Journal of Alloys and Compounds 408–412 (2006) 1274–1277

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Separation of trivalent actinides from lanthanides by using R-BTP resins and stability of R-BTP resin

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Abstract

For the development of advanced aqueous reprocessing system, it is one of the most important subjects to separate minor trivalent actinides (MA = Am and Cm). MA are α-emitters with long half-life, therefore it is desired to separate MA from fission products. However, it is very difficult to separate MA from lanthanides (Ln) owing to their chemical similarity. For the separation of these two groups of elements, solvent extraction process has been widely studied based on the difference in complex formation with extractants. Extraction chromatography is one of the most promising separation techniques for recovering small amounts of target components from solution. For this purpose, we prepared novel silica-based extraction resins by impregnating some R-BTP molecules into a macroreticular styrene–divinylbenzene copolymer which is immobilized in porous silica particles with a mean diameter of 50 μm. The impregnated resin has high affinity for Am against Ln(III) not only in sodium nitrate solution but also in nitric acid solution.

Stability of the extraction resin was also examined. The silica-based support was significantly stable against γ-irradiation and nitric acid. A part of R-BTP was dissolved into nitric acid solution from the extraction resin due to protonation. However, the branched R-BTP (*iso*-Bu-BTP) resin was much more stable than a normal R-BTP in nitric acid solution ($\leq$3 M).

Keywords: R-BTP; Chromatography; MA; Lanthanides

1. Introduction

For the development of nuclear fuel cycle, it is one of the most important tasks to improve reprocessing process more economically and efficiently [1]. Especially, to establish the Fast Breeder Reactor (FBR) cycle system for the future, it is strongly desirable to develop a new reprocessing process which uses more compact equipments and produces less radioactive wastes compared to the present PUREX process. For this purpose, we have proposed a novel aqueous reprocessing system named ERIX Process (The Electrolytic Reduction and Ion Exchange Process for Reprocessing Spent FBR-MOX Fuel) to treat spent FBR-MOX fuels as shown in Fig. 1. This process consists of (1) Pd removal by selective adsorption using a specific anion exchanger; (2) electrolytic reduction for the valence adjustment of the major actinides including U, Pu, Np and some fission products (FP) such as Tc and Ru; (3) anion exchange separation for the recovery of U, Pu and Np using a new type of anion exchanger, AR-01; and (4) selective separation of long-lived minor actinides (MA = Am and Cm) by extraction chromatography.

Recently, excellent selectivity for MA(III) over Ln(III) has been found on some extractants containing soft donor, such as S or N [2,3,4]. Kolarik et al. reported that a new N-donor ligand, 2,6-bis(5,6-dialkyl- 1,2,4-triazine-3-yl)-pyridine (R-BTP), shows high selectivity for MA (III) over Ln(III) [5,6]. The MA separation is achieved in two column units. Firstly, MA(III) and trivalent lanthanides (Ln(III)) are separated from other FP elements in the HLLW containing concentrated nitric acid by the first column packed with the silica-based

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doi:10.1016/j.jallcom.2005.04.128

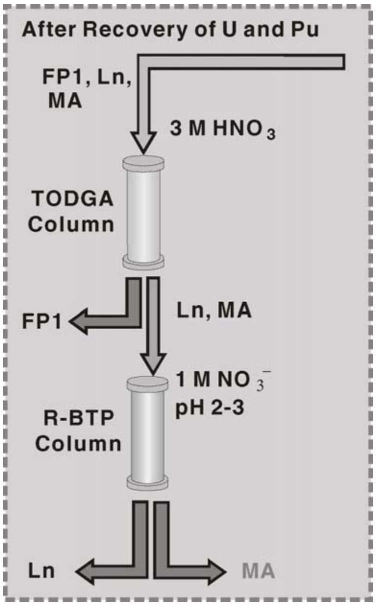

Fig. 1. MA separation process in "ERIX Process". FPI: Cs, Sr, Mo, Rh, etc.; Ln: La, Nd, Y, etc.; MA: Am and Cm.

TODGA (*N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane-1,5-diamide) extraction resin [7]. Secondly, MA(III) and Ln(III) are mutually separated from each other using the second column packed with the silica-based R-BTP extraction resin [8].

This work is focused on the recent study on mutual separation of MA(III) and Ln(III) from simulated high-level liquid waste (HLLW) using the silica-based extraction resin containing the newly developed chelating extractant, R-BTP. The extraction resin was prepared by impregnating R-BTP into a macroreticular styrene–divinylbenzene copolymer which is immobilized in porous silica particles with a mean diameter of 50 μm, as described in previous studies [1,9].

2. Experimental

2.1. Preparation of silica-based extraction resin

Spherical silica particles with a diameter of 40–60 μm, a mean pore size of 600 nm and a pore fraction of 0.69 were used. As the support of extractant, an inert copolymer of formylstyrene and divinylbenzene was synthesized and embedded into the pores of the silica particles. The preparation method of the polymer-immobilized silica particles (SiO_2-P) was reported previously [9]. Some molecules of 2,6-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridine (R-BTP) as shown in Fig. 2, were used. The extractant was impregnated into the SiO_2-P particles as follows: 5 g of extractant was placed in a glass flask and dissolved using 20 cm^3 of dichloromethane as a diluent. Subsequently, 10 g of the dried SiO_2-P particles was added to the solution and was shaken mechanically for 2 h at 298 K. The diluent was removed under reduced pressure and finally dried up in vacuo. Since there was no loss of extractant during impregnation, the resultant extraction resin (R-BTP/SiO_2-P) contains 0.5 g of R-BTP in 1.0 g of SiO_2-P.

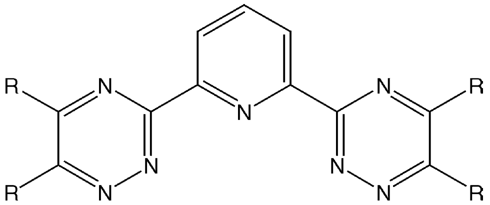

Fig. 2. R-BTP extractant. Et-BTP: R = C_2H_5; Pr-BTP; R = *n*-C_3H_7; *n*-Bu-BTP: R = *n*-C_4H_9; *iso*-Bu-BTP; R = *iso*-C_4H_9; *n*-Hex-BTP: R = *n*C_6H_{13}; *n*-C_8H_{17}.

2.2. Adsorption experiment

All distribution coefficients (K_d) were measured by batch experiment. A definite amount of extraction resin (0.25 g) was combined in a glass vial with screw cap with a measured volume (5 cm^3) of an aqueous solution. The glass vial was packed in a vinyl bag and was shaken mechanically for 3 h in a water bath at 25 °C. The aqueous phase was filtrated through a membrane filter with 0.45 μm pore. The concentration of metal was determined by ICP-AES (ICPS-1000IV; Shimadzu) modified to handle radioactive samples in a glove box and gamma-activity of ^{241}Am was determined by gamma spectrometry (SEIKO EG&G). The distribution coefficient was calculated by:

$$K_d = \frac{C_0 - C_s}{C_s} \times \frac{V}{W} \qquad (1)$$

or

$$K_d = \frac{A_0 - A_s}{A_s} \times \frac{V}{W} \qquad (2)$$

where C_0, A_0, C_s, and A_s denote the concentration of metal or activity in the aqueous phase before and after adsorption, respectively. V indicates the volume of aqueous phase and W is the weight of the dry extraction resin.

2.3. Stability of the extraction resin

An amount of *n*-Bu-BTP resin and pure water or $NaNO_3$ solution were packed in glass vial and irradiated by ^{60}Co-γ source. After prescribed term, total organic carbon (TOC) concentration in liquid phase was determined by TOC analyzer (TOC-V; Shimadzu). Calibration curve was made by using sodium phthalate (Wako Chem.) solution.

3. Results and discussion

3.1. Adsorption behavior of Am(III) and Ln(III)

Adsorption kinetics of Am(III) and Ln(III) onto *iso*-Bu-BTP resin was examined experimentally by contacting with

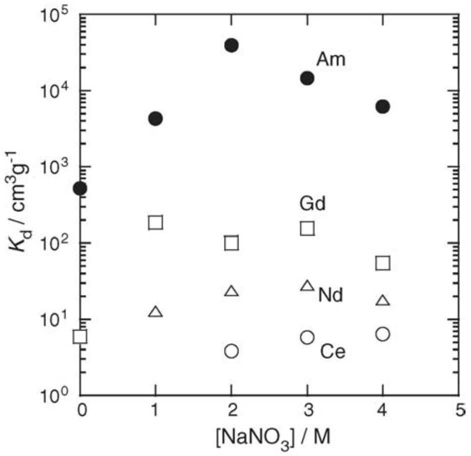

Fig. 3. Distribution coefficients of Am and Ln onto *iso*-Bu-BTP resin from sodium nitrate solution.

a mixture of 0.1 HNO_3 and 3 M $NaNO_3$. The adsorption of Am(III) reached an equilibrium state within 2 h with distribution coefficient over 10^4 cm^3/g.

Adsorption behavior of Am(III) and Ln(III) onto *iso*-Bu-BTP resin from sodium nitrate solution at a constant nitric acid concentration of 0.1 M, was shown in Fig. 3. Separation factor (SF) between Am(III) and Ln(III) were calculated as the ratio of K_d values and summarized in Table 1. Distribution coefficient of Am increased with increasing $NaNO_3$ concentration and then reached a maximum value of over 3×10^4 cm^3/g at 2 M $NaNO_3$. The decrease of K_d at high $NaNO_3$ concentration is owing to the competition adsorption of $NaNO_3$ or HNO_3. Separation factor between Am and Gd was also obtained as a maximum value of about 400 at 2 M $NaNO_3$.

Adsorption behavior of Am(III) and Ln(III) onto *iso*-Bu-BTP resin from 3 M nitric acid solution is shown in Fig. 4. The distribution coefficient of Am(III) increased to more than 10^4 cm^3/g in 2 h contact and attained to an equilibrium state. The adsorption of both Ce(III) and Nd(III) also attained to equilibrium states in 2 h, however, the adsorption kinetics of Gd(III) was slightly slow and needed 3 h for equilibration. From these results, it is obvious that *iso*-Bu-BTP resin can strongly and selectively adsorb Am(III) form nitric acid solution, though *n*-Bu-BTP had adsorption affinity only from nitrate solution with low acidity [8].

Table 1
Separation factors between Am and Ln in sodium nitrate solution.

[NaNO$_3$] (M)	Ce(III)	Nd(III)	Gd(III)
0	$>10^3$	$>10^3$	8.82×10^1
1	$>4 \times 10^3$	3.35×10^2	2.32×10^1
2	1.04×10^4	1.64×10^3	3.92×10^2
3	2.49×10^3	5.14×10^2	9.41×10^1
4	9.71×10^2	3.44×10^2	1.13×10^2

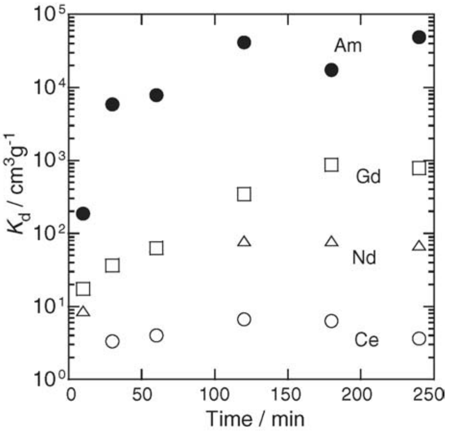

Fig. 4. Adsorption of Am and Ln onto *iso*-Bu-BTP resin from 3 M nitric acid solution.

Table 2
TOC from SiO_2-P after γ-irradiation

Initial nitric acid concentration (M)	After irradiation	
	[TOC] (ppm)	[H^+] (M)
0	ND	4.68×10^{-4}
1	0.623	1.12
3	24.7	3.03

3.2. *Stability of the extraction resin*

Firstly, the stability of SiO_2-P against γ-irradiation was examined. TOC concentration in liquid phase after γ-irradiation is shown in Table 2. The negligibly small TOC concentration indicates that the SiO_2-P is stable against γ-irradiation.

The stability of extraction resin against γ-irradiation was examined. *n*-Bu-BTP extraction resin was irradiated in pure water or sodium nitrate solution. TOC concentration in liquid phase after γ-irradiation is shown in Fig. 5. After the irradiation in water, the TOC concentration increased with

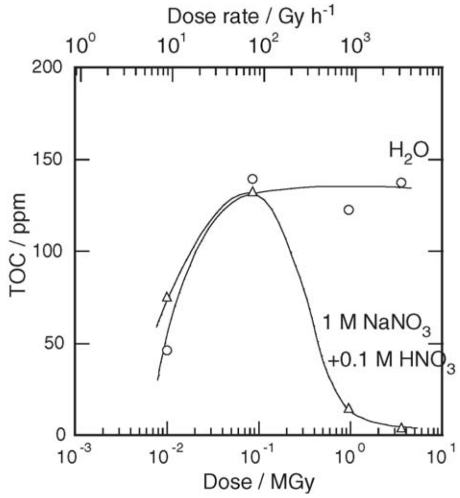

Fig. 5. TOC concentration after γ-irradiation.

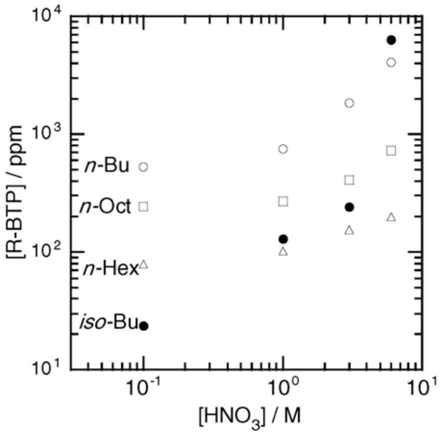

Fig. 6. Leakage of R-BTP from resin into nitric acid solution.

increasing γ-dose and was steady at more than 0.1 MGy. On the other hand, after the irradiation in sodium nitrate solution, the TOC concentration increased with increasing γ-dose up to 0.1 MGy and then decreased drastically with γ-dose. These are presumed to be caused by the following reactions: C−H bonds of hydrocarbon are dissociated to free radical of hydrogen atom and carbon by irradiation [10]. Hydrogen atom abstracts hydrogen atom from molecules existing nearby and is stable. Free radicals of carbon become stable by such as cross-linking each other or making double-bond between molecules.

$$-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-CH_2-\dot{C}H-CH_2- + H \qquad (3)$$

$$-CH_2-CH_2-CH_2-CH_2- + H \rightarrow -CH_2-CH_2-\dot{C}H-CH_2- + H_2 \qquad (4)$$

$$-CH_2-CH_2-\dot{C}H-CH_2- + H \rightarrow -CH_2-CH{=}CH-CH_2- + H_2 \qquad (5)$$

On the other hand, hydrocarbons at end is dissociated and generate gasses such as methane, ethane, ethylene, propane or propylene if short chain such as methyl group, ethyl group or long chain is existent. Especially in the presence of oxygen, free radicals preferentially react with oxygen and cleave C−C bond of backbone, releasing CO or CO_2. Therefore, the concentration of TOC decreased owing to decomposition of hydrocarbon in the sodium nitrate solution.

R-BTP extractant is liable to dissolve in concentrated acid because of protonation [11]. Stability of some R-BTP extraction resins was examined by contacting with nitric acid solution. The leakage behavior of R-BTP extractant from resin is shown in Fig. 6. The leakage of all the R-BTP resins increased with increasing nitric acid concentration. Branched R-BTP resin (*iso*-Bu-BTP) has a remarkable stability in dilute nitric acid solution compared to normal R-BTP (*n*-Bu-BTP).

4. Conclusions

A novel silica-based extraction resin impregnated with *iso*-Bu-BTP was prepared. Adsorption of metal ions attained to an equilibrium state rapidly, since fine porous silica particles of 50 μm was used as a support. It had high adsorption affinity for Am(III) in not only sodium nitrate solution but also concentrated nitric acid solution.

Stability of the extraction resin was also examined. The silica-based support was significantly stable against γ-irradiation and nitric acid. A part of R-BTP was dissolved into nitric acid solution from the extraction resin due to protonation. However, the branched R-BTP (*iso*-Bu-BTP) resin was much more stable than a normal R-BTP in nitric acid solution (≤3 M).

Acknowledgment

This work was financed by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) under the framework of “The Development of Innovative Nuclear Technologies”.

References

[1] Y.-Z. Wei, T. Arai, M. Kumagai, A. Bruggeman, L. Vos, Proceeding of the 13th Pacific Basin Nuclear Conference (PBNC-2002), Shenzen, China, October 21–25, 2002.
[2] Y. Zhu, Radiochim. Acta 68 (1995) 95.
[3] C. Madic, M.J. Hudson, Nucl. Sci. Technol. EUR 18038 (1998) 140.
[4] M.J. Hudson, M.R. Foreman, C. Hill, N. Huet, C. Madic, Solv. Extr. Ion Exch. 21 (5) (2003) 637–652.
[5] Z. Kolarik, U. Müllich, F. Gassner, Solv. Extr. Ion Exch. 17 (1999) 23.
[6] Z. Kolarik, Solv. Extr. Ion Exch. 21 (3) (2003) 381–397.
[7] H. Hoshi, Y.-Z. Wei, M. Kumagai, T. Asakura, Y. Morita, J. Alloys Comp. 374 (2004) 451–455.
[8] Y.-Z. Wei, H. Hoshi, M. Kumagai, T. Asakura, Y. Morita, J. Alloys Comp. 374 (2004) 447–450.
[9] Y.-Z. Wei, M. Kumagai, Y. Takashima, G. Modolo, R. Odoj, Nucl. Technol. 132 (2000) 413–423.
[10] Y. Haruyama, H. Sunaga, K. Arakawa, T. Seguchi, JAERI-Tech 2002-084 (2002) (in Japanese).
[11] Z. Kolarik, U. Mullich, F. Gassner, Solv. Extr. Ion Exch. 17 (4) (1999) 1155–1170.