Synthesis of two novel macroporous silica-based impregnated polymeric composites and their application in highly active liquid waste partitioning by extraction chromatography

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Abstract

Two kinds of novel macroporous silica-based chelating polymeric adsorption materials, TODGA/SiO$_2$-P and CMPO/SiO$_2$-P, were synthesized by impregnating and immobilizing two chelating agents, *N,N,N′,N′*-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphoshine oxide (CMPO), into the pores of SiO$_2$-P particles. To separate minor actinides (MA(III)) such as Am(III) and Cm(III), the adsorption and elution of 13 typically simulated fission products from a 3 M HNO$_3$ were performed. It was found that in the first column packed with TODGA/SiO$_2$-P, all of the simulated elements were separated effectively into four groups: (1) Cs(I), Mo(VI), and the most portion of Ru(III) (non-adsorption group), (2) Sr(II), small portion of Gd(III) and all of light REs(III) (MA–*l*RE–Sr group), (3) most of Gd(III) and all heavy RE(III) (*h*RE group), and (4) Zr(IV), Pd(II), and a little of Ru(III) (Zr–Pd group) by eluting with 3.0 M HNO$_3$, 1.0 M HNO$_3$, distilled water, and 0.5 M H$_2$C$_2$O$_4$, respectively, at 298 K. MA(III) was predicted to flow into the second group along with Nd(III) because of their close adsorption-elution onto TODGA/SiO$_2$-P. In the second column packed with CMPO/SiO$_2$-P, MA–*l*RE–Sr group was separated into (1) Sr(II), (2) middle RE(III) such as Gd(III), Eu(III), Sm(III), and quite small portion of Nd(III) (MA–*m*RE), and (3) light RE(III) such as La(III), Ce(III), and most of Nd(III) by eluting with 3.0 M HNO$_3$ and 0.05 M DTPA-pH 2.0, respectively, at 323 K. MA(III) was believed to flow into MA–*m*RE group along with Gd(III) due to their similar adsorption properties towards CMPO/SiO$_2$-P. Based on positions of MA(III) appeared in light and heavy RE(III), an improved MAREC process for MA(III) partitioning from HLW was proposed.
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1. Introduction

One of the main purposes of unclear spent fuel in reprocessing process is to recover some valuable metals such as uranium and plutonium by well-known Purex process and its modified process employing slat-free forming reductants such as the derivatives of hydroxylamine and hydrazine [1–5]. As a result of reprocessing process, it is unavoidable to produce long-lived minor actinides such as Am(III) and Cm(III) as well as a large quantity of radioactive fission products such as RE(III), Cs(I), Sr(II), and Tc(II–VII) in highly active liquid waste (HLW). Consideration of the adverse impact of these radionuclides on environment, a variety of extraction processes such as TRUEX, UNEX, SETFICS, and SANEX have been developed to separate these radionuclides especially minor actinides from the acidic HLW [6–10]. For this purpose, the variously conventional and newly synthesized organic chelating agents such as octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphoshine oxide (CMPO), 2,6-bis(5,6-dialkyl-1,2,4,-triazine-3-y1)pyridine (R-BTP), and bis(2,4,4-tri-methylpentyl)dithiophosphinic acid (Cyanex 301) etc. have been investigated widely. However, it is well-known that these solvent extraction processes will generate a great amount of organic waste from the hydrolytic and radiolytic degradation of organic extractants and diluents [11,12].

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In addition, a large number of equipments are required for the muti-stage extraction, stripping and solvent-washing processes. A separation technique utilizing a minimal organic solvent and compact equipment is therefore expected for HLW partitioning.

Based on the SETFICS process [13,14], we developed recently an advanced partitioning technology called minor actinides recovery from HLW by extraction chromatography (MAREC) process to separate and recover Am(III) and Cm(III) from HLW using a novel silica-based octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide extraction resin (CMPO/SiO$_2$-P) synthesized by impregnating and immobilizing CMPO into macroporous SiO$_2$-P particles with a mean diameter of 50 μm [15,16]. Two main adsorption columns packed with CMPO/SiO$_2$-P extraction resins are utilized for the chromatographic separation of the elements through selective adsorption and elution procedures. In the first column, the elements can be effectively separated into the following three groups depending on their different adsorption and elution behavior which result from the complexation ability of the metal ions with CMPO and DTPA (diethylenetriaminepentaacetic acid, DTPA) [17]: (1) Cs, Sr, Rh and Ru (non-adsorptive FP); (2) minor actinides (MA), heavy rare earths (*h*RE) (Eu-Lu and Y), Zr, Mo and Pd (noted MA–*h*RE–Zr–Mo); (3) light rear earths (*l*RE). Subsequently, the MA containing effluent is applied to the second column where the elements are separated to (1) Pd, (2) MA–*h*RE, and (3) Zr–Mo, respectively, by using water and 0.5 M H$_2$C$_2$O$_4$ or 0.05 M DTPA-pH 2.0 as eluents [18]. The Zr and Mo containing effluent is capable of separating from 0.5 M H$_2$C$_2$O$_4$ or 0.05 M DTPA by the third column utilizing 3.0 M or 6.5 M HNO$_3$, 0.1 M HNO$_3$, water and 0.5 M H$_2$C$_2$O$_4$ as eluents [19,20]. The resistance behavior of the main adsorbents used in partitioning process against nitric acid, heat, and γ-irradiation was also investigated [21,22].

However, the separation of Sr(II) and Cs(I), the two main heat-generator elements, from the non-adsorptive elements group seems to be unreasonable, in where two columns packed with a novel silica-based 4,4′,(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6/SiO$_2$-P) [23] and a calix[4]arene-*bis*-(*t*-octylbenzo-crown-6) (BOB Calix[4]/SiO$_2$-P) adsorbents are required to employ. Moreover, 0.05 M DTPA-pH 2.0 as an available chelating agent of metal ions is employed both in the first and second columns. This is adverse for effectively reducing the quantity of liquid waste produced in the reprocessing process and the capital cost. The significant reduction of the adsorption columns and the quantity of the eluents employed is much desired. The simplification and optimization of MAREC process is therefore necessary.

Anew diamide-containing extractant titled N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide (TODGA), a neutral chelating agent having the hard-atom oxygen, has been developed recently. It is reported that in the liquid–liquid solvent extraction process, TODGA exhibits strong affinities for many kinds of elements such as actinides(III) and lanthanides(III) in comparison with the older reference diamide such as N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide (DMDBTDMA) [24–27]. However, the application of TODGA-containing polymeric adsorbent in the separation of MA(III), RE(III) or FPs from acidic HLW has been hardly reported [28].

Compared to original MAREC process proposed previously, the main purpose of present work is focused on (1) simplification and optimization of MAREC process to achieve a more appropriate separation of minor actinides and other fission products from the simulated HLW. It can be done by synthesizing two new kinds of novel macroporous silica-based polymeric adsorption materials, TODGA/SiO$_2$-P and CMPO/SiO$_2$-P, utilizing an advanced sucking technique developed recently in our laboratory, and (2) elution of Sr(II) and Cs(I), both heat generators, to different groups to reduce the quantity of additional column used to separate them further. The special separation of Sr(II) from Cs(I) by the third column packed with the highly specific adsorbent DtBuCH18C6/SiO$_2$-P will be discarded. A more reasonable and improved MAREC separation process was proposed.

2. Experimental

2.1. Reagents

Various RE(NO$_3$)$_3$·nH$_2$O (RE = La, Ce, Nd, Sm, Eu, Y and Gd, n = 3 or 6), fission products nitrates (FP = Cs(I), Sr(II), and Zr(IV)), as well as (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were of analytical grade. Ruthenium (III) nitrosyl nitrate solution containing 1.5% of Ru(III) was purchased from the Strem Chemicals, American. Palladium nitrate solution containing 4.5 wt.% of Pd(II) was purchased from Tanaka Noble Metal Co. Inc., Japan. The concentrations of all metal ions used were ~5.0×10^{-3} M. The purity of N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide purchased from Kanto Chemical Co. Inc., Japan was more than 99%. Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphoshine oxide, with a purity greater than 99.5%, was purchased from Hokuko Company of Chemical Industry, Japan. They were used without further purification. The solutions of various concentrations of HNO$_3$ and H$_2$C$_2$O$_4$ as well as the feed solution used were prepared temporarily.

An acidic chelating agent diethylenetriaminepentaacetic acid (DTPA), dichloromethane, methanol, and other reagents were of analytical grade and were used without further treatment. To avoid the precipitate of DTPA in weakly acidic solution, prior to experiment the 0.05 M DTPA-pH 2.0 solution prepared temporarily was heated slightly.

In reprocessing process, fission products (FPs) usually refer to those kinds of reaction products generated by the fission process of uranium, plutonium, or other actinides in nuclear reactors as well as a series of radioactive decay of adjacent species produced from fission reaction. It is known that all of

rare earths, part of transition elements Tc, Mo, Zr, Pd, Pt, Ru etc., some alkali metals and alkaline earths such as Cs, Sr, Ba etc. are fission products.

2.2. Synthesis of silica-based CMPO and TODGA impregnated polymeric materials

The macroporous silica-based chelating polymeric adsorption materials, TODGA/SiO$_2$-P and CMPO/SiO$_2$-P, were synthesized in our laboratory by impregnating organic compound TODGA or CMPO into ~50 μm of macroporous SiO$_2$-P particles, which was synthesized as described previously [23,29], i.e., by a series of polymerization reactions between macroporous SiO$_2$ and a mixture of m/p-divinlbenzene, α,α-azobisisobutyronitrile, 1,1-azobiscyclohexane-1-carbonitrile, m/p-formylstyrene, methylbenzoate, and diotylphthatate utilizing an advanced immobilization technique. P contained in SiO$_2$-P particles refers to the styrene-divinylbenzene copolymer, which was prepared by means of a polymerization reaction taking place inside the macroporous SiO$_2$.

To increase the affinity of copolymer inside of the SiO$_2$-P particles for an organic octyl-(phenyl)-N,N-diisobutylcarbamoylmethylphoshine oxide molecule, prior to synthesis the SiO$_2$-P particles used were mixed with a given quantity of methanol, shaken mechanistically for 60 min, and then separated by filtering. Such a pretreatment procedure was repeated three times. CMPO/SiO$_2$-P polymeric adsorbent was prepared by impregnating the organic CMPO molecule into the pores of the SiO$_2$-P particles through a vacuum sucking technology based on the intermolecular interaction of CMPO and the polymeric compound contained in SiO$_2$-P particles. The synthesis procedure was described as follows:

Ten grams of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphoshine oxide dissolved in 100 cm^3 of dichloromethane and twenty grams of SiO$_2$-P particles pretreated were mixed into a 300 cm^3 of flask and stirred mechanistically for 90 min at room temperature. Subsequently, the mixture was moved into a silicon-oil bath controlled by an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co. Ltd., Japan) and further stirred for about 180 min at ~323 K to impregnate and immobilize octyl(phenyl)-N,N-diisobutylcarbamoylmethylphoshine oxide molecule into the pores of macroporous SiO$_2$-P particles. After drying in a vacuum drying oven at around 323 K for 24 h, the polymeric adsorption material CMPO/SiO$_2$-P was obtained. It was characterized by TG-DSC and elementary analysis, respectively. Its composition (wt.%) was determined as 33.3% CMPO, 11.4% organic copolymer and 55.3% SiO$_2$ substrate, respectively. The schematic diagram of synthesizing CMPO/SiO$_2$-P extraction resin was illustrated in Fig. 1.

In terms of the identical method mentioned above, another polymeric adsorption material used, TODGA/SiO$_2$-P, was synthesized by impregnating and immobilizing TODGA
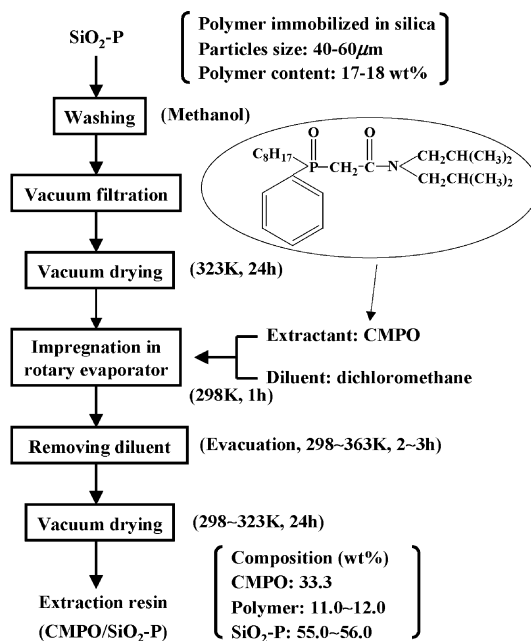

Fig. 1. Schematic diagram of synthesizing silica-based CMPO/SiO$_2$-P polymeric materials.

molecule into the pores of the macroporous SiO$_2$-P particles by the vacuum sucking technique. The related structure and physical properties of TODGA/SiO$_2$-P were listed in Table 1.

2.3. HLW partitioning by extraction chromatography

In group separation operated in the first column, Nd(III) as a light rare earth was used to simulate Am(III) and Cm(III)

Table 1
Structure and physical properties of silica-based TODGA polymeric composite

Organic/inorganic polymeric composite	TODGA/SiO$_2$-P
Chelating functional group	
	Dark brown
Bead diameter	40–60 μm
TODGA content	33% (w/w)
Support of polymeric material	66.7% (w/w) of macroporous SiO$_2$ following copolymer-containing -CH$_2$-CH-CH$_2$-CH-
Appearance	Light yellow powder
Affinity for water or acidic solution	Fine

because of their similar adsorption and elution properties towards TODGA/SiO$_2$-P. Similarly, Gd(III) as a heavy rare earth was used in the second column separation to simulate Am(III) and Cm(III) based on their similar adsorption and elution properties towards CMPO/SiO$_2$-P.

In the improved MAREC partitioning process proposed, both silica-based TODGA/SiO$_2$-P and CMPO/SiO$_2$-P as the polymeric adsorption materials selected were employed to perform the group separation in the main separation engineering of HLW.

Separation experiments for simulated HLW solutions were carried out using a pyrex-glass column with 10 mm in inner-diameter and 300 mm or 500 mm in length. The polymeric adsorption material was packed to the column in the slurry state under 0.3–0.5 MPa of N$_2$ gas pressure. The space of head and end of the column used was adjusted with a mobile plug. The mass, density, and volume of the resin in the column were about 23.5 g, 0.61 g/cm^3, and 38.5 cm^3 for CMPO/SiO$_2$-P as well as about 14.2 g, 0.62 g/cm^3, 22.8 cm^3 for TODGA/SiO$_2$-P. No working pressure was found inside the column because of the silica-based support, which is quite different from the conventional polymer-based support. Prior to 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 323 K by circulating the thermostated water through an EYELANTT-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. After a 3.0 M HNO$_3$ solution containing ∼5.0 × 10^{-3} M of Pd(II), Cs(I), Ru(III), Sr(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Y(III), Mo(VI), and Zr(IV), which were used as feed solution in the first column packed with TODGA/SiO$_2$-P, or ∼5.0 × 10^{-3} M of Sr(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), and Y(III) employed as the feed solution in the second column packed with CMPO/SiO$_2$-P passed through the column, the given volumes of 3.0 M HNO$_3$, 1.0 M HNO$_3$, distilled water, and 0.5 M H$_2$C$_2$O$_4$ as well as 3.0 M HNO$_3$ and 0.05 M DTPA-pH 2.0 as the eluents employed in the first and second columns, respectively, were subsequently pumped down-flow through the column. Effluent fractions were collected by an auto-fractional collector in 10 ml aliquots. The concentrations of various metal ions in effluent were then analyzed.

2.4. Main instrumentation

A SPS-5000 Model inductively coupled plasma-atomic emission spectrometer (ICP-AES, Seiko Co., Japan) was used for analyzing the concentrations of various metal ions in effluent except Cs(I), which was determined using an AA-6800 Model atomic adsorption spectroscopy (Shimadzu, Japan). An EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co. Ltd., Japan) was used to collect effluent fraction. The pH value of fraction effluent was measured using an AUT-301 Model titrator/pH meter (TOA Electronics Ltd., Japan).

3. Results and discussion

3.1. Partitioning of the simulated HLW in the first column packed with TODGA/SiO$_2$-P

The TODGA/SiO$_2$-P adsorbent was newly developed macroporous silica-based adsorption material. To examine the separation behavior of the heavy rare earths, light rare earths, Am(III), Cm(III) and other fission products, a group separation experiment for a simulated HLW solution con-
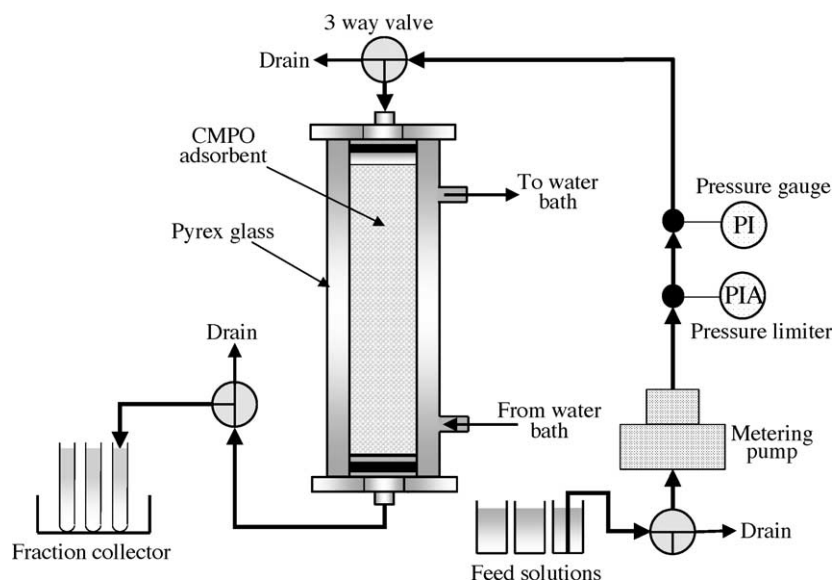

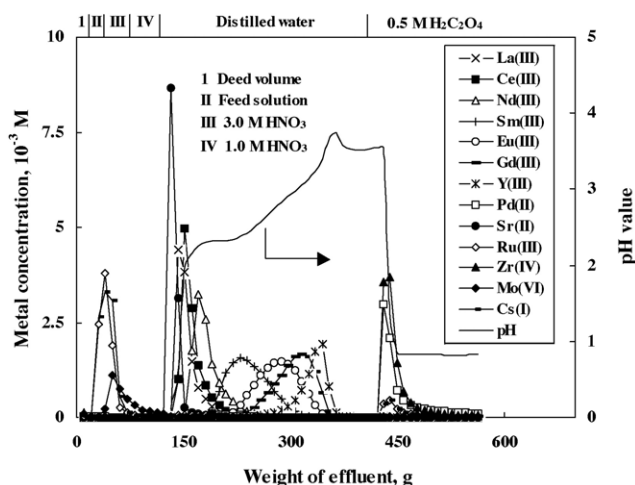Fig. 2. Experimental apparatus of the column chromatographic separation.

Fig. 3. Group separation of $\sim 5.0 \times 10^{-3}$ M typical fission products from a simulated solution of 3.0 M HNO$_3$ by TODGA/SiO$_2$-P packed column eluting with water and 0.5 M H$_2$C$_2$O$_4$ at 298 K.

taining $\sim 5.0 \times 10^{-3}$ M of 13 typically simulated elements Ru(III), Pd(II), Mo(VI), Pd(II), Zr(IV), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Y(III), Cs(I), Sr(II) and 3.0 M HNO$_3$ was performed by the TODGA/SiO$_2$-P adsorbent packed column at 298 K. To ensure effective adsorption of these metal ions, prior to column experiment TODGA/SiO$_2$-P adsorbent used was equilibrated with 3.0 M HNO$_3$. The elution curves of various elements and the pH values in the column chromatography were illustrated in Fig. 3.

Obviously, the fission products Cs(I), Mo(VI), and most portion of Ru(III) showed almost no adsorption towards TODGA/SiO$_2$-P and quickly leaked out column along with the feed solution and the 3.0 M HNO$_3$ washing solution. Subsequently, after eluting with 1.0 M HNO$_3$, with the continuous supplement of distilled water, Sr(II) and all of rare earths adsorbed firmly by TODGA/SiO$_2$-P were eluted out effectively, and the elution order appeared in the elution curves was as follows: Sr(II), light rare earths and heavy rare earths, i.e., Sr(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), and Gd(III). As one special rare earth, Y(III) appeared behind Gd(III). Such an elution order in the elution curves was due to the decomposition of the complexes of these metal elements with TODGA contained in TODGA/SiO$_2$-P with a decrease in the NO$_3^-$ concentration in the resin bed by supplying water to the column. Namely, the elution order depended on the complex stability constants of these metals with TODGA/SiO$_2$-P. Because the stability constant of the complex of rare earth with TODGA increased with an increase in atomic number, i.e., from La(III) to Lu(III), so, the complex stability of the heavy rare earth with TODGA/SiO$_2$-P was higher than that of the light one, which was therefore eluted effectively by distilled water and flowed into effluent before the heavy one. The fission products Zr(IV), Pd(II), and small portion of Ru(III) adsorbed strongly by TODGA/SiO$_2$-P were finally eluted off by 0.5 M H$_2$C$_2$O$_4$. The elution effect was considered to result from the complex formation between these

metals and H$_2$C$_2$O$_4$, while the complexes were not adsorbed by TODGA/SiO$_2$-P.

On the other hand, the pH value in effluent was found to increase rapidly from pH 0.0 (1.0 M HNO$_3$) to around pH 2 and then gradually to below pH 3.8 as distilled water as an eluent was used. Subsequently, the pH value decreased quickly to about pH 0.88 when employing 0.5 M H$_2$C$_2$O$_4$ as an eluent. The fact that in the elution process with distilled water, the pH value in effluent was below pH 3.8 showed that in the adsorption stage of metal onto TODGA/SiO$_2$-P, a part of HNO$_3$ molecule was adsorbed simultaneously by TODGA/SiO$_2$-P adsorbent and probably formed to 1:1 or 1:2 type of the complex, i.e., HNO$_3$·TODGA or HNO$_3$·2TODGA. Regarding the detailed composition of the associated complex of HNO$_3$ and TODGA has not been investigated yet.

The previous studies performed by the batch experiments in our laboratory showed that in HNO$_3$ solution, the adsorption behavior of Am(III) and Cm(III) towards TODGA/SiO$_2$-P was very similar with that of Nd(III) [28], a light rare earth. The preliminary results obtained recently also indicated that the elution property of Am(III) and Cm(III) from the loaded TODGA/SiO$_2$-P was close to Nd(III). So, in this experiment, it is predicted that Am(III) and Cm(III) will be eluted effectively by distilled water and flowed into effluent along with Nd(III).

From the above results and discussions, it was found obviously that all the tested elements contained in the simulated HLW could be separated into four groups: (1) non-adsorption elements such as Cs(I), Ru(III), and Mo(VI) (noted as non-adsorption group); (2) Sr(II) and light RE(III) such as La(III), Ce(III), Nd(III), a part of Sm(III) and Eu(III) as well as a quite small portion of Gd(III) (noted as MA–*l*RE–Sr group); (3) heavy RE(III) such as the most portion of Gd(III) and Y(III) (noted as *h*RE group); and (4) fission products such as Zr(IV), Pd(II), and a small portion of Ru(III) (noted as Zr–Pd group). Based on the close adsorption and elution of Am(III) and Cm(III) with Nd(III), Am(III) and Cm(III) were believed to be separated into the second group.

3.2. Separation of MA–lRE–Sr in the second column packed with CMPO/SiO$_2$-P

Previous batch experimental studies showed that in 3.0 M HNO$_3$ medium, the adsorption effect of all of the tested metal ions towards CMPO/SiO$_2$-P adsorbent at 323 K was much better than at 298 K. Moreover, the quantity of CMPO leaked from CMPO/SiO$_2$-P, ~ 36 ppm, at 323 K was also obviously lower than that of ~ 48 ppm at 298 K. Such the results in the adsorption of metal and the leakage of CMPO were helpful for selecting the optimum operation conditions in the second column packed with CMPO/SiO$_2$-P. The temperature, 323 K, was therefore selected to employ in this experiment.

To understand the separation behavior of MA–*l*RE–Sr group obtained in the first column packed with TODGA/SiO$_2$-P, the adsorption and elution of a simulated MA–*l*RE–Sr solution containing $\sim 5.0 \times 10^{-3}$ M of Sr(II), La(III),
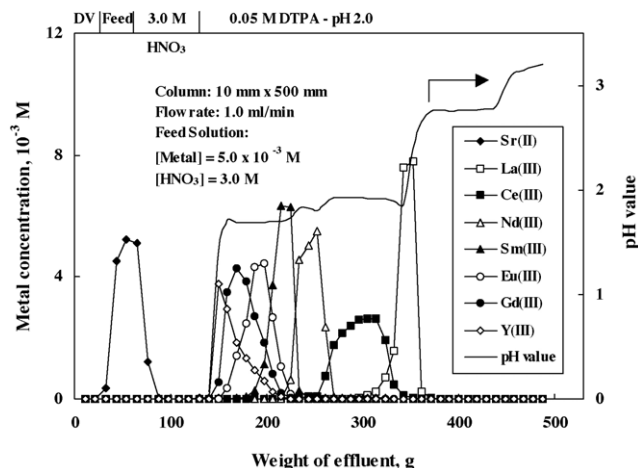
Fig. 4. Separation results of MA–*l*RE–Sr from a 3.0 M HNO₃ solution by CMPO/SiO₂-P polymeric adsorption material packed column utilizing distilled water as an eluent at 323 K.

Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), and Y(III) were performed by CMPO/SiO₂-P packed column at 323 K. Prior to experiment the concentration of HNO₃ in the MA–*l*RE–Sr feed solution was conditioned to 3.0 M to increase the adsorption ability of metal ions towards CMPO/SiO₂-P. The column dimension used was 10 mm in inner-diameter and 500 mm in length. The elution results and the corresponding pH value determined in effluent were illustrated in Fig. 4.

As can be seen, fission product Sr(II) showed no adsorption onto CMPO/SiO₂-P. It leaked out the column quickly and flowed into the effluent along with the feed solution and 3.0 M HNO₃. So, the divalent element Sr(II), one of the main heat generators in HLW, was easily separated in this stage.

On the other hand, it was well-known that CMPO, a bifunctional neutral organophosphorus compound, could extract all of trivalent actinide and lanthanide elements from HNO₃ medium by the following equation:

$$M^{3+} + 3CMPO + 3NO_3^- \leftrightarrow M(NO_3)_3 \cdot 3CMPO$$

$$(M = RE, \ Am, \ Cm, etc.) \qquad (1)$$
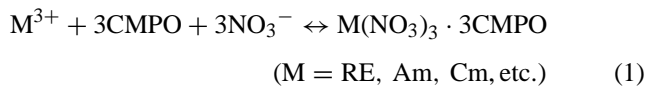
So, it was believed that in the second column, RE(III) and MA(III) contained in the simulated MA–*l*RE–Sr solution were adsorbed strongly towards CMPO/SiO₂-P as the following reaction:

$$M^{3+} + 3NO_3^- + \frac{3CMPO}{SiO_2} - P \leftrightarrow RE(NO_3)_3 \cdot \frac{3CMPO}{SiO_2} - P$$
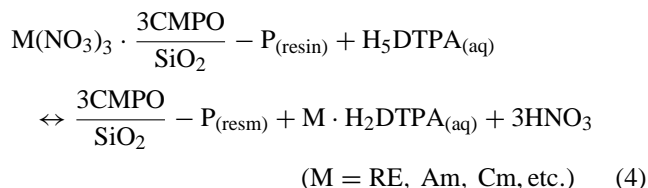
$$(M = RE, \ Am, \ Cm, etc.) \qquad (2)$$
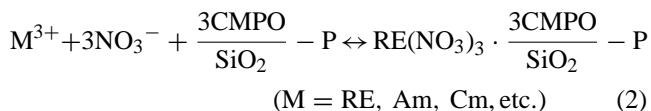
Moreover, diethylenetriaminepentaacetic acid, a multidentate acidic chelating agent containing five carboxyl and three amine groups capable of being protonated, was a pentabasic acid and the acidic dissociation constants at 293 K were reported to be $pK_1 = 1.80$, $pK_2 = 2.55$, $pK_3 = 4.33$, $pK_4 = 8.60$, and $pK_5 = 10.58$ [30], respectively. It had five different species in a wide pH range. Many experimental results

indicated that in a weak and/or middle acidic solution, DTPA could form a series of 1:1 types of quite stable coordination compounds with actinides and lanthanides according to the following reaction [13,31]:

$$M^{3+} + H_5DTPA \leftrightarrow M \cdot H_2DTPA + 3H^+ \qquad (3)$$

Therefore, the adsorbed RE(III) and MA(III) with CMPO/SiO₂-P could be eluted out effectively by DTPA through the following dynamic interconversion reaction between the complexes:

$$M(NO_3)_3 \cdot \frac{3CMPO}{SiO_2} - P_{(resin)} + H_5DTPA_{(aq)}$$

$$\leftrightarrow \frac{3CMPO}{SiO_2} - P_{(resm)} + M \cdot H_2DTPA_{(aq)} + 3HNO_3$$

$$(M = RE, \ Am, \ Cm, etc.) \qquad (4)$$

where subscripts (resin) and (aq) denote the resin phase and aqueous phase, respectively.

As can be seen, with the supplement of 0.05 M DTPA-pH 2.0 to the column, the adsorbed RE(III) onto CMPO/SiO₂-P was complexed efficiently by 0.05 M DTPA and eluted out column, showing an elution order in the elution curves as: Y(III), Gd(III), Eu(III), Sm(III), Nd(III), Ce(III), and La(III). Namely, heavy RE(III) firstly appeared in effluent and then the light one. The elution effect was considered to result from the strongly complex interconversion reaction of substituting RE(III)-DTPA for RE(III)-CMPO based on the different stability constants of the complexes of these metal ions with CMPO and DTPA. The elution order depended strongly on the ability of the complex formation between RE(III) with the ligand DTPA. Since the stability constants of the complexes formed between DEPA and various RE(III) especially the heavy one were very high [30,31], so, the heavy RE(III) was firstly eluted and appeared in the effluent.

The stability constants of the complexes of some minor actinides and DTPA, $\log K_s = -22.92$ for Am(III), $\log K_s = -22.99$ for Cm(III), $\log K_s = -22.79$ for Bk(III), $\log K_s = -22.57$ for Cf(III), $\log K_s = -22.62$ for Es(III), and $\log K_s = -22.70$ for Fm(III) [30], were reported to very similar to those of heavy rare earths especially from Gd(III) to Dy(III). Moreover, our previous studies showed that the adsorption and elution of Am(III) and Cm(III) towards CMPO/SiO₂-P almost consisted with that of Gd(III) [32]. It was therefore assumed that in this experiment, Am(III) and Cm(III) as the representatives of the minor actinides could be eluted out efficiently by 0.05 M DTPA-pH 2.0 and flowed into effluent along with Gd(III) either in theoretical or in practice. Since Sr(II), La(III), Ce(III), and the most of Nd(III) contained in the simulated MA–*l*RE–Sr solution were separated effectively before and after Gd(III), respectively, so, in the finally resulting Am(III) and Cm(III)-containing effluent only contained some middle RE(III) elements such as Gd(III), Eu(III), Sm(III), and quite small portion of Nd(III).

From above results, this experiment demonstrated that the elements contained in the simulated MA–*l*RE–Sr solution

were successfully separated into three groups: (1) Sr(II); (2) Am(III), Cm(III), and some middle RE(III) elements such as Gd(III), Eu(III), Sm(III) and a small portion of Nd(III) (noted as MA–*m*RE), and (3) light RE(III) such as La(III), Ce(III), and the most portion of Nd(III) (noted as *l*RE).

The change of pH value in effluent was in the range of 0–3. With an increase in 0.05 M DTPA-pH 2.0, the pH value of effluent increased quickly to around pH 1.8 and then slowly increased to about pH 2. Such a slow change in the pH value showed that in the elution process, because of the complexation of RE(III) and 0.05 M DTPA, a lot of H$^+$ was released according to Eq. (4), showing that RE(III) adsorbed strongly onto CMPO/SiO$_2$-P was eluted off effectively by 0.05 M DTPA-pH 2.0. The elution of HNO$_3$ molecule associated with CMPO/SiO$_2$-P in the form of 1:1 or 1:2 type of the complex [33,34], i.e., HNO$_3$·CMPO/SiO$_2$-P or HNO$_3$·2CMPO/SiO$_2$-P, was probably another reason.

3.3. An improved MAREC process

Based on the above results obtained, an improved MAREC process for minor actinides partitioning from the acidic HLW by extraction chromatography was proposed as illustrated in Fig. 5. As the main separation engineering, it consisted of two main separation columns packed with TODGA/SiO$_2$-P in the first column and CMPO/SiO$_2$-P in the second column, respectively.

In comparison with MAREC process developed previously, the improved MAREC process had the follow-ing 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) were eluted off effectively only by distilled water. The highly specific chelating agent 0.05 M DTPA-pH 2.0 used to elute RE(III) and MA(III) from the loaded CMPO/SiO$_2$-P in terms of the different stability constants of the complexes of these metals with CMPO and DTPA was cancelled. (2) Radioactive Sr(II), one of the main heat generators, could be separated and recovered efficiently in the second column packed with CMPO/SiO$_2$-P. The additional adsorption column for the special separation of Sr(II) by DtBuCH18C6/SiO$_2$-P and Sr-resin was no more needed and was thus cancelled. Such an effective separation of Sr(II) in the improved MAREC process provided a new pathway for eliminating Sr(II) from HLW. (3) Radioactive Cs(I), another main heat generator, was more easily separated from the non-adsorption group obtained in the first column only by employing BOB Calix[4]/SiO$_2$-P packed column, in where the effect of Sr(II) on the partitioning of Cs(I) was negligible. (4) In the final Am(III) and Cm(III)-containing products only contained a few middle RE(III) elements such as Gd(III), Eu(III), Sm(III), and small portion of Nd(III). This will result in an easy separation of minor actinides from the resultant MA–*m*RE by another silica-based HDEHP/SiO$_2$-P polymeric adsorption materials in next step. (5) Based on the significant simplification of the separation process, to minimize the volume of radioactive waste liquid and reduce noticeably the process capital cost was quite promising.
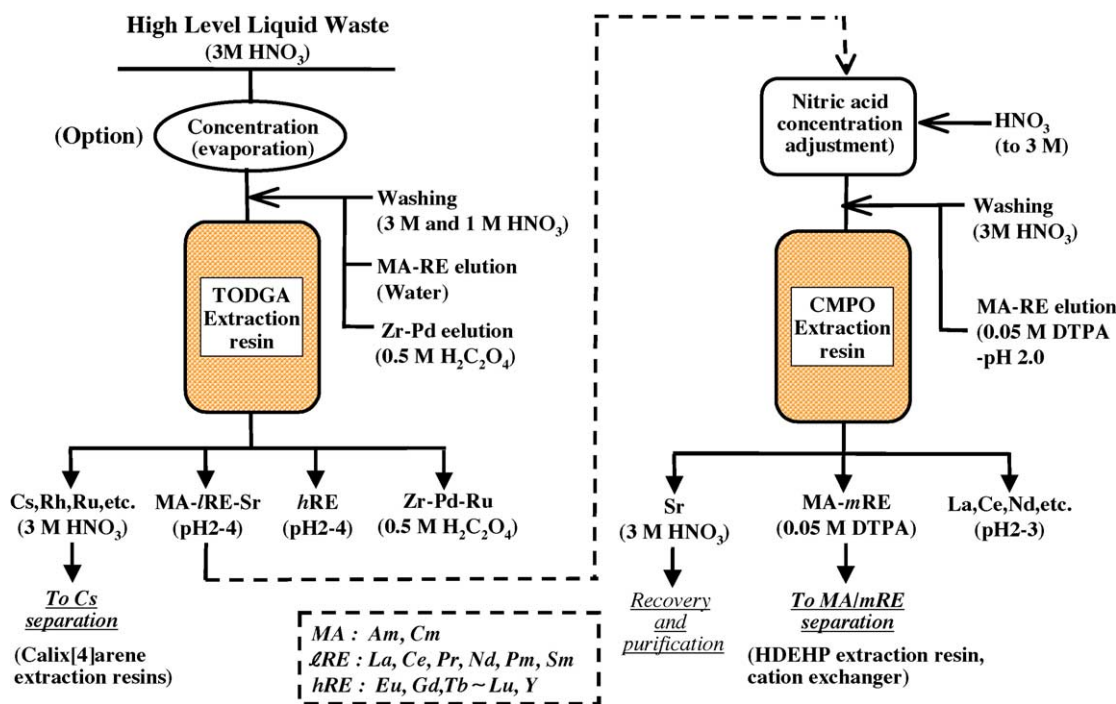

Fig. 5. Improved MAREC process for radionuclides partitioning from HLW by some novel macroporous silica-based extraction chromatography.

4. Conclusions

To minimize the long-term radiological risk and facilitating the management of HLW, significant reduction of the quantity of radioactive waste in reprocessing process is much desirable. For this purpose, an improved MAREC process for minor actinides partitioning from HLW by extraction chromatography with some novel adsorbents was proposed.

The main separation engineering in the improved MAREC process consisted of two columns. In the first column packed with TODGA/SiO$_2$-P, all of the simulated elements were separated into (1) non-adsorption group such as Cs(I), Sr(II), and Ru(III) etc., (2) MA–*l*RE–Sr group, (3) *h*RE, and (4) Zr–Pd group, respectively, at 298 K. MA(III) was predicted to flow into the second group along with Nd(III) because of their similar adsorption properties onto TODGA/SiO$_2$-P. In the second column packed with CMPO/SiO$_2$-P, the simulated elements contained in MA–*l*RE–Sr effluent were separated into three group: (1) Sr, (2) MA–*m*RE, and (3) *l*RE such as La(III), Ce(III), and a little of Nd(III), respectively, at 323 K. Since only a few RE(III) elements contained in the resultant MA–*m*RE product, MA(III) was easily separated by another silica-based adsorbent in next step.

Compared to MAREC process, the improved MAREC process is simplified significantly. Moreover, the separation effect of MA(III) from HLW is much better and the quantity of waste liquid produced in the process decreased evidently. Sr(II), one of the heat generators, is separated simultaneously in the second column packed with CMPO/SiO$_2$-P. The use of an additional column packed with DtBuCH18C6/SiO$_2$-P adsorbent to specially separate Sr(II) from HLW will be discarded.

Acknowledgment

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