Development of MA separation process with TEHDGA/SiO₂-P for an advanced reprocessing

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Abstract
Applicability of tetra2-ethylhexyl diglycolamide (TEHDGA) impregnated adsorbent for minor actinide (MA) recovery from high level liquid waste (HLLW) in extraction chromatography technology was investigated through batch-wise adsorption and column separation experiments. Distribution ratio of representative fission product elements were obtained by the batch-wise experiments, and TEHDGA adsorbent was shown to be preferable to TODGA adsorbent for decontamination of several species. All Ln(III) supplied into the TEHDGA adsorbent packed column was properly eluted from the column, and the applicability of the adsorbent was successfully showed by this study.

Keywords Minor actinide · Lanthanide · Extraction chromatography · TEHDGA · HLLW

Introduction
Trivalent minor actinides (MA(III): Am and Cm) contained in high level liquid waste (HLLW) generated from reprocessing of spent nuclear fuel possess radiotoxicity over the long term, and partitioning and transmutation of those elements are important strategies for sustainable nuclear energy [1]. Development of MA(III) separation technology is being advanced over the world from the viewpoint of reduction of the volume and radiotoxicity of radioactive waste. Japan Atomic Energy Agency has been developing extraction chromatography technology for MA(III) recovery process [2]. A packed column with porous silica based adsorbents is utilized for the extraction chromatography, and it is possible to separate MA(III) from other fission product (FP) through adsorption/desorption reaction. This technology can reduce the amount of secondary wastes in comparison with the solvent extraction process, and it does not require any diluent and the number of stages can easily be increased not by adding equipment but by simply lengthening the column.

Currently, we are developing a flow-sheets consists of two-step column operation; the first column of Tetra 2-ethylhexyl diglycolamide (TEHDGA) impregnated adsorbent for the recovery of MA(III) + Ln(III) and the second column of hexaoctyl-nitrilotriacetamide (HONTA) impregnated adsorbent for MA(III)/Ln(III) separation. TEHDGA and HONTA contains nothing but C, H, O and N and they produce species other than CO₂, NOₓ and H₂O on incineration. So far, N,N′,N′,N′-tetaoctyl diglycolamide (TODGA) has been extensively investigated in the study of extraction of MA(III) + Ln(III) [3–12]. However, MA(III) back-extraction performance was not enough, due to formation of very stable complexes of TODGA with trivalent cations [13]. Therefore, substitution of TODGA with the 2-ethylhexyl group has produced TEHDGA extractant, which has exhibited superior back-extraction performance to TODGA. The chemical structure of TEHDGA is shown in Fig. 1. Importantly, although studies on the TEHDGA in solvent extraction system have been reported, application of TEHDGA to extraction chromatography has not been examined [14]. Therefore, in order to investigate the applicability of TEHDGA to the extraction chromatography technology and to show superiority of TEHDGA to TODGA, it is necessary to evaluate adsorption/elution performance of TEHDGA impregnated adsorbent (referred as TEHDGA/SiO₂-P) through fundamental studies. In this study, the adsorption/elution performance of the TEHDGA/SiO₂-P was investigated with...
batch-wise experiments and column separation experiments on simulated HLLW, in the cold test.

**Experimental**

**Preparation of TEHDGA/SiO₂-P**

Porous silica particles with average particle diameter of 50 μm and average pore diameter of 50 nm were prepared by sol–gel method. Those particles were coated by styrene divinylbenzene copolymer (referred as SiO₂-P), and TEHDGA was impregnated into the polymer as extractant of cross-linkaging of the copolymer was 15%, and the amount of extractant-impregnated adsorbent was 20 wt% of the total adsorbent. The flow-sheet of SiO₂-P preparation and extractant impregnation method are shown in Fig. 2 and Fig. 3, respectively. And, detail preparation procedure is discribed in a reference [15].

**Batch-wise experiments**

The performance of the TEHDGA/SiO₂-P system was discussed through comparison with that of TEHDGA in the solvent extraction system. The TEHDGA solution solvent was prepared by diluting TEHDGA to a final concentration of 0.2 M in 20 vol% 2-ethylhexanol in n-dodecane. 1 cm³ of the prepared solution was contacted with 1 cm³ of feed solution containing 10 mM La(III), Nd(III), Eu(III) and Gd(III) in nitric acid; the mixture thus obtained was shaken for 1 h at 298 K by the shaking water bath. In subsequent tests, Eu(III) was used as a simulated element of MA [16]. The shaking speed was 160 r min⁻¹, and the shaking width was 40 mm. The acidity of the feed solution was parametrically changed at 0.001 M < [HNO₃] < 3 M. In the parallel experiment, 0.2 g of TEHDGA/SiO₂-P were mixed with 4 cm³ of the feed solution and shaken.
for 1 h at 298 K by the shaking water bath. Acidity of the feed solution containing 10 mM Sr(II), Mo(VI), Zr(IV), Pd(II), La(III), Nd(III), Sm(III), Eu(III) and Gd(III) was parametrically changed at 0.001 < [HNO₃] < 10 M.

The concentrations of the metal ions in the aqueous phase before and after the extraction operations were analyzed by ICP-OES, and distribution ratio ($D$ and $K_d$) of the metal ions for the extractant system and adsorbent system were calculated by Eqs. (1), (2) respectively;

\[
D = \frac{C_0 - C_{aq}}{C_{aq}}
\]

\[
K_d = \frac{C_0 - C_s}{C_0} \times \frac{V}{W}
\]

where $C_0$ and $C_{aq}$ are concentrations of metal ions in the solution before and after the extraction operation, respectively. There was no third phase formation or metal adsorption by the container, $C_0 - C_{aq}$ represents assumed metal concentration in the organic phase. $C_0$ and $C_s$ are concentrations of metal ions in the solution before and after the adsorption, respectively. $V$ is volume of the solution, $W$ is weight of the adsorbent. $K_d$ was evaluated to obtain general dependence on acidity, and those experiments were not repeated to obtain precise values.

**Column experiment**

In order to evaluate the adsorption/elution behavior of packed columns, adsorption breakthrough elution experiments were conducted on columns with TEHDGA/SiO₂-P and TODGA/SiO₂-P as adsorbents. TODGA/SiO₂-P was prepared by the same method described for TEHDGA/SiO₂-P. The experimental setup of the column experiments is shown in Fig. 4. The adsorbents were packed in a glass column characterized by a diameter of 1 cm and a length of 5 cm (1 BV = 3.93 cm³). After conditioning the packed column with 3 M HNO₃ solution, 15 BV of feed solution (10 mM of Eu(III) in 3 M HNO₃), 7.6 BV of wash solution (3 M HNO₃) and 23 BV of eluent (distilled water) were sequentially supplied to the column.

The column separation experiment performed on simulated HLLW using the TEHDGA/SiO₂-P packed column was conducted 6 times without exchanging adsorbents to evaluate the reproducibility of the elution curve. Flow-sheet of the operation was designed based on data from a study previously published by our group [12]. In detail, 0.8 BV of simulated HLLW, 4.6 BV of wash solution (3 M HNO₃) and 11.5 BV of eluent (distilled water) were sequentially added to the column, and the effluent discharged from the column was fractionally collected using a fraction collector. The simulated HLLW for the feed solution consists of 1 mM of Sr(II), Mo(VI), Zr(IV), Pd(II), La(III), Nd(III), Sm(III), Eu(III) and Gd(III) in 3 M HNO₃. The concentration of each element in the fraction was analyzed by ICP-OES, and the recovery rate of each element was calculated by Eq. (3).

\[
\text{Recovery rate} \,[\%] = \frac{A_{\text{eluent}}}{A_{\text{supply}}} \times 100
\]

where $A_{\text{eluent}}$ and $A_{\text{supply}}$ are amounts of substance in all eluent and feed solution flow process, respectively.

**Results and discussion**

**Batch-wise experiments**

The distribution ratio of La(III), Nd(III), Eu(III) and Gd(III) by the TEHDGA solvent are shown in Fig. 5. In particular, the adsorption rate at 0.001 M < [HNO₃] < 0.01 M was 0%, and it was not plotted because it could be not expressed in Log. As shown
by Fig. 5, the value of distribution coefficient of Ln(III)s increased with nitric acid concentration. Heavier Ln(III) showed stronger affinity to TEHDGA than lighter Ln(III). TEHDGA is a neutral molecule and the extraction reaction of trivalent metal ion $M^{3+}$ from nitric acid medium is presumed to proceed as follows:

$$M^{3+} + 3NO_3^- + 3\text{TEHDGA} \rightleftharpoons M(NO_3)_3(\text{TEHDGA})_3$$

The extraction reaction proceeds through the formation of a nitrato complex and coordinating with TEHDGA [17]. Generally showing a chemically similar behavior, both MA(III) and Ln(III) are expected to be extracted from the concentrated nitric acid medium and back-extracted into less acidic medium simultaneously.

The value for the log $D$ of metal ions get adsorbed onto TEHDGA/SiO$_2$-P are shown in Fig. 6. It is evident from Fig. 6, Sr(II), Zr(IV) and Ln(III)s were adsorbed on TEHDGA/SiO$_2$-P from the concentrated nitric acid solution, but Pd(II) was scarcely adsorbed. Mo(VI) showed a distinctive adsorption behavior. The distribution ratio of Mo(VI) initially decreased as the nitric acid concentration increased, it then began to increase with the nitric acid concentration. This adsorption behavior might be the result of changes in the chemical form, which depends on the acsidity of nitric acid solution [18]. Chemical form of Mo(VI) depends on acidity of the solution, and several species coexist simultaneously in acidic solution [19]. The change in $K_d$ might be propotional to the ratio of species which are extracted by TEHDGA. Detail extraction mechanism of them should be further investigated. Pd(II) and Mo(VI) are hardly adsorbed on TEHDGA/SiO$_2$-P from acidic solution, and their decontamination from liquid sample should be easily achieved.

At $[\text{HNO}_3]>1$ M, the $K_d$ of Ln(III)s was almost the same value, although log $D$ evaluated for the solvent extraction system at $[\text{HNO}_3]=3$ M depended on the specie. One possible explanation for this phenomenon is as follows, the different behavior of the two extraction system is considered to be caused by difference in concentration of the extractant in the solvent and the adsorbent systems. The log $D$ of different species in the solvent extraction system of TEHDGA depended on TEHDGA concentration, and difference in the log $D$ was distinct when [TEHDGA] was large [20]. Since [TEHDGA] in the adsorbent is less dense than that in the solvent, log $D$ of the adsorbent system might be less sensitive to the Ln(III) species. Consequently, MA(III) and all Ln(III) must be adsorbed onto the adsorbent from the high nitric acid solution simultaneously. Sr(II) and Zr(IV) were adsorbed onto TEHDGA/SiO$_2$-P from the high nitric acid concentration. Adsorption of Sr(II) onto DGA impregnated adsorbent was also observed in the case of the TODGA system [13], and it should be possible to separate Sr(II) from MA(III) and Ln(III) at elution part or next MA(III)/Ln(III) separation step with HONTA/SiO$_2$-P. Zr(IV) is reported to have strong affinity to three O atoms in the TEHDGA molecule [21]. Zr(IV)-based species might be eluted in less acidic solution with MA(III) and Ln(III); therefore, Zr(IV) must be separated from MA(III) by the 2nd column or a masking should be employed in the 1st column. Nevertheless, the $K_d$ of Sr(II) and Zr(IV) for TEHDGA/SiO$_2$-P had lower value than those for TODGA/SiO$_2$-P [7]; in fact, TEHDGA/SiO$_2$-P has an advantage over TODGA/SiO$_2$-P with respect to affording the decontamination of Sr(II) and Zr(IV).

### Column experiment

The elution curves of Eu(III) obtained by TEHDGA and TODGA/SiO$_2$-P column operations are shown in Fig. 7, where $C_0$ and $C$ represent to concentrations of metals in the feed solution and effluent, respectively. The TEHDGA/SiO$_2$-P column showed earlier breakthrough than the TODGA/SiO$_2$-P column. The adsorption capacities of the TEHDGA/SiO$_2$-P and TODGA/SiO$_2$-P adsorbents, calculated from each of breakthrough curves, were 0.04 and 0.06 mmol cm$^{-3}$, respectively. The amount of feed solution supplied to the column should be adjusted based on these values.

Eu(III) was observed to be promptly eluted from the TEHDGA/SiO$_2$-P column, whereas elution from the TODGA/SiO$_2$-P column was slow and the elution curve was broad. According to results from previous studies, short alkyl chain of DGA molecules weaken stability of complex [22]. It will lead to difference in different elution behavior and adsorbent capacity. TEHDGA/SiO$_2$-P is preferable to TODGA/SiO$_2$-P as an adsorbents, in the respect of rapid elution i.e.
reduction in the effluent volume, although adsorption capacity is slightly smaller.

Elution curves obtained by the repeated column experiment with TEHDGA/SiO₂-P on simulated HLLW are shown in Fig. 8. In this work, all elements evaluated showed almost the same elution profiles over 6 times of the operation. The values of recovery rate for each element is shown in Table 1. The recovery rate is the value obtained by dividing the amount of substance isolated in the eluent by the amount of substance in the feed solution in each cycle. Most of the Pd(II) and Mo(VI) were not adsorbed by TEHDGA/SiO₂-P, so they were washed out with the wash solution. On the other hand, a part of Pd(II) and Mo(VI) remained in the adsorbent even after adding the eluent to the column. In order to prevent accumulation of those metal ions in the column, another wash solution or
Fig. 8 Elution curves obtained from the repeat column experiments with the TEHDGA/SiO₂-P adsorbents on simulated HLLW. A: Dead volume, B: feed solution, C: wash solution (3 M HNO₃), D: eluent (distilled water), E: conditioning solution (3 M HNO₃)

Table 1 Recovery rate for each elements

| Cycle | La(III) | Nd(III) | Sm(III) | Eu(III) | Y(III) | Pd(II) | Mo(VI) | Zr(IV) | Sr(II) |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1     | 100    | 100    | 100    | 100    | 100    | 92     | 80     | 0      | 100    |
| 2     | 98     | 100    | 99     | 100    | 99     | 91     | 82     | 0      | 100    |
| 3     | 100    | 100    | 100    | 100    | 100    | 100    | 84     | 0      | 100    |
| 4     | 95     | 98     | 99     | 99     | 96     | 90     | 79     | 1      | 97     |
| 5     | 100    | 100    | 100    | 100    | 100    | 100    | 88     | 15     | 100    |
| 6     | 96     | 100    | 99     | 100    | 97     | 94     | 75     | 29     | 98     |
addition of masking reagent should be adopted. EDTA is one of the candidates for masking those elements. Ln(III) and Sr(II) were immediately eluted by supplying distilled water and they were separated from other FPs. Recovery ratios of them are almost 100\%, and MA(III) are expected to show similar behavior with those metal ions. In the 2nd column, MA(III) are separated from Ln(III) and Sr(II) by HONTA/SiO₂-P adsorbent packed column [23].

Properly adsorbed Zr(IV) in the column hardly eluted through the column operation. From Fig. 8 and Table 1, all of the supplied Zr(IV) accumulated inside the column from the 1st to 3rd cycle, and a part of loaded or supplied Zr(IV) were eluted in the 4th to 6th cycle. Breakthrough of adsorption capacity of TEHDGA for Zr(IV) might be the reason of the elution. Up to 6th cycle, accumulation of Zr(IV) did not influence on elution behavior of other elements. However, more cycles of operation are suspected to lead change in the column performance due to occupation of adsorption sites by the accumulated elements, thus discharge of accumulated Zr(IV) is indispensable for practical use of the column. Appropriate reagents for elution or masking of Zr(IV) have to be employed. Removal of Zr(IV) in the HLLW using HDEHP/SiO₂-P adsorbent in advance with the 1st column operation is also one of options [24].

Based on the above discussion, combination of TEHDGA/SiO₂-P column and HONTA/SiO₂-P column is promising for MA(III) recovery from HLLW. However, improvement in the flow-sheet is required to prevent accumulation of FP elements in the column. Fundamental investigation for the improvement is currently underway.

**Conclusions**

Applicability of TEHDGA/SiO₂-P packed column for MA(III) + Ln(III) co-recovery by extraction chromatography technology was experimentally investigated through back-wise and column separation experiments on several fission product elements. TEHDGA was shown to have an advantage over TODGA in the respect of elution performance of Ln(III) from the adsorbent. MA(III) separation process with TEHDGA/SiO₂-P can achieve not only high MA(III) + Ln(III) co-recovery performance but also reduction in the effluent volume. 6 times repeated column separation operation showed excellent reproducibility in the adsorption/elution curves.

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