Alpha-ray irradiation on adsorbents of extraction chromatography for minor actinide recovery

Sou Watanabe, Sachiko Miura, Yuichi Sano, Kazunori Nomura, Yoshikazu Koma, Yasuo Nakajima
Japan Atomic Energy Agency, Japan

Abstract

Alpha-ray durability of adsorbents used in an extraction chromatography technology for MA recovery process was experimentally investigated. For representative adsorbents (TODGA/SiO_2-P, CMPO/SiO_2-P, isoHex-BTP/SiO_2-P and HDEHP/SiO_2-P), alpha-ray of ^{241}Am was irradiated and influences of the irradiation were examined through distribution coefficient, desorption ratio and thermal characteristics. Those systematic experiments and our previous study revealed that the alpha-ray durability of the adsorbents is less significant than their gamma-ray durability. The difference between a charged particle and γ-ray is considered to cause the different interaction between the system (adsorbents with nitric acid) and the radiations.

Introduction

Extraction chromatography technology is one of the promising methods to recover minor actinides (MA; Am and Cm) from spent FBR fuel, and the Japan Atomic Energy Agency has been conducting R&D studies for the implementation [1]. We have carried out the design of an appropriate flow sheet [2], laboratory scale separation experiments on a genuine high-level liquid waste [3], development of the engineering scale apparatus [4] and inactive repeated separation experiments [5].

This technology uses an adsorbent consisting of an extractant for interacting with MA and of porous silica particles coated by styrene divinyl benzene polymer (referred as SiO_2-P) to support the extractant. Radioactive elements such as MA form complexes with the extractant in the adsorbent, therefore degradation of those materials by irradiation is unavoidable. Previous studies have reported that radiation degradation of the adsorbent lead to a distinct change in adsorption/elution behaviours [6] [7]. In order to design operational condition and to evaluate the frequency of exchange for the adsorbent, durability of the adsorbents is indispensable information. Although effects of γ-ray irradiation and exposure to acid on adsorption/elution performances of the adsorbents have been investigated before [2], resistance against α-ray irradiation has not been reported yet.

In this study, α-ray irradiation experiments on the representative adsorbents for the extraction chromatography process (TODGA[8]/SiO_2-P, CMPO[9]/SiO_2-P, isoHex-BTP[10]/SiO_2-P and HDEHP[11]/SiO_2-P) were carried out and influences of alpha-ray irradiation on the fundamental characteristics of the adsorbents were investigated.

Experimental

α-ray irradiation

The experimental conditions are shown in Table 1. Nitric acid solutions containing ^{241}Am with 0.87 ~ 8.7 mM was prepared as α-ray sources (E = 5.5 MeV, Half life = 432.2 y). 0.5 g of the adsorbent was contacted with 10 mL of the source solution and was shaken for 3 hours to adsorb ^{241}Am onto the adsorbents. The particles bearing ^{241}Am were left for a certain period to irradiate with the α-ray. During the irradiation, the amount of ^{241}Am elute from the adsorbent was measured to evaluate stabilities of adsorbents against α-ray irradiation. In this study, the concentration of ^{241}Am was analysed by γ-ray spectrometry.

Elution ratio

After the irradiation, ^{241}Am were desorbed by contacting with 40 mL of eluents. H_2O or 1M HNO_3 were used as the elutent for TODGA/SiO_2-P, CMPO/SiO_2-P and iso-Hex-BTP/SiO_2-P or HDEHP/SiO_2-P. The elution ratio of the adsorbed ^{241}Am was obtained to evaluate influences of α-ray irradiation on the desorption performance of the adsorbents. The α-ray irradiated adsorbent was dried and then supplied to the following experiments.

Absorption performance

Distribution coefficients of ^{241}Am onto the α-ray irradiated adsorbents were obtained to evaluate influences of α-ray irradiation on the adsorption performance of the adsorbents. 0.2 g of the adsorbent was contacted with 4 mL of the HNO_3 solution containing ^{241}Am and was shaken for 3 hours.

Thermal characteristics

The thermal characteristics of the α-ray irradiated adsorbents were also investigated to examine the possibility of hazardous reaction due to the formation of radiolysis products. Thermogravitry/Differential Thermal Analysis (TG/DTA) measurements on 0.01 g of the dried adsorbents were carried out at from room temperature to 800°C with 10°C/min under air atmosphere.

Table 1: Experimental conditions for α-ray irradiation

Extractant	^{241}Am source solution	Irradiation period	Eluent
TODGA	[H^+] = 5 M [^{241}Am] = 3.9 mM	~7 Day	H_2O
CMPO	[H^+] = 3 M [^{241}Am] = 8.7 mM	~ 65 Day	H_2O
Iso-Hex BTP	[H^+] = 1 M [^{241}Am] = 3.8 mM	~8 Day	H_2O
HDEHP	[H^+] : 0.01 M [^{241}Am] = 0.87 mM	~ 65 Day	1M HNO_3

Result and discussion

α-ray irradiation and influences on adsorption/desorption performances

TODGA/SiO_2-P

The amount of ^{241}Am kept on the TODGA/SiO_2-P adsorbent during α-ray irradiation is shown in Figure 1, where absorption dose was calculated assuming that all energy of alpha-ray from ^{241}Am was transferred to the adsorbent. More than 99% of ^{241}Am initially adsorbed was kept after 1.3 MGy irradiation. Figure 2 shows the desorption ratio of ^{241}Am from the irradiated TODGA adsorbent. The elution ratio did not change clearly and it was at ca. 60%.

The distribution coefficient of ^{241}Am onto the α-ray irradiated TODGA/SiO_2-P, calculated from the following equation, is shown in Figure 3

$$K_d = \frac{W_0 - W_s}{W_s} \times \frac{V}{w}$$

where, W_0 is radioactivity of ^{241}Am in the feed solution (Bq), W_S is radioactivity ^{241}Am in the solution after the adsorption, V is volume of the solution (cm^3), and w is the weight of the adsorbent (g). The irradiated adsorbents showed a lower distribution coefficient than that of the new one, however, the distribution coefficient did not depend on the irradiated dose. 1.3 MGy α-ray irradiation did not significantly affect the adsorption performance.

In our previous study, the adsorption capacity and distribution coefficient of Eu on γ-ray irradiated TODGA/SiO_2-P decreased to 90% and 10%, respectively, after 1 MGy irradiation [2]. According to an article, γ-ray and α-ray irradiation on the mixture of TODGA with dodacane revealed that the γ-ray irradiation is dominant for degradation of TODGA [12]. Another report suggested that the radical of dodecane produced by γ-ray irradiation degrades TODGA, according to the following equations [13]:

$$DD \rightarrow DD^+ + e^-$$

$$DD^+ + TODGA \rightarrow DD + TODGA^+$$

where DD and TODGA denote dodecane and TODGA molecules, respectively.

In the case of the extraction chromatography system, nitric acid solution or the polymer possibly play a similar role of dodacane in the solvent system. As polystyrene tends to form excited states rather than radicals by γ-ray irradiation [14], radicals produced from nitric acid solution must be the most dominant component to degrade TODGA extractant. Since molecular species such as H_2 or H_2O_2 have been reported to be produced by α-ray irradiation [15], degradation of the extractant by α-ray irradiation is considered to be caused by direct interaction of α-ray with the extractant. The different interactions between the extractant and the radiations seem to result in different degradation products and adsorption performances. Regarding adsorption performance, the influence of γ-ray irradiation is more significant than that of α-ray irradiation. Stabilities of the degradation products will be discussed in the next section through thermal characteristics of the adsorbent.

Figure 1: The amount of ^{241}Am kept in the TODGA/SiO_2-P adsorbent during α-ray irradiation

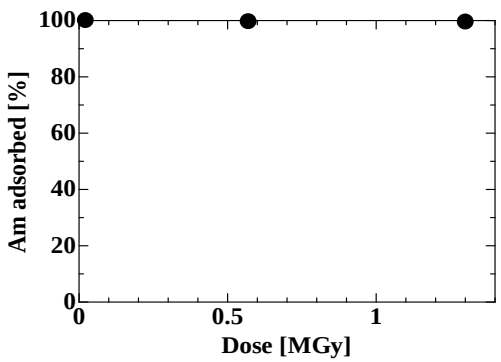


Figure 2: Elution ratio of ^{241}Am from the α-ray irradiated TODGA/SiO_2-P

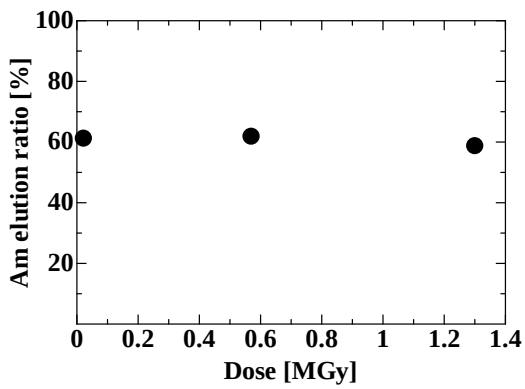
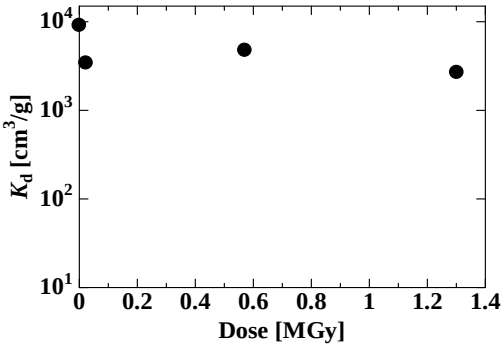


Figure 3: Distribution coefficient of ^{241}Am onto the α-ray irradiated TODGA/SiO_2-P adsorbent



CMPO/SiO_2-P

Figure 4 shows the amount of ^{241}Am kept on the adsorbent during the α-ray irradiation. About 35% of the adsorbed ^{241}Am was kept until 26.5 MGy irradiation. Degradations of CMPO and/or polymer must be progressed by the irradiation. The elution ratio of ^{241}Am after the irradiation is shown in Figure 5. More than 60% of ^{241}Am was desorbed by H_2O even after 26.5 MGy irradiation.

Figure 6 shows the distribution coefficient of ^{241}Am onto the α-ray irradiated CMPO/SiO_2-P. The distribution coefficient decreased with increasing the radiation dose, and the adsorption ability of the CMPO almost disappeared after 26.5 MGy α-ray irradiation. Up to 0.4 MGy irradiation, the influence of the irradiation on the distribution coefficient was not obvious. The distribution coefficient of Nd onto γ-ray irradiated CMPO/SiO_2-P also decreased with increasing radiation dose [16], and the influence of γ-ray irradiation is more distinct than that of α-ray irradiation like in the case of TODGA/SiO_2-P. The degradation mechanism of CMPO/SiO_2-P can be explained in the same manner with that for the degradation of TODGA/SiO_2-P.

Figure 4: The amount of ^{241}Am kept in the CMPO/SiO_2-P adsorbent during α-ray irradiation

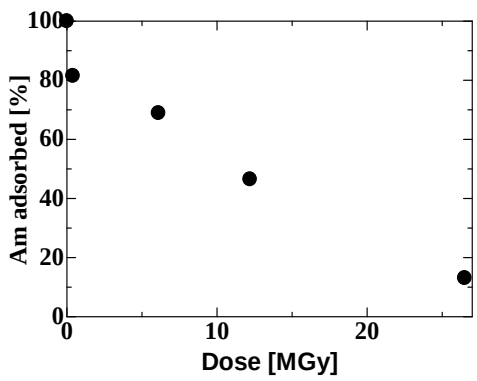


Figure 5: Elution ratio of ^{241}Am from the α-ray irradiated CMPO/SiO_2-P

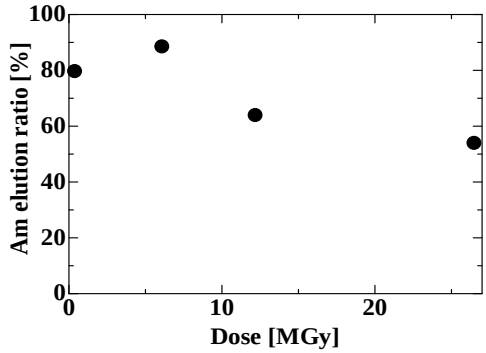
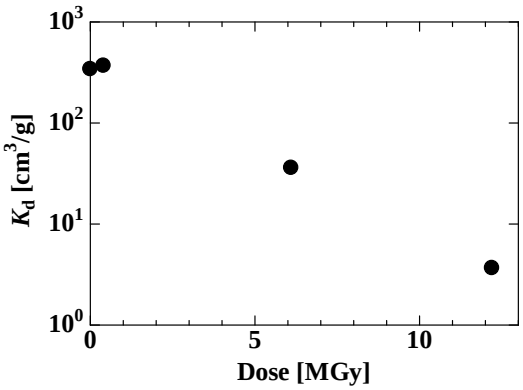


Figure 6: Distribution coefficient of ^{241}Am onto the α-ray irradiated CMPO/SiO_2-P adsorbent



Iso-Hex BTP/SiO_2-P

Figure 7 shows the amount of ^{241}Am kept in the adsorbent during α-ray irradiation. About 60% of ^{241}Am was kept after 1.3 MGy irradiation. The elution ratio of ^{241}Am from α-ray irradiated adsorbent is shown in Figure 8. The elution ratio was almost constant at 50% until 0.5 MGy irradiation, however, it decreased to be less than 1% after 1.3 MGy irradiation. ^{241}Am initially adsorbed by the adsorbent is considered to form the complex with degradation product of iso-Hex-BTP. The elution ratios of cations from iso-Hex BTP/SiO_2-P adsorbent decreased in 5-20% after 1 kGy γ-ray irradiation [7]. Thus, a change in the performance of iso-Hex BTP/SiO_2-P is more sensitive to γ-ray irradiation than α-ray irradiation although the influence of α-ray irradiation on iso-Hex BTP is larger than that on TODGA or CMPO. Those results could be consistent with previous reports of γ-ray and α-ray irradiations on CyMe4-BTBP which is analogous to iso-Hex BTP [17].

Figure 7 shows the distribution coefficient of ^{241}Am onto the α-ray irradiated adsorbent. Although the distribution coefficient did not change after 0.6 MGy, 1.3 MGy irradiated adsorbent completely lost its adsorption capacity for ^{241}Am. Iso-Hex-BTP impregnated may be almost degraded through the irradiation.

Figure 7: The amount of ^{241}Am kept in the iso-Hex-BTP/SiO_2-P adsorbent during α-ray irradiation

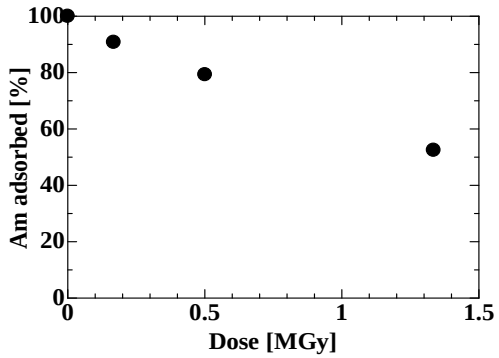


Figure 8: Elution ratio of ^{241}Am from the α-ray irradiated iso-Hex-BTP/SiO_2-P

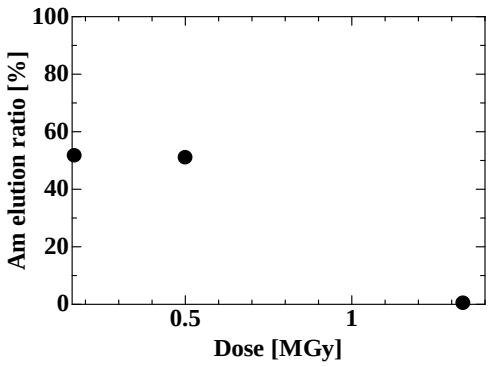
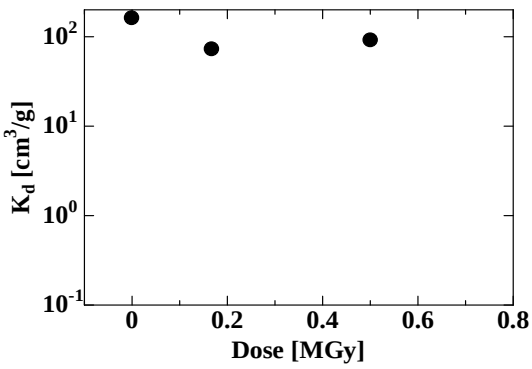


Figure 9: Distribution coefficient of ^{241}Am onto the α-ray irradiated iso-Hex-BTP/SiO_2-P adsorbent



HDEHP/SiO_2-P

Figure 10 shows the amount of ^{241}Am kept on the adsorbent during α-ray irradiation. More than 99% of ^{241}Am was kept on the HDEHP/SiO_2-P up to 15 MGy irradiation, and more than 80% of ^{241}Am was still kept up to 30 MGy irradiation. Figure 7 shows the elution ratio of ^{241}Am from the α-ray irradiated HDEHP/SiO_2-P. The elution ratio increased with increasing the radiation dose and reached 87% after 30 MGy irradiation.

Figure 8 shows the distribution ratio of ^{241}Am onto the α-ray irradiated HDEHP/SiO_2-P. There was no distinct decrease in the distribution ratio up to 15 MGy irradiation. A

previous study revealed that the degradation of HDEHP is mainly caused by hydrolysis rather than radiolysis [16], and those results should be consistent with that conclusion.

Figure 10: The amount of ^{241}Am kept in the HDEHP/SiO_2-P adsorbent

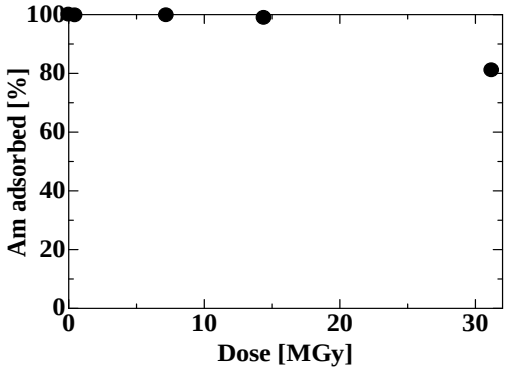


Figure 11: Elution ratio of ^{241}Am from the α-ray irradiated HDEHP/SiO_2-P

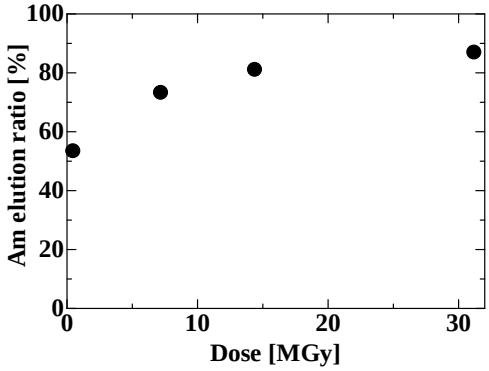
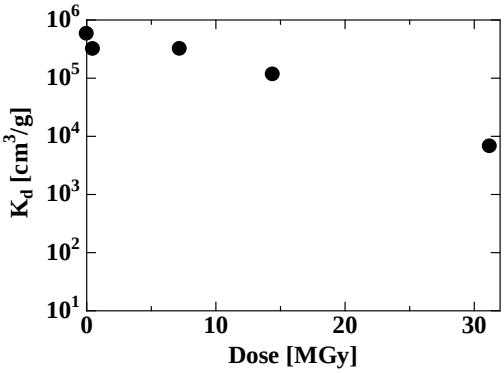


Figure 12: Distribution ratio of ^{241}Am onto the α-ray irradiated HDEHP/SiO_2-P



Thermal characteristics

Figures 13-16 show TG/DTA curves of α-ray irradiated adsorbents. A previous study has shown that exothermal peaks at 300, 400 and 580°C can be attributed to the thermal decomposition of the styrene-divinyl benzene polymer [18]. Therefore, the thermal decomposition of TODGA can be attributed to exothermal peaks at 200 and 350°C. The exothermal peak at 200°C decreased with increasing the radiation dose. In TG/DTA curve of CMPO/SiO_2-P, the decrease in mass caused by thermal decompositions of CMPO and

the polymer disappeared after 26.5 MGy irradiation. Therefore, the polymer as well as the extractant is possibly damaged by the irradiation. However, no exothermal peaks were observed after the irradiation. An endothermal peak at 80°C and an exothermal peak at 420°C could be attributed to the decomposition of iso-Hex BTP. α-ray irradiation made the endothermal peak disappear, therefore the iso-Hex BTP must be decomposed by the irradiation. The decomposition of HDEHP easily belonged to an endothermal peak at 220°C. Peak intensity decreased with increasing the irradiation dose.

According to these results, distinct exothermic peaks were not observed at under 100°C in the DTA curves, even after the irradiation. In the extraction chromatography system, the temperature of the system is controlled at under 100°C to prevent boiling of the mobile phase. Therefore, degradation which is suspected to lead to abnormal events such as fire or explosion will not be anticipated for the use of the adsorbents.

Figure 13: TG/DTA curves of α-ray irradiated TODGA/SiO_2-P

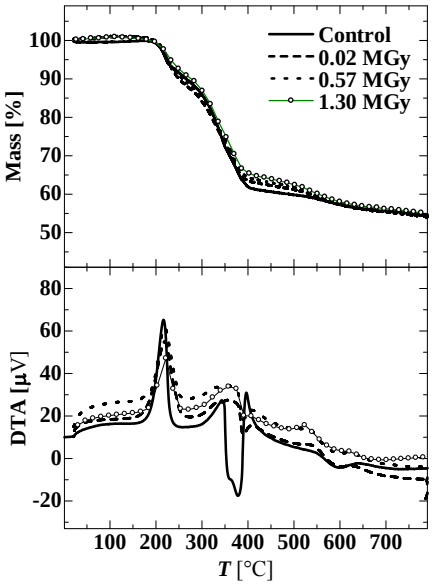


Figure 14: TG/DTA curves of α-ray irradiated CMPO/SiO_2-P

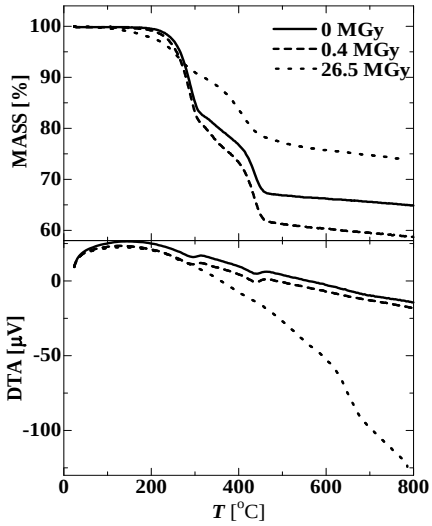


Figure 15: TG/DTA curves of α-ray irradiated iso-Hex BTP/SiO_2-P

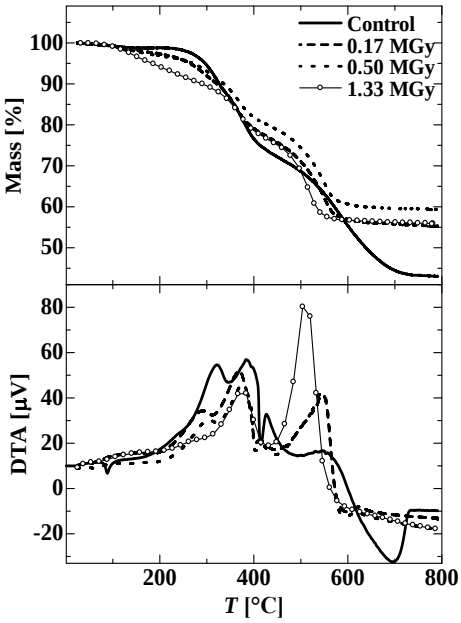
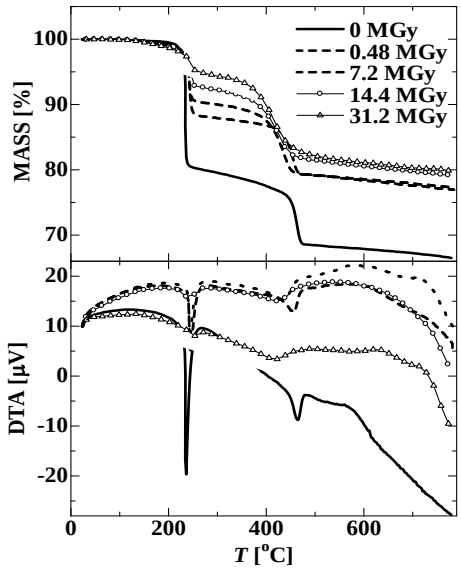


Figure 16: TG/DTA curves of α-ray irradiated HDEHP/SiO_2-P



Summary

In order to evaluate the α-ray durability of representative adsorbents for the extraction chromatography system, α-ray irradiations on the adsorbents were carried out through adsorption of ^{241}Am onto them. The α-ray irradiations influenced the adsorption/desorption performances, and that should correspond to the degradations of extractants impregnated in the adsorbents and of polymers supporting the extractants. Comparison of the influences of α-ray with γ-ray on those properties under the same radiation doses condition shows that radiation damage suffered from the α-ray irradiations are less significant for all the adsorbents. The difference between a charged particle and γ-ray is considered to cause the different interaction between the system (adsorbents with nitric acid) and the radiations. TG/DTA measurements on the α-ray irradiated adsorbents revealed that they are stable under operating conditions.

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