Development of ARTIST process, extraction and separation of actinides and fission products by TODGA

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Abstract –Total recovery of TRU from nitric acid solution was studied by using TODGA whose extractant is a tridentate ligand showing the high extractability for An(III) and An(IV). TODGA extracts Pu(IV), Am(III) and Cm(III) effectively but not Np(V), therefore Np(V) has to be reduced to Np(IV) prior to extraction. From the results of the extraction of fission products, Sr(II), Zr(IV) and lanthanides(III) give high distribution ratios in TODGA-HNO_3 system. After extraction of TRU with Sr(II) and Zr(IV), these FP elements can be stripped by using 0.2M oxalic acid in 2M HNO_3 or diluted HNO_3, while TRU remains in the organic phase. After separation of Sr(II) and Zr(IV), the backward extraction of total TRU into aqueous phase was also studied.

INTRODUCTION

The development of a novel separation method of actinides(An) and fission products(FP) is very important task for the treatment and disposal of the spent nuclear fuel(SF). We have proposed an innovative chemical separation process (ARTIST, Amide-based Radio-resources Treatment with Interim Storage of Transuranics)(1). ARTIST process consists of two main steps, i.e., the first step is the employment of BAMA (Branched Alkyl Mono Amide) for the isolation of matrix U and the second one is the use of N,N,N',N'-tetraoctyl-3-oxapentanediamide (TODGA) for the total recovery of transuranium elements (TRU). TODGA, which was developed in our laboratory, is one of the tridentate diamide extractants, and has the high solubility in n-dodecane and very high extraction ability for An(III) and An(IV) from nitric acid solution(2-5). Concerning TODGA extraction process for high level liquid waste (HLLW), the preliminary evaluation of actinide separation was already performed(6). We can employ TODGA as a key extractant for total recovery of TRU in ARTIST process. In order to prevent the third phase formation and to give the high radiation resistance(7), we can adopt the mixed solvent of TODGA and DHOA (di-n-hexyl-octanamide) in n-dodecane.

In this paper, the extraction of An(III), (IV), (V), (VI) and FP, the separation of Sr(II) and Zr(IV) from TRU, and the extraction capacity of metals by using TODGA or TODGA-DHOA were studied. Using these results, the preliminary flow-sheet was proposed.

EXPERIMENTAL

After pre-equilibration, a certain volume (0.5-2 ml) of an organic phase containing TODGA was taken in an extraction tube with an equal volume of an aqueous nitric acid solution spiked with radioactive tracer or metal standard solution. The concentrations of metal ions used in the extraction experiments were, in $mol/dm^3 (= M)$, 5×10^{-3} or higher concentration for Sr(II), Zr(IV), and Nd(III) 5×10^{-7} for U(VI), 1×10^{-6} for Np(V), 1×10^{-10} for Pu(IV), 1×10^{-9} for Am(III), and 5×10^{-10} for Cm(III). The extraction tube contained two phases was shaken mechanically for 2 hours at 25 ± 0.1 °C. In order to reduce the oxidation states of Np and Pu to Np(IV) and Pu(III), 5mM of Fe(II) and 5mM of hydrazine were employed as the reductants(8). After centrifugating and separating both phases, the duplicate 0.50 ml aliquots were taken and the alpha activities of ^{233}U, ^{237}Np, ^{238}Pu, ^{241}Am and ^{244}Cm were measured by liquid scintillation counter (Tri-Carb 1600 TR, Packard Instrument Company) with 5 ml of PICO-AQUA cocktail. The amounts of non-radioactive metal ions in the organic phase were measured after preparation by the following methods, stripping Zr(IV) from the organic phase by 0.2M oxalic acid in 2M HNO_3, and decomposing the organic phase containing Sr(II) or Nd(III) by HNO_3-$HClO_4$, the

residue was dissolved by 0.5M HNO$_3$. The aqueous phase after extraction was prepared to 0.5M HNO$_3$ by using the nitric acid and the distilled water. ICP-AES (SPS 1200AR, Seiko-EG & G) was employed to measure the metal concentration.

RESULTS AND DISCUSSION

TRU Extraction by TODGA

The extraction behavior of An ions by TODGA was illustrated in Fig. 1. D(An) were plotted against HNO$_3$ concentration. Normally, the extractability of An ions are in the order of An(IV) > An(VI) > An(III) > An(V), by using TBP, TOPO and HTTA(9-11), and the order of D values for these An ions in the same oxidation state was followed by the atomic number. From our detailed investigation(12), the order of extractability of An by TODGA was An(IV) > An(III) > An(VI) > An(V) and the D values obtained from the heavy atomic number of An(III) and probably An(IV) were higher than those of the light ones. Most of extractants employed in SF reprocessing and partitioning of HLLW are mono- or bi-dentate ligands. TODGA is the tridentate ligands, which may exhibits the different extraction behavior from the mono- and bi-dentate ones. For actinyl ions, e.g., U(VI) and Np(V), having the coordination sites in the equatorial surface of the central An ion, TODGA may work as the bidentate chelation rather than tridentate one, which results in low D of them compared to those of An(III) and An(IV). From Fig. 1, it appears that D of all An ions by TODGA shows the remarkable increase with HNO$_3$ concentration, which might be due to the extraction reaction accompanying HNO$_3$ in addition to the counter anion, NO$_3^-$(13).

In ARTIST process, the purpose of the employment of TODGA is the extraction for total recovery of TRU. Because of the low D value, Np(V) should be changed to the other oxidation states, prior to the extraction. One of the possibility to extract Np by TODGA is to prepare Np(IV), where the reducing condition may change the oxidation state of Pu from (IV) to (III). In Fig. 1, the extraction behavior of Np(IV) and Pu(III) by TODGA was shown. We obtained the similar results as the same oxidation state of other An and confirmed that at the reducing condition, all An ions, i.e., Np(IV),
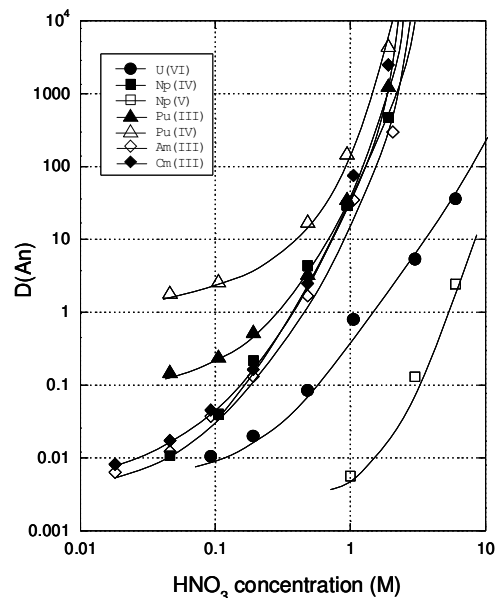

Fig. 1 Extraction behaviors of An(III), (IV), (V) and (VI) by TODGA
aqueous phase: HNO$_3$, organic phase: 0.1M TODGA/n-dodecane

Pu(III), Pu(IV), Am(III) and Cm(III) can be extracted by TODGA into the organic phase with high D values from concentrated nitric acid solution. We also studied the extraction behavior of Np(VI) and Pu(VI) by TODGA after oxidation by HClO$_4$ fuming, whose preparation method was followed by the reference(14). We found that Np(VI) and Pu(VI) were rather unstable during the extraction by TODGA, and the satisfactory results of such An(VI) ions were never obtained.

Sr(II) and Zr(IV) Extraction and Separation from TRU

From the results described above, An(III), and An(IV) are very extractable by TODGA. Among FP elements, Sr(II), Zr(IV) and lanthanides (Ln)(III) have high D values for TODGA extraction(5,13,15). Here, Sr(II) is one of the aimed elements in ARTIST process, because Sr(II) in FP includes the radioactive nuclide, e.g., ^{90}Sr, of the heat source. We summarized the D(Zr) and D(Sr) and separation factors (α) against An(III) in Tables 1 and 2, where α is defined as D(An)/D(M). In Table 1, α of Sr(II) against An(III) and An(IV) are considerably high, whereas concerning to Sr(II) extraction, the highest D(Sr) is 4 under the condition of 0.1M TODGA and 3M HNO$_3$.

Table 1 D of Sr(II), Am(III) and Pu(IV) and α

HNO$_3$ (M)	D			α	
	Sr(II)	Am(III)	Pu(IV)	Am/Sr	Pu/Sr
0.1	0.006	0.04	2.7	7	450
0.2	0.0065	0.13		20	
0.5	0.022	1.68	18	76	820
1	0.16	35	150	220	940
2	2	300	> 1000	150	> 500
3	4	> 1000	> 1000	> 250	> 250
6	0.28	> 1000	> 1000	> 360	> 360

TODGA concentration: 0.1M in n-dodecane

These D values decrease with increase and decrease of HNO$_3$ concentration from 3M. From these results, we can separate Sr(II) and Am(III) or Pu(IV) by using diluted or concentrated HNO$_3$, e.g., 1M or 6M HNO$_3$ after extraction of these ions. From Table 2, D(Zr) increases with increase of HNO$_3$ concentration and the maximum value is reached to 700, which is somewhat similar extraction behavior as Pu(IV) and Am(III) in TODGA/n-dodecane-HNO$_3$ system. D(Zr) is very low under the aqueous condition containing oxalic acid, therefore Zr(IV) can be stripped by using 0.1M oxalic acid/2M HNO$_3$ from Am(III) and Pu(IV) in the organic phase.

Table 2 D of Zr(IV), Am(III) and Pu(IV) and α in HNO$_3$ and oxalic acid

HNO$_3$ (M)	oxalic aicd (M)	D			α	
		Zr(IV)	Am(III)	Pu(IV)	Am/Zr	Pu/Zr
0.1	-	1.6	0.04	2.7	0.025	1.7
1	-	300	35	150	0.12	0.51
2	-	700	300	> 1000	0.43	> 1.4
2	0.1	0.025	300	6.7	> 1000	270

TODGA concentration: 0.1M in n-dodecane

Extraction Capacity of Sr(II), Nd(III) and Zr(IV)

In Table 3, we summarized the maximum metal ion concentrations in the organic phase, whose metal ions employed are Sr(II), Nd(III) and Zr(IV). DHOA, di-n-hexyloctanamide, is used as a modifier to suppress the third phase formation in TODGA extraction system. Nd(III) is representative of Ln(III) and An(III). In Table 2, Zr(IV), which has relatively high concentration in HLLW, has the same oxidation state as Pu(IV) and its D value is as high as D(Pu) by TODGA, therefore we can consider Zr(IV) as an example of An(IV) in this study. In Table 3, the maximum concentrations of metal ions in the organic phase obtained by using the different concentration of TODGA with and

without DHOA were shown. The TODGA/n-dodecane extraction solvent without DHOA forms the third phase when the metal concentration is excessively high. The extracted species determined by the slope analysis are mainly Sr(TODGA)$_2$(NO$_3$)$_2$, Nd(TODGA)$_3$(NO$_3$)$_3$, and Zr(TODGA)$_3$(NO$_3$)$_4$. From the extraction reactions (or equilibria), the stoichiometric concentrations as the extraction capacity of the metal ions in the organic phase are calculated to be 50, 33 and 33 mM for Sr(II), Nd(III) and Zr(IV), respectively, when 100 mM TODGA is used. The observed concentrations for Nd(III) and Zr(IV) in Table 3 are close to the capacity under 0.1M TODGA-1M DHOA. Following these results, An(III) and An(IV) are well-extractable and have high metal concentration in the mixture of DHOA and TODGA in n-dodecane. Concerning with Sr(II) extraction, because of low D values (4 at maximum in Table 1) compared to Nd(III) and Zr(IV), the maximum concentration of Sr(II) was 10.3 mM in 0.1M TODGA-1M DHOA. However, the concentration of Sr(II) is ca. 3.7 mM after dissolving SF (LWR burn-up; 49000 MWD/t) in 3M HNO$_3$, according to the calculation usnig ORIGEN II code. From these results, all extraction solvents in Table 3 are applicable to extract completely Sr(II) in HLLW.

Table 3 Maximum metal concentrations in the organic phase

Extraction solvent	concentration in n-dodecane (mM)		
	Sr(II)	Nd(III)	Zr(IV)
0.1M TODGA	7.87	6.4	7.7
0.2M TODGA	28.1	12.2	10.6
0.1M TODGA+1M DHOA	10.3	29.7	40
0.2M TODGA+1M DHOA	34.0	-	> 70

aqueous phase condition: 3M HNO$_3$

An Example of Schematic Diagram for Total Recovery of TRU

In Fig. 2, one of the preliminary schematic diagrams for total recovery of TRU by TODGA is illustrated. After U extraction by BAMA, the dissolved solution of SF with addition of the redox reagent is shaken with 0.1-0.2M TODGA/n-dodecane with or without DHOA. The overall extraction of TRU including Sr(II) and Zr(IV) can be achieved, and the aqueous solution after extraction contains FP mainly such as Cs(I), Rh(III), Te(IV), Se(IV) etc. The first

stripping solution is 0.1M oxalic acid/ 2M HNO$_3$ for backward extraction of Zr(IV), and the next stripping solution is 0.5-1M HNO$_3$ for washing oxalic acid in the organic phase and backward extraction of Sr(II).   The last stripping solution for the back-extraction of TRU is considered as follows: one is 0.2M HNO$_3$ including the complexing agent of An(IV) or another is 0.01M HNO$_3$ with reductant of Pu(IV) to Pu(III).   We will accumulate the basic data and fix the optimum conditions for the extraction and separation of TRU.
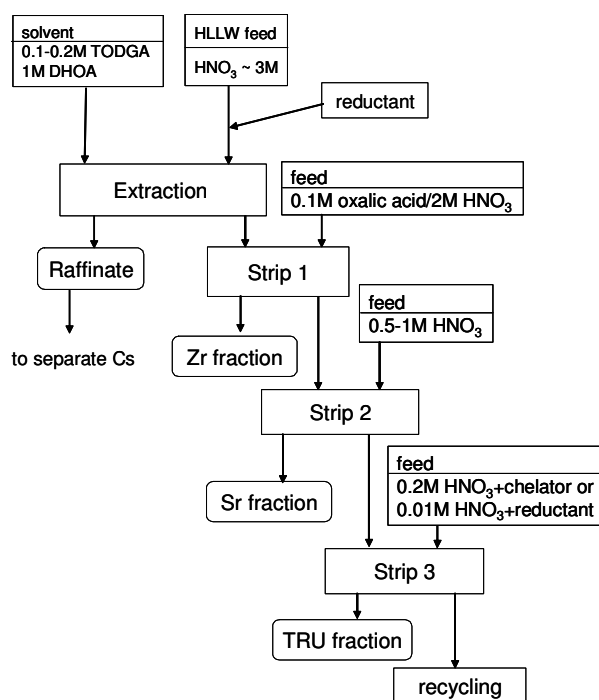

Fig. 2 Preliminary schematic diagram for total recovery of TRU by TODGA

REFERENCES

1. S. Tachimori, S. Suzuki, Y. Sasaki, J. At. Energy Soc. Japan. **43**, 1235-1241 (2001).
2. Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, Solv. Extr. Ion Exch., **19**, 91-103 (2001).
3. Y. Sasaki and S. Tachimori. Solv. Extr. Ion Exch., **20**, 21-34 (2002)
4. H. Narita, T. Yaita and S. Tachimori, Sol. Extr. Ind. Appl., Vol.1, ISEC99, P.693 (2000).
5. Y. Sasaki, Y. Sugo and S. Tachimori, Proceedings of the International Conference ATALANTE 2000 Avignon, France, Paper No. O2-07 (2000).
6. Y. Morita, Y. Sasaki and S. Tachimori. Proceedings of International Conference on "Back-End of the Fuel Cycle: From Research to Solution" (Global 2001), Paris, France, Paper No. 036 (2001).
7. Y. Sugo, Y. Sasaki, S. Tachimori, Radiochim. Acta, **90**, 161-165 (2002).
8. J.J. Katz, G.T. Seaborg and L.R. Morss, The Chemistry of the Actinide elements vol. 1, Chapman and Hall, London, p. 473 (1986).
9. J.J. Katz, G.T. Seaborg and L.R. Morss, The Chemistry of the Actinide elements vol. 1, Chapman and Hall, London, p. 528 (1986).
10. G.R. Choppin, Radiochim. Acta, **32**, 43-53 (1983).
11. G.R. Choppin, Sep. Sci. Tech., **19**, 911-925 (1984-1985).
12. Y. Sasaki, S. Suzuki, S. Tachimori and T. Kimura, Proceedings of Global 2003, New Orleans, USA, (2003).
13. H. Suzuki, Y. Sasaki, Y. Sugo, A. Apichaibuol, T. Kimura, Radiochim. Acta in press.
14. H. Takeishi, Y. Kitatsuji, T. Kimura, Y. Meguro, Z. Yoshida, S. Kihara, Anal. Chim. Acta, **431**, 69 (2001).
15. S. Tachimori, S. Suzuki, Y. Sasaki and A. Apichaibukol, Solv. Extr. Ion Exch., **21**, 707-716 (2003).