

## Extraction Chromatography for Am and Cm Recovery in Engineering Scale

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**Abstract** – JAEA has been developing the extraction chromatography for An(III) recovery from HLLW aiming at an engineering scale application. For process development, we started to assess the characteristics of adsorbents with some extractants by laboratory scale experiments. The experimental results with HDEHP/SiO<sub>2</sub>-P adsorbent suggested that An(III) is separated from other FP by adjusting pH of a feed solution and/or an eluent containing DTPA to be an appropriate value. The durability of CMPO/SiO<sub>2</sub>-P and HDEHP/SiO<sub>2</sub>-P adsorbents for gamma-ray irradiation were estimated to be 1 and 0.5MGy, respectively. In the system development, system experiments for fluidics, safety and durability using engineering scale column as well as studies on remote control/maintenance are now under progress.

### INTRODUCTION

In the framework of the feasibility study on commercialized FR cycle system, Japan Atomic Energy Agency (JAEA) evaluated Am and Cm (An(III)) recovery processes on design basis, and the extraction chromatography technique, which uses SiO<sub>2</sub> support coated with styrene-divinylbenzene polymer (SiO<sub>2</sub>-P) and an extractant on its surface, was evaluated as the promising process for establishing more compact equipments and a less amount of secondary waste than those of the solvent extraction methods [1], [2]. Compared to conventional polymer-matrix adsorbents, the SiO<sub>2</sub>-P particle (Fig. 1) used in our extraction chromatography process is characterized by the following advantages; (a) low content of organic compounds, which decreases the risk of fire and explosion, (b) high mechanical strength, which allows the operation at high flow rate (high pressure), (c) small swelling and shrinking, which brings the steady operation.

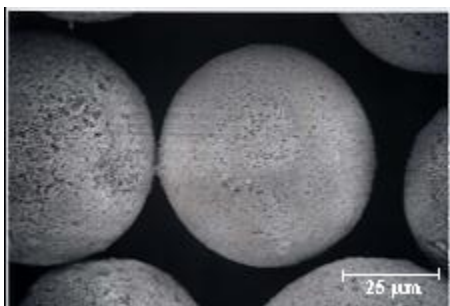


Fig. 1. Photo of the CMPO/SiO<sub>2</sub>-P adsorbent.

In addition, any extractants (even if it is difficult to use them in solvent extraction processes due to a low solubility into a diluent) can be impregnated into the SiO<sub>2</sub>-P particles.

Although the previous laboratory scale experiments using a simulated and a real HLLW showed the efficiency of this technique for high recovery yields of An(III) with sufficient decontamination [3], application of extraction chromatography to reprocessing process in engineering scale has not been discussed deeply. As it is well known, the engineering scale columns packed with ion exchange resin are used as adsorbent columns for nuclear industry, e.g. in nuclear power plants for purifying the reactor water. It is demanded to treat higher radioactivity and to have the ability of chromatographic separation for An(III) recovery from HLLW. It is, therefore, important to choose the best extractant and to design a flowsheet correspond to the extractant in the view of performance, safety and durability.

Based on these backgrounds, JAEA launched process and system developments of extraction chromatography for An(III) recovery in engineering scale with the capacity of ~ 750 L HLLW/day (~ 1.7kg An(III)/day). The prerequisites for the development are as follows:

- Separation: An(III) recovery yields  $\geq 99.9\%$  (with DF of other elements  $\geq 100$ )
- Safety: preventing fire and explosion in normal and abnormal operations
- Instrumentation and control: promoting the automation of control and operation
- Remote handling: introducing module/package/unit replacements with considering the operational condition

In this paper, the latest experimental results mainly on the process development as well as details of R&D programs are described.

## PROCESS DEVELOPMENT

There is no extractant for selective An(III) separation from a highly acidic HLLW at present, and the combination of some extractants with the following abilities is required; (a) An(III) and lanthanides (Ln(III)) recovery from a highly acidic HLLW, (b) An(III)/Ln(III) separation in a low acidity.

In consideration of the recent studies of extractants, we selected 4 extractants (CMPO and TODGA for An(III) and Ln(III) recovery, HDEHP and R-BTP for An(III)/Ln(III) separation) and started to assess the characteristics of SiO<sub>2</sub>-P adsorbents impregnated with these extractants by laboratory scale experiments; adsorption/elution properties of FP and An, safety data on acid, gamma-radiation and heat resistance.

### Adsorption and elution properties onto/from HDEHP/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents

The adsorption and elution properties of some FP and An onto/from the HDEHP/SiO<sub>2</sub>-P adsorbent were investigated by batch and column experiments. In addition, the effects of SiO<sub>2</sub>-P particle and pore sizes on separation properties, pressure drop and strength of particle were studied using several SiO<sub>2</sub>-P or CMPO/SiO<sub>2</sub>-P adsorbents.

#### Experimental

The particle and pore sizes of SiO<sub>2</sub>-P used in this study are summarized in Table I. The particle size distribution and pore size of SiO<sub>2</sub>-P were measured by the laser diffraction analysis and the mercury porocimetry analysis, respectively.

TABLE I. The particle and pore sizes of SiO<sub>2</sub>-P

	Particle size (μm)	Pore size (nm)
SiO <sub>2</sub> -P	37-74	600
SiO <sub>2</sub> -P (M)	37-74	50
SiO <sub>2</sub> -P (L)	74-150	50

The HDEHP/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents were prepared by the previous report [4].

The distribution coefficients ( $K_d$ ) were measured by batch experiments using a definite amount of adsorbent and measured volume of 40 - 50mM DTPA-HNO<sub>3</sub> solution (pH 1 - 3). The mixture of adsorbent and solution was shaken mechanically for 3h. The distribution coefficient was calculated by

$$K_d = \frac{(C_0 - C_s)}{C_s} \times \frac{V}{W}, \quad (1)$$

where  $C_0$  and  $C_s$  denote the concentration of metal in the aqueous phase before and after adsorption, respectively.  $V$  indicates the volume of aqueous phase and  $W$  is the weight of the dry adsorbent. The concentration of metal was determined by ICP-AES or alpha/gamma-ray spectrometry.

Column experiments with simulated feed solutions were carried out using a Pyrex-glass column with 10 mm diameter and 300 mm (HDEHP/SiO<sub>2</sub>-P) or 500 mm (CMPO/SiO<sub>2</sub>-P) in length. The column was kept at a constant temperature (25°C (HDEHP/SiO<sub>2</sub>-P) or 50°C (CMPO/SiO<sub>2</sub>-P)) with a water jacket. The composition of the simulated feed solutions was summarized in Table II.

TABLE II. Composition of the simulated feed solutions

Element	Conc. (mM)	Element	Conc. (mM)
Ce	16.4	Zr	1.6
Pr	8.5	Y	3.1
Nd	27.0	Mo	30.2
Sm	8.6	Pd	21.6
Eu	0.92	Sr	5.4
Gd	1.1	Cs	30.1
Ru*	9.9	U*	0.042

\* 4.76 M HNO<sub>3</sub> solution containing Ru and U for the experiments using CMPO/SiO<sub>2</sub>-P, 50 mM DTPA solution of pH 2.0 without Ru and U for the experiments with HDEHP/SiO<sub>2</sub>-P

All the mobile phase was pumped at 1cm<sup>3</sup>/min and the eluents were collected by a fractional collector. The metal concentrations in the eluents were determined by ICP-AES except for Cs which was determined by atomic adsorption spectroscopy or ICP-MS.

The pressure drops were measured by feeding 4.76M HNO<sub>3</sub> into the Pyrex-glass column with

10 mm diameter and 500 mm in length, which was packed with SiO<sub>2</sub>-P or CMPO/SiO<sub>2</sub>-P adsorbent, at 50°C. The strength of SiO<sub>2</sub>-P particles was estimated by the change of particle size distribution before and after static pressurizing (max. 2MPa) up to 2 weeks.

### Results and Discussion

The pressure drops observed in the experiments with several SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents are summarized in Fig. 2. The results of the SiO<sub>2</sub>-P particles without the CMPO impregnation indicated that large particle (SiO<sub>2</sub>-P (L)) and pore (SiO<sub>2</sub>-P) sizes brought the low pressure drop, which was better for operation. Especially, the SiO<sub>2</sub>-P particles with large pore size kept the low pressure drop even after the CMPO impregnation (CMPO/SiO<sub>2</sub>-P).

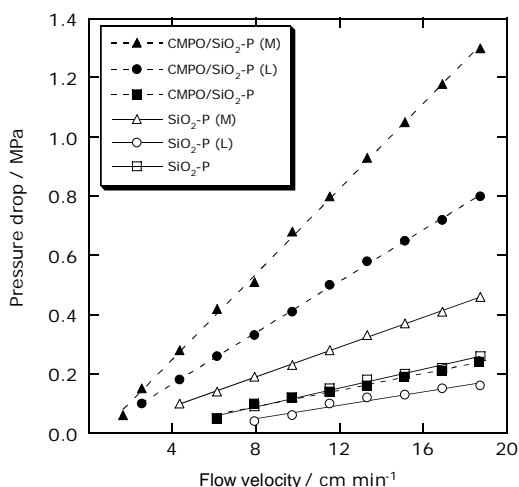


Fig. 2. Pressure drops for several SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents.

The averages of the SiO<sub>2</sub>-P particle sizes after the static pressurized tests are shown in Fig. 3. All of the SiO<sub>2</sub>-P particles showed no significant change of the particle sizes after the pressurized test up to 2 weeks. It is concluded that the effect of SiO<sub>2</sub>-P particle and pore sizes on the strength of particle was negligible under the experimental conditions.

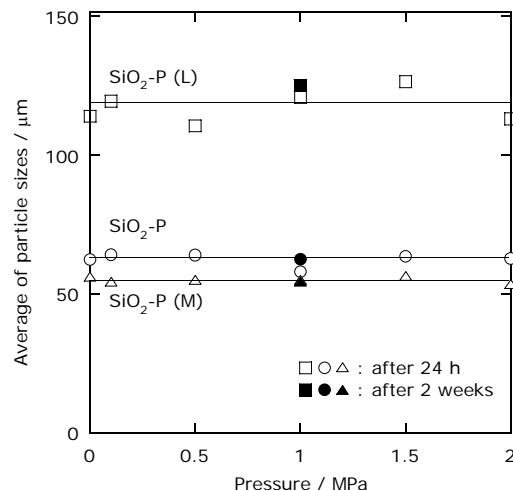


Fig. 3. Average of the SiO<sub>2</sub>-P particle sizes after the static pressurized tests.

The result of the chromatographic separation of a simulated feed solution (simulated HLLW) by a CMPO/SiO<sub>2</sub>-P column is shown in Fig. 4.

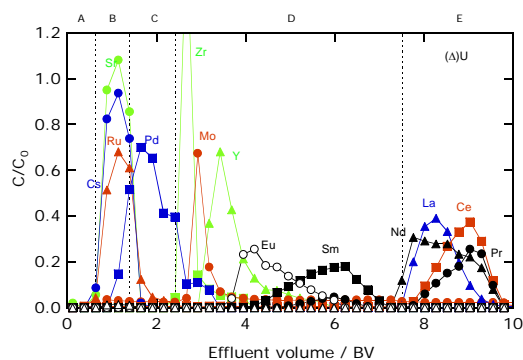


Fig. 4. Chromatographic separation of a simulated HLLW by a CMPO/SiO<sub>2</sub>-P column: (A) dead volume, (B) simulated HLLW, (C) 4.76M HNO<sub>3</sub>, (D) 50mM DTPA-pH<sub>2</sub>, (E) H<sub>2</sub>O

Firstly, Sr, Ru, Cs and a part of Pd passed through the CMPO/SiO<sub>2</sub>-P column without adsorption. The adsorbed Pd was eluted by 4.76M HNO<sub>3</sub>. All of the Zr, Mo and Ln were adsorbed on the CMPO/SiO<sub>2</sub>-P adsorbent, and Zr, Mo and heavy Ln were eluted by the supply of 50mM DTPA-pH<sub>2</sub> solution, showing the order of elution; Zr, Mo, Y, Eu and Sm. The light Ln (Nd, La, Ce and Pr) were eluted out by H<sub>2</sub>O. These adsorption and elution behaviors were almost same as in the experiments with the CMPO/SiO<sub>2</sub>-P (M) and CMPO/SiO<sub>2</sub>-P (L) columns, but the solution volume for eluting the adsorbed elements was less in the experiments with the CMPO/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P (M) columns. For minimizing the volume of waste

solutions, therefore, it is desirable to use the SiO<sub>2</sub>-P with small particle size.

The above experimental results about the effects of SiO<sub>2</sub>-P particle and pore sizes can be summarized as follows:

- Pressure drop; larger particle size, and especially larger pore size are better
- Strength; no effect of particle and pore sizes
- Separation; smaller particle size is better

The SiO<sub>2</sub>-P with small particle size and large pore size (SiO<sub>2</sub>-P in Table I) was used for preparing HDEHP/SiO<sub>2</sub>-P adsorbent and investigating the adsorption and elution properties of FP and An onto this adsorbent. Figure 5 shows the distribution coefficients of some FP and TRU elements onto HDEHP/SiO<sub>2</sub>-P adsorbent in 50mM DTPA-HNO<sub>3</sub> solution. The elements except for An(III) and Ln were not adsorbed around pH=2. The difference between the distribution coefficients of An(III) and Ln was not so significant under low pH condition, but it became greater with increasing pH and only Ln showed quantitative adsorption around pH=3.

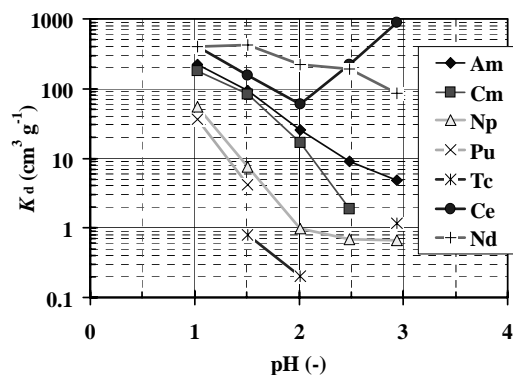


Fig. 5. Distribution coefficients of some FP and TRU elements onto HDEHP/SiO<sub>2</sub>-P adsorbent. HDEHP/SiO<sub>2</sub>-P adsorbent; 0.25g, solution; 5cm<sup>3</sup> (Am 3.8 - 4.0x10<sup>-4</sup>, Cm 4.2 - 4.8x10<sup>-6</sup>, Np 0.93 - 1.0, Pu 2.1-2.7x10<sup>-2</sup>, Ce 0.48 - 0.57, Nd 0.58 - 0.68, DTPA ~ 40 (unit in mM))

These An(III) and Ln behaviors are attributed to the change of the contribution of adsorption (extraction) reaction by HDEHP and complexing reaction by DTPA with varying pH, and suggests that An(III) can be separated from Ln by adjusting pH of a feed solution and/or an eluent containing DTPA to be an appropriate value.

One of the results of the chromatographic separation of a simulated feed solution by an HDEHP/SiO<sub>2</sub>-P column is shown in Fig. 6. In this experimental condition, Cs, Sr, Zr and Pd showed no adsorption, and leaked out with the feed solution and 0.01M HNO<sub>3</sub>. On the contrary, all the Ln were adsorbed onto the HDEHP/SiO<sub>2</sub>-P column, and were eluted by 1M HNO<sub>3</sub>. An(III) would similarly behave as Ln in the experimental condition; i.e. adsorption onto the HDEHP/SiO<sub>2</sub>-P column and elution with Ln by 1M HNO<sub>3</sub>.

For the effective separation of An(III) from other elements by the HDEHP/SiO<sub>2</sub>-P column, it is required to change the composition of feed solution and/or eluents with reference to the result in Fig. 5, e.g. elution with DTPA solution (pH=3) before supplying 1M HNO<sub>3</sub>, which will bring a selective An(III) elution from the HDEHP/SiO<sub>2</sub>-P column.

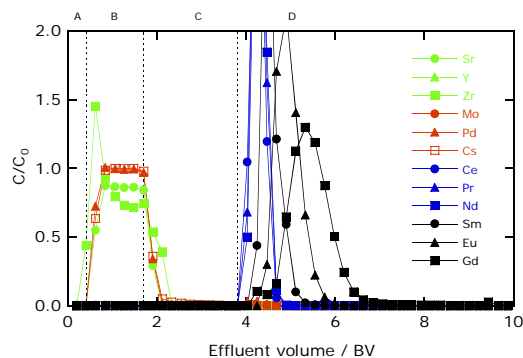


Fig. 6. Chromatographic separation of a simulated feed solution by a HDEHP/SiO<sub>2</sub>-P column: (A) dead volume, (B) simulated feed solution, (C) 0.01M HNO<sub>3</sub>, (D) 1M HNO<sub>3</sub>

### Safety data of HDEHP/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents

#### Experimental

Resistances of the HDEHP/SiO<sub>2</sub>-P and the CMPO/SiO<sub>2</sub>-P adsorbents to nitric acid, to gamma-ray irradiation and to heat were investigated to evaluate durability of the adsorbents. The CMPO/SiO<sub>2</sub>-P adsorbent was kept in HNO<sub>3</sub> solution with the concentration of 0.1 and 4.7M for 30 days, while the HDEHP/SiO<sub>2</sub>-P adsorbent was contacted with 0.01 and 1M HNO<sub>3</sub>. The adsorbents separated from the acid solution were provided for the batch adsorption/elution experiments, and the concentrations of the TOC and P in the residual

acidic solution were evaluated to estimate the amount of the eluted extractants.

The adsorbents immersed in the acid solution were irradiated at room temperature with the gamma-ray at the dose rate of 3kGy/h generated by Co-60 source, and the maximum accumulated dose was 4MGy. The gamma-ray resistances of the adsorbents were evaluated by the same manner with the case of acid resistance tests. The heat resistances of the adsorbents were evaluated by TG/DTA measurements.

### Results and Discussion

The adsorption/elution properties of the adsorbents were slightly changed by contacting with  $\text{HNO}_3$ , therefore degradation of the adsorbents by  $\text{HNO}_3$  should be insignificant under those conditions.

Gases were generated in the vial that contained the adsorbents and  $\text{HNO}_3$  solution during gamma-ray irradiation, and colors of the adsorbents turned from white to yellow or brown by the irradiation.

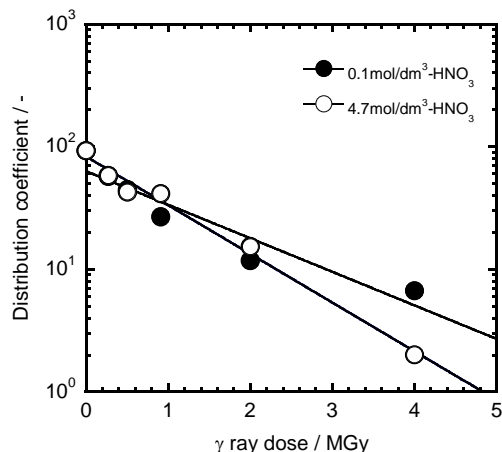


Fig. 7. The distribution coefficients of Nd onto the CMPO/SiO<sub>2</sub>-P adsorbent (Feed;  $[\text{HNO}_3]=4.7\text{M}$ ,  $[\text{Nd}]=10\text{mM}$ , contact time; 3h, temp.; 25°C)

Figure 7 shows the distribution coefficients of Nd onto the CMPO/SiO<sub>2</sub>-P adsorbent irradiated with the gamma-ray. The distribution coefficient decreased with increasing irradiation dose, and degradation by the irradiation was apparently observed through the change of appearance of the adsorbent.

As shown in Fig. 8, the HDEHP/SiO<sub>2</sub>-P adsorbent also showed degradation by the irradiation, besides the concentration of the  $\text{HNO}_3$  influenced on the distribution coefficient.

Thus, hydrolysis of the HDEHP extractant rather than degradation by  $\text{HNO}_3$  is considered to affect on decrease in the distribution coefficient.

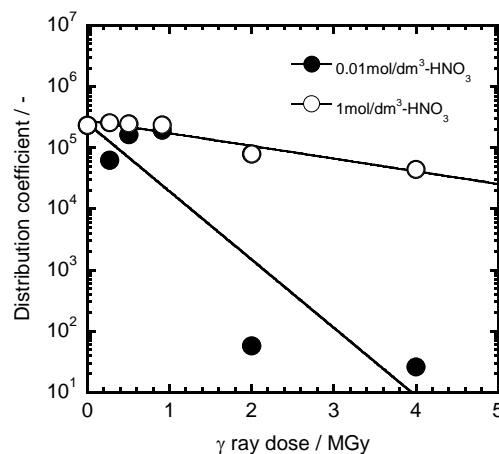


Fig. 8. The distribution coefficients of Eu onto the HDEHP/SiO<sub>2</sub>-P adsorbent (Feed;  $[\text{HNO}_3]=0.01\text{M}$ ,  $[\text{Eu}]=10\text{mM}$ , contact time; 3h, temp.; 25°C)

The amount of the eluted HDEHP was evaluated from the concentration of P in the residual  $\text{HNO}_3$  solution, and showed a reasonable agreement with the decrease in the adsorption capacity of the adsorbent, however the TOC in the solution led an underestimate for the amount of the eluted extractant. The difference in the amount of eluted extractant evaluated from the concentration of TOC and P is considered to be caused by radiolysis of HDEHP to another organic phosphorous compound and  $\text{CO}_2$  gas. On the other hand, the amounts of the eluted CMPO calculated from the amounts of TOC and P significantly differed from the decrease in the adsorption capacity. Since the adsorption capacity of the irradiated CMPO/SiO<sub>2</sub>-P adsorbents was lower than the calculated values, CMPO should decompose into  $\text{CO}_2$  and soluble product with a lower adsorption capacity than that of CMPO. For further discussion about the decomposition of the extractants in the adsorbents, the radiolysis products of the extractants and components of the gases have to be identified.

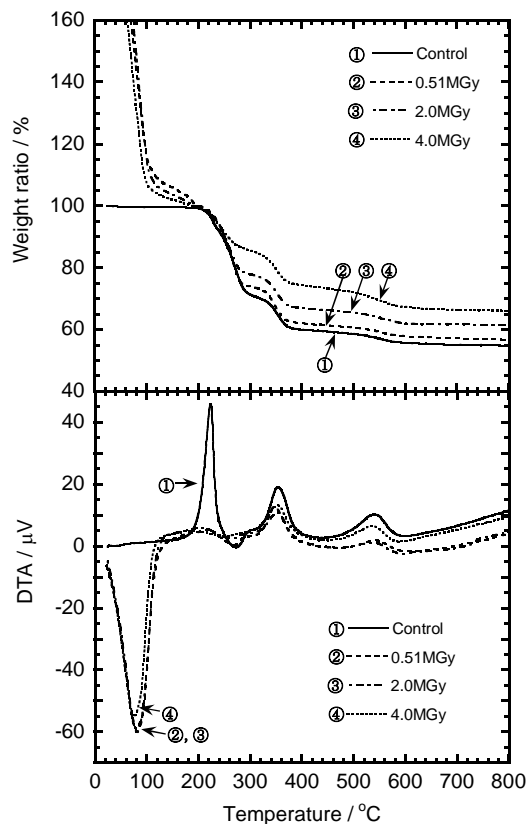


Fig. 9. TG/DTA curves of the CMPO/SiO<sub>2</sub>-P adsorbent ([HNO<sub>3</sub>]=4.7M, heating rate; 10°C/min, in air)

The TG/DTA curves of the CMPO/SiO<sub>2</sub>-P and the HDEHP/SiO<sub>2</sub>-P adsorbent are shown in Fig. 9 and 10, respectively. Exothermic and endothermic peaks observed at ca. 220°C for the controlled adsorbent of unirradiation, which correspond to the sharp decreases in thermo gravity at ca. 220°C, represents the thermal degradation of the CMPO and HDEHP, respectively, and the exothermic peaks observed at ca. 350 and 550°C correspond to thermal degradation of the styrene-divinylbenzene. Although the amount of extractants in the adsorbents decreased by the irradiation, different decomposing behavior was not observed.

Those tests conclude that the degradation of the adsorbents mainly depends on the irradiation dose and that the thresholds for the durability of the CMPO/SiO<sub>2</sub>-P and HDEHP/SiO<sub>2</sub>-P adsorbents for gamma-ray irradiation are 1 and 0.5MGy, respectively, in the respect of the adsorption/elution properties of the adsorbents.

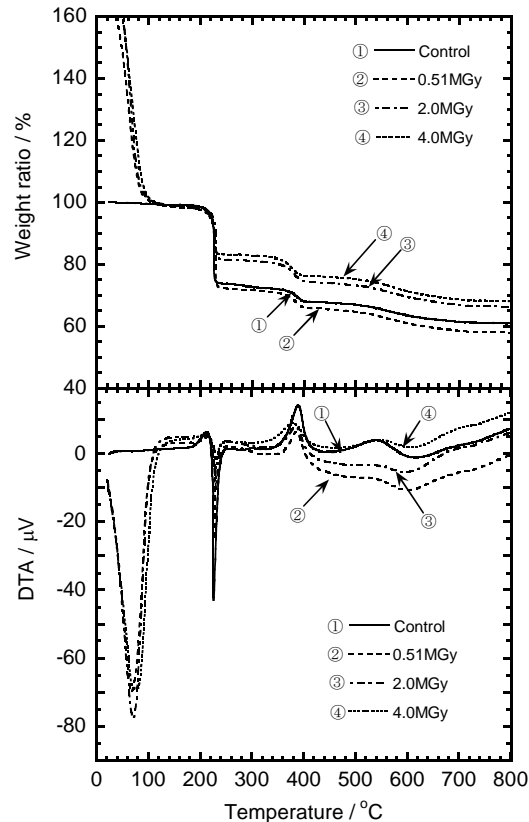


Fig. 10. TG/DTA curves of the HDEHP/SiO<sub>2</sub>-P adsorbent ([HNO<sub>3</sub>]=1M, heating rate; 10°C/min, in air)

## FUTURE R&D PROGRAM

Figure 11 shows our R&D program from JFY2006 to JFY2009.

### Process Development

We will continue to study the characteristics of SiO<sub>2</sub>-P adsorbents impregnated with CMPO, TODGA, HDEHP and R-BTP; i.e. adsorption/elution properties of some FP and An, safety data on acid, gamma-irradiation and heat resistance, and treatment methods after using, by laboratory scale experiments. Based on the results of these studies, several flowsheets for An(III) recovery will be designed and evaluated.

### System Development

The system development is at the first stage at present, therefore, we have given priority to the developments for sufficient separation performance and safety operation although the investigation of remote control/maintenance and instrumentation also started.

In order to achieve steady operation for An(III) separation and recovery, it is required to establish the operational condition for obtaining the stabilized and uniform flow through a column, and to assure the separation performance through a long-term operation (multi-cycle operations).

For the safety operation preventing fire and explosion, it is important to assess the effect of degradation products of the adsorbents, and to control the temperature in a column. The former was partially carried out as the process development as mentioned in the previous chapter, but the behavior of gas products in a column should be also investigated for preventing the gas accumulation which will decrease the separation performance and increase the risk of explosion in a column.

*Fluidics of solid, liquid and gas in a column*

The condition of packing the adsorbents into a column will be investigated and be optimized to make a uniform bed. The effects of column diameter and liquid flow direction on the liquid fluidics in a column will be also studied for the stabilized and uniform flow in a column. Furthermore, the gas behavior will be discussed for preventing its accumulation in a column.

*Safety in a column operation*

The thermal properties of a column filled with the adsorbents will be investigated under the

condition where the liquid flow exists. With reference to this result, several methods for controlling the temperature in a column on normal and abnormal operations will be studied.

*Durability through a long-term operation*

The variation of separation performance (adsorption/elution properties, loss of extractants from the adsorbents, deformation of the adsorbents) will be investigated through a long-term operation (multi adsorption/elution cycle operations).

For these experiments, we fabricated the column system consisting of a column with 20cm or 40cm diameter, utilities, such as tanks and pumps, and several instrumentations. Experiments using this system are now under progress.

We also surveyed the remote control and instrumentation used in the existing industry for column operations, and studied the control system required for automatic operation. In addition, the control system for abnormal events is now being studied, and the remote handling required for maintenance will be defined.

The results obtained in these developments will be applied to engineering scale system development; i.e. fabrication of the engineering scale system and experiments using this system.

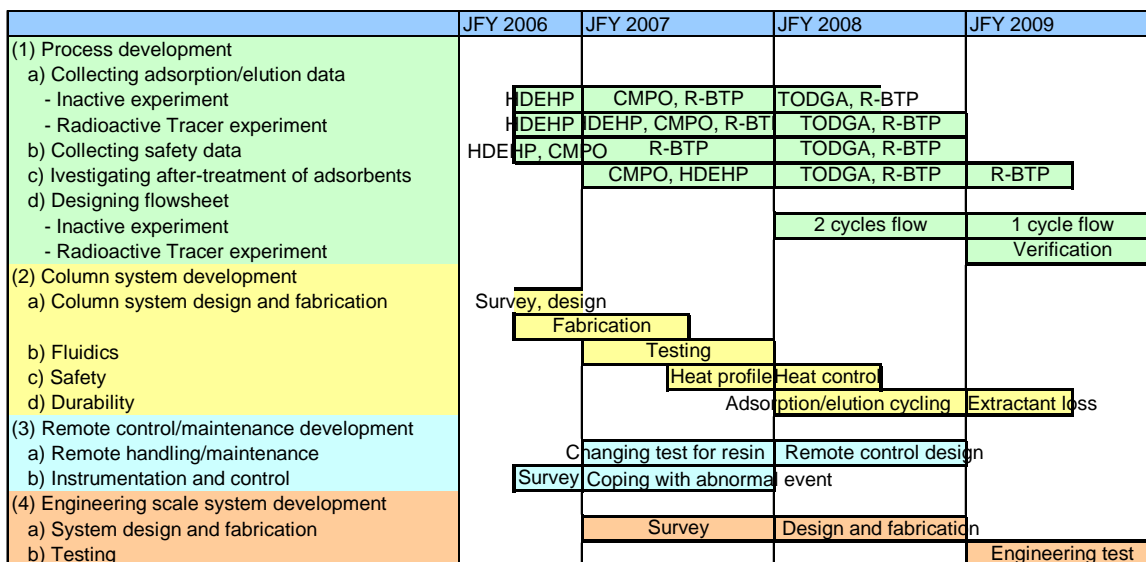


Fig. 11. R&D program for Am and Cm recovery by extraction chromatography



In the experiments using the engineering scale system, we will have overall assessments of separation performance, safety, instrumentation and control, and remote handling, and will confirm the fundamental performance of the extraction chromatography for An(III) recovery in engineering scale.

## CONCLUSION

In the development of the extraction chromatography for An(III) recovery from HLLW aiming at an engineering scale application, the adsorption/elution properties and safety data on HDEHP/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents were collected and assessed.

The effects of SiO<sub>2</sub>-P particle and pore sizes on separation properties, pressure drop and strength of particle showed that the SiO<sub>2</sub>-P particle with small particle size and large pore size was suitable for the support of adsorbent.

The experimental results with HDEHP/SiO<sub>2</sub>-P adsorbent suggested that An(III) is separated from Ln by adjusting pH of feed solution and/or eluent containing DTPA to be an appropriate value.

The degradation of HDEHP/SiO<sub>2</sub>-P and CMPO/SiO<sub>2</sub>-P adsorbents by HNO<sub>3</sub> was insignificant, while the durability of CMPO/SiO<sub>2</sub>-P and HDEHP/SiO<sub>2</sub>-P adsorbents for gamma-ray irradiation were estimated to be 1 and 0.5MGy, respectively. These adsorbents showed thermal degradation of the extractants at ca. 220°C, and no difference of decomposing behavior was observed regardless of gamma-ray irradiation.

In the system development, system experiments for fluidics, safety and durability using engineering scale column as well as studies on remote control/maintenance are now under progress.

## ACKNOWLEDGMENTS

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