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VI. 1. Development of a Simplified MA Separation Process Using Novel R-BTP Adsorbents – II

Kuraoka E., Usuda S., Liu R., Xu Y., Kim S.Y., Yamazaki H., and Ishii K.

Cyclotron and Radioisotope Center, Tohoku University

Introduction

In recent years, many soft-donor ligands have been developed for liquid-liquid solvent extraction separation of trivalent minor actinides (MA: Am and Cm) and/or rare earths (RE) from the other fission products (FP) in the high level radioactive liquid waste (HLLW), which is generated by spent fuel reprocessing. Especially, a new type of nitrogen-donor ligand, R-BTP (BTP: 2,6-Bis-(5,6-Dialkyl-1,2,4-Triazin-3-yl)Pyridine, R: alkyl group [C_nH_{2n+1}]), which was discovered by Kolarik *et al.*[1,2)], shows high extraction selectivity for Am(III) over RE(III) and attracts a great deal of attention because its constituent elements are C, H, O and N which are combustible after use up. Figure 1 shows the chemical structure of the R-BTP.

On the other hand, to overcome the demerits of solvent extraction method and to advantage the merits of R-BTP, another technology of extraction chromatography for separation of MA(III) has been proposed, which combines the selectivity of solvent extraction with the ease of operation of column chromatography. Kuraoka *et al.* have synthesized several R-BTP adsorbents with different alkyl groups for the extraction chromatography and investigated their fundamental properties such as adsorbability and stability[3-9)]. It was found that separation property and stability of the R-BTP adsorbents depended on the structure of alkyls, i.e. number of carbons (length of chain) and different branched chain. Separation factors between Am(III) and Eu(III) are relatively high in the case of normal R-BTP adsorbents with straight 3~7 carbon chain[6,7)], and the branched R-BTP (*iso*buthyl-BTP [C=4]) adsorbent is more stable than normal R-BTP adsorbents in ≤3 M HNO_3 solution[5,7)].

The final object of this work is, by synthesizing novel R-BTP adsorbents (*i.e.*

extraction resins), to establish a simplified MA direct separation process (see Fig. 2). In the fiscal year (FY) 2008, *i) iso*hexyl-BTP [C=6] and *iso*heptyl-BTP [C=7] extraction resins were synthesized by impregnating the R-BTP ligands (*i.e.* extractants) into the macroporous silica/polymer composite support (SiO_2-P particles), then, *ii)* adsorption properties of typical FP including RE(III) with HNO_3 solution onto the resins, and *iii)* chemical and thermal stabilities of the resins were examined[10,11]. In the FY 2009, *(1)* adsorption and desorption properties of Am(III) including typical FP elements and U with HNO_3 solution onto the resins, *(2)* radiolytic stabilities of the resins were examined, and *(3)* another type of novel R-BTP resins (*Cy*heptyl-BTP/SiO_2-P) was prepared and attempted to obtain its fundamental properties.

Experimental

As the novel R-BTP adsorbents, *iso*hexyl-, *iso*heptyl- and *Cy*heptyl-BTP extraction resins were prepared by impregnating the respective R-BTP extractants into the macroporous silica/polymer composite support (SiO_2-P particles), according to the reported procedures[9].

Adsorption and desorption properties were evaluated by batch experiment. The former was obtained by measuring distribution coefficient, K_d[10,11]. The concentration (or radioactivity) of ^{241}Am, which is one of typical MA nuclides, and simulated FP (Cs, Sr, Zr, Mo, Pa, *etc.*) including RE (Y, Ce, Nd, Eu, Dy, *etc.*) in solution was analyzed by γ-ray spectrometer (well-type NaI(Tl) scintillation counter) and ICP-AES (inductively coupled plasma–atomic emission spectrometer), respectively.

Radiolytic stabilities of the resins were examined under relatively low dose (about 40 Gy/h) contacting with various concentration of HNO_3 concentration by irradiating γ-rays from ^{60}Co. Leakage of R-BTP extractants, degradation evalution and thermal stabilities of the resins under γ-ray irradiation were examined with TOC (total organic carbon analyzer), FT-IR (Fourier transform infrared spectrophotometer), and TG-DTA (thermogravimetry-differential thermal analyzer).

Results and Discussion

(1) Adsorption and desorption properties

Figures 3 and 4 show dependence of K_d on HNO_3 concentration onto *iso*hexyl- and *iso*heptyl-BTP resins, respectively, in 3 h at 25°C. In 2~3 M (mol/m^3) HNO_3 solution, Am(III) seems to be possibly separated from main FP including even heavy RE(III). Separation factor between Am and heavy RE were ≈100 and more. It was found that Am was probably separated from U and Tc, and the separation of Am from Pd required further investigating.

On the other hand, adsorption rate with 3 M HNO_3 solution and desorption rate with H_2O onto *iso*hexyl- and *iso*heptyl-BTP resins at 25ºC were extremely slow. Consequently, it was difficult to separate Am from FP by column experiment at 25ºC. As compared with two resins, the adsorption and desorption rates onto *iso*hexyl-BTP resin were much higher than those onto *iso*heptyl-BTP resin. Therefore the column experiment using *iso*hexyl-BTP resin at 50ºC will be worth performing.

(2) Radiolytic stabilities

In relation to the radiolytic stability, *i)* effects of γ-ray irradiation on adsorbability of RE onto *iso*hexyl- and *iso*heptyl-BTP resins, *ii)* leakage of R-BTP extractants from the resins with TOC, *iii)* degradation of the resins with FT-IR, and *iv)* thermal decomposition of the resins with TG-DTA were investigated during 30~120 d.

The adsorbability of RE (Eu, Gd and Dy) onto the both resins was evaluated by obtaining the K_d values. The values seriously decreased with increasing dose (30~120 kGy) and concentration of HNO_3 (0.01~3 M) except for 0.01 M HNO_3, as compared with those by non-irradiation. As a result of TOC analysis of liquid phase, generally, but not always, increasing irradiation dose and concentration of HNO_3 (0.1~3 M) tended to increase leakage of R-BTP extractants from R-BTP resins. Degradation of the resins examined with FT-IR was observed a little in 0.1 M HNO_3, and it increased with acid concentration. The phenomena seemed to be accelerated by γ-ray irradiation. Concerning thermal stabilities, serious difference between irradiation and non-irradiation was not observed with TG-DTA. Blow about 120 kGy, the resins were decomposed by HNO_3 rather than γ-ray irradiation.

(3) Synthesis of another type of R-BTP resin

Quite recently, similar types of ligands to the R-BTP extractants have been vigorously developed[12-16)], which contain plural-pyridine structure and/or plural phenyl groups, and are expected to be improved in hydrolysis (stability of HNO_3) and radiolysis. One of the authors has also designed and synthesized another type of ligand, *Cy*heptyl-BTP (*cyclic*-heptyl-BTP) extractant, as shown in Fig. 5, and then prepared another novel adsorbent, *Cy*heptyl-BTP/SiO_2-P resin, by impregnating the extractant into the macroporous SiO_2-P particles. Its fundamental properties, except for adsorbability and radiolytic stabilities, were investigated by analyzing the resin with FT-IR, TG-DTA, *etc*. The chemical structure of the resin was verified by analyzing the *Cy*heptyl-BTP extractant, SiO_2-P particles and *Cy*heptyl-BTP/SiO_2-P resins with FT-IR and so on. Table 1 shows the TG-DTA results of *Cy*heptyl-BTP resin, comparing with *iso*hexyl- and *iso*heptyl-BTP resins. It was found that thermal decomposition property of *Cy*heptyl-BTP resin was similar to that of *iso*hexyl- and *iso*heptyl-BTP resins.

Conclusions

Adsorbability of Am in 2~3 M HNO_3 solution onto *iso*hexyl- and *iso*heptyl-BTP adsorbents (*i.e.* extraction resins) showed excellent property for main FP including RE (separation factor ≥100), but adsorption rate with 3 M HNO_3 solution and desorption rate with H_2O were considerably slow at 25°C. In addition, stabilities of the resins against γ-ray irradiation during 30~120 d showed the poor quality in adsorbability of RE, leakage of R-BTP extractants, degradation and thermal decomposition of the resins, as compared with the case of non-irradiation. Therefore, another type of R-BTP resin (Cyheptyl-BTP/SiO_2-P) was synthesized and its evaluation study has started. Batch and column experiments at not only 25°C but also 50°C will be necessary to accelerate the adsorption and desorption rates.

This work has started from October, 2008, and will be over the end of FY2010. More detailed adsorption/desorption (or elution) properties and hydrolytic/radiolytic stabilities will be examined by batch and column experiments in order to construct the simplified MA direct separation process.

Acknowledgments

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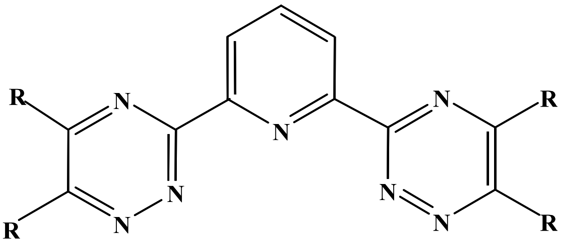
Table 1. Comparison with TG-DTA results of three R-BTP/SiO_2-P resins.

R-BTP resins	Weight (mg)	Loss weight (%)					
		<100 ℃	100~170 ℃	170~234 ℃	234~368 ℃	368~600 ℃	<600 ℃ (Total)
*Cy*heptyl-BTP	21.2	1.08	2.18	3.88	25.8	17.2	50.1
*iso*hexyl-BTP	35.0	0.96	2.45	6.21	24.8	14.8	49.2
*iso*heptyl-BTP	19.3	0.71	3.17	6.18	25.8	13.8	49.7

Atmosphere gas: O_2, gas flow rate: 30 mL/min, temperature elevating rate: 1 ℃/min.



R-BTP

Figure 1. Chemical structure of R-BTP (**BTP**: 2,6-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine, **R**: alkyl group [C_nH_{2n+1}]).

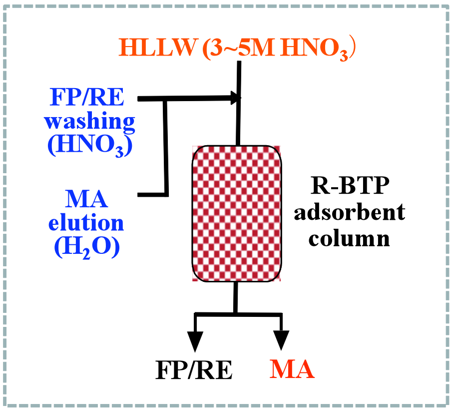


Figure 2. Simplified MA direct separation process by use of novel R-BTP adsorbent column (**MA**: Am, Cm, **RE**: Y, Nd, Eu, *etc*., **FP**: Cs, Sr, Zr, Mo, Tc, Ru, Rh, RE, *etc*.).

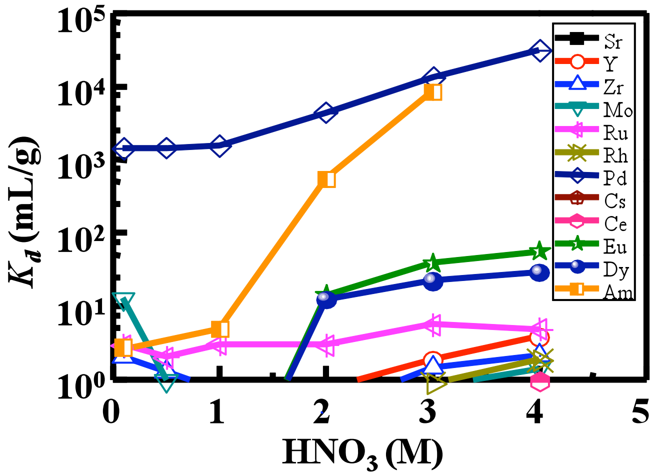


Figure 3. Dependence of K_d on HNO_3 concentration onto *iso*hexyl-BTP/SiO_2-P resin in 3 h at 25ºC. [K_d (U): 1~5, K_d (Tc): 3~20, K_d (Cs, Sr, Y, Mo, Ce, Rh)≤10^0].

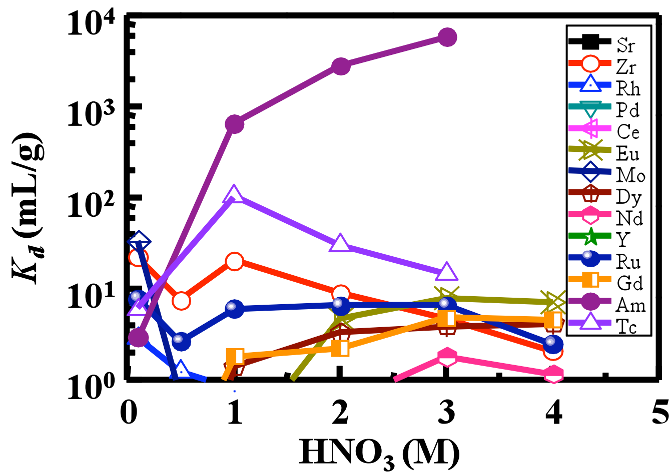


Figure 4. Dependence of K_d on HNO_3 concentration onto *iso*heptyl-BTP/SiO_2-P resin in 3 h at 25ºC. [K_d (Pd)>10^4, K_d (U): 2~3, K_d (Cs, Sr, Y, Mo, Ce, Rh)≤10^0] .

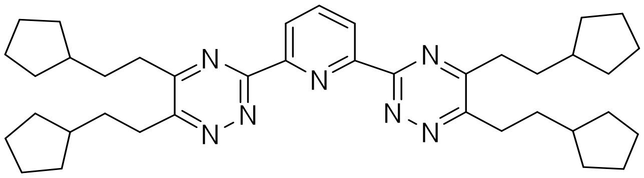


Figure 5. Chemical structure of *Cy*heptyl-BTP.