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ARTICLE

Safety Improvement in the Packed Column of Extraction Chromatography System for Trivalent Minor Actinides Recovery

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Systematic studies to develop extraction chromatography technology for Am and Cm (MA(III)) recovery from spent MOX fuel are progressing. Developments in the extraction chromatography system especially focusing on safety and stable operation are required for the practical application of the technology. MA(III) are separated from other fission products through adsorption/elution reactions inside the adsorbent-packed column. In order to reduce the pressure drop of the packed column to prevent the accumulation of heat and gas inside the bed, an improvement in the structure of porous silica support for the adsorbent was carried out. A new adsorbent with larger particle and pore sizes than the original adsorbent achieved these objectives without losing column separation performance.

KEYWORDS:* *minor actinides, extraction chromatography, safety, adsorbent, packed column

I. Introduction

Extraction chromatography is one of the promising technologies for the recovery of trivalent minor actinides (Am and Cm: MA(III)) from spent nuclear fuels, and Japan Atomic Energy Agency has carried out systematic studies for the implementation of the technology.1) Porous silica-based, extractant-impregnating adsorbent is packed in a column, and separation of elements can be achieved using solvent extraction principle. A nitric acid solution involving MA(III) and other fission products such as Cs, Sr, Mo, Zr, rare earth elements, platinum group elements, etc. is generated as a raffinate of solvent extraction procedure for U and Pu recovery, and selective recovery of MA(III) from the raffinate is a main goal of the technology. MA(III) recovery from genuine raffinates has been successfully done with small-scale packed columns in our previous studies,2,3) and an engineering scale apparatus has been developed to demonstrate the feasibility of this technology for industrial reprocessing, especially for the aspects of safety and remote handling.4)

In the current phase of this research, a new study project is progressing to show the robustness of the technology considering long-time operation and safety.5) In this project, flow sheet and system designs considering safety and stability are systematically studied. A process flow for the MA(III) recovery proposed by the project is a two-step column operation consisting of MA(III)+RE(III) co-recovery by the 1st column using 2-ehylhexyl diglycolamide (TEHDGA) extractant-impregnated adsorbent and MA(III)/RE(III) separation by the 2nd column using hexaoctyl-nitrilotriacetamide (HONTA) impregnated adsorbent. A series of batch-wise and column separation tests showed the applicability of the flow sheet.6-8)

One of the most important issues for the safety of the extraction chromatography technology is preventing fire and explosion which are caused by accumulation of decay heat and explosive gases radiolytically generated. During normal operation, heat and gas are discharged from the column with mobile phases.9) In cases of troubles in a pump for the mobile phase and loss of power, cooling water should be supplied into the packed bed with gravity. Particle and pore sizes of the original adsorbent which was produced by the sol-gel method are 50 μm and 50 nm, respectively. Typical pressure drop of the engineering scale column packed with original adsorbent is about 0.3 – 0.4 MPa.10) The pressure has to be reduced to less than one-half of the current value to cool inside the bed with the gravity flow coolant. The accumulated heat and gas are desired to be discharged as quickly as possible after supplying the coolant, thus not only a reduction in the pressure drop but also higher heat and gas transfer ability of the bed is required. Reduction in the pressure drop and enhancement in the heat and gas transfer are expected to be attained simultaneously by improvement in the structure of the porous silica particle i.e. enlargement of particle and pore sizes.

Although the larger particle and pore sizes are desirable for safety reasons, a certain amount of pressure drop is required for uniform flow velocity distribution inside the bed.4) Therefore, improvements in the particle structure might lead poor separation performance of the column. The mechanical strength of the particle has to be checked since the improvement might weaken the physical durability of the particle. The optimized structure of the porous silica particle should be designed to achieve both required separation and safety performances.

Our previous study succeeded in granulation of porous silica particles with control of particle and pore sizes by spray drying granulation and spinodal decomposition techniques, respectively.11) Pressure drop of the packed bed could be decreased to one-third of the original one, which was enough

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*Corresponding author, E-mail: watanabe.sou@jaea.go.jp for emergency cooling by the gravity flow. The distribution coefficients of lanthanide ions onto the new adsorbent were almost the same as those of the original adsorbent. However, other important characteristics of the particle and the packed bed are still missing.

In this study, the mechanical strength of the improved adsorbent was measured, and the safety performance of the packed column was evaluated through the discharge performance of heat and gas. The fundamental separation performance of the packed column was also investigated, and the applicability of the new adsorbent was discussed in respect of the separation and safety performances.

II. Experiments

1. Preparation of Adsorbent

Porous silica particles were produced by the spray drying granulation and the spinodal decomposition for pore formation. A spray dryer with a rotating disk-type atomizer (PRECI, P260) was used for the granulation tests. A feed solution containing 10 nm silica particles was fed into the drying chamber through the atomizer, and the dried powder product was gathered at the bottom of the chamber. Porous particles were obtained after heat treatment and washing. Detailed procedure is described in Ref. 11). Styrene-divinyl benzene copolymer was coated around the particles, and TEHDGA extractant was impregnated into the copolymer. The preparation procedure is written in Ref. 6).

2. Mechanical Strength of the Adsorbent

The crushing strength of the particle was measured by a micro compression testing machine (MCT-510, Shimazu). A particle was pressed with increasing the load, and the crushing strength was calculated from the force at which the particle was broken and the particle size. Mechanical strength was evaluated as an average of the crushing strength of more than 10 particles.

3. Characterization of the Packed Bed

(1) Thermal Conductivity Measurement

The adsorbent was packed into a glass column (47.1 cm^3, 20 mm diameter and 150 mm height) by slurry transfer, the thermal conductivity of the packed bed (mixture of water and the adsorbent) was measured. An overview of the experimental apparatus is shown in **Fig. 1**. The thermal conductivity of the bed was measured by a sensor (KD2Pro, DECAGON) inserted into the bed where temperature of the bed was kept at 298 K by circulating cooling water in a column jacket. For comparison, thermal conductivity of the original adsorbent bed was also measured.

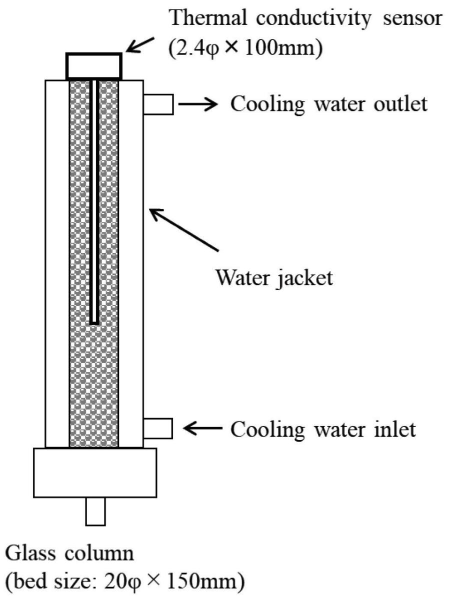


Fig. 1 Experimental apparatus for the thermal conductivity measurement

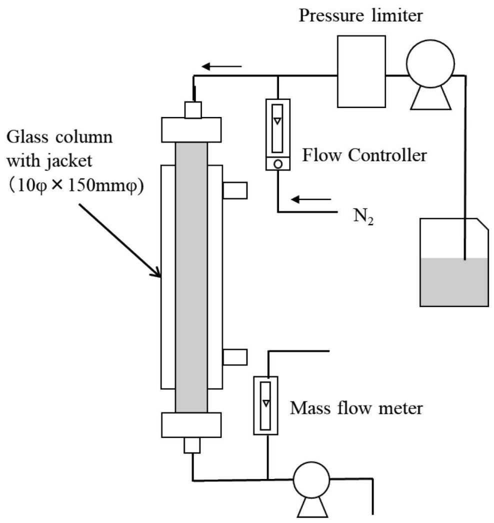


Fig. 2 Experimental apparatus of the gas recovery test

(2) Gas Discharge Behavior

The adsorbent was packed into a column (47.1 cm^3, 20 mm diameter and 150 mm height), and gas behavior inside the bed was evaluated. **Figure 2** shows the experimental apparatus of the gas recovery test. 1-2 mL of N_2 gas was supplied into the column with 1mL/min, and then water was supplied into the column to push out the gas from the column. The amount of gas discharged from the column was measured downstream of the column. The ratio of gas remaining inside the bed was calculated from the results. The gas discharge behavior of the new adsorbent-packed bed was compared to that for the original adsorbent.

(3) Column Separation Performance

A feed solution, a wash solution, an eluent, and another wash solution were sequentially supplied into a packed column, and then the effluent was fractionally collected at every 0.5 BV and concentrations of elements in the fractions were analyzed by ICP-AES. The temperature of the column was controlled at 323 K by cooling water supplied into a column jacket. The composition of the feed solution and the experimental conditions are shown in **Tables 1** and **2**, respectively.

Table 1 Composition of the feed solution

Component	Concentration
Pd	252 ppm
Mo	588 ppm
Sr	156 ppm
Nd	1560 ppm
Eu	25 ppm
Zr	539 ppm
H^+	2.8 M

Table 2 Conditions of the column separation experiments

Column size		10 mmΦ×150 mmH (1 BV = 11.8 cm^3)
Flow rate		3 cm/min
Solutions	Feed	Simulated HLLW: 2 BV
	Wash	7 M HNO_3: 6 BV
	Eluent	H_2O: 5 BV
	Wash2	50 mM EDTA-Na: 5 BV

III. Results and Discussion

1. Characterization of the Particle

Average particle and pore sizes obtained by the granulation with the spinodal decomposition were 100 µm and 300 nm, respectively. The porosity of the new particle was about 0.44, whereas that of the original particle was 0.26. Appearances of the newly obtained porous silica particles and original particles are shown in **Fig. 3**. Both particle and pore sizes of the new particles were larger than the original ones, and the shape of the new particles seemed more uniform. The average crushing strength of the original and the new particles were 4.5 and 28.7 MPa, respectively. The mechanical strength increased by 6 times with the improvement in the particle, and the increase is favorable for the slurry transfer of the adsorbent for the packing.

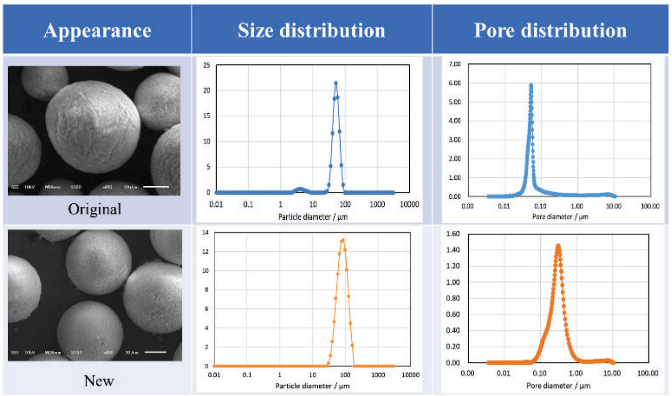


Fig. 3 Fundamental information of original and new porous silica particles

2. Characterization of the Packed Bed

(1) Thermal Conductivity

The thermal conductivities of the packed beds for new and original adsorbents are shown in **Table 3**. The thermal conductivity of the new adsorbent bed was larger than that of the original one. A simple model for the thermal conductivity of a porous media and a fluid can be written as the following equation:

$$K_{\mathrm{eff}} = K_{\mathrm{s}}\,(1-\rho) + \rho K_{\mathrm{f}}$$

where K_{eff}, K_{s}, K_{f} and ρ are effective thermal conductivity, thermal conductivity of the solid material, thermal conductivity of the fluid, and porosity of the medium. The thermal conductivities of water at 284 and 298 K are about 0.58 and 0.61 W/m·K, respectively.[12] The original particle's thermal conductivity (in the packed bed, containing liquid) was 0.58 W/m·K, and for the new particle it is 0.64 W/m·K. The new particles are more porous, contain more water, and therefore have a higher thermal conductivity. This characteristic is suitable for discharging decay heat from the packed column.

Table 3 Thermal conductivity of the packed bed

Adsorbent	Temperature [K]	Thermal conductivity [W/m·K]
Original	284	0.57
	298	0.58
New	298	0.64

(2) Behavior of Gas Discharge

Amounts of the remaining gas inside the packed beds during the operation are shown in **Fig. 4**. More than 20 % of the supplied gas remained inside the column with the original adsorbent 10 minutes after restarting the mobile phase. This result is consistent with our previous experiments performed with the engineering-scale apparatus.[4] On the other hand, almost all the supplied gas was quickly discharged from the packed bed with the new adsorbent. The larger flow channel between particles and inside the particles should enhance the gas discharge. Radiolytically generated gas inside the new adsorbent-packed bed is expected to be discharged immediately after supplying emergency coolant.

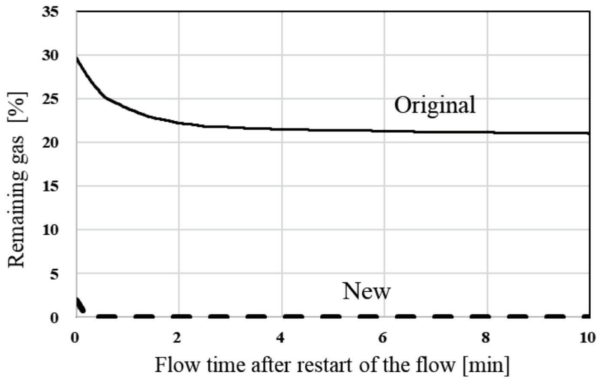
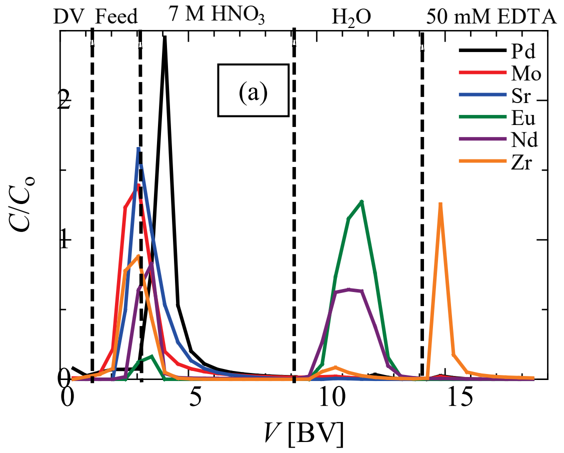


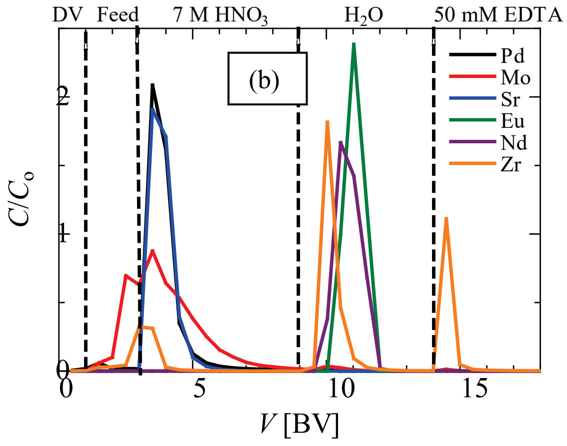
Fig. 4 Amount of remaining gas inside the packed bed

(3) Column Separation Performance

Elution curves obtained by the column separation experiments on columns with the original and the new adsorbents are shown in **Fig. 5**. Pd, Mo, and Sr were not adsorbed on the column and eluted with the feed solution and 7 M HNO_3. Eu and Nd were adsorbed on the column and then eluted by H_2O. Zr was stripped by 50 mM EDTA solution. These features reasonably agree with our previous report.[6)] Pd, Mo and Sr were properly recovered from the new column before the H_2O supply although elution peaks of Mo and Sr slightly shifted to the right hand of the figure by the improvement. Elution curves of Eu and Nd became sharp with the improvement. The quick elution must be an outcome of the enlargement of the pore size which can enhance the diffusion of the eluent inside the particle. Elution properties of Am and Cm are also expected to be improved. The amount of Zr mixed in the H_2O fractions increased with the improvement. The result must be caused by change in the adsorption capacity of Zr. However, Zr can be decontaminated by the next HONTA column, and the result would not influence MA(III) recovery performance significantly. The accumulation behavior of the elements inside the packed bed was also not influenced by the improvements. Consequently, improvements in the adsorbent do not have negative impacts on separation performance of the TEHDGA column. In order to evaluate separation behavior of MA(III) in the HONTA column, further experiments are required.



(a) Original adsorbent



(b) New adsorbent

Fig. 5 Elution curves of TEHDGA adsorbent columns

IV. Conclusion

Improvements in the structure of porous silica support for extraction chromatography were performed to enhance the safety of the system. Enlargement in particle and pore sizes increased the thermal conductivity of the packed bed and enhanced gas discharge properties from the bed. These characteristics prevent the accumulation of gas and heat radiolytically generated inside the column. The improvement did not influence separation behavior. Therefore, the safe operation of the system without losing column separation performance will be achieved by using the new adsorbents.

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