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ARTICLE

Study on the Development of Flow Sheet for the Separation of MA(III) and Ln(III) Fission Products using Two-Step Process with Impregnated Adsorbents

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The separation of minor actinides (MA) from lanthanides (Ln) in high-level radioactive liquid waste (HLLW) is a challenging task. In this study, a flow sheet was developed for the separation of MA(III) and Ln(III) using a two-step separation column system with silica-based microporous adsorbents. In a column packed with a TEHDGA-impregnated adsorbent, MA(III) and Ln(III) were simultaneously recovered from a HLLW solution containing the radioactive isotopes ^{241}Am and ^{152}Eu. In a second column using a HONTA-impregnated adsorbent, MA(III) was separated from the MA(III)–Ln(III) mixed solution.

KEYWORDS: minor actinide, lanthanide, extraction chromatography, TEHDGA, HONTA

I. Introduction

The energy obtained from nuclear power generation is used in many countries as a highly reliable base load power source that does not emit CO_2. However, a large amount of spent nuclear fuel is generated after power generation. High-level radioactive liquid waste (HLLW) generated by reprocessing spent nuclear fuel contains many minor actinides (MA).[1)] By separating these elements and transmuting them, the number of long-lived and heat-generating nuclides can be reduced, which allows reducing the long-term risk of radiation, the amount of vitrified HLLW, and the area of the disposal site.

To address this issue, extraction chromatography methods using porous silica adsorbents impregnated with extractants are being actively investigated.[2-5)] In particular, particles containing styrene-divinylbenzene polymer in the pores of porous silica particles (SiO_2-P) exhibit high chemical resistance to nitric acid and are promising candidates for research aimed at improving radiation resistance.[6,7)]

The SiO_2-P adsorbent is suitable for solid-liquid extraction, which is easier than liquid–liquid extraction. Moreover, compared with other separation methods such as solvent extraction, extraction chromatography using the SiO_2-P adsorbent requires less amount of organic diluent and exhibits higher mechanical strength and interfacial stability.[8)]

However, MA(III) exhibits the same valence and similar chemical properties, such as ionic radius, as those of lanthanides (Ln(III)).[9)] Furthermore, the content of Ln(III) in HLLW is up to 50 times that of MA(III), which renders nuclide separation a challenging task.[10)] Our group has been investigating a two-step method for the separation of MA(III) and Ln(III) using adsorbents impregnated with *N*,*N*,*N*′,*N*′-tetra(2-ethylhexyl)diglycolamide (TEHDGA) and hexaoctylnitrilotheroacetamide (HONTA).[11)]

To study the coseparation of MA(III) and Ln(III) in TEHDGA columns and the subsequent separation of MA(III) from Ln(III) in HONTA columns, the feasibility of the separation flow in the presence of other coexisting metal elements and under flow velocity conditions, which are assumed to be important in practical treatment process, should be evaluated. To this aim, a MA(III) recovery flowsheet was examined in this study using a simulated HLLW solution spiked with ^{241}Am and ^{152}Eu to emulate a real adsorption separation process.

II. Experiment

1. Materials

All chelating agents and modifiers were of analytical grade. The reagents used in the preparation of the simulated HLLW solution were lanthanum(III) nitrate hexahydrate, cerium(III) nitrate hexahydrate, neodymium(III) nitrate hexahydrate, samarium(III) nitrate hexahydrate, europium(III) nitrate hexahydrate, gadolinium(III) nitrate hexahydrate, cesium(I) nitrate, strontium(II) nitrate and barium(II) nitrate (all purchased from Kanto Chemical Co.). Nitrosyl ruthenium(III) nitrate solution, palladium(II) nitrate solution, and rhodium(III) nitrate solution were purchased from Sigma–Aldrich. Zirconium(IV) nitrate dihydrate and ammonium hepta-molybdate tetrahydrate were purchased from Kanto Chemical Co. Rhenium(VII) oxide was purchased from Mitsuwa Chemicals Co. Solutions of these metal ions were

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*Corresponding author, E-mail: sonyun.kimu.d7@tohoku.ac.jp prepared by dissolving the reagents in a HNO_3 solution. Ultrapure water with a specific resistivity of at least 18.3 MΩ cm was used in all experiments. The simulated HLLW (La: 1.88 mM, Ce: 2.12 mM, Pr: 1.08 mM, Nd: 3.60 mM, Sm: 0.911 mM, Eu: 0.170 mM, Gd: 6.70 mM, Sr: 0.593 mM, Ba: 2.99 mM, Ru: 4.08 mM, Rh: 1.16 mM, Pd: 3.72 mM, Zr: 4.09 mM, Mo: 4.76 mM, Ag: 0.251 mM, Cr: 0.0998 mM, Mn: 2.55 mM, Fe: 1.90 mM, Ni: 0.203 mM and [HNO_3]: 2.8 M) used in the column test of TEHDGA/SiO_2-P was manufactured by Toyama Pharmaceutical Co. The ^{241}Am and ^{152}Eu radioactive isotopes were used to evaluate the adsorption behavior for MA(III) and Ln(III), respectively. The solution was diluted to prepare a ^{241}Am–^{152}Eu mixed solution with ^{241}Am and ^{152}Eu concentrations of 100 and 500 kBq/mL, respectively, which was used in the batch and column tests.

2. Preparation of Silica-based Microporous Adsorbents

Before synthesizing the TEHDGA/SiO_2-P (20 wt%) and HONTA/SiO_2-P (20 wt%) adsorbents, microporous SiO_2-P particles were washed three times with methanol to remove any impurities and dried under vacuum at 313 K for one day. The chelating extractants TEHDGA (10 g) and HONTA (10 g) were dissolved in a round-bottom flask using 200 cm^3 of dichloromethane as the diluent.

Then, 40.0 g of dried SiO_2-P particles was added and rotated for 60 min at room temperature. The diluent was removed at 323 K with gradual decompression using a rotary evaporator to impregnate and immobilize the extractant in the pores of the SiO_2-P particles. Residual dichloromethane was further removed by drying overnight in a vacuum drying oven at 313 K to obtain the silica-based adsorbent, which was characterized via scanning electron microscopy (SEM, Hitachi TM3030Plus).

3. Batch Adsorption Experiments

The TEHDGA/SiO_2-P and HONTA/SiO_2-P adsorbents were subjected to radioactive adsorption experiments for ^{241}Am and ^{152}Eu ions at a temperature of 298 K in a constant-temperature shaker with varying HNO_3 concentrations. The working solution was prepared by adding stock solutions of ^{241}Am and ^{152}Eu to simulated HLLW containing Ln elements prepared with HNO_3 at different concentrations. Next, 0.2 g of the TEHDGA/SiO_2-P or HONTA/SiO_2-P adsorbent was placed in a 13.5 mL glass bottle with a plastic cap and mixed with 4 mL of the working solution. The mixed solution was shaken vigorously for a certain period of time to allow contact, and the solid and liquid phases were separated from each other using a syringe and a nylon mesh filter. The radioactivity of ^{241}Am and ^{152}Eu before and after the adsorption experiment was measured using a Canberra germanium semiconductor detector with gamma rays of 59.5 keV (^{241}Am) and 122 keV (^{152}Eu), respectively. The other metal elements were measured using ICP-AES. The results of the radioactivity measurements were analyzed using Canberra software (Genie 2000). The distribution coefficient (K_d; cm^3/g) of each metal ion is expressed by the following formula: [12)]

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \qquad (1)$$

where C_0 is the concentration of metal ions in the aqueous phase at the initial point, C_e is the corresponding concentration (mg/dm^3) after adsorption equilibrium, and V and m indicate the volume of the aqueous phase and the weight of the dried TEHDGA/SiO_2-P and HONTA/SiO_2-P adsorbents, respectively.

4. Column Separation Experiments

To investigate the effect of ^{241}Am, ^{152}Eu, and other metal ions on the dynamic adsorption behavior of the adsorbent, adsorption separation tests were conducted using a column system consisting of a Pyrex glass column, a jacket for circulating hot water, a quantitative pump, a fraction collector, and a constant-temperature water circulation device. As in the batch test, a simulated HLLW feed solution was prepared by mixing ^{241}Am, ^{152}Eu, and Ln elements and adjusting the HNO_3 concentration. First, the fractionated adsorbent was soaked in pure water to remove air from its surface. The degassed adsorbent was then packed into a glass column. Details on the volumes of the feed solution, washing solution, and eluent solution are shown in **Table 1**.

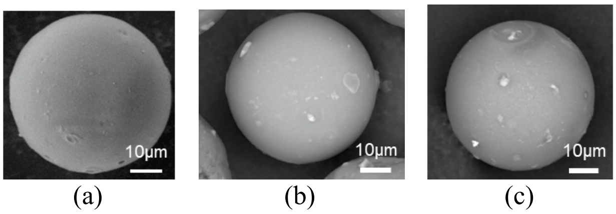
Table 1 Conditions for the column separation tests

TEHDGA/SiO_2-P		HONTA/SiO_2-P	
Feed Solution	24.0 mL	Feed Solution	15.7 mL
Washing Solution (200 mM EDA in 7 M HNO_3)	72.0 mL	Washing Solution (0.2 M HNO_3)	60.0 mL
Eluting Solution (H_2O)	60.0 mL	Eluting Solution (1 M HNO_3)	80.0 mL
Eluting Solution (50 mM EDTA)	60.0 mL		

III. Results and Discussion

1. Characterization of the Adsorbents

SEM observations were performed to evaluate the surface morphology of the adsorbent (**Fig. 1**), which was found to be similar to that of the SiO_2-P particle. Moreover, no extractant precipitation was observed, confirming that the extractant was impregnated and supported in the pores of the SiO_2-P particle.



(a) (b) (c)

Fig. 1 SEM image of (a) SiO_2-P, (b) TEHDGA/SiO_2-P adsorbent, and (c) HONTA/SiO_2-P adsorbent

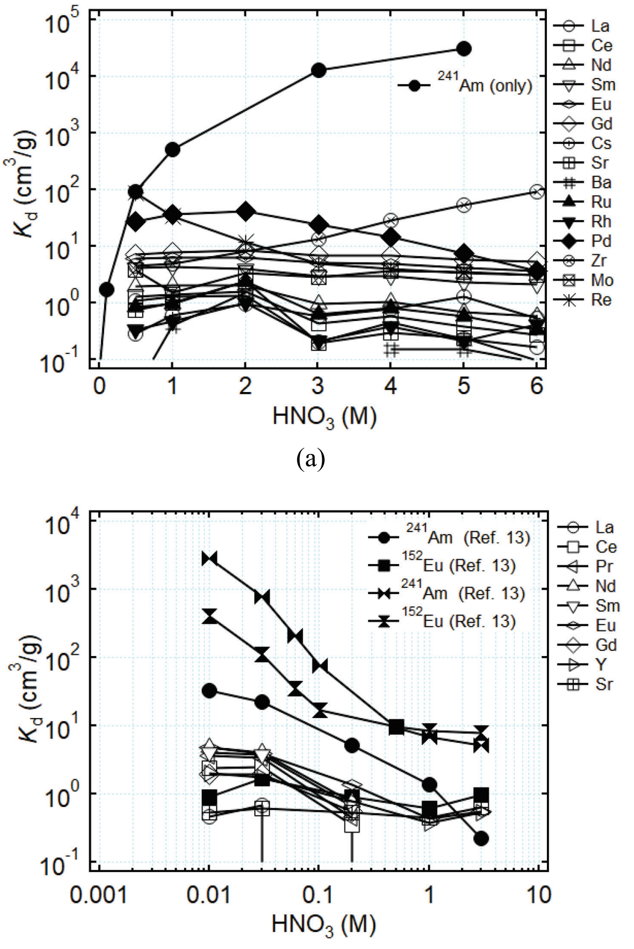
3. Effect of HNO_3 Concentration

Figure 2 shows the K_d of ^{241}Am and ^{152}Eu at HNO_3 concentrations ranging from 0.1 to 6.0 M, revealing that

^{241}Am was adsorbed on the TEHDGA/SiO$_2$-P adsorbent in the high nitric acid concentration range.

In a previous study, ^{241}Am and ^{152}Eu were not adsorbed on HONTA/SiO$_2$-P in the high nitric acid concentration range. In addition, the K_d values differed depending on the presence or absence of coexisting metal ions. Differences in the adsorption of ^{241}Am and ^{152}Eu were observed in the nitric acid concentration range from 0.01 to 3.0 M.[13)]

Thus, column separation can be achieved by changing the concentration of nitric acid on the basis of the difference in K_d values.



(a)

(b)

Fig. 2 Effect of HNO$_3$ concentration on the adsorption of (a) TEHDGA/SiO$_2$-P and (b) HONTA/SiO$_2$-P adsorbents. Conditions: [metal] = 5 mM (TEHDGA/SiO$_2$-P) and 1 mM (HONTA/SiO$_2$-P); ^{241}Am and ^{152}Eu = tracer; V/m = 20 cm^3/g; shaking speed: 160 rpm; temperature: 298 K; time: 5h.

4. Column Separation Method

(1) TEHDGA/SiO$_2$-P Adsorbent

The results of the column tests using the TEHDGA adsorbent with a flow rate of 3 mL/min are shown in **Fig. 3**. First, a 200 mM EDA solution was introduced as a washing solution to elute elements other than ^{241}Am, Ln(III), and Zr. The non-adsorbed components were immediately eluted, whereas the adsorbed components were retained in the adsorbent. Next, distilled water was introduced to elute and recover the target elements, i.e., ^{241}Am, ^{152}Eu, and Ln(III), which were retained in the adsorbent. Finally, a 50 mM EDTA solution was introduced as a chelating agent, and the Zr element was eluted alone.

The experimental results showed that the TEHDGA adsorption column can coseparate ^{241}Am and Ln(III) in a solution containing various metal elements, including ^{241}Am, even at a relatively high flow rate, by virtue of the fast reaction between the metal elements and the extractant.

The recovery ratios for each element in the column test are shown in **Table 2**. High recovery rates were obtained for almost all elements, achieving complete recovery of the target elements ^{241}Am, ^{152}Eu, and Ln(III).

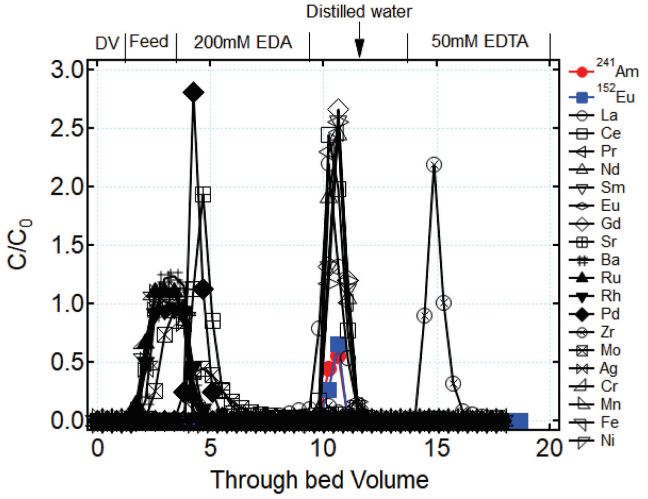


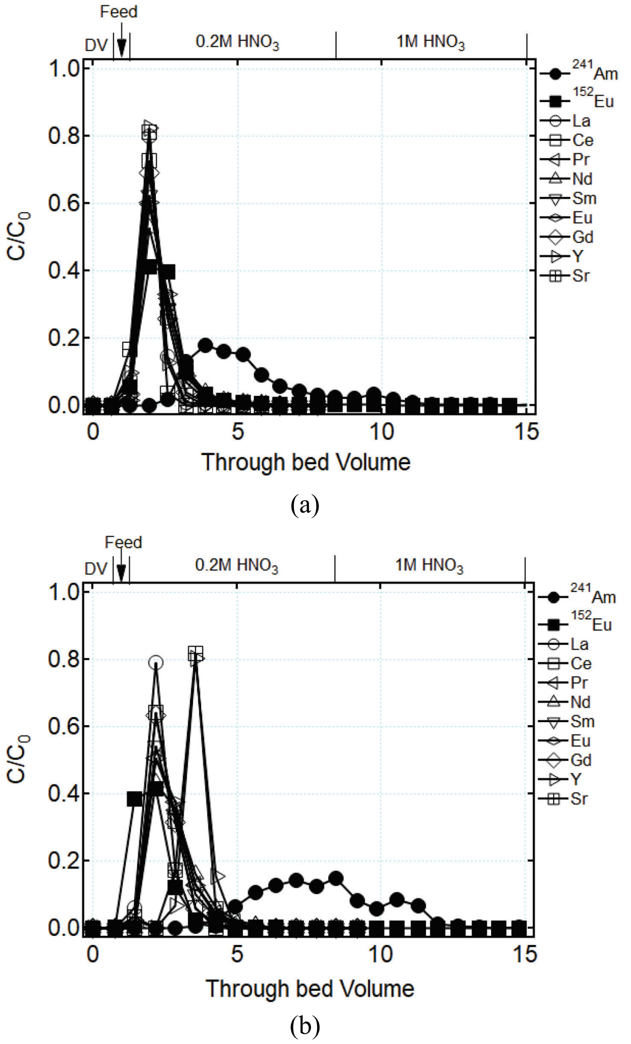
Fig. 3 Chromatographic separation results using TEHDGA/SiO$_2$-P. Conditions: [metal] = Simulated HLLW; ^{241}Am and ^{152}Eu = tracer; flow rate = 3 cm^3/min; bed height = 150 mm; inner diameter of the column = 10 mm; temperature = 323 K.

Table 2 Recovery ratios of ^{241}Am and ^{152}Eu using the TEHDGA-packed column in the presence of Ln elements

	Recovery ratio (%)		Recovery ratio (%)		Recovery ratio (%)
^{241}Am	100	Eu	100	Zr	100
^{152}Eu	100	Gd	100	Mo	100
La	100	Ru	100	Ag	87.9
Ce	100	Rh	100	Cr	100
Pr	100	Pd	92.9	Mn	100
Nd	100	Sr	97.0	Fe	100
Sm	100	Ba	100	Ni	96.1

(2) HONTA/SiO$_2$-P Adsorbent

The results of the column tests using the HONTA adsorbent at flow rates of 5 and 1.5 mL/min are shown in **Fig. 4**. After the feed and washing solutions were passed through the column, Ln(III), Sr, and ^{152}Eu, which are non-adsorbed components, were quickly eluted. Subsequently, ^{241}Am was eluted. The close proximity of the Ln(III) and MA(III) peaks suggests that the adsorption and desorption reactions between the metal elements and the extractant are slow and that the contact time required for adsorption to the adsorbent is not sufficient. Although further optimization of the flow rate conditions and column length is required for application to real processes, the results suggest that Am(III) and Ln(III) can be separated. As a result of this test, high recovery rates were obtained for most elements regardless of the flow rate conditions, and complete recovery of the target elements ^{241}Am, ^{152}Eu, and Ln(III) was achieved.



(a)

(b)

Fig. 4 Chromatographic separation results for ^{241}Am, ^{152}Eu, and Ln(III) using HONTA/SiO$_2$-P. Conditions: [metal] = 1 mM; ^{241}Am and ^{152}Eu = tracer; flow rate = (a) 5 cm^3/min and (b) 1.5 cm^3/min; bed height = 100 mm; inner diameter of the column = 10 mm; temperature = 298 K.

IV. Conclusion

Toward the development of a practical MA separation and recovery technology, the performance of a two-step MA recovery flow sheet with columns packed with TEHDGA and HONTA adsorbents, respectively, was evaluated using ^{241}Am and ^{152}Eu. In the column test using the TEHDGA adsorbent, ^{241}Am and ^{152}Eu were added to the simulated solution, and it was confirmed that Ln(III) and Am were eluted simultaneously. In the column test using the HONTA adsorbent, Am was eluted after the rare-earth elements were eluted. The results suggest that MA(III) and Ln(III) could be efficiently separated by tuning the flow rate.

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References

1) R. C. Ewing, "Long-term storage of spent nuclear fuel," *Nat. Mater.*, **14**[3], 252-257 (2015).
2) J. Fan, L. Duan, Y. Wang, P. Qiu, M. Fan, P. Shang, Y. He, T. Kang, "Adsorption of actinides (III) and lanthanides (III) on silica-based BCPDTPA resin: kinetics, thermodynamics, and isotherms," *Colloids Surf. A Physicochem. Eng. Aspects*, **670**[5], 131547 (2023).
3) S.-Y. Kim, Y. Xu, T. Ito, Y. Wu, T. Tada, K. Hitomi, E. Kuraoka, K. Ishii, "A novel partitioning process for treatment of high level liquid waste using macroporous silica-based adsorbents," *J. Radioanal. Nucl. Chem.*, **295**[2], 1043-1050 (2013).
4) J. Shi, J. Wang, W. Wang, X. Wu, H. Wang, J. Li, "Efficient and selective removal of palladium from simulated high-level liquid waste using a silica-based adsorbent NTAamide(C8)/SiO$_2$-P," *Nanomaterials (Basel)*, **14**[6], 544 (2024).
5) S. Zhang, Q. Huang, L. Chen, X. Yin, M. F. Hamza, Y. Wei, S. Ning, "Fast removal of strontium from nitric acid solution using an acid-resistant silica-based adsorbent," *J. Environ. Chem. Eng.*, **11**[5], 110529 (2023).
6) Q. Shu, A. Khayambashi, X. Wang, X. Wang, L. Feng, Y. Wei, "Effects of γ irradiation on bis(2-ethylhexyl)phosphoric acid supported by macroporous silica-based polymeric resins," *Radiochim. Acta*, **106**[3], 249-258 (2018).
7) T. Ito, R. Nagaishi, T. Kimura, S.-Y. Kim, "Study on radiation effects on (MOTDGA–TOA)/SiO$_2$-P adsorbent for separation of platinum group metals from high-level radioactive waste," *J. Radioanal. Nucl. Chem.*, **305**[2], 419-427 (2015).
8) S.-C. Zhang, S.-Y. Ning, J. Zhou, S.-Y. Wang, W. Zhang, X.-P. Wang, Y.-Z. Wei, "New insight into the adsorption of ruthenium, rhodium, and palladium from nitric acid solution by a silica-polymer adsorbent," *Nucl. Sci. Tech.*, **31**[4], 34 (2020).
9) C. S. Cao, H. S. Hu, J. Li, W. H. E. Schwarz, "Physical origin of chemical periodicities in the system of elements," *Pure Appl. Chem.*, **91**[12], 1969-1999 (2019).
10) R. Malmbeck, C. Nourry, M. Ougier, P. Souček, J. P. Glatz, T. Kato, T. Koyama, "Advanced fuel cycle options," *Energy Procedia*, **7**, 93-102 (2011).
11) T. Akuzawa, S.-Y. Kim, M. Kubota, H. Wu, S. Watanabe, Y. Sano, M. Takeuchi, T. Arai, "Design of MA(III)/Ln(III) separation process of extraction chromatography technology," *J. Radioanal. Nucl. Chem.*, **331**[12], 5851-5858 (2022).
12) J. Zhou, X. Zhang, B. Deng, Y. Huang, X. Liu, S. Ning, S. Kuang, W. Liao, "Separation and purification of heavy rare earth elements by a silica/polymer-based β-aminophosphonic

acid resin from chloride media," *Sep. Purif. Technol.*, **354**([7], 129342 (2025).

13) M. Kubota, S. -Y. Kim, H. Wu, S. Watanabe, Y. Sano, M. Takeuchi, T. Arai, "Development of a process for the separation of MA(III) from Ln(III) fission products using HONTA impregnated adsorbent," *J. Radioanal. Nucl. Chem.*, **333**[5], 2413-2420 (2024).