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ARTICLE

Recovery of Minor Actinides from High-Level Liquid Waste by *N,N,N',N',N'',N''*-Hexaoctyl Nitrilotriacetamide (HONTA) using Mixer-Settler Extractors

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A continuous counter-current extraction experiment was performed using mixer-settler extractors to recover minor actinides (MA; Am and Cm) from high-level liquid waste. Using *N,N,N',N',N'',N''*-hexaoctyl nitrilotriacetamide (HONTA) as an extractant, 0.17 g of MA was recovered in the MA fraction.

KEYWORDS: minor actinide, solvent extraction, mixer-settler, HONTA

I. Introduction

The reprocessing of spent nuclear fuel is vital for the sustainable utilization of nuclear energy, and several commercial-scale reprocessing plants are in operation today. Partitioning and transmutation is a strategy for reducing the volume and radiotoxicity of high-level liquid waste (HLLW) generated by nuclear reprocessing. HLLW contains various elements, including minor actinides (MA), such as Am and Cm. Such actinides have nuclides with long half-lives and/or high heat release. Thus, the burden of final disposal can be reduced by transmuting them into stable or short-lived nuclides. Accordingly, many hydrometallurgical processes, such as SANEX,1) i-SANEX,2) EURO-GANEX,3) and TALSPEAK,4) have been developed for this goal.

Recently, we proposed a separation process called SELECT (Solvent Extraction from Liquid waste using Extractants of CHON-type for Transmutation.5-7) This process involves four steps: (i) recovery of U and Pu from the dissolution solution of the spent nuclear fuel, (ii) recovery of MA and rare earths (RE), (iii) mutual separation of MA and RE, and (iv) mutual separation of Am and Cm. **Figure 1** shows a conceptual flow sheet of the current SELECT process, and the candidate extractants are shown in **Figure 2**. Monoamide (a and b), diglycolamide (c), nitrilotriacetamide (d), and alkyldiamideamine (e) were studied as extractants for steps (i), (ii), (iii), and (iv), respectively. These extractants comprise C, H, O, and N atoms and can be decomposed into gases via incineration, thereby reducing the volume of secondary waste. Although the extraction properties of these extractants have been fundamentally investigated by single-stage batch experiments, limited studies have conducted continuous counter-current extraction experiments with nitrilotriacetamides as extractants.

Herein, we explored *N,N,N',N',N'',N''*-hexaoctyl nitrilotriacetamide (HONTA) as an extractant for step (iii). A continuous counter-current extraction experiment was

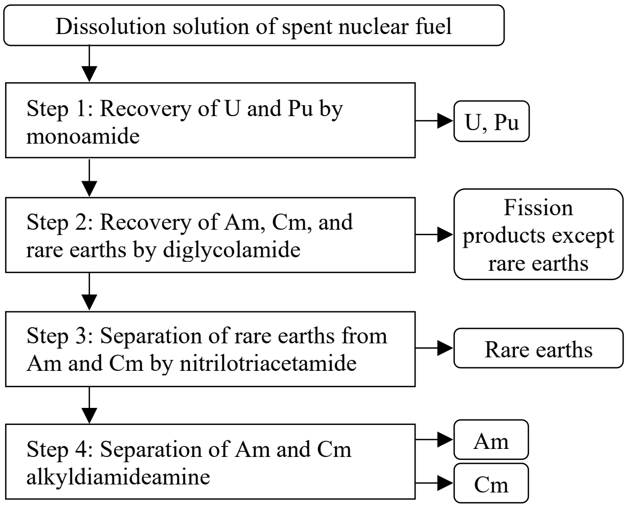

Fig. 1 Conceptual flowsheet of the current SELECT process

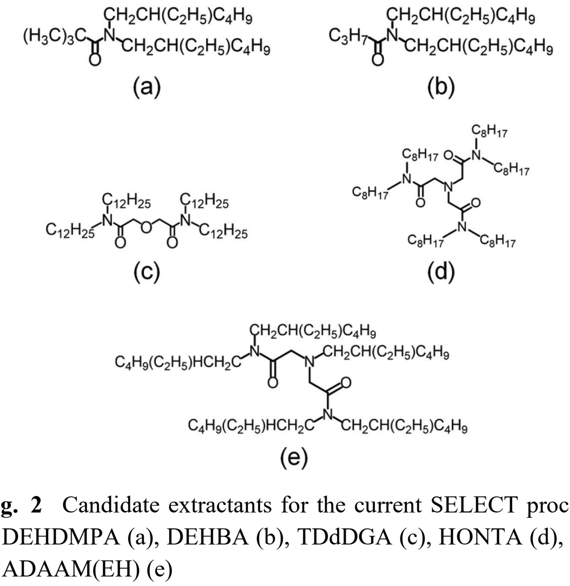

Fig. 2 Candidate extractants for the current SELECT process: DEHDMPA (a), DEHBA (b), TDdDGA (c), HONTA (d), and ADAAM(EH) (e)

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*Corresponding author, E-mail: ban.yasutoshi@jaea.go.jp conducted, and the applicability of HONTA was evaluated in terms of its MA-recovery efficiency (Am and Cm) from HLLW.

II. Experimental

1. Reagents

HONTA (96% purity) was purchased from Chemicrea, Inc. Nitric acid and *n*-dodecane of analytical grade were used without further purification.

2. Continuous Counter-Current Test

Two mixer-settler extractors, labeled Bank 1 and Bank 2, with 20 stages each were installed in a hot cell in NUCEF (NUclear Fuel Cycle Safety Engineering Research Facility) at the Nuclear Science and Research Institute. The volume of each settling part was 41 cm^3 for the 1st and 20th stages and 25 cm^3 for the 2nd to 19th stages.

Figure 3 shows the conditions of the continuous counter-current extraction experiment. Bank 1 comprised a 4-stage diluent wash step, a 10-stage MA-extraction step, and a 6-stage scrub step. Bank 2 comprised a 4-stage diluent wash step and a 16-stage MA back-extraction step. The feed was prepared from a HLLW sample stored in the hot cell after separating MA and RE using tetoradodecyl diglycolamide.[5] Subsequently, after adjusting the nitric acid concentration to 0.047 mol/dm^3 (M), the feed was supplied to the 5th stage. The concentrations of ^{241}Am, ^{244}Cm, Y, La, Nd, and Eu in the feed are 4.4×10^{-4} M, 3.1×10^{-5} M, 3.6×10^{-4} M, 7.9×10^{-4} M, 2.7×10^{-3} M, and 1.1×10^{-4} M, respectively.

HONTA diluted to 0.05 M with *n*-dodecane was fed to the 14th stage for the mutual separation of MA and RE. A portion of the RE extracted by HONTA was scrubbed using the 0.047 M nitric acid fed to the 20th stage. The organic phase leaving the 20th stage was fed to the 25th stage in Bank 2, and the organic phase leaving the 40th stage was fed to the 5th stage for reuse. The 0.5 M nitric acid fed to the 40th stage was adopted for MA back-extraction. After 11 h from the start of the experiment, the aqueous phase leaving the 21st stage was collected as an MA fraction until the end of the experiment. The cumulative operation time of the experiment was 43.5 h, during which the organic phase in Bank 1 was replaced 16.5 times, and that in Bank 2 was replaced 8.2 times. The residence time of the organic and aqueous phases in each mixing part was approximately 2.2 minutes. A previous study showed that Am and Eu extracted by HONTA reached equilibrium within 2-4 min,[8] and the extraction in the continuous counter-current test either reached or closely approached equilibrium.

The organic and aqueous phases were sampled from the settling part of each stage after halting the operation of the mixer-settlers. The concentrations of the acid and metal ions were measured for some samples. The concentrations of Y, La, Nd, and Eu were measured by inductively coupled plasma atomic emission spectrometry. The concentrations of ^{241}Am were measured using a gamma-ray counter with a Ge detector. The concentrations of ^{244}Cm were measured using an alpha-ray counter with semiconductor detectors. The error in each analysis was assumed to be at most 10% and similar in size to the data points shown in the figures.

III. Results and Discussion

The organic and aqueous phases were separated into two phases in the settling part of each stage, and no appreciable third phase and precipitation were observed throughout the experiment. **Figure 4** shows the concentrations of Am and Cm in the organic and aqueous phases of some stages in Bank 1 and Bank 2. The concentrations of Am and Cm increased from the 5th to the 11th stage, highlighting the high extraction efficiency of HONTA for Am and Cm at the MA extraction step. The concentrations of Am and Cm in the organic phase from the 12th to the 20th stages were almost constant, and most of the Am and Cm contents entered Bank 2. The Am and Cm concentrations decreased rapidly from the 25th to the 40th stage, and 0.5 M nitric acid fed to the 40th stage was demonstrated to be effective for the back-extraction of Am and Cm.

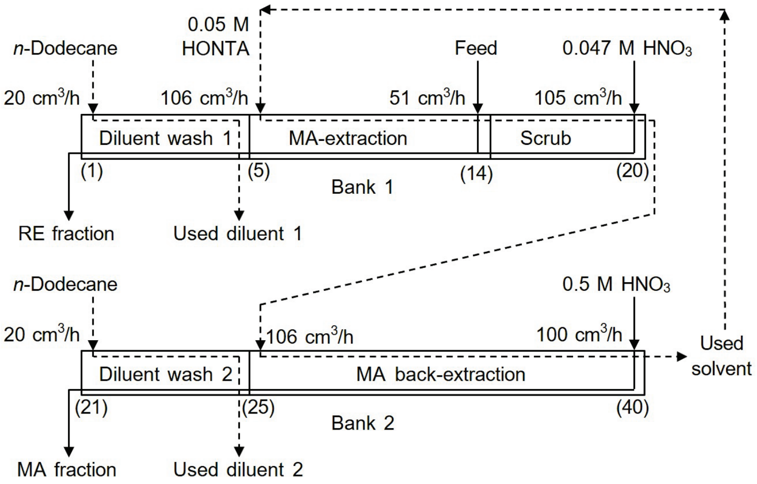


Fig. 3 Conditions for the continuous counter-current experiment using mixer-settler extractors installed in a hot cell. The dashed lines and the solid lines represent the organic phase and the aqueous phase, respectively. The numbers in parentheses indicate the stage number.

Figure 5 shows the concentrations RE in the organic and aqueous phases of some stages in Bank 1 and Bank 2. As for Bank 2, the samples taken from the 21st, 25th, 28th, 32nd, 36th, and 40th stages were subjected to the quantitative analysis. However, some had undetectably low concentrations, and thus, no data points were shown in the figure.

The concentrations of Y and La in the aqueous phase at the MA-extraction step were considerably higher than those in the organic phase. These concentrations remained almost unchanged at the MA-extraction step and substantially decreased along with the stage number at the Scrub step. These results indicate that Y and La in the feed were less extractable by HONTA, and most of them were distributed to the RE fraction. The concentrations of Nd in the organic and aqueous phases in Bank 1 were similar, and no remarkable decrease was observed at the Scrub step. Similar behavior was observed for the Eu concentration in Bank 1, indicating that the present experimental condition was less effective for the

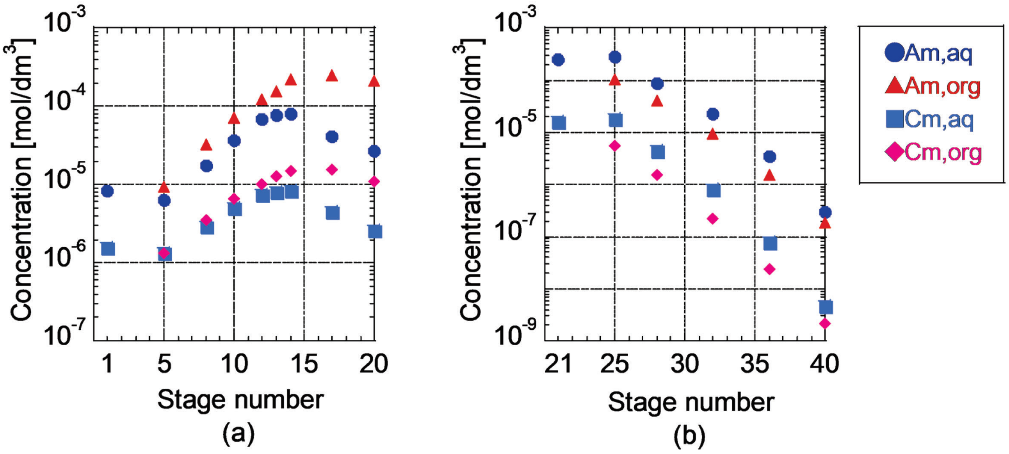
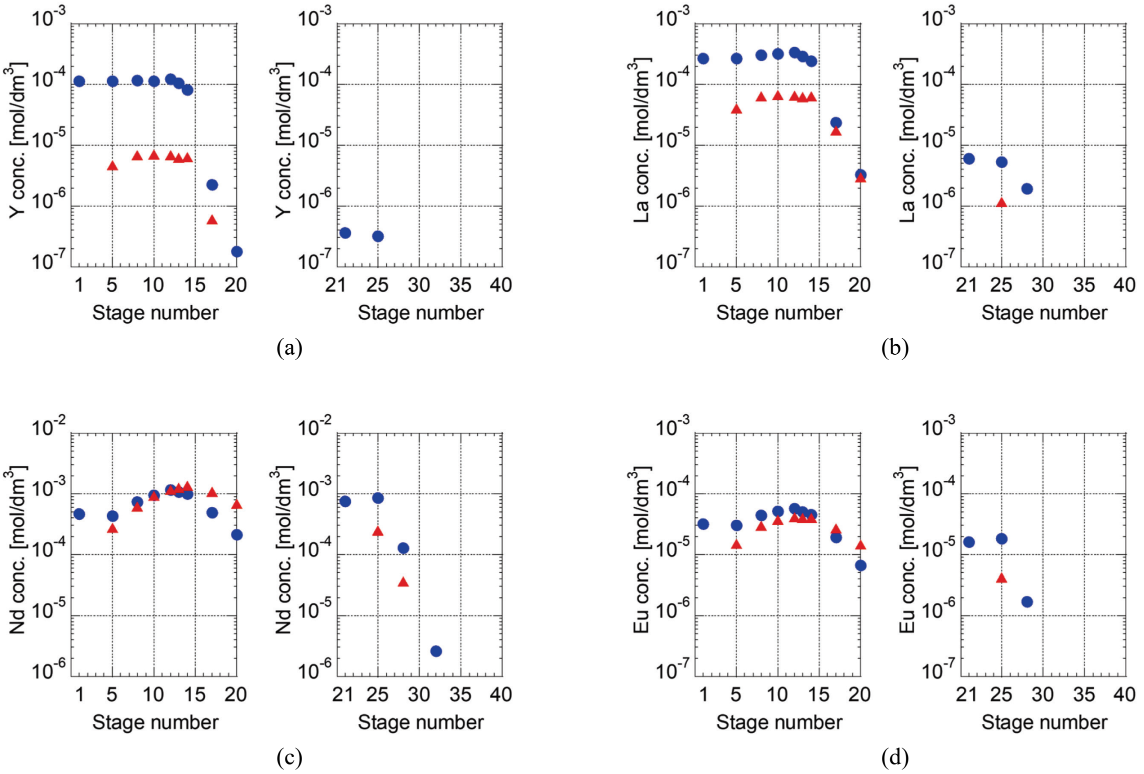


Fig. 4 Concentrations of Am and Cm in Bank 1 (a) and Bank 2 (b). Subscripts org and aq in the legend indicate the organic and the aqueous phases, respectively



(a)

(b)

(c)

(d)

Fig. 5 Concentrations of Y (a), La (b), Nd (c), and Eu (d). Solid circle and solid triangle represent the aqueous phase and the organic phase, respectively

Table 1 Experimentally measured and calculated concentrations of Y, La, Nd, Eu, Am, and Cm in the MA fraction.

	Y	La	Nd	Eu	Am	Cm
Measured [mol/dm^3]	1.8×10^{-7}	2.3×10^{-6}	5.0×10^{-4}	1.0×10^{-5}	2.1×10^{-4}	1.3×10^{-5}
Calculated [mol/dm^3]	1.6×10^{-7}	1.7×10^{-6}	2.3×10^{-4}	3.3×10^{-6}	2.2×10^{-4}	1.4×10^{-5}

recovery of Nd and Eu to the RE fraction.

The concentrations of Y, La, Nd, Eu, Am, and Cm in the MA fraction were calculated using the PARC-MA numerical code.[9,10] Equations (1)-(7) show the distribution ratios input in the code, which were derived from the results of single-stage extraction experiments.[6]

$$\log D_{\mathrm{Am}} = -1.23 - 1.32 \cdot \log\,[\mathrm{NO_3^-}] \tag{1}$$

$$\log D_{\mathrm{Cm}} = -1.50 - 1.36 \cdot \log\,[\mathrm{NO_3^-}] \tag{2}$$

$$\log D_{\mathrm{Y}} = -3.01 - 1.13 \cdot \log\,[\mathrm{NO_3^-}] \tag{3}$$

$$\log D_{\mathrm{La}} = -1.80 - 0.64 \cdot \log\,[\mathrm{NO_3^-}] \qquad 0.1\ \mathrm{M} \leq [\mathrm{NO_3^-}] \tag{4}$$

$$\log D_{\mathrm{La}} = 0.14 + 1.29 \cdot \log\,[\mathrm{NO_3^-}] \qquad [\mathrm{NO_3^-}] < 0.1\ \mathrm{M} \tag{5}$$

$$\log D_{\mathrm{Nd}} = -1.50 - 1.03 \cdot \log\,[\mathrm{NO_3^-}] \tag{6}$$

$$\log D_{\mathrm{Eu}} = -2.00 - 1.26 \cdot \log\,[\mathrm{NO_3^-}] \tag{7}$$

Table 1 shows the calculated and experimentally measured results. The calculated RE concentrations were lower than the experimentally measured values, whereas the calculated and experimentally measured MA concentrations were similar. The difference particularly observed in the RE concentrations could be attributed to the complexity of the experimental procedures in a shielded cell via manipulators and the precision of the distribution ratios used in the calculations. Although further studies are necessary for the comprehensive discussion of this difference, the calculation code could be useful for estimating the performance of the separation process.

The proportions of Y, La, Nd, Eu, Am, and Cm distributed in the MA fraction were 0.01%, 0.58%, 40.6%, 18.5%, 94.7%, and 84.7%, respectively. Since the concentrations of Nd and Eu decreased along with the stage number at the Scrub step, the proportions of Nd and Eu in the MA fraction could be increased by optimizing the experimental conditions. Based on the volume of the MA fraction and the concentrations of Am and Cm in this fraction, the corresponding amount of MA recovered was approximately 0.17 g. We performed another continuous counter-current extraction experiment using HONTA as the extractant and recovered 0.12 g of MA from HLLW.[7] Approximately 0.3 g of MA in total was recovered from the two experiments, demonstrating the utility of HONTA.

IV. Conclusion

A continuous counter-current extraction experiment was performed using mixer-settler extractors with HONTA diluted in *n*-dodecane as an extractant. HONTA effectively extracted MA from HLLW, and the extracted MA was back-extracted using 0.5 M nitric acid. The proportions of Am and Cm distributed in the MA fraction were 94.7% and 84.7%, respectively, corresponding to a total MA-recovery amount of 0.17 g. Although improvements are necessary, the present results support the applicability of HONTA as an extractant for the mutual separation of MA and RE.

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