



Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Local structure and distribution of remaining elements inside extraction chromatography adsorbents

Sou Watanabe^{a,*}, Yuichi Sano^a, Hideaki Shiwaku^b, Tsuyoshi Yaita^b, Simpei Ohno^c, Tsuyoshi Arai^c, Haruaki Matsuura^d, Masashi Koka^e, Takahiro Satoh^e^aJapan Atomic Energy Agency, 4-33, Muramatsu, Tokai-mura, Ibaraki 319-1194, Japan^bJapan Atomic Energy Agency, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan^cShibaura Institute of Technology, 3-7-5, Toyosu, Koutouku, Tokyo 135-8548, Japan^dTokyo City University, 1-28-1, Tamazutsumi, Setagayaku, Tokyo 158-8557, Japan^eNational Institute for Quantum and Radiological Science and Technology, 1233, Watanukicho, Takasaki, Gunma 370-1292, Japan

ARTICLE INFO

Article history:

Received 8 August 2016

Received in revised form 9 November 2016

Accepted 23 January 2017

Available online xxxxx

Keywords:

Extraction chromatography

Minor actinides

Lanthanides

PIXE-CT

EXAFS

ABSTRACT

A new adsorbent of the extraction chromatography technology impregnating CMPO and HDEHP extractants for minor actinide recovery process was prepared and fundamental performance were evaluated by batch-wise adsorption/elution experiments, EXAFS analysis and PIXE-CT analysis. Selective minor actinides recovery from the adsorbent charging minor actinides and lanthanides was revealed to be possible owing to synergistic extraction of lanthanides by CMPO and HDEHP. Discharging the residual lanthanides is essential for repeated use of the adsorbent, and ammonium acetate solution was proposed as an appropriate eluent although the elution ratio is not large enough. In order to enhance the elution performance of the lanthanides, improvements in structure of the adsorbent as well as in the eluent were shown to be important.

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1. Introduction

Partitioning and transmutation of radiotoxic elements such as minor actinides (MA(III): Am(III) and Cm(III)) and other long lived fission products is an important strategy to reduce a potential hazard of the final vitrified waste [1]. Extraction chromatography is one of the most promising technology for MA(III) recovery from high level liquid waste (HLLW) generated in the reprocessing [2]. In this technology, an extractant is impregnated into styrene-divinyl benzene copolymer coating around porous silica particle and the particles are utilized as an adsorbent [3]. MA(III) can be recovered through adsorption/elution processes inside the packed column. In our current flow-sheet, MA(III) are recovered by 2 steps column operations [4]. MA(III) and lanthanides (Ln(III)) are co-recovered from the HLLW by the 1st column, and then MA(III) are separated from Ln(III) by the 2nd column. For the 1st and 2nd columns, octyl(phenyl)-*N,N*-diisobutylcarbonylmethylphosphine oxide (CMPO) [5] and bis(2-ethylhexyl)hydrogen phosphate (HDEHP) [6] extractants are used for the adsorbents, respectively. CMPO extracts trivalent cations from acidic solution, and they

are stripped into less acidic solution. The back-extracted trivalent cations are extracted by HDEHP, and then MA(III) can be selectively stripped by using an appropriate complexing reagent. In these ways, MA(III) are separated from other elements though the 2 steps operations. MA(III) in genuine HLLW were successfully recovered by the current flow-sheet in our previous study [7], however further simplification of the process is desirable to reduce volumes of equipment and amount of secondary wastes such as spent adsorbents and waste solutions.

In order to simplify the current process, we propose application of an adsorbent with mixture of CMPO and HDEHP extractants. The CMPO in the binary system should extract MA(III) and Ln(III) from acidic media as it is solely used. According to extraction and back-extraction behavior of MA(III) and Ln(III) by CMPO or HDEHP at various acidity, the charged cations might be released from the CMPO and be extracted by the HDEHP alternatively under low acidic environment. Then, MA(III) can be selectively stripped from HDEHP by Diethylenetriaminepentaacetic Acid (DTPA) solution which is used as an eluent of MA(III) in our current flow-sheet. Consequently, MA(III) and Ln(III) co-recovery from the HLLW and MA(III)/Ln(III) separation can be achieved in single column with the adsorbent with the binary extractants. Preparation of the adsorbent with binary extractants and evaluation of basic

* Corresponding author.

E-mail address: watanabe.sou@jaea.go.jp (S. Watanabe).

performance of the adsorbent are required to design a practical condition for column operation.

In this study, adsorption/elution performances of the adsorbents and fundamental information of complexes formed in the adsorbent were investigated. Adsorption/elution property of the adsorbent was evaluated through batch-wise adsorption/elution experiments on $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$. Chemical state and distribution of $\text{Eu}(\text{III})$ inside the adsorbent before and after contacting with candidate eluents for $\text{MA}(\text{III})$ or $\text{Ln}(\text{III})$ were evaluated by Extended X-ray Absorption Fine Structure (EXAFS) analysis and Particle Induced X-ray Emission-Computed Tomography (PIXE-CT) analysis, respectively.

2. Experimental

2.1. Preparation of the adsorbent

Porous silica particle with about 600 nm and about 60 μm pore and particle diameters, respectively, were coated by styrene-divinyl benzene copolymer with 15% degree of the cross linkage. CMPO and HDEHP were impregnated into the copolymer with the same manner with that described in the article [3]. Amount of CMPO impregnated was fixed at 20 wt% of total weight of the adsorbent, and mole ratio of CMPO:HDEHP was parametrically changed 2:1 or 1:1 to evaluate influence of the composition on the performance. For comparison, adsorbent without HDEHP was also prepared and supplied to series of the experiments.

2.2. Adsorption/elution experiments

Batch-wise adsorption elution experiments on $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ were carried out to evaluate fundamental performance of the adsorbent. 1.47×10^5 Bq/mL of $^{241}\text{Am}(\text{III})$ or 20 mM of $\text{Eu}(\text{III})$ were in 1 M nitric acid solution. 10 mL of the solution was mixed with 0.5 g of the adsorbent and then shaken for 3 h at the room temperature. The supernatant solution was separated from the adsorbent, and concentrations of $^{241}\text{Am}(\text{III})$ or $\text{Eu}(\text{III})$ were analyzed by γ -ray spectrometry or ICP-AES, respectively, to evaluate distribution coefficients. The adsorbent was dried and supplied to the elution experiment.

0.2 g of the adsorbent charging $^{241}\text{Am}(\text{III})$ or $\text{Eu}(\text{III})$ was contacted with 4 mL of 50 mM DTPA solution at $\text{pH} = 2.3$, and shaken for 3 h at the room temperature. Elution ratios of $^{241}\text{Am}(\text{III})$ or $\text{Eu}(\text{III})$ were evaluated from concentrations of them in the supernatant solutions.

2.3. EXAFS analyses

Eu-K edge (48.5 keV) EXAFS measurements were carried out at BL11XU beamline of SPring-8, Japan. Adsorbents charging Eu and those after contacting with the eluent were put in glass vials and set at ionization chambers for measuring intensities of incident and transmitted X-ray. X-ray absorption spectra were analyzed to give information about the nearest neighboring atoms around Eu ions. The X-ray absorption spectra were analyzed by WinXAS 2.3 software [8] and FEFF8.0 code [9].

2.4. PIXE-CT analysis

The PIXE-CT analysis was carried out at a light-ion microbeam line connected to a 3-MV single-ended accelerator in Takasaki Ion accelerators for Advanced Radiation Application (TIARA) of National Institute for Quantum and Radiological Science and Technology, Japan. Proton beam energy was 3 MV, and the beam spot size and projection area were $1 \times 1 \mu\text{m}^2$ and $150 \times 150 \mu\text{m}^2$,

respectively. The same samples with the EXAFS analysis were analyzed to give distribution of Eu ions inside the adsorbent. The particle was set on a carbon fiber fixed on top of a needle. The needle was rotated, and projection images were collected every 9° . 3D image reconstruction was carried out according to the previous study [10].

3. Results and discussion

3.1. Adsorption/elution experiments

Distribution coefficients of $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ are shown in Fig. 1. Both $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ were adsorbed by the new adsorbent, and the distribution coefficient of Eu slightly increase with the ratio of HDEHP. The change in the adsorption behavior can be attributed to synergistic effect of CMPO and HDEHP reported in the solvent extraction system [11]. On the other hand, distribution coefficient of ^{241}Am slightly decreased with the ratio of HDEHP which is possibly an antagonistic effect of CMPO and HDEHP. Nevertheless, the decrease in the adsorption performance of ^{241}Am might not affect the process since the distribution coefficient is still large.

Elution ratios of $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ are shown in Fig. 2. Elution of $\text{Eu}(\text{III})$ was not confirmed for the binary extractant system. Although elution ratio of ^{241}Am also slightly decreased with the ratio of HDEHP, selective stripping of $^{241}\text{Am}(\text{III})$ was confirmed for the new adsorbent. About 60–70% of the elution ratio in the batch-wise experiment is expected to show enough recovery ratio of $\text{MA}(\text{III})$ in the column operation. Decontamination factor of $\text{Eu}(\text{III})$ was calculated to be more than 10^3 , and that is larger than our targeted value i.e. 10^2 . As elution of $\text{Ln}(\text{III})$ after selective stripping of $\text{MA}(\text{III})$ is essential for repeated use of the adsorbent, selection of an appropriate eluent for $\text{Ln}(\text{III})$ is important. If $\text{Ln}(\text{III})$

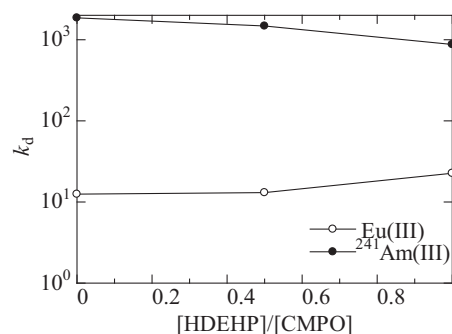


Fig. 1. Distribution coefficients of $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ onto the adsorbent.

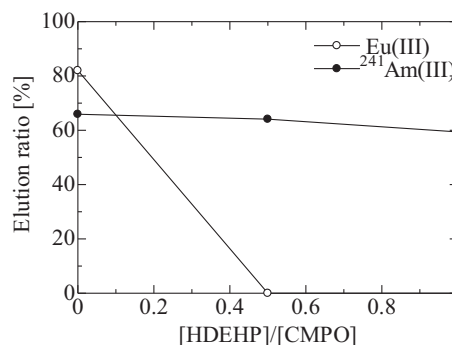


Fig. 2. Elution ratio of $^{241}\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$.

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