinks are shown to be light brown.

In addition, Table 3 exhibited the results of the resin synthesis according to the size of crosslink and the elementary analysis. When the crosslink became increased, the nitrogen content was decreased. As the results shown like this, the increase of the crosslink also brought on the increase of the DVB content, which subsequently decreased the chlorine content during the substitution reaction because the porosity was lowered due to the increase of crosslink density. Consequently, this influenced the macrocyclic ligand to be displaced, and caused the decrease of the nitrogen content.

Table 3. Compositions of 1-aza-12-C-4-styrene- DVB-resins with various crosslinked

Degree of crosslinking (%)	C (%)	H (%)	N (%)	O (%)
1	76.92	8.37	3.32	11.39
2	76.96	8.38	3.26	11.40
3	77.00	8.40	3.18	11.42
6	77.05	8.44	3.06	11.45

3.2. Effects of pH

To confirm the acidic zone possible to adsorb metal ions for the resin, uranium, lutetium, and iron ions of 3.0 mM were stirred in methanol solvent for 2 hours, and the adsorption characteristics were examined according to the pH changes of the resin representatively having 1% of crosslink as shown in Fig. 1. The adsorbability of uranium ion became slowly increased and the stable complexes of uranium were rapidly increased at pH 3 or over. The adsorbability of iron ion was gradually increased between pH 3 and pH 4, and the stable complexes of iron was suddenly increased at pH 4 or over. This phenomenon can be explained by the assumption that because the cryptand resin is basic amine, the nitrogen atom of the resin becomes protonated in a strong acidic solution (pH<2) and obstructs the adsorption of the metal cations, however, uranium and iron ions with the products generated from hydrolysis of the non-protonated resin form stable complexes^[11] and yield high adsorptivity in a weak acidic solution (pH>3). On the other hand, lutetium ion cannot form a complex even in a strong acidic zone, and the complex formation is not easy because +3 value rare earth element ions are strongly hydrated and this hydration energy should be overcome to form cryptand resin and complexes. Hydration enthalpies^[15] of uranium and

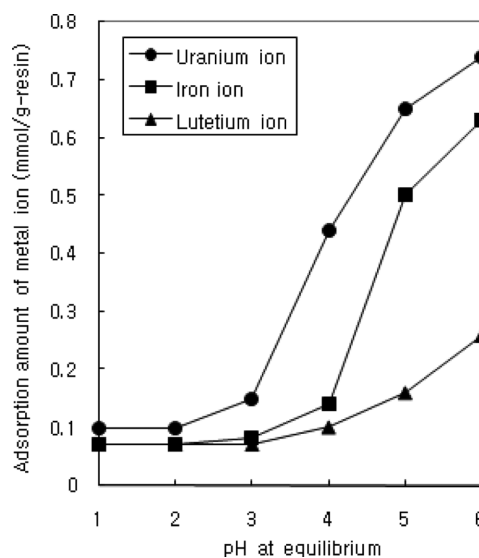


Fig. 1. Adsorption rate of UO_2^{2+} , Fe^{3+} , and Lu^{3+} on 1% crosslinked 1-aza-12-C-4-styrene-DVB resin at various pH in methanol (concentration : 3.0 mM, time : 2 h).

iron ions easily forming the complexes were -2990.5 kJ/mole and -3285.3 kJ/mole, respectively, and the hydration enthalpy of lutetium ion not well forming the complexes was -4062.2 kJ/mole. The cryptand resin used in the current study was alkaline, and therefore, the adsorption experiment was performed only in the acidic solution under pH 6.

3.3. Effects of Equilibrium Arrival Time

One of necessities to be resin is to quickly reach the adsorption equilibrium. Accordingly, Fig. 2 showed the adsorption equilibrium time of uranium, lutetium and iron ions of 3.0 mM taken to reach the resin having 1% crosslink in methanol solvent of pH 6. The adsorptivities were as large as 74% and 63% each for uranium and iron ions easily forming resin and complexes^[11], but 26% for lutetium ion that did not form the cryptand resin and complexes well. Also, the adsorbability of each metal ion to the resin showed to decrease in an order of uranium > iron > lutetium ions. In investigating the ratios of the size of UO_2^{2+} (2.38 Å), Fe^{3+} (1.75 Å), and Lu^{3+} (2.23 Å) to the resin (2.45 Å) by a theory^[16] that the electrostatic attraction is very large and forms the stable complexes well when the ratios of the metal ion size to the resin cavity is between 0.7–0.9 the ratios

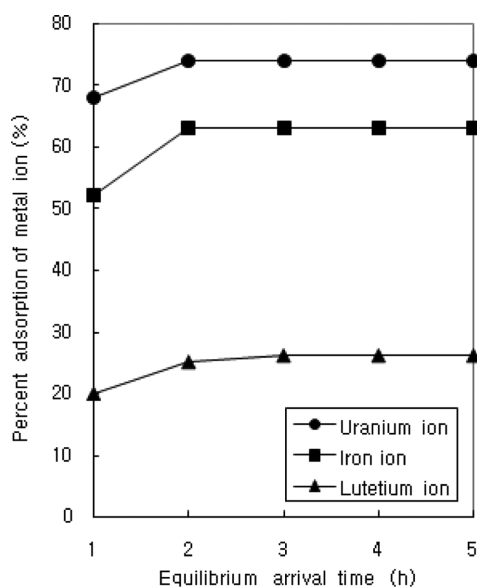


Fig. 2. Adsorption rate of UO_2^{2+} , Fe^{3+} , and Lu^{3+} on 1% crosslinked 1-aza-12-C-4-styrene-DVB resin at various time in methanol (concentration : 3.0 mM, pH : 6.0).

were 0.97 (UO_2^{2+}), 0.71 (Fe^{3+}), and 0.91 (Lu^{3+}) and seemed to form the complexes very well, however, lutetium ion showed low adsorption owing to an influence of hydration energy. Moreover, these kinds of metal ions have the addition of covalent bonds by electrostatic bonding and resin nitrogen atom during the formation of 1% resin and complexes regardless of the adsorbability, and accordingly, the metal ions easily reach the adsorption equilibrium only after 2 hours. On account of this, not only the conception of ion diameter-cavity radius but also the covalent bond between metal ions and resins and the hydration energy of metal ions react complicately in a case of cryptand-type metal complexes having nitrogen donor atom.

3.4. Effects of Resin Crosslink

Fig. 3 shows the adsorption amount of uranium ion investigated by using the resins having 1%, 2%, 3%, and 6% crosslinks through a variation of uranium ion concentrations within a range from 1.0 – 6.0 mM by methanol solvent.

As shown in Fig. 3, the resins having 1% and 2% crosslinks adsorbed approximately 0.5 mmol/g in 1.0 mM whereas the resins having 3% and 6% crosslinks adsorbed 0.10 mmol/g only. The result of the adsorption

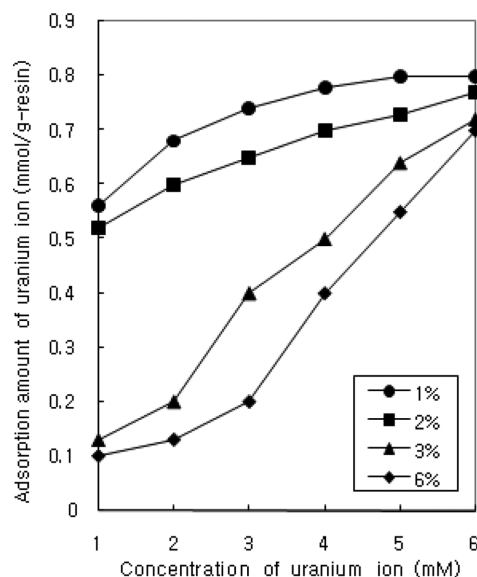


Fig. 3. Adsorption rate of UO_2^{2+} on 1%, 2%, 3%, and 6% crosslinked 1-aza-12-C-4-styrene-DVB resin at various concentration in methanol (time : 2 h, pH : 6.0).

presenting as 1% \approx 2% > 3% \approx 6% resins can be considered due to the reason that the crosslink is dependent on the amount of DVB during the synthesis of styrene-DVB copolymers, and the resin crosslink density is decreased with the decrease of the DVB content, whereas the porosity becomes higher and the diffusion velocity of uranium ion into the resin is large in the 1% and 2% resins compared with the 3% and 6% resins. However, the 3% and 6% resins adsorbed at almost the same level as the 1% and 2% resins within the high range (6.0 mM) of uranium ion.

A point expressing the maximum adsorption observed in an adsorption curve of Fig. 3 is the apparent capacity of resins. The apparent capacity of uranium ion for 1%, 2%, 3%, and 6% resins were 0.80, 0.77, 0.72, and 0.70 mmol/g, respectively.

3.5. Effects of Solvent Dielectric Constant

For verifying the adsorption effects of uranium ion according to different solvent kinds, the adsorption rates of uranium ion were examined in the solvents of distilled water (78.54), acetonitrile (37.50), and methanol (32.63) having different dielectric constants (ϵ , 25°C) as shown in Fig. 4.

The resins having 3% and 6% crosslinks in Fig. 3 had generally lower metal ion adsorption rates than the resin

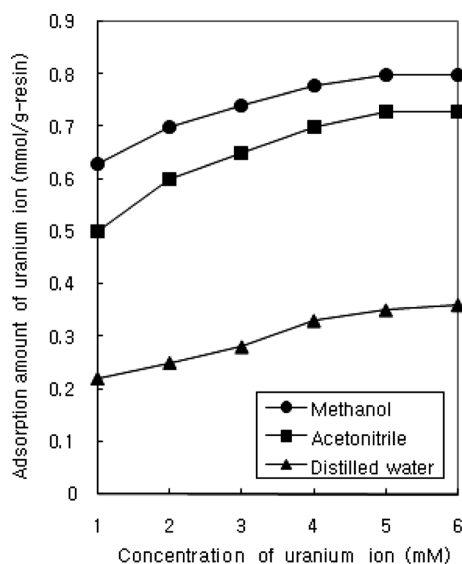


Fig. 4. Adsorption rate of UO_2^{2+} on 1% crosslinked 1-aza-12-C-4-styrene-DVB resin in methanol, acetonitrile, and distilled water (time : 2 h, pH : 6.0).

having 1% crosslink. Therefore, the resin having 1% crosslink was selected from Fig. 4, and the adsorption rates of uranium ion were investigated under the varied uranium ion conditions controlled within a range from 1.0–6.0 mM and increased in an order of methanol > acetonitrile > distilled water. This is probably due to the reason that the power of electrostatic bond (the power of Coulomb) is large as the dielectric constant value is smaller.

4. Conclusion

To selectively separate and collect uranium ion, resin with styrene hazardous material was synthesized and its adsorption was examined according to diverse conditions. The results are as follows.

The increase of crosslinks in synthetic resin leads to the increase of crosslink density but the lowering of porosity, and subsequently, the chlorine content is reduced. This course influences the macrocyclic ligand, which reduced the nitrogen content.

The nitrogen atom in synthetic resins was protonated under methanol solvent and pH 2 or lower (strong acid) and inhibited the adsorption of uranium ion, but uranium ion showed high adsorptivity through the formation of stable complexes with the products by the hydrolysis of non-protonated resins, at pH 3 or over (toward weak acid).

The metal ion adsorbability for the resin was shown to be uranium > iron > lutetium ions, which is affected by a ratio of metal ion to resin cavity, covalent bond between metal ion and resin, and hydration energy of metal ions. Also, the electrostatic bond and the covalent bond by resin nitrogen atom are added when the resin and uranium ion form complexes, and therefore, the adsorption equilibrium can be quickly reached only 2 hours passed.

The resins having 1% and 2% crosslinks have lower crosslink density and higher porosity due to the small amount of the DVB content than the resins with 3% and 6% crosslinks. Accordingly, the diffusion velocity of uranium ion into the resin was large even in a dilute solution, which makes it well to adsorb uranium ion.

The adsorption rates of uranium ion for the resin having 1% crosslink were methanol > acetonitrile > distilled water in order, and increased as the dielectric constant of the solvent becomes smaller.

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