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

Yusuke Horiuchi^{1,2} · Sou Watanabe¹ · Yuichi Sano¹ · Masayuki Takeuchi¹ · Fukuka Kida² · Tsuyoshi Arai²

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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, NO_x and H₂O on incineration.

So far, *N,N,N',N'*-tetraoctyl 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

✉ Yusuke Horiuchi
horiuchi.yusuke@jaea.go.jp

¹ Japan Atomic Energy Agency, 4-33, Muramatsu,
Tokai-mura, Ibaraki 319-1194, Japan

² Shibaura Institute of Technology, 3-7-5, Toyosu, Koutouku,
Tokyo 135-8548, Japan

Fig. 1 Structure of TEHDGA

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 described in a reference [15].

Fig. 2 Flow-sheet of SiO₂-P preparation

Fig. 3 TEHDGA impregnated method onto SiO₂-P

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 $0.001 < [\text{HNO}_3] < 10 \text{ M}$.

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;

$$D = \frac{C_0 - C_{aq}}{C_{aq}} \quad (1)$$

$$K_d = \frac{C_0 - C_s}{C_0} \times \frac{V}{W} \quad (2)$$

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).

$$\text{Recovery rate [\%]} = \frac{A_{\text{eluent}}}{A_{\text{supply}}} \times 100 \quad (3)$$

where A_{eluent} and A_{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 $0.001 \text{ M} < [\text{HNO}_3] < 0.01 \text{ M}$ was 0%, and it was not plotted because it could be not expressed in Log. As shown

Fig. 4 Experimental setup for the column separation experiments

Fig. 5 Extraction behavior of Ln(III)s for TEHDGA extractant

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:

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/SiO₂-P are shown in Fig. 6. It is evident from Fig. 6, Sr(II), Zr(IV) and Ln(III)s were adsorbed on TEHDGA/SiO₂-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 acidity 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 the K_d might be proportional 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/SiO₂-P from acidic solution, and their decontamination from liquid sample should be easily achieved.

At $[HNO_3] > 1$ M, the K_d of Ln(III)s was almost the same value, although $\log D$ evaluated for the solvent extraction system at $[HNO_3] = 3$ 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/SiO₂-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/SiO₂-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/SiO₂-P had lower value than those for TODGA/SiO₂-P [7]; in fact, TEHDGA/SiO₂-P has an advantage over TODGA/SiO₂-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/SiO₂-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/SiO₂-P column showed earlier breakthrough than the TODGA/SiO₂-P column. The adsorption capacities of the TEHDGA/SiO₂-P and TODGA/SiO₂-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/SiO₂-P column, whereas elution from the TODGA/SiO₂-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/SiO₂-P is preferable to TODGA/SiO₂-P as an adsorbents, in the respect of rapid elution i.e.

Fig. 6 Distribution coefficient of FPs onto TEHDGA/SiO₂-P adsorbent

Fig. 7 Elution curves of Eu(III) obtained from the column experiments with the TEHDGA, TODGA/SiO₂-P adsorbents. A: Dead volume, B: feed solution, C: wash solution (3 M HNO₃), D: eluent (distilled water)

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	Recovery rate [%]								
	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 batch-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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References

- Oigawa H, Tsujimoto K, Nishihara K, Sugawara T, Kurata Y, Takei H, Saito S, Sasa T, Obayashi H (2011) Role of ADS in the back-end of the fuel cycle strategies and associated design activities; The Case of Japan. *J Nuclear Mater* 415:229–236
- Watanabe S, Sano Y, Kofuji H, Takeuchi M, Shibata A, Nomura K (2018) Am,Cm recovery from genuine HLLW by extraction chromatography. *J Radioanal Nucl Chem* 316:1113–1117
- Du H, Peng X, Cui Y, Sun G (2019) Effect of DGA substituent structure on rare earth extraction in nitric acid media. *Earth Environ Sci* 310:042023
- Tachimori S, Sasaki Y, Suzuki S (2002) Modification of TODGA-n-dodecane solvent with a monoamide for high loading of lanthanide(III) and actinide(III). *Solvent Extr Ion Exch* 22(4):687–699
- Ansari SA, Pathak PN, Manchanda VK, Husain M, Prasad AK, Parmar VS (2005) N,N,N',N'-tetraoctyl diglycolamide (TODGA): a promising extractant for actinide-partitioning from high-level waste (HLW). *Solvent Extr Ion Exch* 23:463–479
- Zhu Z, Sasaki Y, Suzuki H, Suzuki S, Kimura T (2004) Cumulative study on solvent extraction of elements by N,N,N,N'-tetraoctyl-3-oxapentanediamide(TODGA) from nitric acid into n-dodecane. *Anal Chim* 527:163–168
- Hoshi H, Wei Y-Z, Kumagai M, Asakusa T, Morita Y (2004) Group separation of trivalent minor actinides and lanthanides by TODGA extraction chromatography for radioactive waste management. *J Alloys Compd* 374:451–455
- Tachimori S, Suzuki S, Sasaki Y, Apichabukol A (2003) Solvent extraction of alkaline earth metal ions by diglycolic amides from nitric acid solutions. *Solvent Extr Ion Exch* 21:707
- Sugo Y, Sasaki Y, Tachimori S (2002) Studies on hydrolysis and radiolysis of N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamine. *Radiochim Acta* 90:161–165
- Sasaki Y, Rapold P, Arisaka M, Hirata M, Kimura T, Hill C, Cote G (2007) An additional insight into the correlation between the distribution ratios and the aqueous acidity of the TODGA system. *Solvent Extr Ion Exch* 25:187–204
- Ansari S, Mohapatora PK, Prabhu DR, Manchanda VK (2007) Evaluation of N,N,N',N'-tetraoctyl-3-oxapentane diamide (TODGA) as a mobile carrier in remediation of nuclear waste using supported liquid membrane. *J Membr Sci* 298:169–174
- Nave S, Modolo G, Madić C, Testard F (2004) Aggregation properties of N,N,N',N'-tetraoctyl-3-oxapentane diamide (TODGA) in n-dodecane. *Solvent Extr Ion Exch* 22(4):527–551
- Watanabe S, Senzaki T, Shibata A, Nomura K, Koma Y, Nakajima Y (2011) MA recovery experiments from genuine HLLW by extraction chromatography. In: *Proceedings of the Global 2011, Makuhari, Japan, December 11–16*
- Horwitz EP, McAlister DR, Bond AH, Barrans RE Jr (2005) Novel extraction of chromatographic resins based on

- tetraalkyldiglycolamides: characterization and potential applications. *Solvent Extr Ion Exch* 23:319–344
15. Wei Y, Kumagai M, Takashima Y (2000) Studies on the separation of minor actinides from high-level wastes by extraction chromatography using novel silica-based extraction resins. *Nucl Technol* 132:413–423
 16. Fan Y, Li Y, Shu X, Wu R, Chen S, Jin Y, Xu C, Chen J, Huang C, Xia C (2021) Complexation and separation of trivalent actinides and lanthanides by a novel DGA derived from macrocyclic crown ether: synthesis, extraction, and spectroscopic and density functional theory studies. *ACS Omega* 6:2156–2166
 17. Petit S, Bertolo L, Petitjean F, Marie C, Conocar O, Thiebaut V (2016) TEHDGA, DMDOHEMA and mixed sorbents: characterization and Am(III) uptake properties. *Procedia Chem* 21:9–16
 18. Goto M, Kakoi T, Narisako M, Kondo K, Nakashino F (1992) *Kagaku Kogaku Ronbunshu* 18:767–769
 19. Sano M, Shibata J, Harada M, Nishimura S (1987) Extraction of Molybdenum and Tungsten with D2EHPA and LIX63. *Nippon kogyokaishi* 104:475
 20. Nayak PK, Kumaresan R, Venkatesan KA, Antony MP, VasudevaRao PR (2013) A new method for partitioning of trivalent actinides from high-level liquid waste. *Sep Sci Technol* 48:1409–1416
 21. Sasaki Y, Saeki M, Yoshizuka K (2019) Extractions and spectroscopic studies of various metals with diglycolamide-type tridentate ligands. *Solvent Extr Res Dev Japan* 26:21–34
 22. Deepika P, Sabharwal KN, Srinivasan TG, VasudevaRao PR (2010) Studies on the use of N,N,N',N'-tetra(2-ethylhexyl) diglycolamide(TEHDGA) for actinide partitioning. I: Investigation on third-phase formation and extraction behavior. *Solvent Extr Ion Exch* 28:184–201
 23. Takeuchi M, Watanabe S, Sano Y, Kofuji H, Suzuki H, Matsumura T (2019) Characterization of HONTA/SiO₂-P adsorbent for MA(III)/Ln(III) separation flow-sheet. *Global* 2019:11
 24. Abe R, Nagoshi K, Arai T, Watanabe S, Sano Y, Matsuura H, Takagi H, Simizu N, Koka M, Sato T (2017) Microscopic analyses of complexes formed in adsorbent for Mo and Zr separation chromatography. *Nuclear Instrum Methods Phys Res Sect B Beam Interact Mater Atoms* 404:173–178

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