Americium and curium separation from simulated acidic raffinate from the reprocessing process by extraction chromatography

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Abstract

As a part of the Fast Reactor Cycle Technology Development Project (FaCT), research and development of a reprocessing system for fast breeder reactor spent fuel has been conducted. In the system, trivalent actinides [An(III) = Am(III) and Cm(III)] are recovered by the method of extraction chromatography from an acidic raffinate from the reprocessing process that recovers U, Np and Pu. In general, an extractant for solvent extraction can be used as an adsorbent for extraction chromatography. The principle of separation for extraction chromatography is similar to that of solvent extraction, therefore, chemical flow sheet is composed of a two-cycle system; An(III)-lanthanides [Ln(III)] recovery and An(III)/Ln(III) separation. A best combination of extractants should be considered on the latest extractant development for application. In the course of development, CMPO [noctyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphineoxide] and TODGA (N,N,N',N'-tetraoctyl-diglycolamide) for An(III)–Ln(III) recovery, and HDEHP [bis(2-ethylhexyl)hydrogen phosphate], isoHEX-BTP [2,6-bis(5,6-di-iso-hexyl-1,2,4-triazine-3-yl-pyridine] and TOPEN [N,N,N',N'-tetrakis((5-octyloxypyridin-2-yl)methyl)ethylenediamine] for An(III)/Ln(III) separation were investigated. The adsorbent for the extraction chromatography is based on the composite material of porous silica support and polystyrenedivinylbenzene (SiO_2-P) impregnated with the extractants. The flow sheet tests using simulated acidic raffinate from reprocessing process containing TRU tracers were carried out. This paper gives results of the research and development of the flow sheet of extraction chromatography.

Introduction

As a part of the Fast Reactor Cycle Technology Development Project (FaCT), research and development of a reprocessing system for fast breeder reactor spent fuel has been conducted [1]. In the system, Am and Cm is recovered by the method of extraction chromatography from an acidic raffinate from the solvent extraction process that recovers U, Np and Pu. In general, an extractant for solvent extraction can be used as an adsorbent. The principle of separation for extraction chromatography is similar to that of solvent extraction, therefore, chemical flow sheet assumed is composed of the two cycles system; trivalent actinides [An(III)] – lanthanides [Ln(III)] recovery and An(III)/Ln(III) separation. A best combination of extractants should be considered on the latest extractant development for application. In the course of our development, CMPO [n-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphineoxide] and TODGA [*N,N,N',N'*-tetraoctyldiglycolamide] for An(III)-Ln(III) recovery, and HDEHP [bis(2-ethylhexyl)hydrogen-phosphate], *iso*HEX-BTP [2,6-bis(5,6-di-iso-hexyl-1,2,4-triazine-3-yl-pyridine] and TOPEN [*N,N,N',N'*-tetrakis((5-octyloxypyridin-2-yl)methyl)ethylenediamine] for An(III)/Ln(III) separation were investigated. CMPO is the principal extractant of the TRUEX process [2] for An(III) recovery. And the TRUEX process is a major method to extract transuranics from highly acidic solutions. TODGA is an amide extractant and is also capable to recover An(III) [3,4] and recently extensively studied. From the both processes, a dilute nitric acid solution is obtained as an intermediate An(III)-Ln(III) product. As a low acidity is employed to mutually separate the groups, the dilute acid solution is preferred. HDEHP is used for the TALSPEAK process that is a traditional method for An(III)/Ln(III) separation [5]. DTPA (diethylenetriamine-pentaacetic acid) is combined to preferentially make a complex of An(III) cations for separation. BTP which is a selective extractant for An(III) [6] has been studied on various compounds to improve its performance. TOPEN is one of novel extractants which have TPEN structure, and has high performance of An(III)/Ln(III) separation [7,8]. The chemical structures of the extractants are shown in Figure 1. Choosing an extractant has important on process development. The extractants employed should be selected with a careful consideration on property of adsorption/elution, stability towards acid, radiation and heat, and also treatment for reuse and disposal. In this paper that follows the previous works [9,10], the flow sheet experiments were carried out for choosing extractants and making a flow sheet for An(III) separation and recovery.

Experiment

Adsorbents

The chemical structures of the aforementioned extractants are shown in Figure 1. Among some variants of BTP, iso-Hex-BTP was used because of the low solubility into water owing to its long and isotypealkyl chain [11]. And similarly, among some variants of TRPEN, TOPEN was used because of the low solubility into water owing to its long alkyl chain and its reasonable synthetic method [7,8]. The extractants were used as received. The porous silica particle coated with styrenedivinylbenzene polymer, SiO_2-P, as a support had 50 μm of mean diameter. The SiO_2-P purchased from Fuji Silysia Chemical Ltd. The extractants were impregnated into the SiO_2-P support by the procedures described by Wei, *et al.* [12]. The resultant adsorbents contained 0.5 g of extractant in 1.0 g of SiO_2-P.

Simulated raffinate

The simulated raffinate from reprocessing process for the separation experiment contains 18 elements described in Table 1. The composition of the simulated raffinate was based on the NEXT process for spent fuel from fast reactors.

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Figure 1: Chemical structures of the extractants for the flow sheet experiments

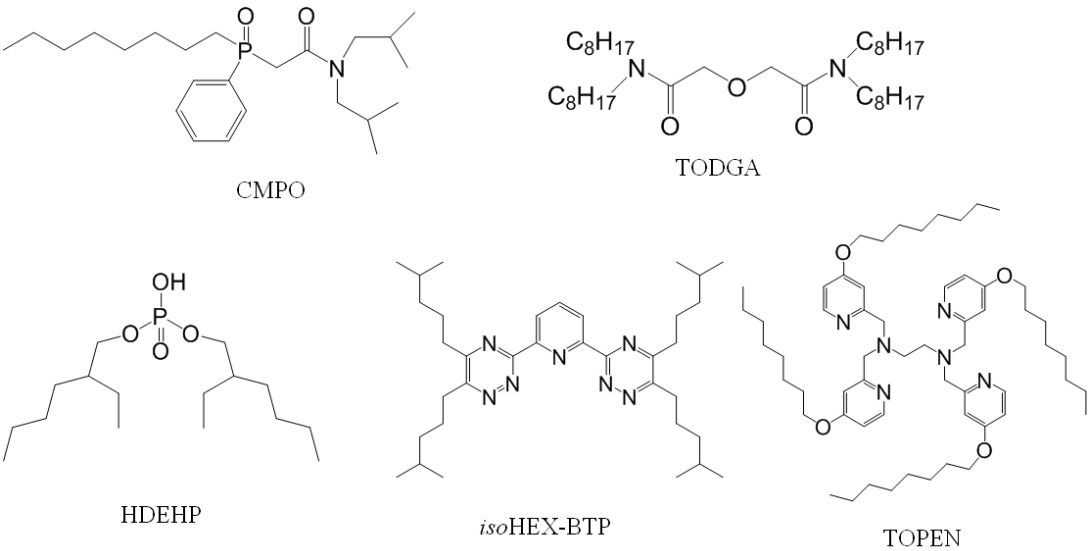


Table 1: Concentration of various elements in the simulated raffinate from reprocessing process

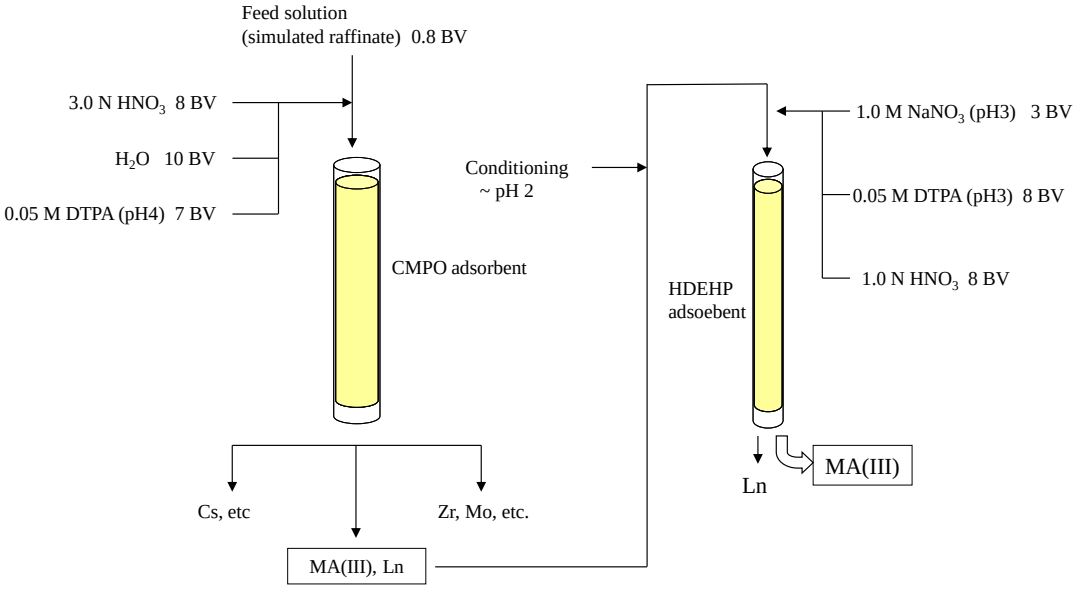
Elements	Metal concentration $\times 10^{-3}$ M	Radioactivity MBq/L
Cs	6.300	
Sr	1.103	
Y	0.666	
Zr	0.299	
Mo	6.811	
Ru	2.414	
Pd	5.299	
La	1.727	
Ce	3.268	
Pr	1.724	
Nd	1.440	
Sm	1.642	
Eu	0.195	
Tc	0.624	
^{243}Am		23.402
^{237}Np		39.111
^{137}Cs		39.111
^{239}Pu+^{240}Pu		36.722
^{244}Cm		28.109

Flow sheet using CMPO-HDEHP adsorbents

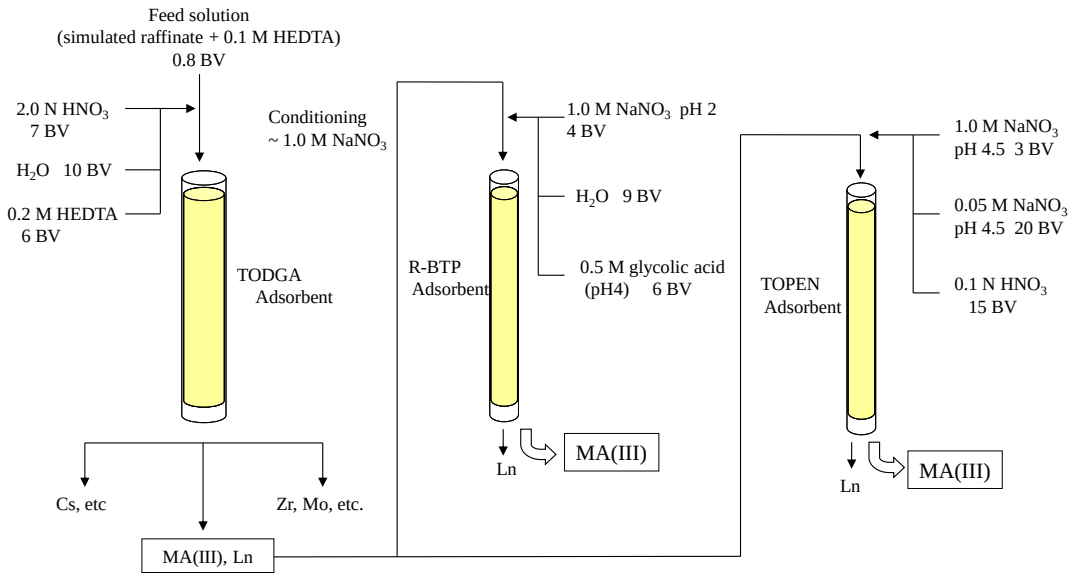
The separation experiments using the CMPO and HDEHP adsorbents were carried out using Pyrex glass columns with inner diameter of 8 mm and length of 300 mm. The adsorbents (dry weight: 7.0 g) were transferred to the columns in a slurry state. The volumes of the adsorbent bed (BV) were 15 cm^3. The columns and throughput solutions were at 50°C for CMPO adsorbent column and room temperature for HDEHP adsorbent column. Prior to the chromatographic operation, the adsorbent was conditioned by passing 100 cm^3 of HNO_3 solution through the columns. A schematic view of the experimental flow is shown in Figure 2(a).

Figure 2: Schematic flow sheet of the experiment

(a) A flow sheet using CMPO and HDEHP adsorbents



(b) A flow sheet using TODGA and *iso*HEX-BTP or TOPEN adsorbents



Flow sheet using TODGA-isoHEX-BTP/TOPEN adsorbents

The separation experiments using the TODGA, *iso*HEX-BTP and TOPEN adsorbents were carried out using Pyrex glass columns with inner diameter of 10 mm for the TODGA adsorbent and 8 mm for isoHEX-BTP and TOPEN adsorbents and length of 300 mm. The adsorbents (dry weight: 7.0 g) were transferred to the columns in a slurry state. The volumes of the adsorbent bed (BV) were 23.5 cm^3 and 15 cm^3. The columns and throughput solutions were at 40°C for TODGA adsorbent column and TOPEN adsorbent column and room temperature for *iso*HEX-BTP adsorbent column. Prior to the chromatographic operation, the adsorbent was conditioned by passing 100 cm^3 of HNO_3 solution through the columns. A schematic view of the experimental flow is shown in Figure 2(b).

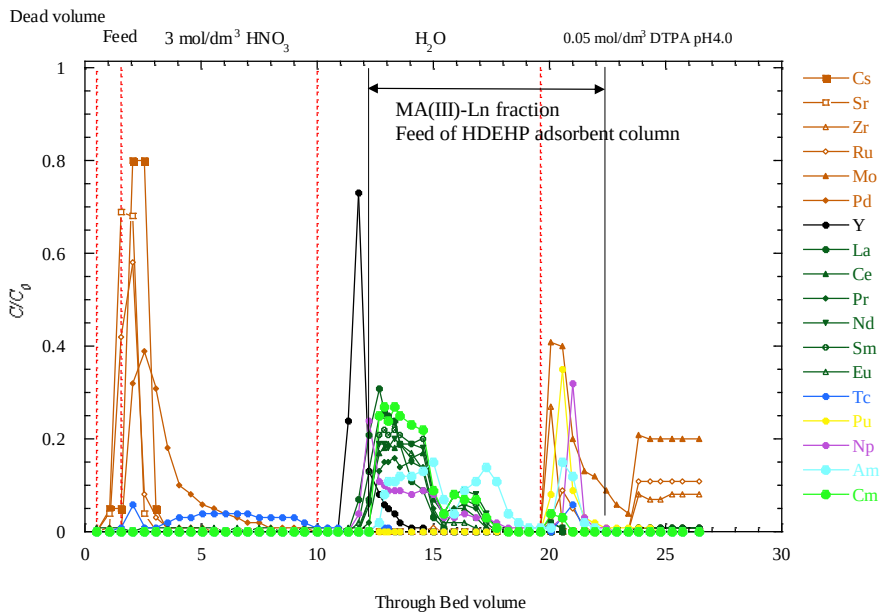
Results and discussion

Flow sheet using CMPO and HDEHP adsorbents

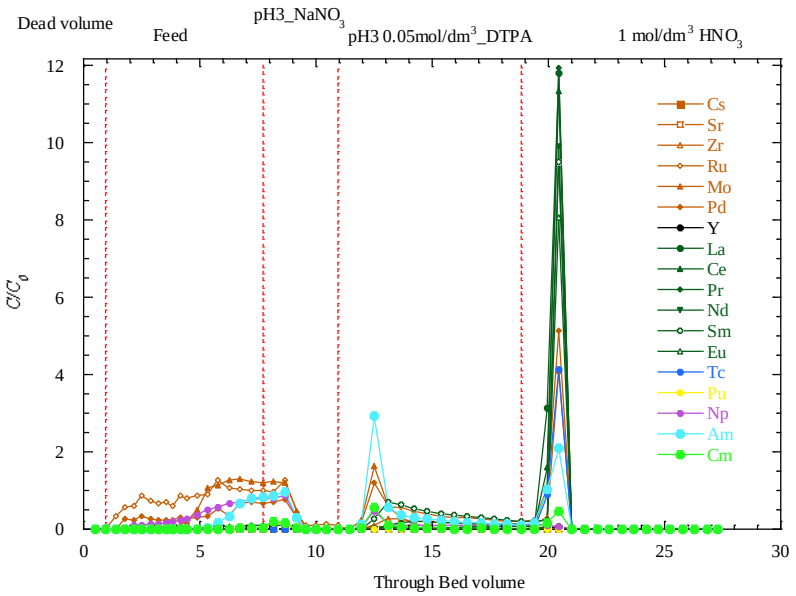
The chromatograms of the experiments using the CMPO and HDEHP adsorbents are shown in Figure 3. The MA(III)-Ln fraction from the CMPO adsorbent column for the feed solution of the HDEHP adsorbent column were 180 cm^3 (12 BV). In the chromatogram of the HDEHP adsorbent column, MA(III) eluted in the fraction of feed solution, DTPA solution and 1 M HNO_3. MA(III) were separated from Ln in the fraction of DTPA solution, however, the recovery rate were 25%.

Figure 3: Results of the flow sheet experiment using CMPO and HDEHP adsorbents

(a) A chromatogram of the experiment using the CMPO adsorbent column



(b) A chromatogram of the experiment using the HDEHP adsorbent column

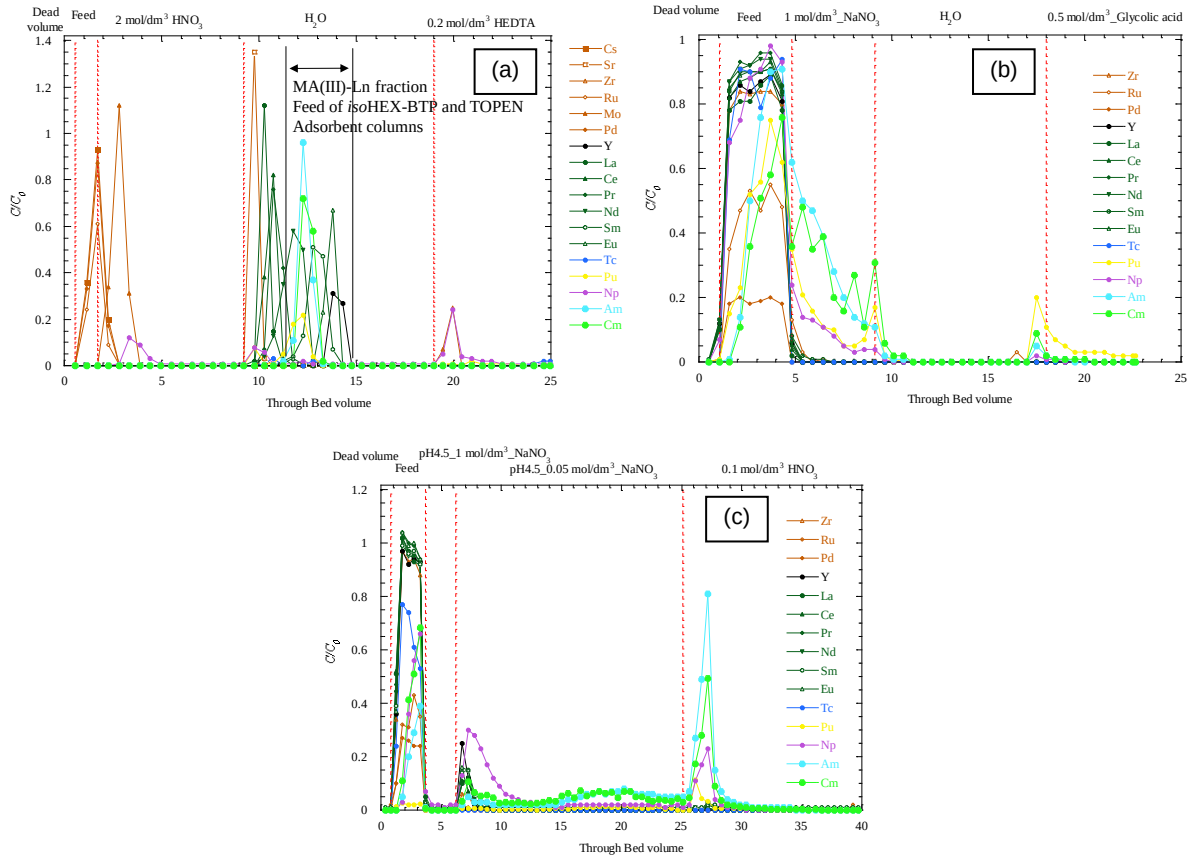


Flow sheet using TODGA, isoHEX-BTP and TOPEN adsorbents

The chromatograms of the experiments using the TODGA, *iso*HEX-BTP and TOPEN adsorbents are shown in Figure 4. The MA(III)-Ln fraction from the TODGA adsorbent column for the feed solution of the *iso*HEX-BTP adsorbent column and the TOPEN adsorbent column were 92 cm^3 (4 BV). The fraction was pH 2.7, and contains 99.9% of Am, 100% of Cm, 100% of Y, 2.3% of Ce, 34% of Pr, 90% of Nd, 100% of Sm, 100% of Eu. The other FP were not contained in the fraction. The moiety of the fraction was conditioned the ionic strength to 1.0 by addition of $NaNO_3$ and supplied to the isoHEX-BTP adsorbent column, and other moiety supplied to the TOPEN adsorption column without any conditioning. Am(III) and Cm(III) were separated by the *iso*HEX-BTP adsorbent column. The trivalent actinides were mainly expected to be eluted in H_2O fraction but were adsorbed by the *iso*HEX-BTP adsorbent more weakly than the predicted behaviour. Small amounts of Am(III) and Cm(III) were eluted in the feed solution because Am(III) and Cm(III) adsorption on *iso*HEX-BTP adsorbent is slow, as described in previous reports [11,13]. MA(III) and FP elements will be more effectively separated by improving conditions such as flow velocity and column length. Am(III) and Cm(III) were also separated by the TOPEN adsorbent column. The trivalent actinides were mainly eluted in 0.1 M HNO_3 fraction. Small amounts of Am(III) and Cm(III) were eluted in the feed solution because Am(III) and Cm(III) adsorption on TOPEN adsorbent is slow. MA(III) and FP elements will be more effectively separated by improving conditions such as flow velocity and ionic strength of feed solution.

Figure 4: Results of the flow sheet experiment using TODGA and *iso*HEX-BTP or TOPEN adsorbents

(a) Chromatogram of the experiment using the TODGA adsorbent column, (b) chromatogram of the experiment using the isoHEX-BTP adsorbent column, (c) Chromatogram of the experiment using the TOPEN adsorbent column



Conclusions

In this study, it was demonstrated that Am and Cm can be separated from simulated raffinate in the reprocessing process with combinations TODGA adsorbent column and *iso*HEX-BTP adsorbent column or TOPEN adsorbent column. The flow sheets using the two column units will separate MA(III) effectively by improving condition of flow velocity, column length and ionic strength of the feed solution.

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