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**INTRODUCTION:** In order to develop resins with selectivity to U(VI) in  $\text{HNO}_3$  media, we have synthesized several silica-supported polymer beads with the structure of a monoamide as the functional group. The examination on their adsorptivities to various metal ions has clarified that among these resins those consisting of *N,N*-dimethylacrylamide (Silica-DMAA) and *N*-methyl-*N*-vinylbenzylacetamide (Silica-MVBAA) have selectivity to U(VI) and U(IV), respectively, where major fission product (FP) ions are found to show no or very little adsorption from  $\text{HNO}_3$  ranging up to 6 mol/dm<sup>3</sup> (= M) [1, 2]. For wider applications of these resins including treatment of highly-radioactive solutions, it is necessary to investigate their stability under irradiation conditions. In this study, the above two resins were irradiated by  $\gamma$ -ray in  $\text{HNO}_3$  and adsorptivities to FP ions were examined. The structure change in the resins by irradiation was also studied.

**EXPERIMENTS:** Silica-DMAA and MVBAA resins were synthesized in a similar manner as previously reported[1, 3]. The resins and  $\text{HNO}_3$  of up to 6 M were mixed in a Pyrex sample tube at a ratio of 5 cm<sup>3</sup>/g, respectively, and used as the samples for  $\gamma$ -ray irradiation. Irradiation by the <sup>60</sup>Co source was performed at max. 16.3 kGy/h up to 1.6 MGy at room temperature under ambient atmosphere. The irradiated resins were separated from the supernatant and washed using distilled water to avoid further degradation of the resins by  $\text{HNO}_3$ . The resulting resins and the supernatants were analyzed by IR and <sup>1</sup>H NMR (400 MHz, solvent : D<sub>2</sub>O), respectively. Adsorptivities of the irradiated resins to FP ions were examined by the batch method similar to the previous studies[1-3]. Samples of the conditioned resins irradiated in 3 or 6 M  $\text{HNO}_3$  were mixed with 0.01 - 6 M  $\text{HNO}_3$  solutions containing 10 mM FP ions at a ratio of wet 0.05 g/cm<sup>3</sup>, respectively, and shaken at 298 K in a thermostatic shaking bath for 1 h. After shaking, samples of the supernatant were taken and the concentrations of FPs were measured using ICP-AES or ICP-MS. Adsorptivities were evaluated by the distribution ratio,  $K_d$ , defined as,

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{W} \quad (\text{cm}^3/\text{g}) \quad (1)$$

where  $C_0$  and  $C$  denote the concentrations of the FP ions in the solution before and after contact with the resin, respectively.  $V$  and  $W$  represent the volume of the solution and the weight of the dry resin, respectively.

**RESULTS:** For the IR analyses, a new peak generated at around 1700 cm<sup>-1</sup> for DMAA irradiated in  $\text{HNO}_3$  of

higher concentration. While, no clear changes in the spectra were observed in the irradiated MVBAA. <sup>1</sup>H NMR spectra of the supernatants after irradiation showed exclusively distinguished peaks which would be attributed to *N,N*-dimethylamine (ca. 2.7 ppm (vs. DSS), CH<sub>3</sub>, singlet) for DMAA irradiated in 6 M  $\text{HNO}_3$  at 1.6 MGy and acetic acid (ca. 2.1 ppm (ditto), CH<sub>3</sub>, singlet) for MVBAA irradiated in 6 M  $\text{HNO}_3$  at 0.90 MGy, respectively.

Based on the above results, it would be proposed that both two resins were mainly degraded simply by the break of each amide bond, followed by the formation of polyacrylic acid from DMAA and secondary-amine-type weakly-basic anion exchange resin from MVBAA, respectively (see Fig.1). These degradation properties are similar to those of chain-type monoamide extractants[4]. Considering the degradation properties of these monoamide compounds, the two resins are expected to be stable against irradiation in  $\text{HNO}_3$  of lower concentration such as 0.1 M.

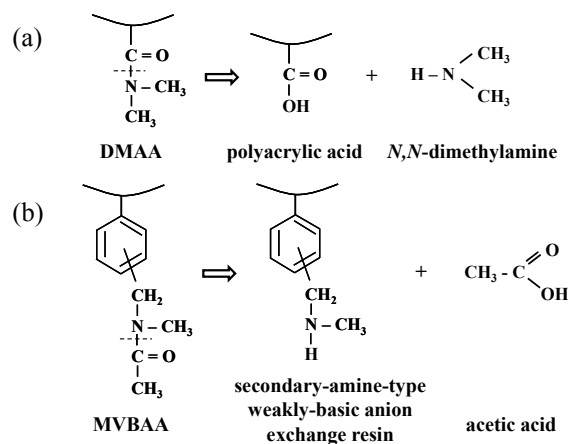


Fig. 1. Expected major degradation routes of monoamide resins by  $\gamma$ -ray irradiation in  $\text{HNO}_3$ ; (a) Silica-DMAA, (b) Silica-MVBAA.

The irradiated resins showed weak adsorptions for Zr(IV) and Pd(II) from  $\text{HNO}_3$  of lower concentration ranges and no or little adsorptions were found for other FP ions, which was in accordance with the expected adsorptivities of the degraded resins. Besides, it is expected that the two irradiated resins keep the selectivity to U species, respectively, in  $\text{HNO}_3$  of ca. 3 M and higher.

### REFERENCES:

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**INTRODUCTION:** Technetium with atomic number 43 is an artificial radioactive element that is not found in nature, and it is used as a tracer in medicine and environmental analysis. In particular, technetium-95m (half-life: 61 days) and technetium-99m (half-life: 6 hours) are frequently used as tracers. Because commercially available technetium-95m is isolated from fission products, the influence of other technetium isotopes cannot be avoided. Technetium-99m, however, is obtained as a decay product of molybdenum-99, and it does not sustain any effects from other technetium isotopes. Technetium-99m, therefore, is superior as a tracer with its higher isotopic purity compared to technetium-95m. Nonetheless, the supply of technetium-99m from overseas has recently been unstable. Consequently, a variety of alternative efforts have been examined in Japan, such as the study of production methods using accelerators. The present research employed molybdenum metal to production molybdenum-99/technetium-99m through reactor neutron irradiation. The handling of molybdenum metal is easy, but the generated specific radioactivity is low. Thus, methods for efficient extraction of technetium from molybdenum must be studied, and the usability of the technetium extracted as a tracer must be confirmed.

**EXPERIMENTS:** Technetium-99m was determined to be obtained through the production and subsequent decay of its parent nuclide, molybdenum-99, as a decay product. Approximately 50 mg of natural molybdenum metal foil (0.05 mm in thickness) was used for the production of molybdenum-99. The foil was irradiated in the Pn-2 radiation tube of the Kyoto University Research Reactor for 50 minutes at 5 MW. Upon cooling for approximately 2 hours after irradiation, the foil sample was heated and dissolved in 7 N nitric acid and aqueous hydrogen peroxide. The solution was left to cool, followed by adsorption to an Empore filter[1, 2] (made by 3M Ltd.), and finally elution from the filter by varying the nitric acid concentration from 1 N to 8 N. The eluent was subjected to gamma-ray analysis at 739 keV emitted from molybdenum-99 and at 142.7 keV emitted from technetium-99m with a well-type HP-Ge detector to determine the filter adsorption and elution characteristics. The same chemical process was employed respectively for the an-

ion-exchanged resin, activated alumina, and TEVA resin[3] as adsorbents for a column volume of 2 ml. Filter adsorption and elution characteristics for these were also determined.

**SUMMARY:** This experiment was adopted in the second half of fiscal 2011. To date, the irradiation was performed on twice, and the chemical separation on four times experiments. Although the results are preliminary, the experimental conditions enabled the production of the requisite amount of radioactivity for a tracer. Experimentation work will continue in 2012 for chemical separation in order to improve reproducibility and to determine the optimum separation conditions. Based on the current data, chemical separation employing the TEVA resin and anion-exchanged resin yielded better results for separation and recovery rates, in comparison to the activated alumina and Empore filter. The obtained technetium-99m as a tracer is planned for use in determining technetium-99 recovery yield from respective samples of tap water, sea water, soil, and sea weed. Quantitative analysis of the separated and collected technetium-99 is planning to use the liquid scintillation counter and ICP-MS.

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