

# RADIOLYTIC STABILITY OF THE TEHDGA-IMPREGNATED SILICA-BASED ADSORBENT FOR EXTRACTION CHROMATOGRAPHY

Yasunori Miyazaki<sup>1</sup>\*, Yuichi Sano<sup>1</sup>, and Ryoya Ishigami<sup>2</sup>

<sup>1</sup>Japan Atomic Energy Agency (JAEA). Oarai Research and Development Institute  
4002 Narita-cho, Oarai-machi, Higashi-ibaraki-gun, Ibaraki, 311-1393, Japan

<sup>2</sup>Wakasa Wan Energy Research Center (WERC). 64-52-1 Nagatani, Tsuruga 914-0192, Japan

\* Corresponding author

**Abstract.** Gamma-ray and He<sup>2+</sup> ion beam (which is simulating alpha-ray from Am-241, for example) were applied to the TEHDGA adsorbent to evaluate hydrogen gas production, leaching of organics by 3 M HNO<sub>3</sub> solution, thermal characteristics and speciation of degradation products. These elements were brought together to assess the stability of the adsorbent after a run of MA separation from an irradiating raffinate of 1 kGy/h dose rate.

## 1. Introduction

In the global challenge to achieve carbon neutrality by 2050, nuclear power is attracting attention as a cost-effective source of energy with low greenhouse gas emissions and long-term stable supply. The closed nuclear fuel cycle is promoted as a means of utilising the energy resources of uranium (U) and plutonium (Pu), but many countries are struggling with the management of spent nuclear fuel and/or high-level radioactive waste generated from spent nuclear fuel after reprocessing. The separation of minor actinides (MA), which are long-lived and thermogenic nuclides, has been reported to be useful in reducing the volume and radiotoxicity of radioactive wastes for geological disposal [1]. Since then, a new avenue of research has been initiated to separate trivalent MA i.e. Am<sup>3+</sup> and Cm<sup>3+</sup> from the reprocessed liquid waste, which are difficult to recover with TBP in the PUREX process. Various extractants have been investigated and several now known processes are proposed for different MA cycle patterns, such as DIAMEX-SANEX, GANEX and EXAM in France [2-4], TALSPEAK in the USA [5-6] and TRUEX/SETFICS in Japan [7-8].

In recent years, JAEA has adapted the solid phase separation method (hereafter referred to as extraction chromatography) as an alternative to the solvent extraction method [9-10]. The concept is to minimise the amount of liquid waste in order to design a low cost plant. The previous studies showed the flowsheet using the phosphorus-based extractants such as CMPO and HDEHP [11-12], but the increasing waste was still a serious concern. Therefore, the applicability of TEHDGA, one of the CHNO-type extractants, was evaluated with reference to the SELECT process. A typical flowsheet implemented in a hot cell has already been reported [13]. The next stage is to determine the duration of repeated use in an irradiating environment. In contrast to solvent extraction, the degradation products formed by the radiolysis are retained in the SiO<sub>2</sub>-based support particle, resulting in a loss of selectivity for MA and a decrease in adsorption capacity. In addition, from a safety perspective, a safety assessment is required in the event of an accident and/or spill. In the last two decades, radiolysis has been performed by external gamma-ray irradiation, probably because of the pursuit of the elementary reactions stems from the low linear energy transfer (LET) effect. This paper presents the He<sup>2+</sup> ion beam irradiation experiment to simulate the alpha-rays emitted by Am-241, for example, and to compare the degradation with that of gamma-ray. These data were combined to support the safety demonstration of a 1st run of column separation.

## 2. Experimental

### 2.1 Preparation

The impregnation procedure is described in details elsewhere [9–13]. Briefly, an adequate amount of TEHDGA was diluted with acetone and added to the SiO<sub>2</sub>-P support, which had an average particle diameter of 55 μm and a pore diameter of 50 nm, in a flask. The mixture was swirled in a rotary evaporator for 30 minutes. After one hour, acetone was completely evacuated and a TEHDGA-impregnated adsorbent was obtained. It is hereafter referred to simply as the adsorbent. The porosity of the TEHDGA adsorbent was 0.3 and its bulk density was 0.5 g/mL.

The white jelly TEHDGA was purchased from Chemicrea Inc. with a purity of 97.0 % and used without any further purification.

### 2.2 Gamma-ray irradiation

The gamma-ray irradiation experiment was performed at the Co-60 irradiation facility of the Takasaki Institute for Advanced Quantum Science, National Institute for Quantum Science and Technology. Samples were prepared by mixing 2 g of the adsorbent and 40 mL of a 3 M HNO<sub>3</sub> solution in a 100 mL glass vial sealed with the silicone septum. These were irradiated at an average dose rate of 3 kGy/h at room temperature up to the total dose of 3,000 kGy. After irradiation, the amount of hydrogen gas was measured using Gas Chromatograph GC-2014 (Shimadzu Corp.) to determine the G-value (H<sub>2</sub>) by the following equations.

$$C_{conv} = C_{measure} \times \frac{T_{std}}{T_{std}+T} \times \frac{P}{P_{std}} \times \frac{V_{gas}}{V_{std}} \times 10^{-3} \quad (1)$$

where  $C_{conv}$  is the unit-converted amount of hydrogen gas in mol,  $C_{measure}$  is the measured amount of hydrogen gas in ppm,  $V_{std}$  is the molar volume of ideal gas at the standard conditions in L/mol,  $V_{gas}$  is the volume excluding liquid in the glass vial in mL,  $T_{std}$  and  $T$  are the standard temperature and the irradiated temperature in K, respectively, and  $P_{std}$  and  $P$  are the standard pressure and irradiated pressure in Pa, respectively. For simplicity, the internal pressure in the glass vial was assumed to be unchanged from the standard condition during the irradiation.

$$G - \text{value} = \frac{C_{conv}}{D \times w} \quad (2)$$

where G-value is the hydrogen gas production in mol/J,  $D$  is the integrated dose in kGy (or J/g), and  $w$  is the dry weight of the adsorbent in g.

The irradiated adsorbent and immersed solution were separated by filtration. The former was carried out for analysis of thermal characteristics and degradation products described in 2.4, and the latter was provided to the Total Organic Concentration (TOC) measurement (TOC-L CSH, Shimadzu Corp.). The TOC values were evaluated by subtracting the immersed 3 M HNO<sub>3</sub> solutions including the TEHDGA adsorbents with and without irradiations from the standard 3 M HNO<sub>3</sub> solution.

### 2.3 He<sup>2+</sup> ion beam irradiation

Figure 1 shows the scheme of He<sup>2+</sup> ion beam irradiation experiment. An appropriate amount of adsorbent was immersed in a 3 M HNO<sub>3</sub> solution, in a glass vial, and the resulting slurry was added to the sample holder. The loading depth was 100 μm, and the irradiated area was 120 mm<sup>2</sup>; thus, a total volume of 12 mm<sup>3</sup> or 6 mg of adsorbent could be packed at maximum theoretically.

The covered sample holder with O-ring and Ti film was placed in a vacuum chamber, evacuated to the order of 10<sup>-4</sup> Pa, and irradiated with 10 MeV He<sup>2+</sup> ion beam using the tandem accelerator at the Wakasa Wan Energy Research Center [14]. The ion beam was scanned vertically in 25 mm increments and horizontally in 35 mm increments to ensure an equivalent dose over the irradiated area. The typical ion flux was 4.8×10<sup>10</sup> cm<sup>-2</sup>s<sup>-1</sup>.

The Ti film was used not only to pack the slurry in the sample holder but also to decelerate the  $\text{He}^{2+}$  ion after transmitted. The SRIM code indicated the initial energy of 10 MeV was down to 4.7 MeV for a 30  $\mu\text{m}$  thickness, which was energetically comparable to an alpha-ray emitted, for example, by Am-241. In addition, the energy loss of the packed adsorbent that was mostly composed of silica with a true density of 1.6 g/mL was predicted to be 5.65 MeV. It means that the  $\text{He}^{2+}$  ion beam reached the top one or two layers near the Ti film, as highlighted in red in Figure 1.

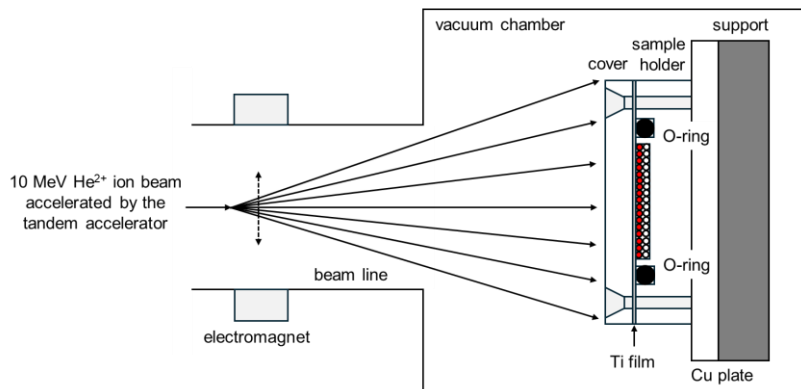


Figure 1. Scheme of the  $\text{He}^{2+}$  ion beam irradiation experiment.

## 2.4 analysis

For both gamma and  $\text{He}^{2+}$  ion beam irradiation experiments, the irradiated adsorbent was dried and subjected to thermogravimetry-differential thermal analysis (TG/DTA) measurements to determine the thermal properties. Approximately 10 mg of the adsorbent before and after irradiation were placed in the alumina dish and the temperature was raised from 298 to 1000 K at a rate of 10 K/min in Thermo plus EVO 2 (Rigaku Corp.). Note that no inert gas was circulated to investigate the flash point and ignition point.

The degradation products generated after irradiations were analyzed by gas chromatography-mass spectrometry (GC/MS). The TEHDGA adsorbent was rinsed with acetone. The obtained organic compounds were diluted with acetone, injected into the evaporation chamber that was heated at 573 K, split into the He gas at a flow rate of 1.0 mL/min and separated from each other by the column DB-1 (Agilent Technologies, Inc.) with a temperature gradient of 423 K (2 min)  $\rightarrow$  598 K (10 K/min)  $\rightarrow$  598 K (10 min) in GC-17A (Shimadzu Corp.). The separated species were ionised by the electron impact (EI) method and detected in the  $m/z$  range of 40 ~ 800 in GCMS-QP5050 (Shimadzu Corp.). The degradation products were estimated based on the fragment patterns in their mass spectra.

## 3. Results and discussion

### 3.1 Emissions from the adsorbent after irradiation

Figure 2 (a) shows the amount of hydrogen gas produced from the gamma-ray irradiated adsorbent in the 3 M  $\text{HNO}_3$  solution, with that from the 3 M  $\text{HNO}_3$  solution subtracted as a background. The hydrogen gas was produced at an increased dose because the hydrogen atom of the styrene-divinylbenzene (St/DVB) copolymer and TEHDGA was likely abstracted by the radicals generated by the radiolysis of water and nitric acid. From the equations (1) and (2), the G-value determined for the 1 g adsorbent was  $2.23 \times 10^{-7}$  mol/J. This value would be underestimated due to the sinking effect, which in the experiment the liquid was filled with half of a glass vial and hydrogen gas was partially dissolved by the high pressure.

Figure 2 (b) shows the percentage loss of organic compounds from the  $\text{SiO}_2$ -P support before and after gamma-ray irradiation. Subtracting the background amount of the 3 M  $\text{HNO}_3$  solution, TEHDGA leached from the  $\text{SiO}_2$ -P support at a constant rate of 150 mg/L over the immersion time period. This

was much higher than the solubility of TODGA alone in water, i.e. 20 mg/L [15], due to the branched structure. The amount of organics leaching was dramatically increased by irradiation. The degradation products were generated by the OH radical substitution and/or ether linkage dissociation, etc., which changed the water solubility. The specification of these water soluble degradation products is under investigation.

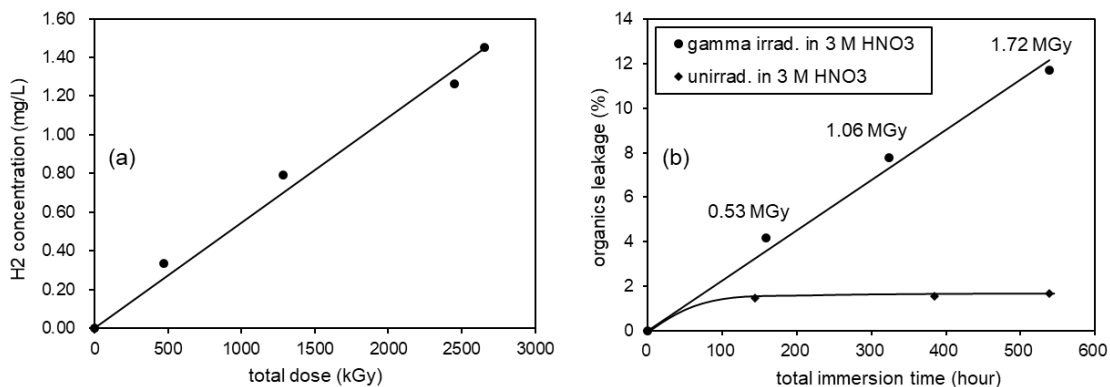


Figure 2. (a) hydrogen gas production and (b) leaching percent of organics in a 3 M HNO<sub>3</sub> solution after gamma-ray irradiation.

### 3.2 Residues of the adsorbent after irradiation

Figure 3 (a) and (b) show the DTA and TG of the adsorbent before and after irradiation, respectively. The black solid line is the unirradiated adsorbent as reference. Based on the weight loss by an oxidative exothermic reaction, the flash point of TEHDGA was 488 K and that of the St/DVB copolymer was 615 K, both of which were comparable to the thermal properties of the TODGA adsorbent [16]. On the other hand, the spontaneous ignition point of the St/DVB copolymer was found to be 786 K.

The coloured solid lines show the gamma-ray irradiated adsorbent. The new exothermic peak appeared at 437 K, while that of TEHDGA became weaker with the irradiation dose, indicating that the degradation products were accumulating in the SiO<sub>2</sub>-P support. The mass balance of impregnating TEHDGA before and after gamma-ray irradiation matches with the sum of the accumulating and leaking amounts.

The purple dotted line shows the one irradiated with the He<sup>2+</sup> ion beam. It is obvious that the thermal characteristics were different from those of gamma-ray irradiation. For example, there was another exothermic peak at 535 K in addition to the original peak of TEHDGA at 490 K. It was rationalised that the unexpectedly high irradiation dose of an accelerator experiment generated the radicals in a short distance. Polymerisation of TEHDGA itself and/or St/DVB polymer may occur.

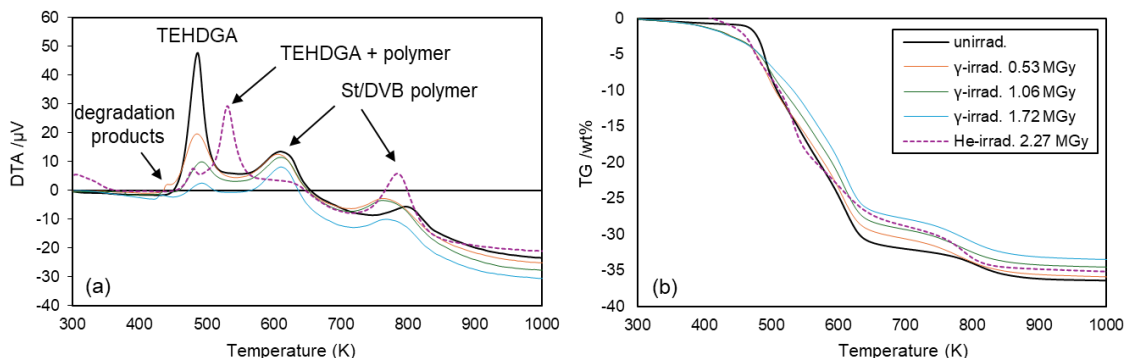


Figure 3. (a) DTA and (b) TG of the adsorbent before and after irradiation.

Figure 4 shows the GC-MS chromatogram of the organic compounds trapped in the adsorbent. The black solid line is the unirradiated one used as reference. There were two peaks; one was diisooctyl

phthalate at 16.99 min and the other was TEHDGA at 22.55 min (data not shown). The former was added to the mixture of styrene and divinylbenzene in SiO<sub>2</sub> to prepare the SiO<sub>2</sub>-P support [17] and remained even after washing with copious amounts of acetone. It was therefore excluded from further considerations as it was independent from radiolysis.

The green and purple lines are those irradiated with gamma-ray and He<sup>2+</sup> ion beam, respectively. Surprisingly, their degradation products were almost identical, at least in the detected m/z range. The polymerised molecules would not be found due to the insufficient evaporation temperature in the GC set-up. Figure 5 shows the major products labelled at from A to H and estimated from the mass spectra. The dissociation sites were the ether oxygen and its surroundings, where the HOMO and LUMO were distributed in the electronic structure. In general, the bond dissociation originates from either a radical cation of TEHDGA and/or an electronic excited state after the geminate recombination of the emitted electron and the radical cation of TEHDGA. The latter would be the most likely case, but such a reaction mechanism is addressed by the advanced Monte Carlo simulation to understand the fate of the emitted electron after ionisation.

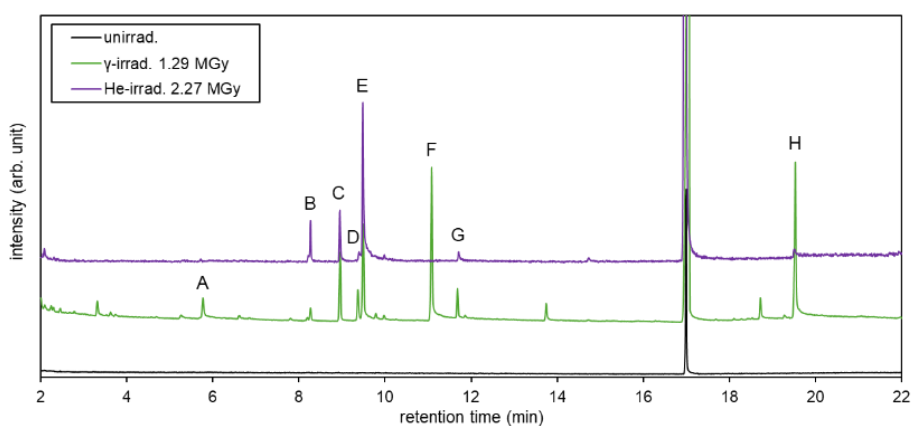


Figure 4. GC-MS chromatogram for organics before and after irradiations.

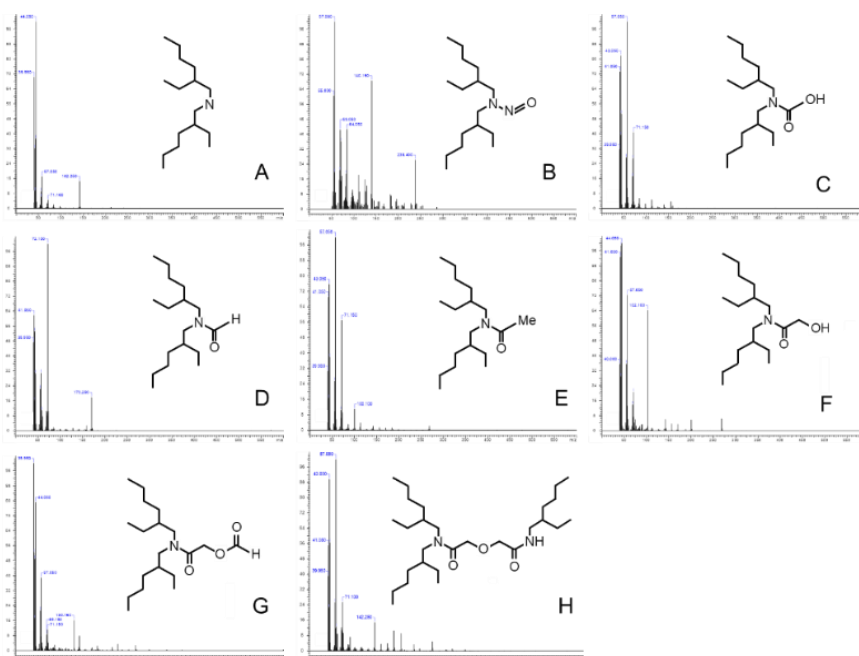


Figure 5. Mass spectra of the major degradation products and their molecular structures.

Figure 6 shows a summary of the degradation products for gamma-ray irradiation. Most of them are formed even at 2.45 MGy, as TEHDGA continuously absorbed the irradiation energy.

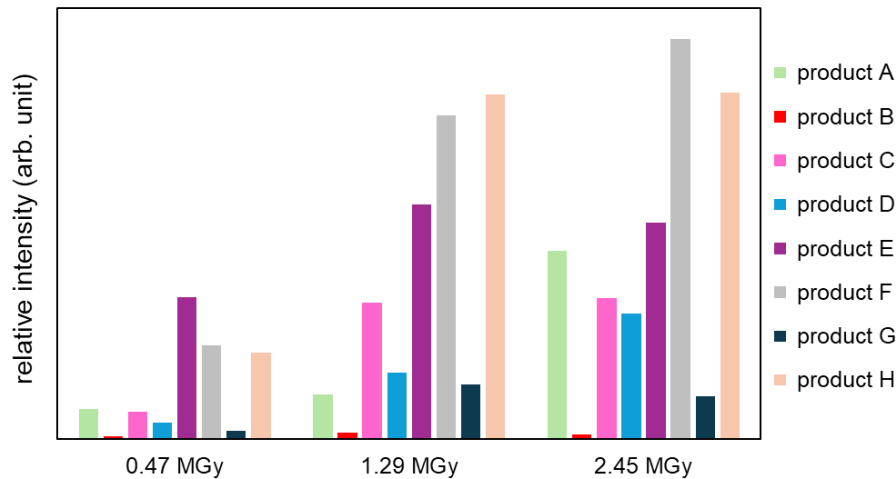


Figure 6. Degradation behaviour of TEHDGA with respect to the irradiation dose.

### 3.3 Stability assessment

Combining these results, the stability of the column separation for a 1<sup>st</sup> run was evaluated for the raffinate of reprocessed PWR MOX fuel with a U-235 enrichment of 4.8 wt%, which was burned at 49 GWd/t and cooled 20 years after reactor discharge. Figure 7 shows the adsorption scheme of MA. In this case, some of the radioactive nuclides that influence the irradiation and heat load such as Sr-90 ( $1.60 \times 10^{-1}$  W/g), Y-90 ( $3.01 \times 10^3$  W/g), Cs-137 ( $9.67 \times 10^{-2}$  W/g), Ba-137 ( $1.91 \times 10^6$  W/g), Eu-154 ( $2.44 \times 10^0$  W/g), Am-241 ( $1.14 \times 10^{-1}$  W/g) and Cm-244 ( $2.83 \times 10^0$  W/g) were considered for a realistic picture. Based on the flowsheet [13], the raffinate containing 250.93 g fission products in the 3 M HNO<sub>3</sub> solution was fed to adsorb the MA (6.52 g) and lanthanides (52.17 g) with a volume of 6.59 L in the upper column bed. The rest was eluted from the column. The adsorption band was present for 52 minutes until water was added as eluent. As the dose being applied to the adsorbent band was 0.81 kGy, the degradation effect was small. The heat load was 0.85 W and raised the temperature by 1.08 K, still below the flash point of the degradation products. The hydrogen gas was produced at 1.59 mol, which was almost equivalent to the dissolution amount of 1.97 mol in the volume of the column bed at the typical applied pressure of 2.5 MPa at 323 K [18]. In summary, the column separation was feasible without any additional treatment for heat load and gas production when the separation process of the 1<sup>st</sup> run was applied.

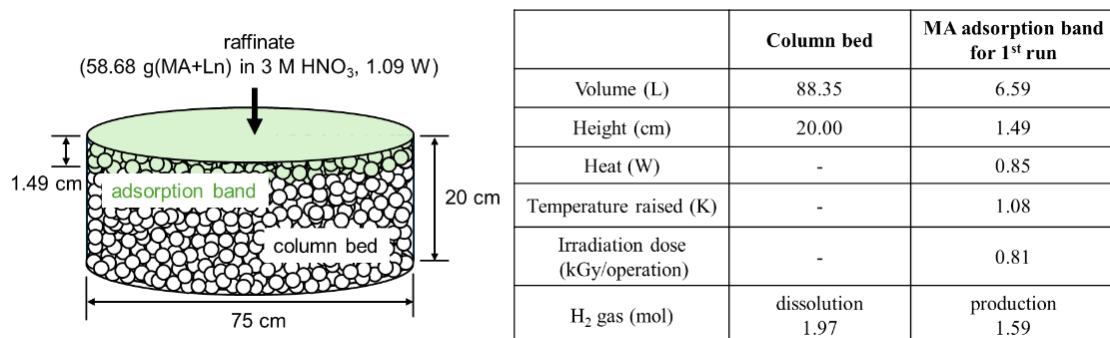


Figure 7. Adsorption scheme of MA and Ln in the column from the raffinate.

For the future, the data sheet will be re-applied to assess not only the stability but also the separation performance of the column. With repeated uses, the adsorbability is reduced and the MA adsorption band is broadened, resulting in alternating elution behaviour from the current flowsheet.

## 4. Conclusions

In this study, the fundamental data set of hydrogen gas production, leaching amounts of organic compounds in the immersion solution, thermal properties and speciation of degradation products were collected for the TEHDGA adsorbent after gamma-ray and He<sup>2+</sup> ion beam irradiations. The He<sup>2+</sup> ion beam (or simulating alpha radiation from Am-241, for example) induced degradation of TEHDGA more than the gamma ray as expected. The stability assessment was carried out to demonstrate that any additional treatment for heat load and hydrogen gas production is not required for the 1st run of the MA separation process.

## Acknowledgments

This work was carried out as a part of the research project "Basic Research Programs of Vitrification Technology for Waste Volume Reduction (JPJ010599)", commissioned by the Ministry of Economy, Trade and Industry (METI), in FY2019 - 2021. The author would like to thank Dr. Fukumoto of Ibaraki University for helpful advice of GC/MS analysis.

## References

- [1] M. Salvatores and G. Palmiotti, *Progress in Particle and Nuclear Physics*, 66, 144-166 (2011).
- [2] C. Rostaing, C. Poinssot, D. Warin, P. Baron and B. Lorraina, *Procedia Chemistry*, 7, 367-373 (2012).
- [3] V. Vanel, M.-J. Bollesteros, C. Marie, M. Montuir, V. Pacary, F. Antégnard, S. Costenoble and V. Boyer-Deslys, *Procedia Chemistry*, 21, 190-197 (2016).
- [4] R. Taylor, M. Carrott, H. Galan, A. Geist, X. Hères, C. Maher, C. Mason, R. Malmbeck, M. Miguirditchian, G. Modolo, C. Rhodes, M. Sarsfield and A. Wilden, *Procedia Chemistry*, 21, 524-529 (2016).
- [5] K. L. Nash, *Solvent Extraction Ion Exchange*, 33, 1-55 (2014).
- [6] K. L. Nash, G. Johnson, D. Brigham, C. Marie, T. S. Grimes and J. C. Braley, *Procedia Chemistry*, 7, 45-50 (2012).
- [7] M. Ozawa, Y. Koma, K. Nomura and Y. Tanaka, *Journal of Alloys and Compounds*, 271-273, 538-543 (1998).
- [8] T. Tanaka, Y. Koma, K. Sato, M. Kamiya, A. Shibata, K. Nomura, H. Ogino, T. Koyama and S. Aose, *Journal of Nuclear Science and Technology*, 41, 307-314 (2004).
- [9] Y. Wei, A. Zhang, M. Kumagai, M. Watanabe and N. Hayashi, *Journal of Nuclear Science and Technology*, 41, 315-322 (2004).
- [10] Y. Wei, M. Kumagai and Y. Takashima, *Nuclear Technology*, 132, 413-423 (2000).
- [11] S. Watanabe, K. Nomura, S. Kitawaki, A. Shibata, H. Kofuji, Y. Sano and M. Takeuchi, *Procedia Chemistry*, 21, 101-108 (2016).
- [12] S. Watanabe, T. Senzaki, A. Shibata, K. Nomura, M. Takeuchi, K. Nakatani, H. Matsuura, Y. Horiuchi and T. Arai, *Journal of Radioanalytical and Nuclear Chemistry*, 322, 1273-1277 (2019).
- [13] Y. Horiuchi, S. Watanabe, Y. Sano, M. Takeuchi, F. Kida and T. Arai, *Journal of Radioanalytical and Nuclear Chemistry*, 330, 237 (2021).
- [14] S. Hatori, T. Kurita, Y. Hayashi, M. Yamada, H. Yamada, J. Mori, H. Hamachi, S. Kimura, T. Shimoda, M. Hiroto, T. Hashimoto, M. Shimada, H. Yamamoto, N. Ohtani, K. Yasuda, R. Ishigami, M. Sasase, Y. Ito, M. Hatashita, K. Takagi, S. Fukumoto and M. Kondo, *Nuclear Instruments and Methods in Physics Research B*, 241, 862-869 (2005).
- [15] S. Kumar, *Journal of Radioanalytical and Nuclear Chemistry*, 333, 4995-5001 (2024).
- [16] Y. Xu, Y. Wei, R. Liu, S. Usuda, K. Ishii and H. Yamazaki, *Journal of Nuclear Science and Technology*, 48, 1223-1229 (2011).
- [17] Y. Miyazaki, I. Goto, S. Watanabe, Y. Sano, H. Kofuji, M. Takeuchi and T. Satoh, *International Journal of PIXE*, 29, 67-79 (2019).
- [18] D. Li, C. Beyer and S. Bauer, *International Journal of Hydrogen Energy*, 43, 512-529 (2018).