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Characteristics of TPDN/SiO₂-P adsorbent for MA(III) recoveryHirohide Kofuji^{a*}, Sou Watanabe^a, Masayuki Takeuchi^a, Hideya Suzuki^b, Tatsuro Matsumura^b,
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Applicability of newly developed MA(III)/RE(III) separation extractant TPDN for the extraction chromatography technology was evaluated through series of fundamental characterizations. The adsorbent selectively extract ²⁴¹Am from diluted high level liquid waste and sufficient performance for MA(III)/RE(III) separation process was confirmed. Durability and behavior in the vitrification process of the adsorbent also suggested that the new adsorbent can be employed as a material for reprocessing of spent fuels.

Keywords: minor actinides; extraction chromatography; adsorbent; vitrification

1. Introduction

Partitioning and transmutation program of trivalent minor actinides (MA(III): Am(III) and Cm(III)) is an important strategy for reduction in volume and radiotoxicity of the vitrified waste. Japan Atomic Energy Agency has been developing the extraction chromatography technology for the recovery of MA(III) from spent nuclear fuel [1]. In this technology, particle based porous silica coated by styrene divinyl benzene copolymer (referred as SiO₂-P) and impregnated extractant is utilized as the adsorbent. Series of fundamental studies for charactering the adsorbents and designing an appropriate flow-sheet have been carried out on adsorbents with several extractants such as CMPO, TODGA, and HDEHP etc [2]. However, a deciding extractant which possesses enough durability against acid or radiations and ability to separate MA(III) from trivalent lanthanides (Ln(III)) with simple operation has not been discovered so far.

We currently focus on a newly developed soft donor extractant N,N,N',N'-tetrakis(2-pyridylmethyl) ethylenediamine (TPDN) as one of the most promising extractants regarding its excellent performance obtained in solvent extraction system [3]. In this study, TPDN impregnated as the adsorbent was prepared, and then applicability of the extractant for the extraction chromatography technology was mainly evaluated through batch-wise adsorption/elution experiments, durability of the extractant, behavior of the adsorbent in the vitrification process.

2. Experimental

2.1. Preparation of adsorbent

N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (**Figure 1**) was impregnated into styrene-divinyl benzene co-polymer coating around porous silica particles with an average diameter of 50 μm and an average pore size of 50 nm. Detail procedure of the preparation was based on an article [4]. The weight ratio of TPDN of the product particles was 20 wt%, and degree of cross linkage of the polymer was 15 %. Those particles were used as the adsorbent.

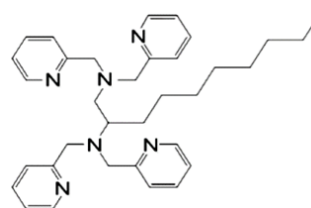


Figure 1. TPDN (N,N,N',N'-tetrakis(pyridin-2-ylmethyl) - decane-1,2-diamine).

2.2. Performance of the adsorbent

2.2.1 MA(III)/Ln(III) separation

Distribution coefficients and elution ratio of ²⁴¹Am, ¹⁵⁵Eu and ¹³⁷Cs were evaluated through batch-wise adsorption/elution experiments using diluted high level liquid waste (HLLW) obtained from solvent extraction experiments on irradiated Joyo fuel, which is an experimental FBR in Japan, for U/Pu/Np co-recovery. The distribution coefficients was derived from

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

where, C_0 and C_s are concentrations of cations in the solution before and after the adsorption, respectively, V is volume of the solution, W is weight of the adsorbent. Composition of the feed solution is shown in **Table 1**, where only concentrations of representative nuclides are shown. 2×10^{-4} kg g of the TPDN/SiO₂-P adsorbent was mixed with 4 cm³ of the feed solution, and then shaken for 1.08×10^4 s at room temperature. After separation of the solid and liquid, 5×10^{-5} kg of the adsorbent was mixed with 1 cm³ of 1 mol·dm⁻³ HNO₃ for elution of charged cations. Concentration of those nuclides in the solution were analyzed by gamma-spectrometry.

Table 1. Composition of the feed solution.

HNO ₃	0.01 mol·dm ⁻³
¹³⁷ Cs	3.13×10^5 Bq·cm ⁻³
¹⁵⁵ Eu	8.15×10^3 Bq·cm ⁻³
²⁴¹ Am	1.25×10^5 Bq·cm ⁻³

2.2.2 Local structure of complex in the adsorbent

In order to evaluate the extraction mechanism of TPDN immobilized in the adsorbent for trivalent cations, Extended X-ray Absorption Fine Structure (EXAFS) analysis on charged Eu(III) into the adsorbent was carried out. For comparison, XAFS on Eu(III) in TOPEN/SiO₂-P [5] was also carried out. Eu-K edge XAFS measurements were carried out at BL11XU beamline of SPring-8 in the transmission mode.

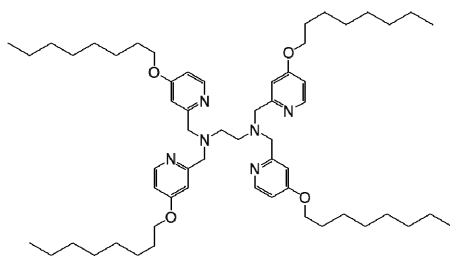


Figure 2. TOPEN (N,N,N',N'-tetrakis((5-octyloxy)pyridin-2-yl)methyl)ethylene diamine).

2.2.3 Durability of the adsorbent

Adsorbents are desirable to be used long time for the practical use, however degradation of the organic compounds in the adsorbent is inevitable due to acidic and radiation environment [6]. Durability of the adsorbent was evaluated by the adsorption/elution experiments using adsorbent exposed to acid or irradiation and by analysis on chemical structure of the degradation product formed in the exposed adsorbent.

Gamma-ray irradiation was carried out at irradiation room No. 1 of Co-60 Gamma-ray Irradiation Facility No. 1 in Takasaki Advanced Radiation Research Institute of National Institute for Quantum and Radiological Science and Technology, Japan. The adsorbent was mixed with

0.01 mol·dm⁻³ HNO₃ and then irradiated up to 1 MGy. After solid/liquid separation, the irradiated adsorbent was supplied to the adsorption/elution experiments. Chemical structure of organic compounds in both of the separated solid and liquid were analyzed. The analytical procedure is written in Ref [7]. For the reference, adsorbent exposed to the acid was also supplied to series of the evaluations.

2.3. Disposal of the adsorbent

2.3.1 Thermal behavior

Thermal properties of the adsorbent were investigated by measurements of flash point and ignition point, Thermogravimetry/Differential Thermal Analysis (TG/DTA) measurements and Temperature Programmed Desorption/Mass Spectrometry (TPD/MS). The flash point and the ignition point were measured by Setaflash closed cup test [8] and Krupp ignition temperature test [9], respectively. In the TG/DTA and the TPD/MS analyses, 1×10^{-5} kg of the dried adsorbents was heated with 10 K·min⁻¹ up to 1073 K under air atmosphere.

2.3.2 Vitrification test

Based on the thermal behavior of the adsorbent at high temperature, vitrification experiment using SiO₂ in the adsorbent as a constituent material of the glass was carried out to propose a disposal procedure of the adsorbent.

Certain amount of the adsorbent was heated at 873 K to decompose all organic compound in advance with the vitrification process. The calcined inorganic compounds were mixed with glass matrix with composition of **Table 2**, where Eu₂O₃ was added in the glass not as the glass matrix but for investigating influence of trivalent cations remaining inside the adsorbent on the vitrification process. Then the mixture was heated with 10 K·min⁻¹ up to 1473 K and kept 7.2×10^3 s for melting. Cooled glass was characterized by powder X-ray diffraction and SEM observation.

Table 2. Composition of raw materials for the vitrification.

Oxide	[kg]
SiO ₂ (from the adsorbent)	4.5×10^{-2}
H ₃ BO ₃	1.6×10^{-2}
CaCO ₃	3.3×10^{-3}
Li ₂ CO ₃	4.6×10^{-3}
ZnO	1.9×10^{-3}
Al ₂ O ₃	3.1×10^{-3}
Na ₂ CO ₃	1.0×10^{-2}
Eu ₂ O ₃	5.2×10^{-3}

3. Results and discussion

3.1. Performance of the adsorbent

Table 3 shows results of adsorption experiments. Only ²⁴¹Am was adsorbed on the new adsorbent, and the

adsorbed ^{241}Am was properly eluted from the adsorbent into $1 \text{ mol}\cdot\text{dm}^{-3}$ HNO_3 solution. Selective MA(III) recovery is expected to be achieved using the adsorbent without any complex reagents for elution. Acidity of the solution was drastically decreased by contacting with the adsorbent. Protonation of TPDN is considered to be significant, and longtime conditioning must be essential before the column operation to show the expected performance of the adsorbent. An appropriate process flow of column separation operation using TPDN adsorbent is currently designed and will be demonstrated in near future.

Adsorption amount of ^{241}Am increased by exposing the adsorbent to the acid or irradiation environments. However, not only ^{241}Am but also ^{155}Eu was adsorbed after those treatments. These changes must be caused by degradation of TPDN and are not desirable in the respect of MA(III)/Ln(III) separation. In the practical use, adsorbent has to be exchanged before the distinct change in the performance and durability of the adsorbent have to be investigated more precisely. Since all adsorbed ^{241}Am and ^{155}Eu were eluted by HNO_3 solution, some risks such as accumulation of decay heat or explosive gas inside the column must be avoided even if the degraded adsorbent is mixed inside the packed bed.

Table 3. Adsorption performance of TPDN/SiO₂-P adsorbent.

	Adsorption amount [Bq/kg resin]		
	Not irradiated		Irradiated
	—	HNO ₃ exposure	1.0 MGy
^{137}Cs	N.D.	N.D.	N.D.
^{155}Eu	N.D.	2.0×10^6	9.8×10^7
^{241}Am	2.4×10^8	3.6×10^8	1.3×10^9
Eq. pH	4.4	4.4	4.3

Radial structure function around Eu charged in the adsorbent obtained by the EXAFS measurements are shown in **Figure 3**. Predominant peak observed at $R = 0.2 \text{ nm}$ must be contributions from N of the TPDN or TOPEN molecules and from O of NO_3^- ion according to structure of Ln(III)-TPEN complexes formed in solvent extraction system [10]. Curve fitting analysis on the peak were carried out by assuming the structural models of the solvent extraction system with double shells of O and N around Eu as reported in reference [11]. The local structural parameters around Eu are shown in **Table 4**, where R , N and σ^2 are interatomic distance, coordination number and Debye-Waller factor, respectively. The fittings on both adsorbents were successfully finished with the double shell structural model and those results suggest that coordination geometry around Eu in the adsorbent is similar to those evaluated for the solvent extraction system and that molecular ratio of the cation to the ligand in the complexes should be 1 : 1. TOPEN must have stronger affinity to Eu than TPDN in the respect of the local structural parameters, and which might give a reasonable explanation for difference in MA(III)/Ln(III) separation performances of those

adsorbents. Comparison in performance of those adsorbents is currently underway.

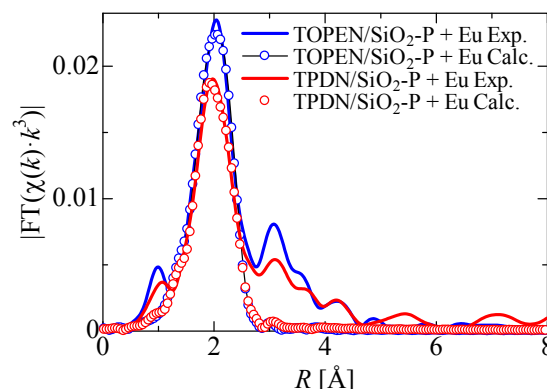


Figure 3. Radial structure functions around Eu inside the adsorbent.

Table 4. Local structural parameters around Eu.

Sample	atom	R [nm]	N	σ^2 [10^{-4} nm^2]	Residual [%]
TPDN	O	0.248 ± 0.001	3.88 ± 0.4	0.75 ± 0.05	6.46
	N	0.269 ± 0.001	2.27 ± 0.2	0.18 ± 0.05	
TOPEN	O	0.249 ± 0.001	4.63 ± 0.5	0.97 ± 0.05	6.78
	N	0.268 ± 0.001	3.17 ± 0.3	0.37 ± 0.05	

Table 5 shows degradation products produced by exposure of the adsorbent to the acid and the irradiation environments. Generation of those products is considered to be one of the causes of the poor MA(III)/Ln(III) separation performance after the exposure to the acid or the irradiation. For further discussion on correlation between the change in the adsorption performance with production of the degradation products, amount the degradation products are required to be quantitatively evaluated. In addition to that, adsorption performance of MA(III) and Ln(III) by those products is also necessary to be investigated to explain detail mechanism of change in the performance.

Table 5. Degradation products of TPDN.

	Nitric acid	γ -ray irradiation
Solid phase	<chem>C1=CC=CC=C1C(=O)N</chem>	<chem>C1=CC=CC=C1C(=O)N</chem>
Liquid Phase	<chem>C1=CC=CC=C1C(=O)N</chem> and <chem>C1=CC=CC=C1C(=O)N</chem>	

3.2. Disposal of the adsorbent

Flash and firing points of the adsorbents were evaluated to be 429.1 and 828 K, respectively. Those values are larger than PUREX solvent, therefore special cares for use inside the reprocessing plant are not required.

Amount of gases generated during the heat treatment on the adsorbent are shown in **Figure 4**. Representatively, 7 kind of gases were generated with increase in temperature, and the gas generations almost stopped at around 873 K. Major part of C originated from the styrene divinyl benzene copolymer and TPDN were released as CO₂, however significant quantities of aromatic products were also generated. Some of those have low firing points and those are desirable to be discharged before the vitrification process. Therefore, the vitrification operation on the adsorbent was carried out after annealing the adsorbent for 3.6×10^3 s at 873 K.

TG/DTA curves of the adsorbent is shown in **Figure 5**. Sharp decreases in the weight of the adsorbent corresponded to exothermal peaks observed at 523 K and 623 K, and those must be attributed to decompositions of TPDN and polymer of the adsorbent, respectively [6]. Distinct weight loss and heat generation were not observed at higher than 873 K, thus the vitrification condition proposed above is considered to be appropriate to achieve stable and safety operation.

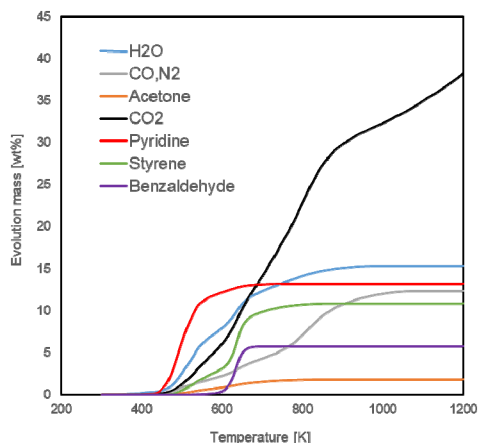


Figure 4. Amount of gases generated from the adsorbent.

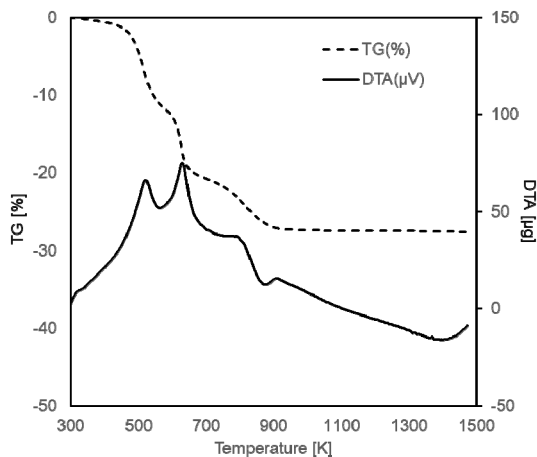


Figure 5. TG/DTA curves of the adsorbent.

Vitrification operation using the annealed adsorbent was successfully done without any problems, and uniform and transparent product solid was obtained. X-ray diffraction pattern of the product is shown in **Figure 6**. Typical halo X-ray diffraction pattern was observed. It is reasonable to consider that the glass was formed from the adsorbent by the vitrification operation employed in this study. Though the chemical and physical stabilities of the glass have to be investigated further, the used adsorbent of the extraction chromatography is expected to be utilized as a raw material of the final disposal waste.

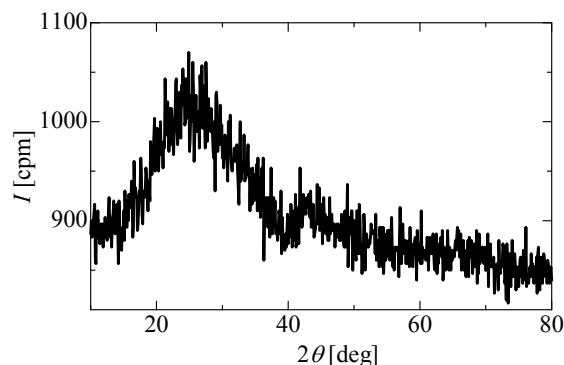


Figure 6. XRD pattern of vitrified adsorbent X-ray source: Cu-K α .

4. Conclusion

Applicability of newly developed soft donor extractant TPDN for the extraction chromatography technology was evaluated through performance and degradation behavior of the adsorbent and vitrification experiments on the used adsorbent. TPDN impregnated adsorbent showed effective MA(III)/Ln(III) separation performance and is expected to be used as raw material for the vitrification of high level active waste. Design of process flow for column separation operation using the adsorbent is underway.

Acknowledgement

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