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Particle induced X-ray emission-computed tomography analysis of an adsorbent for extraction chromatography

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ABSTRACT

Nd, which simulates minor actinides (MAs), was used for investigating residual minor actinides produced during the extraction chromatography separation of spent fuel from fast neutron reactors. A cross-sectional distribution of Nd in a minute globular adsorbent having diameter less than 50 μm was obtained using particle induced X-ray emission-computed tomography with a 3-MeV proton microbeam. The measurement area was 150 × 150 μm^2 corresponding to 128 × 128 imaging pixels in projection images with 9° resolution, image reconstruction was carried out by a modified ML-EM (maximum likelihood expectation maximization) method. As a result, the cross-sectional distribution of Nd in the adsorbent was successfully obtained, and it was first revealed that Nd existed both in the central region and on the outer surface even after an elution. This implies that the internal structure of the adsorbent must be modified for improving of the recovery of MAs.

1. Introduction

Solvent extraction [1–3], ion exchange chromatography [4,5], and extraction chromatography (EXC) [6] have been well employed for the selective separation of actinides or metal impurities from the radioactive materials. Especially, EXC has been extensively applied to the recovery of minor actinides (MAs) from the spent fuel of a fast neutron reactors for separating long-lived MA and minimizing the long-term radiological risk [7]. A solid adsorbent, generally small porous silica (diameter ~50 μm) coated with a polymer (SiO_2-P), is used in the EXC process. The EXC process is simpler than other separation methods and it is thus considered suitable for reprocessing the highly complex and radioactive spent fuel of a fast neutron reactors. However, one of the drawbacks is that the recovery rate (<70%) of MAs [8,9] is well below the targeted rate of 99%. Investigation of distribution of the residual MAs using instruments with high spatial resolution of several μm is considered necessary for improving the recovery rate.

In 1998, an in-air micro particle induced X-ray emission (micro-PIXE) analyzer having 1 μm or less of high spatial resolution was developed at Takasaki ion accelerators for advanced radiation application of the Japan atomic energy agency (JAEA) [10,11]. In a previous study, the authors applied PIXE-computed tomography (PIXE-CT) [12–15], scanning transmission ion microscopy-CT (STIM-CT) [16] and maximum likelihood expectation maximization (ML-EM) iterative image reconstruction method [17] to analyze trace elements in a unicellular organism having diameter less than 100 μm. In that study, STIM-CT was used to measure the density of major elements because energy attenuation of incident particles and absorption of X-rays must be considered in ML-EM image reconstruction. As a result, the yields of characteristic X-rays from trace elements found in unicellular organisms, such as lead, were nondestructively achieved with spatial resolutions of less than 5 μm [18,19]. Since the porous silica adsorbent is very small and fragile, the PIXE-CT analyzer in JAEA was considered well suitable for nondestructive investigation of .the residual MAs.

2. Experiment

An adsorbent target was prepared by impregnating an extractant N,N,N′,N′-tetraoctyl diglycolamide (TODGA) [20,21] into particulate porous silica (~50 μm in diameter) coated with styrene divinylbenzene as a binder. Fig. 1 shows an electron microscope image of the prepared adsorbent particle having spherical shape and roughly diameter ~50 μm. In this experiment, Nd was used as a substitute for MAs because of the safety concerns described

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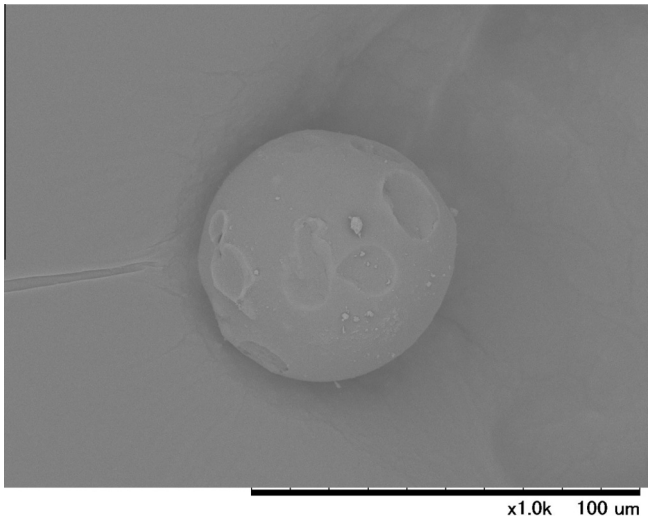

Fig. 1. A scanning electron microscope image of the porous silica adsorbent particle having a diameter of ~50 μm.

in Ref. [22]. Nd was adsorbed from a neodymium nitrate solution ([Nd] = 0.01 M, [H^+] = 5 M), and eluted with 0.01-M nitric acid solution at room temperature for 60 min by a batch process.

The adsorbent backed with polycarbonate film was first studied using a two-dimensional in-air micro-PIXE with a 3-MeV 1-μm-diameter proton microbeam with beam current of ~100 pA. The schematic diagram of the experimental setup is shown in Fig. 2. The adsorbent was placed in air to ensure that conditions match those of actual use. The measuring area was 100 × 100 μm^2, corresponding to 128 × 128 imaging pixels. The distance from the target and angle with respect to the beam axis of the lithium-drifted silicon (Si(Li)) detector (LS30135, PGT) for X-rays were 22 mm and 40°, respectively. A 60-μm-thick polyethylene terephthalate film was used for absorbing the plentiful K X-rays of silicon, which is one of the major components of the adsorbent.

Fig. 3 shows the experimental setup for PIXE-CT and STIM-CT analysis. After the two-dimensional analysis, PIXE-CT was performed under the same X-ray detector conditions. After PIXE-CT, STIM-CT was performed with a planar silicon detector (PD100-12-300RM, CANBERRA) having an active diameter of 19.5 mm placed just behind the target for measuring the density of major elements in the adsorbent. The typical count rate in the STIM-CT was approximately 100 cps. The adsorbent particle sample was affixed on top of a diagonally cut Kapton tube (500 μm in diameter) with polyvinyl acetate glue, as shown in Fig. 4, and the tube was placed on an automatic rotation stage, the stage rotated from 0° to 351° with 9° steps. Consequently, there were 40 projections for one PIXE-CT measurement. The projection area was 150 × 150 μm^2, corresponding to 128 × 128 imaging pixels. Thus, 128 tomographic slices were constructed, and the thickness of each slice was 1.17 μm. To align the rotation axis with the center of projection, another 0.5-μm-resolution linear motion stage was used. As shown in Fig 3, these stages and the adsorbent particle were placed in vacuum because they interfered with the polycarbonate window and its frame, which separated the vacuum and atmosphere regions from each other in in-air micro-PIXE. All projection images were finally obtained after 6 h and 40 min.

Tomographic image reconstruction was carried out using a modified ML-EM method [19]. The calculation formula of the ML-EM algorithm is

$$\lambda_j^{(k+1)} = \frac{\lambda_j^{(k)}}{\sum_{i=1}^{n} C_{ij}} \sum_{i=1}^{n} \frac{y_i C_{ij}}{\sum_{j'=1}^{m} C_{ij'} \lambda_{j'}^{(k)}} \quad (1)$$

where $\lambda^{(k)}$, j, i, y and C_{ij} are the k-th iteration image, pixel index, sinogram bin index, measured sinogram and detection probability of j by i, respectively. In the case of PIXE-CT, the λ_j and y_i denote the cross-sectional map and projection map of X-ray counts per irradiation dose unit, respectively. C_{ij} corrects X-ray counts in each bin in the sinogram based on the cross sections for the production and absorption of X-rays. According to SRIM-2013 [23], the energy of a 3-MeV proton decreases to less than 2 MeV after passing through a 50-μm-thick SiO_2 (2.32 g/cm^3) film. The K_α X-ray production cross section of silicon and the L_α X-ray production cross section of Nd for 2-MeV proton are, 0.86 and 0.54 times lower, respectively than those for 3-MeV proton. Besides, 1.7 keV (K_α of silicon) and 5.2 keV ($L_{\alpha 12}$ of Nd) X-rays are absorbed to ~1/4000 and ~1/4, respectively by the 50-μm-thick SiO_2. Therefore, correction by C_{ij} is critical for proper reconstruction. In this paper, the three-dimensional map of the density of SiO_2 in the target was first obtained using the STIM-CT data and the Bethe-Bloch energy loss formula assuming that SiO_2 was the sole component of the adsorbent particle because of the low density of TODGA. Subsequently, C_{ij} for each X-ray was obtained using the production and absorption cross-sections based on the three-dimensional map of the density of SiO_2 in the target.

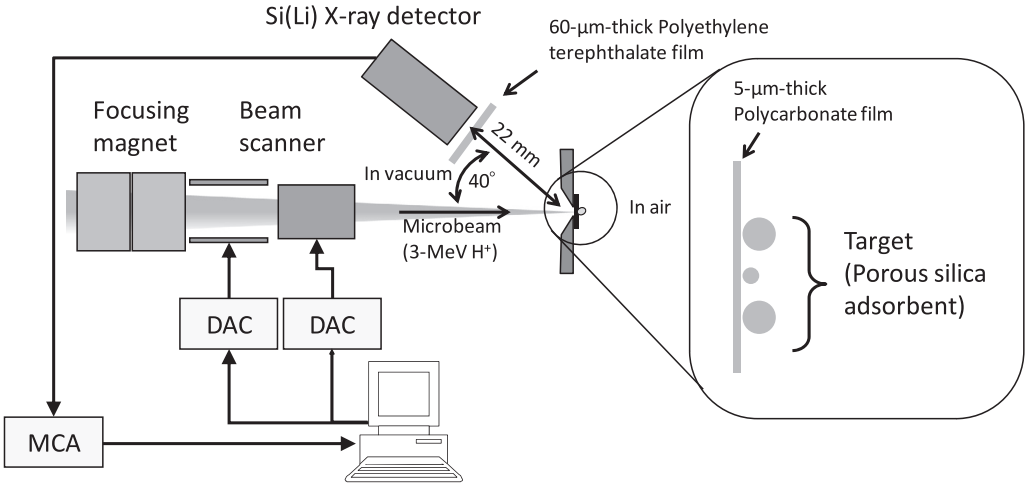

Fig. 2. Schematic diagram of the experimental setup for micro-PIXE analysis.