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Separation of Minor Actinides and Rare Earths from a Simulated High Activity Liquid Waste by Two Macroporous Silica-based Polymeric Composites

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Abstract: To eliminate the long-lived minor actinide (MA) elements from high activity liquid waste (HLW), a group partitioning from a simulated HLW solution containing 14 typical elements and 3.0 M HNO_3 was performed. It was done by utilizing two macroporous silica-based polymeric N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) composites (TODGA/SiO_2-P and CMPO/SiO_2-P). It was found that in the first column packed with TODGA/SiO_2-P, the tested elements were separated to (1) Cs, Ru, and Mo (non-sorption group), (2) minor actinides (MAs), rare earths (REs), Sr, and Pd (MA-RE-Sr-Pd group), and (3) Zr, respectively, by eluting with 3.0 M HNO_3, 0.01 M HNO_3, 0.05 M DTPA-pH 3.75, and 0.5 M $H_2C_2O_4$ at 298 K. MA were considered to flow into MA-RE-Sr-Pd group along with Gd and Dy because of their similar sorption and elution behavior towards TODGA/SiO_2-P. In the second column packed with CMPO/SiO_2-P, the MA-containing effluent was separated to (1) Sr-Pd group and (2) MA-RE group, respectively by eluting with 3.0 M HNO_3 and water at 323 K. MA was believed to flow into MA-RE group. Based on the results obtained, a process entitled GPEC (Group Partitioning of HLW by Extraction Chromatography) for effective partitioning of minor actinides and rare

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earths from HLW utilizing two macroporous silica-based polymeric composites was proposed.

Keywords: Silica-based polymeric composite, group partitioning, minor actinide, extraction chromatography, high activity liquid waste

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INTRODUCTION

To minimize the long-term radiological risk and facilitate the management of high activity liquid waste (HLW), partitioning of the long-lived minor actinide (MA) elements and some specific fission products (FPs) from HLW is required (1, 2). Solvent extraction processes such as TRUEX, DIAMEX, DIDPA, SETFICS, SANEX, etc. using various conventional or newly developed extractants have hence been developed (3–5). In these extractants, a neutral chelating agent octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), a bifunctional organophosphorous compound, is well-known to be able to extract effectively MAs and FPs from an aqueous solution containing concentrated nitric acid (6–8). Since CMPO shows fairly excellent chemical-stability in nitric acid solution and is a commercially available product, it has been extensively studied for the actinides partitioning from an acidic HLW (9, 10).

Extraction chromatography using a special chelating group-containing extraction resin is one of the separation techniques. It seems to be acceptable due to its sorption character such as a minimal organic solvent utilization, less waste accumulation, compact equipment, and simple operation procedure. It is effective to separate radioactive nuclides through the method of concentration or purification in laboratory scale (11, 12). On the other hand, extraction chromatography combines the selectivity of solvent extraction process with the simplicity and multistage character of column chromatographic system (13, 14). This makes extraction chromatography as an alternative separation technique in the application of the chromatographic partitioning of HLW in industry scale promising.

Based on the SETFICS process (15, 16), we have developed a novel partitioning technology entitled MAREC (Minor Actinides Recovery from HLW by Extraction Chromatography) process (17–21). The purpose is to recover the long-lived minor actinides such as Am and Cm from HLW using a macroporous silica-based polymeric CMPO extraction resin (CMPO/SiO_2-P) synthesized by impregnation of CMPO into the porous of SiO_2-P particles with a mean diameter of 50 μm. Two sorption columns packed with CMPO/SiO_2-P extraction resin are utilized for the chromatographic separation of HLW through selective sorption and elution procedures. Some fundamental investigations were performed (22–35).

An acidic chelating agent diethylenetriaminepentaacetic acid (DTPA) as shown in Fig. 1, a multi-dentate containing five carboxyl and three amine

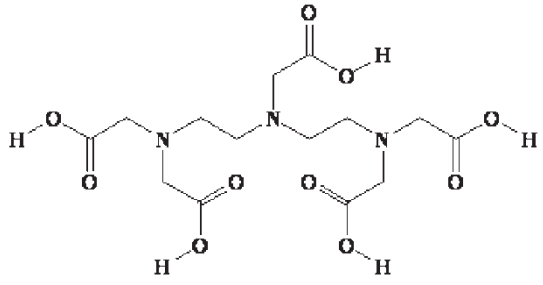

Figure 1. Molecular structure of diethylenetriaminepentaacetic acid (DTPA).

groups capable of being protonated, is a pentabasic acid (36, 37). It has six different species in HNO_3 solutions of different concentrations. N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), a neutral chelating agent having three hard oxygen and two soft nitrogen atoms, was investigated recently. It was found that in HNO_3/*n*-dodecane extraction solution, TODGA extracted effectively RE(III), tri- and tetravalent minor actinides from others (38, 39). In where, DTPA had the obvious effect on the extraction of actinide-s(III) and rare earths(III) from the nitrate solution into TODGA/n-dodecane (40). This makes the separation of MA(III) and RE(III) from HLW by the use of DTPA promising. However, a few works were focused on application of DTPA in partitioning of MA(III) from an acidic HLW by extraction chromatography utilizing TODGA-containing sorbent or ion exchange resin (41, 42).

In the present work, we proposed a process named GPEC (Group Partitioning of HLW by Extraction Chromatography) for the separation of MA(III) and RE(III) from a simulated HLW. It was performed by the impregnation synthesis of two macroporous silica-based TODGA/SiO_2-P and CMPO/SiO_2-P polymeric composites. The elution experiment was conducted by 0.05 M DTPA-pH 3.75 and 0.5 M $H_2C_2O_4$ as eluents in the first column packed with TODGA/SiO_2-P and water in the second one packed with CMPO/SiO_2-P. A possibility in the application of DTPA in the elution of MA(III) and RE(III) from the loaded TODGA/SiO_2-P was discussed.

EXPERIMENTAL

Reagents

$RE(NO_3)_3 \cdot nH_2O$ (n = 3∼6, RE = La, Ce, Nd, Sm, Eu, Gd, Gy, and Y), fission products (FPs) nitrates (FP = Cs(I), Sr(II), and Zr(IV)) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were of analytical grade. A palladium nitrate solution containing 4.5 wt% of Pd(II) was provided by the Tanaka Noble Metal Co. Inc., Japan. A ruthenium (III) nitrosyl nitrate solution containing 1.5% of

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Ru(III) was provided by Strem Chemicals, the United States of America. The concentrations of all the tested elements were about 5.0×10^{-3} M.

A neutral chelating agent, N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) with a purity of more than 99%, was provided by the Kanto Chemical Co. Inc. of Japan. It was used without further purification. The content of TODGA in reagent was determined accurately at a known interval using a high pressure liquid chromatography (HPLC) to ensure its purity. The purity of an acidic chelating agent, diethylenetriaminepentaacetic acid (DTPA) provided by the Tokyo Kasei Kogyo Co. Ltd., Japan, was more than 98%. Prior to the experiment it was dissolved by little of 25% ammonia aqueous solution, then conditioned by the concentrated nitric acid. 0.5 M oxalic acid, the feed solution, the various HNO_3 solutions of different concentrations, and others were prepared temporarily.

Dichloromethane, methanol, and other reagents were of analytical grade and were used without further treatment.

A novel macroporous silica-based support SiO_2-P particles, polymeric CMPO/SiO_2-P and TODGA/SiO_2-P composite were synthesized in our laboratory. A letter P in the SiO_2-P particles refers to the styrene-divinylbenzene copolymer, which was prepared in advance by means of a complicated polymerization reaction taking place inside the pores of the SiO_2 particles (24, 43).

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Synthesis of Silica-Based Polymeric Composites

The macroporous silica-based polymeric composite used was prepared by impregnating an organic compound molecule into the pores of the SiO_2-P particles support through a vacuum sucking technique. The fundamental principle is based on the intermolecular interaction of the chelating agent molecule and the polymeric compounds contained in the SiO_2-P particles.

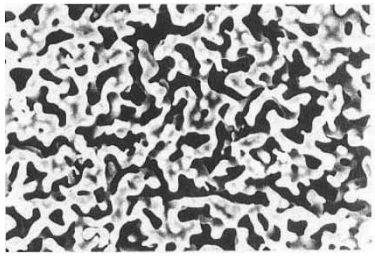
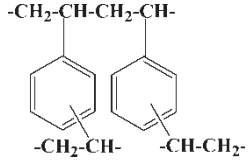
The activity of styrene-divinylbenzene copolymer in the pores of the SiO_2-P particles is small. To increase its affinity for the chelating agent molecule, prior to the synthesis the SiO_2-P particles employed herein were pretreated actively several times with methanol and other organic compounds at room temperature. Then, it was dried in a vacuum drying oven for 24 h at $\sim$323 K. The synthesis procedure of TODGA/SiO_2-P was described as follows:

An accurate quantity of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide dissolved with 100 cm^3 of dichloromethane and the double amount of the SiO_2-P particles were mixed into a 300 cm^3 of conical glass flask. It was then stirred mechanically for 90 min at room temperature to get a uniform solution. Subsequently, the mixture was moved into a silicon-oil bath and stirred for about 180 min at 323 K, which was controlled using an OHB-2000 Model temperature auto-adjustment heater (Tokyo Rikakikai Co. Ltd., Japan), to impregnate and immobilize the TODGA molecule into the pores

of SiO_2-P particles. After drying in a vacuum drying oven at around 323 K for 24 h, the macroporous silica-based polymeric material, TODGA/SiO_2-P, was obtained. It was characterized by TG-DSC and elementary analysis, respectively.

The use of the similar synthesis method to TODGA/SiO_2-P, the macroporous silica-based polymeric composite, CMPO/SiO_2-P, was prepared through impregnating and immobilizing CMPO molecule into the pores of SiO_2-P particles. The corresponding structure and physical properties of CMPO/SiO_2-P and TODGA/SiO_2-P are listed in Table 1.

Table 1. Structure and physical properties of the macroporous silica-based polymeric CMPO or TODGA composite

Organic/inorganic polymeric composite	CMPO/SiO_2-P or TODGA/SiO_2-P
Chelating functional group	CMPO TODGA
Pore fraction	0.69
Mean pore size	0.6 μm
Bead diameter	40–60 μm
CMPO or TODGA content	33.3% (w/w)
Inner structure of the silica-based polymeric composite	
Support of polymeric material	66.7% (w/w) of macroporous SiO_2 particles modified by following copolymer-containing 
Appearance	Colorless CMPO/SiO_2-P: nearly colorless or light yellow micro-ball TODGA/SiO_2-P: yellow micro-ball
Stability	Good resistance against HNO_3, heat, and γ-radiation
Affinity for aqueous solution	Good

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HLW Partitioning by Extraction Chromatography

In the GPEC partitioning process proposed herein, two sorption columns packed with TODGA/SiO_2-P and CMPO/SiO_2-P were selected and used in the main separation engineering of HLW.

In group separation performed in the first column, Nd(III) as a light rare earth was used to simulate Am(III) and Cm(III) because of their similar sorption and elution properties towards TODGA/SiO_2-P. Similarly, Ce(III) as a light rare earth, Gd(III), Dy(III), and Yb(III) as the heavy ones were used in the second column to simulate all of the rare earths, Am(III) and Cm(III) due to their similar sorption and elution behavior onto CMPO/SiO_2-P.

The chromatographic partitioning of the simulated HLW solution was performed using a Pyrex glass column. Its dimension was 10 mm in inner-diameter and 300 mm in length for the first column and 10 mm in inner-diameter and 500 mm in length for the second one. The polymeric sorption composite employed was packed into the column in the slurry state under 0.3 to 0.5 MPa of N_2 gas pressure. The space of head and end of the column used was adjusted with a mobile plug. No significant pressure drop was found through the sorption column because of the silica-based support, which is different from the conventional polymer-based one.

Prior to the separation experiment a given quantity of dry TODGA/SiO_2-P or CMPO/SiO_2-P adsorbent pre-equilibrated fully with 3.0 M HNO_3 was packed into the column. A constant temperature used in the loading and elution cycle was maintained at 298 K or at 333 K through circulating the thermostated water using an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co. Ltd., Japan) as shown in Fig. 2. The flow rate was controlled to 1.0 cm^3/min using a NPG-50UL Model pressure gage (Nihon Seimitsu Kagaku Co. Ltd., Japan) and a 2GN15K Model pressure limiter (Oriental Motor Co. Ltd., Japan).

Following a 3.0 M HNO_3 solution containing $\sim 5.0 \times 10^{-3}$ M of Pd(II), Cs(I), Ru(III), Sr(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III), Mo(VI), and Zr(IV), which were used as feed solution for the first column packed with TODGA/SiO_2-P, or $\sim 5.0 \times 10^{-3}$ M Ce(III), Gd(III), Dy(III), Yb(III), Sr(II), and Pd(II) employed as the feed solution for the second column packed with CMPO/SiO_2-P passed through the column, the given volumes of 3.0 M HNO_3, 0.01 M HNO_3, 0.05 M DTPA-pH 3.75, and 0.5 M $H_2C_2O_4$ or 3.0 M HNO_3, 5.0 10^{-3} M R-BTP-3.0 M HNO_3, and water as the eluents employed in the first and second columns, respectively, were subsequently pumped down-flow through the column. A 10 cm^3 aliquots of effluent fraction was collected using an EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co. Ltd., Japan). The concentrations of metal ions in effluent were analyzed using a SPS-5000 Model inductively coupled plasma-optical emission spectrometer (ICP-OES, SII Seiko Instruments Inc., Japan) except the content analysis of

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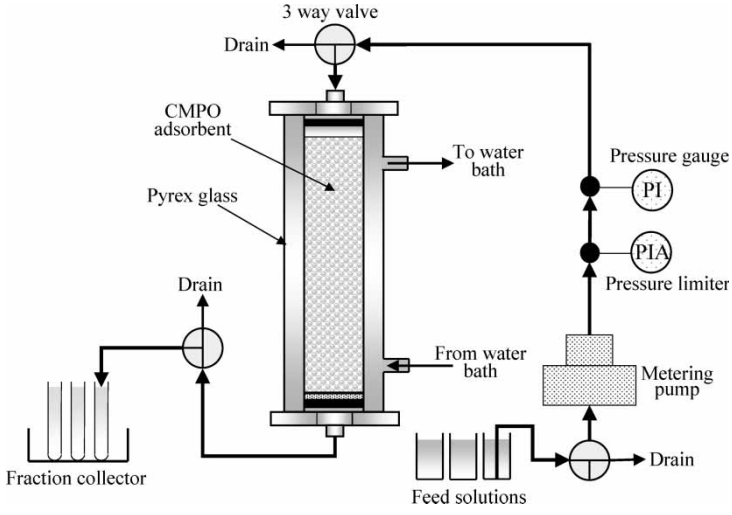

Figure 2. Experimental apparatus of column partitioning by extraction chromatography.

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Cs(I) using an Agilent 7500 series inductively coupled plasma-mass spectrometer (ICP-MS, Agilent Technologies, Japan). The pH value in the effluent was measured using an AUT-301 Model titrator/pH meter (TOA Electronics Ltd., Japan). According to the analysis results, the HLW partitioning efficiency by extraction chromatography was evaluated.

RESULTS AND DISCUSSION

HLW Partitioning by TODGA/SiO_2-P Column

In terms of the batch experimental results, the HLW partitioning from a 3.0 M HNO_3 solution containing $\sim 5 \times 10^{-3}$ M of 8 typical simulated RE(III) elements La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), and Y(III) was well as fission products Pd(II), Ru(III), Mo(VI), Zr(IV), Sr(II), and Cs(I) was performed by the TODGA/SiO_2-P packed column at 298 K. Nd(III) was used to simulate the sorption and elution behavior of the MA elements because of their similarity in chemical properties onto TODGA/SiO_2-P.

To ensure the effective sorption of these tested metals, prior to the partitioning experiment the TODGA/SiO_2-P polymeric composite was pre-equilibrated by 3.0 M HNO_3. The pH value in a diluted HNO_3 solution containing 0.05 M DTPA was conditioned to 3.75 to facilitate the elution of RE(III) and MA(III). The flow rate was controlled to 1 cm^3/min. The

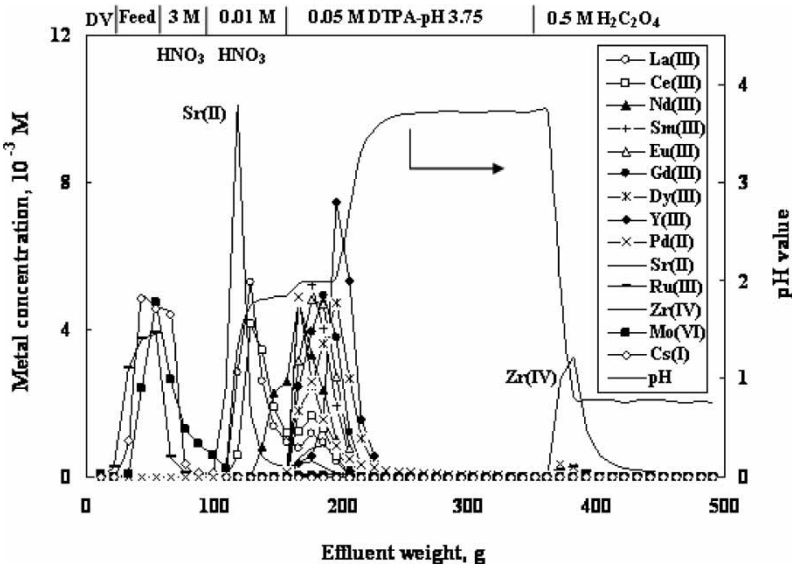

Figure 3. Partitioning results of 15 typically simulated elements from a 3 M HNO_3 solution by TODGA/SiO_2-P polymeric materials packed column utilizing 0.05 M DTPA-pH 3.75 as an eluent at 298 K. Column dimension: Φ 10 mm $\times$ h 300 mm, Flow rate: 1 cm^3/min, [HNO_3] in feed solution: 3.0 M, [Metal] = $\sim 5 \times 10^{-3}$ M.

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elution curves of various metals and corresponding pH values in effluent are illustrated in Fig. 3.

As can be seen, with a supplement of the feed solution to the column, fission products Cs(I), Ru(III), and Mo(VI) showed very weak or almost no sorption towards TODGA/SiO_2-P, quickly leaked out of the column, and flowed into the effluent along with 3.0 M HNO_3. Such an effective elution in the elution curves resulted from the weak or no complexation of these tested metals with TODGA/SiO_2-P.

Subsequently, when 0.01 M HNO_3 was supplied to the column, Sr(II), one of the main heat generators, and the light rare earths La(III) and Ce(III) adsorbed by TODGA/SiO_2-P were eluted out. This was due to the quick decomposition of the complexes of these metals with TODGA contained in TODGA/SiO_2-P with a quick decrease in the NO_3^- concentration in the resin bed. Since the stability of the complex of rare earths with TODGA increased with an increase in atomic number, i.e., the complex stability of the heavy rare earth with TODGA/SiO_2-P was higher than that of the light one, so, the light rare earths from La(III) and Ce(III) were eluted by 0.01 M HNO_3.

After 0.01 M HNO_3, 0.05 M DTPA-pH3.75 as an eluent was supplied to the sorption column. It was found that light, middle, and heavy rare earths

Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), and Y(III) adsorbed strongly towards TODGA/SiO_2-P were efficiently eluted.

It is well-known that DTPA, a multi-dentate acidic chelating agent containing five carboxyl and three amine groups capable of being protonated, is a pentabasic acid. The relevant acidic dissociation constants at 293 K were reported to be $pK_1 = 1.80$, $pK_2 = 2.55$, $pK_3 = 4.33$, $pK_4 = 8.60$ and $pK_5 = 10.58$, respectively (36, 37). It has 6 different species in HNO_3 solution of different concentrations. Its species distribution with a change in pH value is depicted in Fig. 4.

Many experimental results indicated that in a weak and/or middle acidic solution, DTPA could form a series of 1:1 types of the stable coordination compounds with trivalent actinides and lanthanides according to the following reaction:

$$M^{3+} + H_5DTPA \rightleftharpoons M \cdot H_2DTPA + 3H^+ \quad (M(III) = RE(III) \text{ and } An(III)) \tag{1}$$

As can be seen from Eq. (1) and Fig. 4, in pH value range of 2.6–11.0, the main species of DTPA complexed by RE(III) and MA(III) was H_2DTPA^{3-}. In the present work, the acidity employed in the feed solution was pH 3.75. The corresponding pH value in Nd(III)$\sim$Y(III)-containing effluent determined as shown in Fig. 3 was around 2.0. It was clear that the main species of DTPA in this pH value was H_4DTPA^-. On the other hand, our previous experimental results also showed that at around pH 2.0, MA(III) and RE(III) were

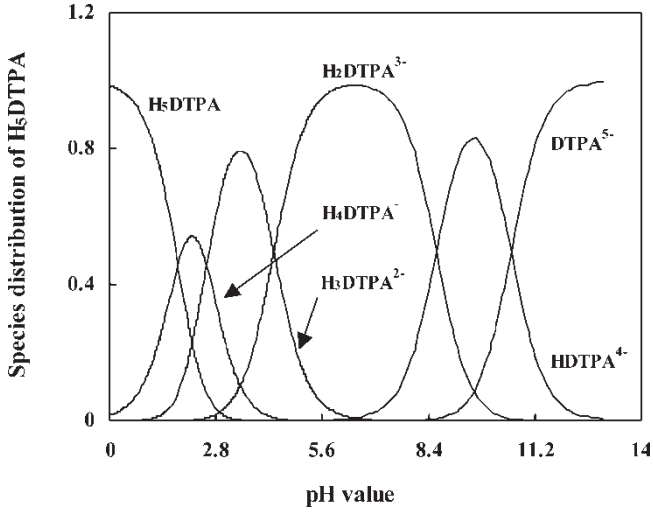

Figure 4. Species distribution of H_5DTPA in a wide pH range.

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complexed strongly with H_4DTPA^- as the following reactions (42):

$$M^{3+} + H_5DTPA \rightleftharpoons M \cdot H_4DTPA^{2+} + H^+ \quad (2)$$

$$M \cdot H_4DTPA^{2+} + 2NO_3^- \rightleftharpoons M(NO_3)_2(H_4DTPA) \quad (M(III) = RE(III) \text{and } An(III)) \quad (3)$$

So, the effective elution of Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), and Y(III) by 0.05 M DTPA-pH 3.75 was ascribed to the strong complexation of H_4DTPA^- with these tested metals. Namely, the substitution of the complex of RE(III) with H_4DTPA^- for the complex of RE(III) with TODGA/SiO_2-P resulted in the elution of these metals from the loaded TODGA/SiO_2-P.

In addition, a few investigations showed that in HNO_3/*n*-dodecane extraction system (38, 39), one RE(III) or MA(III) was extracted efficiently by three TODGA through a neutral extraction mechanism. Our previous experiments also indicated that in the HNO_3 medium, one RE(III) or MA(III) was strongly adsorbed by three TODGA/SiO_2-P. The relevant sorption reaction was described as follows:

$$M^{3+} + 3NO_3^- + 3TODGA/SiO_2\text{-}P \rightleftharpoons M(NO_3)_3 \cdot 3TODGA/SiO_2\text{-}P \quad (M(III) = RE(III) \text{ and } An(III)) \quad (4)$$

So, in combination with the results showing in Eqs. (2)–(4), the elution mechanism of the tested rare earths adsorbed by TODGA/SiO_2-P packed column with 0.05 M DTPA-pH3.75 as an eluent was expressed as follows:

$$RE(NO_3)_3 \cdot 3TODGA/SiO_2\text{-}P + H_4DTPA^- \rightleftharpoons RE(NO_3)_2(H_4DTPA) + 3TODGA/SiO_2\text{-}P + NO_3^- \quad (5)$$

Y(III) is a special rare earth. It was eluted off and flowed into effluent behind all of the tested rare earths. This reflected that the sorption and elution behavior of Y(III) consisted with those of heavy rare earths. So, the elution order by the employed 0.05 M DTPA-pH 3.75 was the following: light RE(III), heavy RE(III) and Y(III).

A long-lived Pd(II) was eluted by 0.05 M DTPA-pH 3.75. Similar to all of the tested RE(III) elements, the elution of Pd(II) was also distributed to the substitution reaction of the complex of Pd(II) with DTPA for the complex of Pd(II) with TODGA/SiO_2-P from the loaded TODGA/SiO_2-P.

The fission product Zr(IV) was finally eluted off by 0.5 M $H_2C_2O_4$. The elution effect was considered to result from the complexation reaction between Zr(IV) and $H_2C_2O_4$, where the $Zr(C_2O_4)_2$ complex was not adsorbed by TODGA/SiO_2-P.

The previous studies performed in our laboratory showed that in HNO_3 solution, the sorption behavior of Am(III) and Cm(III) towards TODGA/

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SiO_2-P was very similar to that of a light rare earth Nd(III). The preliminary investigations obtained recently by the separation experiment verified this conclusion. So, in this experiment, it was believed that minor actinides such as Am(III) and Cm(III) could be eluted effectively by 0.05 M DTPA-pH 3.75 and flowed into effluent along with Nd(III).

From the results and discussions obtained above, it was found obviously that by the use of TODGA/SiO_2-P packed column elution with 0.05 M DTPA-pH 3.75, all of the tested elements contained in the simulated HLW could be separated into three groups:

1. Cs(I), Ru(III), and Mo(VI) (non-sorption group),
2. Sr(II), Pd(II), all RE(III) elements La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), and Y(III) (MA-RE-Sr-Pd group), and
3. Zr(IV). Based on the similar sorption and elution of Am(III) and Cm(III) with Nd(III), the minor actinides were believed to flow into the second MA-RE-Sr-Pd group.

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The pH value in the effluent was determined. It was found that with a supply of 0.01 M HNO_3 to the column, the pH value in effluent increased quickly from 0.08 to 1.74 then slowly to 1.84, showing effective elution of Sr(II), La(III), and Ce(III) from the loaded TODGA/SiO_2-P. With 0.05 M DTPA-pH 3.75 was supplied to the column, the pH value in the effluent increased slightly to 1.97, basically kept in a range of 1.99–2.05, quickly increased to 3.54, and then slowly increased to 3.73. This indicated that the tested RE(III) elements and Pd(II) adsorbed by TODGA/SiO_2-P were eluted effectively. Finally, as 0.5 M $H_2C_2O_4$ was supplied, the pH value in the effluent rapidly decreased to 0.82 and then kept around 0.78, reflecting that the fission product Zr(VI) was eluted efficiently by 0.5 M $H_2C_2O_4$ and flowed into effluent.

MA-RE-Sr-Pd Partitioning by CMPO/SiO_2-P Column

The resultant MA-RE-Sr-Pd group partitioning from Sr(II), Pd(II), and some representative RE(III) elements Ce(III), Gd(III), Dy(III), and Yb(III) was performed by CMPO/SiO_2-P packed column at 323 K.

The effective sorption of the tested metals towards CMPO/SiO_2-P, prior to experiment the MA-RE-Sr-Pd effluent was adjusted to 3.0 M HNO_3. This made dissociation of 0.05 M DTPA from its complexes with MA(III), RE(III), and Pd(II) in MA-RE-Sr-Pd effluent complete. The concentration of the tested metal was also conditioned to about 5×10^{-3} M. The heavy rare earths Gd(III) and Dy(III) were used to simulate the sorption and elution behavior of MA(III) elements because of their similarity in chemical properties towards CMPO/SiO_2-P. The elution results by the use of 3.0 M HNO_3 and water are shown in Fig. 5.

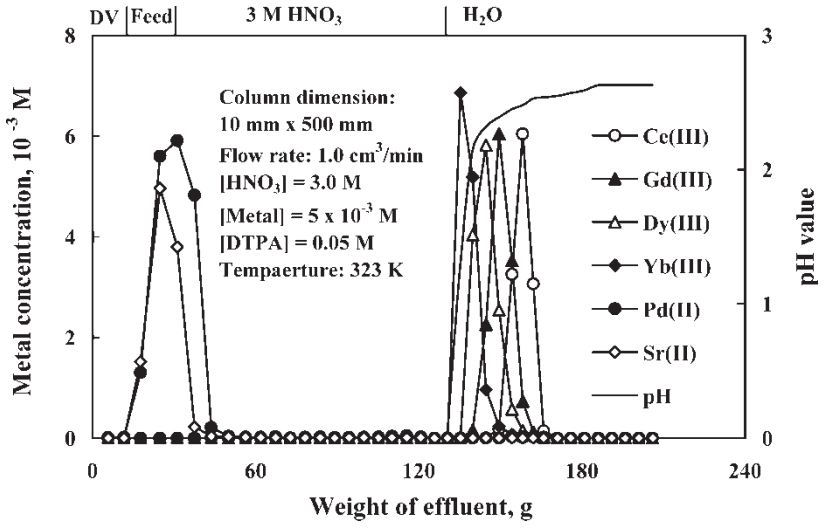

Figure 5. MA-RE-Sr-Pd separation results from a 3 M HNO_3 solution containing 0.05 M DTPA by CMPO/SiO_2-P polymeric composite packed column utilizing 3.0 M HNO_3 and water as eluents at 323 K. Column dimension: Φ 10 mm $\times$ h 500 mm, Flow rate: 1 cm^3/min, [HNO_3] in feed solution: 3.0 M, [DTPA] = 0.05 M, [Metal] = $\sim 5 \times 10^{-3}$ M.

With a supplement of feed solution to the sorption column, fission products Sr(II) and Pd(II) showed no sorption towards CMPO/SiO_2-P and quickly flowed into the effluent along with 3.0 M HNO_3. However, the elution mechanism of Sr(II) and Pd(II) was different.

It was reported that in a wide range HNO_3 concentration even more than 3.0 M, Pd(II) was also complexed strongly by DTPA. Thus, Pd(II) existed in the feed solution in the form of the stable complex with DTPA. So, the effective elution of Pd(II) in its elution curve resulted from its effective complexation with 0.05 M DTPA, while the Pd-DTPA complex was not adsorbed by CMPO/SiO_2-P. On the other hand, Sr(II) usually had no complex ability both with DTPA and CMPO, so, the elution of Sr(II) in its elution curve was due to no sorption towards CMPO/SiO_2-P.

Following 3.0 HNO_3, water as an eluent was supplied to the column. Obviously, the tested Ce(III), Gd(III), Dy(III), and Yb(III) elements adsorbed strongly by CMPO/SiO_2-P were quickly eluted out. The elution peaks were sharp, narrow, and high, showing their effective elution.

It is known that in low HNO_3 concentration solution, all of MA(III) and RE(III) elements were complexed strongly with DTPA and formed the stable complexes. Our previous results showed that in more than 2.0 HNO_3 solution, these complexes were unstable. Free MA(III) and RE(III) was capable of dissociating from their complexes with DTPA. In the present work, the acidity of the feed solution was 3.0 HNO_3, it was undoubtedly that MA(III) and RE(III)

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were fully released from their DTPA-complexes. This resulted in an easy sorption of RE(III) and MA(III) onto CMPO/SiO_2-P and then the effective elution by water. The relevant sorption and elution mechanism were described as follows:

1. In feed solution of 3.0 M HNO_3:

$$RE(H_2DTPA) + 3H^+ \rightleftharpoons RE^{3+} + H_5DTPA \tag{6}$$

2. In sorption process onto CMPO/SiO_2-P

$$RE^{3+} + 3NO_3^- + 3CMPO/SiO_2\text{-}P_{(resin)} \overset{3.0\,MHNO_3}{\rightleftharpoons} RE(NO_3)_3 \cdot 3CMPO/SiO_2\text{-}P_{(resin)} \tag{7}$$

3. In elution process by water

$$RE(NO_3)_3 \cdot 3CMPO/SiO_2\text{-}P_{(resin)} \overset{H_2O}{\rightleftharpoons} 3CMPO/SiO_2\text{-}P_{(resin)} + RE(NO_3)_{3(aq)} \tag{8}$$

Eq. (8) showed that the elution of Ce(III), Gd(III), Dy(III), and Yb(III) in their elution curves resulted from the quick decomposition of the complexes of these metal elements with CMPO contained in CMPO/SiO_2-P with a quick decrease in the NO_3^- concentration in the resin bed.

Our previous results showed that the sorption and elution behavior of the minor actinides towards CMPO/SiO_2-P were very similar to those of the heavy rare earths Gd(III) and Dy(III). So, in this experiment, the minor actinides such as Am(III) and Cm(III) were eluted effectively by water and flowed into the effluent along with Gd(III) and Dy(III).

From the above results and discussions, it was found that all the tested elements contained in the MA-RE-Sr-Pd effluent were separated to

1. Sr-Pd group
2. MA(III)-RE(III) group,

respectively, by eluting with 3.0 M HNO_3 and water at 323 K. Based on the similar sorption and elution properties of Am(III) and Cm(III) with the heavy Gd(III) and Dy(III) elements, the long-lived minor actinides were believed to be separated into the second MA(III)-RE(III) group and flowed into the effluent along with Gd(III) and Dy(III). A mixture composed only of MA(III) and RE(III) was therefore obtained.

The results of pH determination in the effluent showed that with a supply of water to the column, pH value increased rapidly from 0.07 to 2.32, gradually increased to 2.63, and then basically kept constant. This indicated that the tested RE(III) elements were eluted effectively by water and

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quickly flowed into the effluent. So, in the CMPO/SiO_2-P packed column, water was a highly specific eluent for the desorption of MA(III) and RE(III) from the loaded polymeric composite.

A New GPEC Process

According to the results obtained, a new process entitled GPEC (Group Partitioning of HLW by Extraction Chromatography) for minor actinides partitioning from the acidic HLW by extraction chromatography was proposed as illustrated in Fig. 6. As the main separation engineering, it consisted of two main sorption columns packed with the macroporous silica-based TODGA/SiO_2-P in the first column and CMPO/SiO_2-P in the second column, respectively.

In comparison with the MAREC process developed previously, the GPEC process had the following advantages:

1. by substituting TODGA/SiO_2-P for CMPO/SiO_2-P in the first column, all of the RE(III) and MA(III) are eluted off effectively by the use of 0.01 M HNO_3 and 0.05 M DTPA-pH3.75 as eluents. The principle is based on the different stability constants of the complexes of these metals with TODGA/SiO_2-P and DTPA, which are considered to be the competitive reactions. Based on much stronger complexation ability of RE(III) with DTPA compared to TODGA/SiO_2-P, the volumes of various eluents used are reduced significantly.

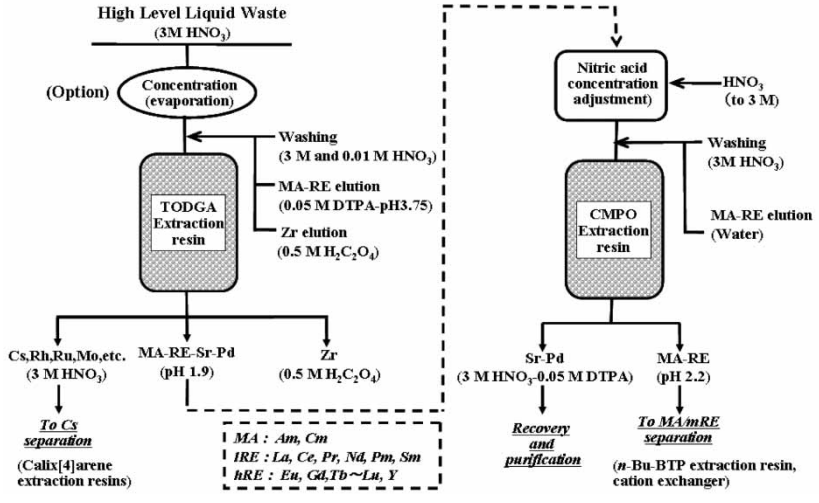

Figure 6. A new GPEC process for radionuclides partitioning from HLW by some macroporous silica-based extraction chromatography.

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2. Radioactive Sr(II), one of the main heat generators, and a long-lived Pd(II), can be separated and recovered efficiently in the second column packed with CMPO/SiO_2-P. The additional sorption column for the special separation of Sr(II) by a novel macroporous silica-based 4,4′,(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6)/SiO_2-P or polymer-based Sr-resin is no more needed and is thus canceled. Such an effective separation of Sr(II) in the GPEC process provides a new pathway for eliminating Sr(II) from HLW.
3. Radioactive Cs(I), another main heat generator, is more easily separated from the non-sorption group obtained in the first column only by employing BOB Calix[4]/SiO_2-P or Calix[4]arene-R14/SiO_2-P packed column, in which the effect of Sr(II) on the partitioning of Cs(I) is negligible.
4. Zr(IV) can be separated and recovered in the first column packed with TODGA/SiO_2-P. The elution of Zr(IV) and Mo(VI) from the loaded CMPO/SiO_2-P as well as the special separation of Zr(IV) and Mo(VI) from 0.05 M DTPA or 0.5 M $H_2C_2O_4$ in original MAREC process are hence discarded.
5. Based on above advantages, the significant simplification of the partitioning process, noticeable reduction of quantities of various radioactive wastes, and obvious reduction of the process capital cost are achieved.

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CONCLUSIONS

To overcome the disadvantages of the MAREC process and its modified process, a new GPEC (Group Partitioning of HLW by Extraction Chromatography) process for radionuclides partitioning from HLW was proposed. It consisted of two main sorption columns. In the first column packed with TODGA/SiO_2-P, a simulated HLW was separated to

1. Cs, Ru, and Mo
2. minor actinides (MAs), rear earths (REs) (La-Lu and Y), Sr, and Pd, (MA-RE-Sr-Pd group), and
3. Zr, respectively.

0.05 M DTPA-pH 3.75 was used to elute RE(III) based on the stronger complexation of RE with DTPA compared to TODGA/SiO_2-P. The long-lived MA(III) flowed into the MA-RE-Sr-Pd group due to the similar chemical properties of Nd(III) and MA(III). In the second column packed with CMPO/SiO_2-P, the MA-containing effluent was separated to

1. Sr-Pd, and
2. MA-RE, respectively.

MA(III) was eluted out by water and flowed into the MA-RE group along with heavy Gd(III) and Dy(III). A group partitioning of MA(III) and RE(III) from a simulated HLW was achieved.

Comparing the proposed GPEC process with MAREC process, it was found that

1. the quantity of various eluents used in two sorption columns was reduced significantly. This makes the elution of the long-lived MA(III) from HLW more effective,
2. Sr(II), one of the main heat generators, and a long-lived Pd(II) were recovered in the second column. The special separation of Sr(II) by another novel macroporous silica-based DtBuCH18C6/SiO_2-P will be canceled,
3. Zr(IV) was separated in the first column packed with TODGA/SiO_2-P.The additional column employed to separate Zr(VI) and Mo(VI) from 0.05 M DTPA or 0.5 M $H_2C_2O_4$ will also be discarded. Thus, the simplification of the partitioning process, the significant reduction of the quantities of various radioactive wastes, and a noticeable reduction of the process capital cost were achieved.

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