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Adsorption behavior of Am with gamma irradiated Thiacalix[4]arene impregnated silica adsorbent

Takahiro Kikuchi*, Kazunori Suzuki

Institute of Research and Innovation (IRI), 1201 Takada, Kashiwa, Chiba 277-0861, Japan

Abstract

Thiacalix[4]arene impregnated silica adsorbent which is called CAPS-SO_2-adsorbent in this paper shows the excellent separative performance of trivalent actinoids, such as Am from the high-level radioactive liquid waste (HLLW) in weak-acid solution. The chemical stability of the adsorbent was investigated under strong irradiation conditions. The amount of dissolved CAPS-SO_2 was only 1% by gamma-ray irradiation at a total dose of 1 MGy. The value of distribution coefficient of Am (Kd_{Am}) at pH 4 by the adsorbent was constant even the high irradiation dose. Moreover, the separation factor of Am to lanthanoids is kept a high value. It was also found that the value of Kd_{Am} by the irradiated CAPS-SO_2-adsorbent increases at pH 2.

Keywords: Americium; Lanthanoids; Separation; Thiacalix[4]arene; Irradiation-stability

1. Introduction

The extraction chromatographic resins have been researched and developed for separation and pre-concentration of actinoid ions, and chemical analysis for biological, environmental and nuclear waste samples. The extraction of chromatographic resins provides a simple and effective method for separation and pre-concentration, and the adsorbed elements in the resins are readily eluted and recovered with the appropriate complexing agents. Horwitz and co-worker developed various chelating ion-exchange resins, such as Diphonix [1], U/TEVA-2 resin [2] and so on for the separation and the pre-concentration of U.

The high-level radioactive liquid waste (HLLW) generated from commercial reprocessing facilities contains various elements, such as Cs, Sr, lanthanoids, actinoids and so on. Cs and Sr group have short half-life period (about 30 years). Radioactivity of lanthanoids is very few. However, ^{241}Am has half-life period of 400 years. So, it is necessary for the waste to be disposal in deep geology, because the waste contains ^{241}Am. The separation of ^{241}Am from HLLW is one of the important items in the radioactive waste management. Authors studied the adsorption method to separate both trivalent actinoids and lanthanoids from HLLW by using a silica adsorbent impregnated octylphenyl-*N*,*N*-diisobutylcarbomoyl phosphine oxide (CMPO-adsorbent) [3]. But CMPO-adsorbent is not able to separate between actinoids and lanthanoids, because CMPO-adsorbent has no selective separation performance for these elements. For this reason, a new adsorbent should be considered for separation of actinoids in the effluent from CMPO-adsorbent. The separation factor of Am to Eu by Diphonix is small [4], and the adsorbed ability of U/TEVA-2 resin for Am shows very smaller than that for U or Pu [2]. Furthermore, the separation factor of Am to Eu by U/TEVA-2 is unknown. Zhu [5] reported that bis(2,2,4-trimethypentyl)-dithiophosphinic acid (Cyanex301) had very high separation factors between Am and Eu. However, the purification of Cyanex301 was necessary to obtain high separation factors [6], and also the purified Cyanex301 was not always stable in aqueous solution [7]. On the other hand, we have found that *p*-tert-butylthiacalix[4]arene compounds impregnated silica adsorbents which we call CAPS-SO_2-adsorbent have the excellent separation performance between Am and lanthanoids in weak-acid (pH 4) solution [8]. CAPS-SO_2 has four *p*-tert-butylphnols which linked by four sulfonyl

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* Corresponding author.
E-mail address: tkikuchi@iri.or.jp (T. Kikuchi).

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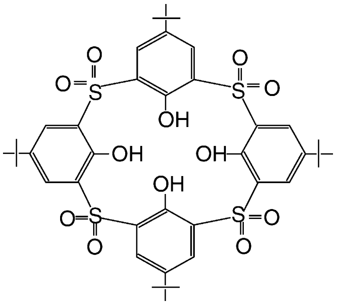

Fig. 1. Structures of CAPS-SO_2.

groups. The structure is shown in Fig. 1. A basic process flow of separation treatment studied by authors was shown in Fig. 2 [3,8]. U and Zr strongly affect adsorption and elution of Am and lanthanoids on CMPO-adsorbent. Therefore, removal of U and Zr before separation between Cs/Sr group and Am/lanthanoids group is important.

CMPO-adsorbents and CAPS-SO_2-adsorbents are always used under the strong irradiated condition in the treatment of actual HLLW. The chemical stability at irradiation is an important item in the reutilization of those adsorbents. The adsorbed amounts of actinoids and lanthanoids on CMPO-adsorbent decreased linearly with increasing irradiation dose. However, the adsorption capacity at a dose of 2 MGy kept 80% of the initial capacity [3]. We estimated that CMPO-adsorbent could be reused for several hundred cycles up to a dose of 2 MGy in the treatment of HLLW. This result shows that reduction of adsorption capacity of CMPO-adsorbent is no problem in the reusing. On the other hand, the irradiation stability of CAPS-SO_2-adsorbent is unknown. In this study, we investigate adsorption performance of gamma-ray irradiated CAPS-SO_2-adsorbent, and compared with the performance of irradiated Cyanex301 impregnated silica adsorbent (Cyanex301-adsorbent).

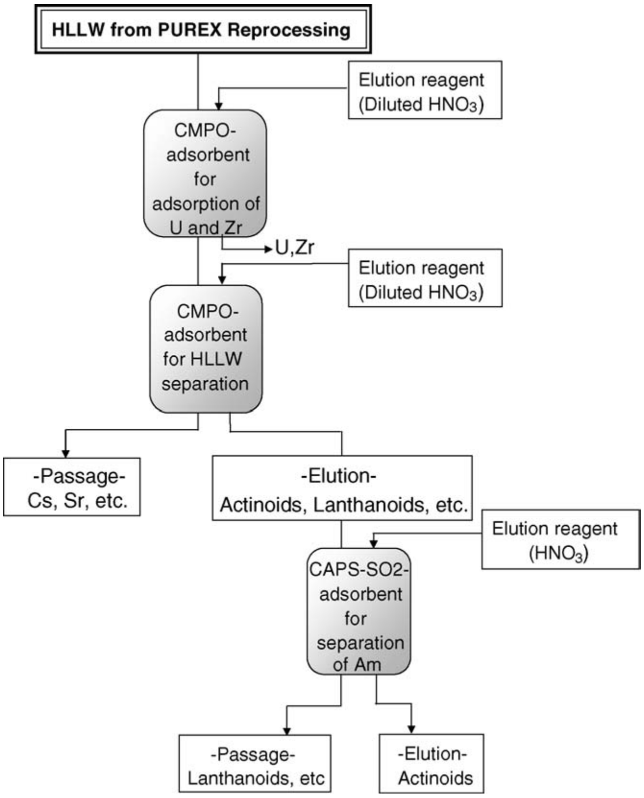

Fig. 2. Basic concept of separation treatment of HLLW.

2. Experimental

2.1. Preparation of CAPS-SO_2- and Cyanex301-adsorbent

Spherical silica particles with a diameter of 36–74 μm, a mean pore size of 500 nm, a pore volume of 0.9 cm^3/g, and a specific surface area of 5 m^2/g were used for the supports of adsorbents. The supports were coated with polyformylstyrene-divinylbenzene, before impregnation of CAPS-SO_2 or Cyanex301. Cyanex301 was purified by using ammonium carbonate according to the method of Modolo and co-worker [6], before loading in the supports. The coating and impregnation method were in detail described previous paper [8].

2.2. Adsorption experiments

The distribution coefficients (Kd) of ^{241}Am, Nd and Eu for those adsorbents were measured by batch adsorption experiments. The pH ranges of experiments were adjusted to 1–4. In the batch adsorption experiment, 0.1 g of the adsorbent was added to 10 cm^3 of the solution containing the predetermined concentration of each element, and was stirred at 298 K for 3 h. The sample solution was separated from the adsorbent by filtration. The concentration of ^{241}Am was determined by scintillation counter, and the concentration of Nd or Eu was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The distribution coefficient was calculated as follows:

$$\mathrm{Kd}\,(\mathrm{cm}^3/\mathrm{g}) = \frac{C_\mathrm{i} - C_\mathrm{e}}{C_\mathrm{e}}\frac{V_\mathrm{s}}{W_\mathrm{e}}$$

where C_i is the initial concentration of element in the solution, C_e is the equilibrium concentration of element in the solution, V_s is the volume of the solution, W_e is the weight of the adsorbent.

2.3. Gamma-ray irradiation

CAPS-SO_2- and Cyanex301-adsorbent is gamma-ray irradiated in pH 4 solution by ^{60}Co irradiator (dose rate, 2800 Gy/h). After the gamma-ray irradiation, those adsorbents were filtered and dried in vacuo at ambient temperature. The adsorption test was carried out by the batch method as noted above. After filtration, the amount of dissolved sulfur in that solution was measured for estimate of degradation ratio by ICP-AES. The degradation ratio (D_r) was calculated as follows:

$$D_r\,(\%) = \frac{S_d}{S_e} \times 100$$

where S_d is the amount of dissolved sulfur after irradiation, S_e is the initial amount of sulfur in the adsorbent.

So, a degradation ratio in this experiment is defined in the amount of dissolved sulfur in the solution. The remained of degradation products in the adsorbents are not taken into consideration in this study.

3. Results and discussion

3.1. Adsorption performance of CAPS-SO$_2$- and Cyanex301-adsorbent

Table 1 shows the adsorption capability of CAPS-SO$_2$-adsorbent and Cyanex301-adsorbent for ^{241}Am, Nd and Eu. Very few of Nd and Eu were adsorbed on those adsorbents. On the other hand, the value of distribution coefficient of ^{241}Am (Kd_{Am}) at pH 4 provides more than 3000 cm^3/g. The high separation factor of Am to Eu was obtained. Also, selective performance of CAPS-SO$_2$-adsorbent indicates the same order of that of Cyanex301-adsorbent. Since the adsorption capability of those adsorbents remarkably decreased at pH 2, then Am is possible to be recovered by acidic eluent, such as nitric acid. As for Nd, adsorption and elution tests on CAPS-SO$_2$-adsorbent by column method have been carried out in pH 5.5 and 1 mol/dm^3 nitric acid solution, respectively. We confirmed that 100% of Nd was recovered with nitric acid.

3.2. Chemical stability of CAPS-SO$_2$- and Cyanex301-adsorbent under gamma-ray irradiation

Under gamma-ray irradiation, amount of dissolved sulfur to the solution from the adsorbent was measured. Fig. 3 shows the radiolytic degradation ratio of CAPS-SO$_2$- and Cyanex301-adsorbent. The degradation ratio of Cyanex301-adsorbent increased with increasing gamma-ray irradiation dose. Thirty percentage of Cyanex301 was dissolved by gamma-ray irradiation at a total dose of 1 MGy. And the pH value of the solution is decreased to 2 up to a dose of 1 MGy. We consider that sulfuric acid is formed by irradiation. On the other hand, only 1% of CAPS-SO$_2$ was dissolved under the irradiation. So, CAPS-SO$_2$-adsorbent is much more stable than Cyanex301-adsorbent. The pH value of that solution was about 3 at a dose of 1 MGy. Moreover CAPS-SO$_2$ which did not contain silica-support was irradiated in the pH 4 solution for measurement of FT-IR. The results showed that the adsorption band between 1350–1310 and 1160–1120 cm^{-1} which assigned sulfonyl group did not make a transformation.

Table 1
Adsorption ability of CAPS-SO$_2$- and Cyanex301-adsorbents

Adsorbent	pH 2			pH 4		
	Kd_{Am}	Kd_{Nd}	Kd_{Eu}	Kd_{Am}	Kd_{Nd}	Kd_{Eu}
CAPS-SO$_2$	13	2	2	5000	10	9
Cyanex301	12	–	2	3800	–	12

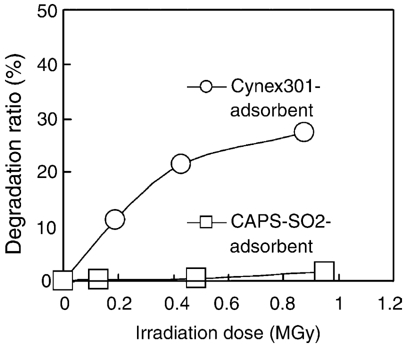

Fig. 3. Radiolytic degradation of CAPS-SO$_2$- and Cyanex301-adsorbent.

3.3. Selectivity degradation behavior of Cyanex301-adsorbent

Fig. 4 shows the change in the adsorption ability of Cyanex301-adsorbent in weak-acid solution (pH 4). Although Cyanex301 was decomposed chemically under irradiation, the value of Kd_{Eu} increased with increasing irradiation dose. But the value of Kd_{Am} slightly decreased. Then, the selectivity for Am disappeared on Cyanex301-adsorbent up to a dose of 1 MGy. The result suggests that Cyanex301 decomposes to Cyanex302 or Cyanex272 in the adsorbent [6].

3.4. Adsorption ability of irradiated CAPS-SO$_2$-adsorbent

Fig. 5 shows the change in the adsorption ability of CAPS-SO$_2$-adsorbent in pH 4 solution. Despite of irradiation dose increased, the value of Kd_{Am} was constant. The distribution ratio of lanthanoids slightly increased up to a dose of 0.2 MGy, but the separation factor was kept a high value even under irradiated condition.

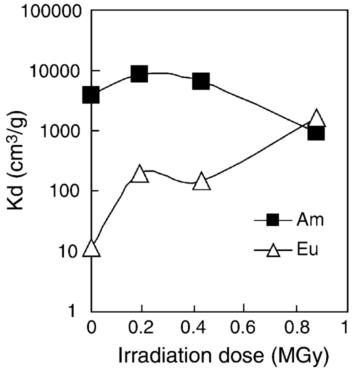

Fig. 4. Change in adsorption ability of irradiated Cyanex301-adsorbent.

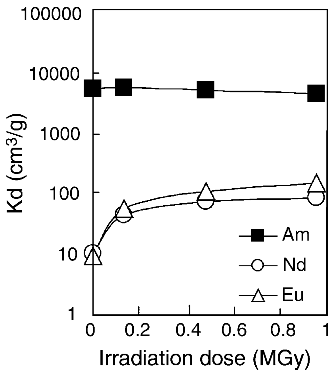

Fig. 5. Change in adsorption ability of irradiated CAPS-SO_2-adsorbent.

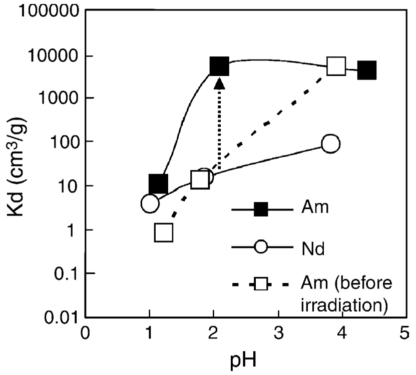

Fig. 6. Adsorption behavior of CAPS-SO_2-adsorbent for Am and Nd after irradiation at a total dose of 1 MGy.

Fig. 6 shows the effect of pH value on adsorption behavior of irradiated CAPS-SO_2-adsorbent (at a total dose of 1 MGy) for Am and Nd. The value of Kd_{Am} by the irradiated CAPS-SO_2-adsorbent increased to almost 5000 cm^3/g at pH 2. Since actinoids and lanthanoids from CMPO-adsorbent were recovered by using 0.01 mol/dm^3 nitric acid, then pH value of the eluent containing both actinoids and lanthanoids was nearly 2. At pH 1–4, the value of Kd_{Nd} by the irradiated adsorbent was very small. It is shown that irradiated CAPS-SO_2-adsorbent can separate actinoids from lanthanoids without any pH control by neutralization or dilution.

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