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SPEC: A New Process for Strontium and Cesium Partitioning Utilizing Two Macroporous Silica-Based Supramolecular Recognition Agents Impregnated Polymeric Composites

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Abstract: To effectively separate two heat generators Cs(I) and Sr(II) from a highly active liquid waste (HLW), two macroporous silica-based polymeric composites (Calix[4]arene-R14 + M)/SiO_2-P and (DtBuCH18C6 + M)/SiO_2-P were synthesized. It was done by impregnating and immobilizing the supramolecular recognition agent, 1,3-[(2,4-diethylheptyl ethoxy)oxy]-2,4-crown-6-calix[4] arene (Calix[4]arene-R14) or 4,4′,(5′)-di-(*tert*-butylcyclo hexano)-18-crown-6 (DtBuCH18C6), into the pores of the macroporous SiO_2-P particles with a mean diameter of 50 μm. It was found that in the first column packed with (Calix[4] arene-R14 + M)/SiO_2-P, all of the tested elements were effectively eluted and separated into two groups: (1) Na(I), K(I), Sr(II), Ba(II), Rh(III), Ru(III), Pd(II), Zr(IV), RE(III) (La-Lu and Y), and Mo(VI) (Sr-containing group), and (2) Cs(I)-Rb(I) (Cs-group) by eluting with 4.0 M HNO_3 and water, respectively, at 298 K. The heat emitting element Cs(I) flowed into the second group along with Rb(I), while Sr(II) showed no sorption and flowed into the Sr-containing group. In the second column packed with (DtBuCH18C6 + M)/SiO_2-P, the Sr-containing group was separated into (1) Na(I), K(I), Rh(III), Ru(III), RE(III) (La-Lu and Y), Pd(II), Zr(IV), and Mo(VI) (non-sorption group), and (2) Sr(II)-Ba(II) (Sr-group), by eluting with 2.0 M HNO_3 and water, respectively. The heat emitting element Sr(II) adsorbed by (DtBuCH18C6 + M)/SiO_2-P flowed into the second group along with Ba(II). Based on the results, a new process entitled SPEC (Strontium/Cesium Partitioning from HLW by Extraction Chromatography) for

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heat generator partitioning from a simulated highly active liquid waste utilizing two macroporous silica-based supramolecular recognition composites has been developed.

Keywords: Chromatographic partitioning, heat generator, highly active liquid waste, silica-based polymeric composite, supramolecular compound

INTRODUCTION

The heat emitting elements ^{137}Cs with a half-life of 30 yr and ^{90}Sr with a half-life of 28.5 yr are the main fission products (FPs) contained in highly active liquid waste (HLW), which is produced in the Purex and its modified reprocessing processes of nuclear spent fuel. It is reported that they are harmful for the vitrification of HLW in final geological disposal. Especially, they can pose a serious radiation hazard to health and environment. On the other hand, as both ^{137}Cs and ^{90}Sr are β-emitters, they are used as the sources of β-radiation and energy generators. Consideration of the environment protection and resource reuse, effective partitioning and recovery of Cs and Sr from an acidic HLW to a great extent is required. However, this task has always been a challenging work.

A few liquid-liquid solvent extraction processes such as SREX (1–3), CSSX (4,5), CCCSX (6), and UNEX (7–9) etc. have been developed for removal of Cs(I) and Sr(II) utilizing a few highly specific extractants containing special chelating functional groups. In these chelating agents, some macrocyclic crown ether and supramolecular calixarene-crown containing agents such as 4,4′,(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) and calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOB CalixC6) showed high extraction selectivity for Sr(II) and Cs(I) over the other tested elements (10–13).

Extraction chromatography is one of the effective separation techniques, wherein an inert support is impregnated with an organic extractant, either alone or in combination with a suitable diluent, to produce a solid sorbent capable of selectively removing certain metal ions from aqueous solution. It provides an effective mean by which the separation and preconcentration of any of a variety of radionuclides can be accomplished. Extraction chromatography combines the selectivity of solvent extraction process with the simplicity and multistage character of column chromatographic system. This allows the use of much simpler equipment, easier materials handling, and reduced capital cost in the construction of process equipment compared to liquid-liquid solvent extraction. Moreover, extraction chromatography can significantly reduce the amount of liquid and solid wastes in processing highly radioactive solutions and the harmful impact of radioactive waste on green environment. It is therefore beneficial to the application in extraction chromatographic partitioning of the long-lived minor actinides and some specific fission products in reprocessing process.

The macroporous silica-based polymeric composite is a novel kind of the adsorption material. Compared to the conventional polymeric matrix resins, the macroporous silica-based types of extraction resins showed rapid sorption-elution kinetics, high mechanical strength, and significantly lower pressure loss in a packed column.

An advanced partitioning technology entitled MAREC process (Minor Actinides Recovery from HLW by Extraction Chromatography) has been developed to recover Am and Cm from HLW using a novel macroporous silica-based octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO/SiO_2-P) extraction resin (14–17). Two main sorption columns packed with CMPO/SiO_2-P are utilized for the separation of the tested metals through selective sorption and elution procedures. In the first column, the elements can be effectively separated into the following three groups depending on their different sorption and elution behavior which result from the complexation ability of the metal ions with CMPO and diethylenetriaminepentaacetic acid (DTPA):

1. Non-adsorptive FP group;
2. MA-*h*RE-Zr-Mo group;
3. *l*RE group.

Then, the MA containing effluent is applied to the second one where the elements are separated to (1) Pd, (2) MA-*h*RE, and (3) Zr-Mo, respectively, by using water and 0.5 M $H_2C_2O_4$ or 0.05 M DTPA-pH 2.0 as eluents. In addition, a series of fundamental investigations related to the MA and other special fission products were carried out (18,19).

To separate Cs(I) and Sr(II) effectively from the non-adsorptive FP group in the MAREC process, the object of the present work is focused on

1. Perfection of the MAREC process to achieve a more satisfactory separation of Cs(I) and Sr(II) from HNO_3 solution containing the similarly simulated elements in the chemical properties. It can be done through synthesizing two novel macroporous silica-based 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) and DtBuCH18C6 impregnated polymeric composites, (Calix[4]arene-R 14 + M)/SiO_2-P and (DtBuCH18C6 + M)/SiO_2-P, utilizing an advanced sucking technique developed recently, and
2. Elution and partitioning of Sr(II) and Cs(I), both heat generators, from the loaded sorbents, while significant reduction of the quantity of liquid and solid waste.

The special separation of Sr(II) from Cs(I) by the third column packed with the highly specific sorbent TODGA(N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide)/SiO_2-P will be discarded. An advanced chromatographic partitioning technique entitled SPEC (Strontium/Cesium Partitioning from HLW by Extraction Chromatography) process was proposed.

EXPERIMENTAL

Reagents

Chemical regents such as alkali metals nitrates $M^{I}NO_3$ (M^{I} = Na, K, Rb, and Cs), $M^{II}(NO_3)_2$ (M^{II} = Sr and Ba), $ZrO(NO_3)_2 \cdot 2H_2O$, $RE(NO_3)_3 \cdot nH_2O$ (RE = Y, La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Lu, $n = 3$ or 6), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ employed were of analytical grade or better. Ruthenium nitrosyl nitrate solution with 1.5 wt% of Ru(III) was provided by the Strem Chemicals, the United States of America. Palladium nitrate solution with 4.5 wt% of Pd(II) was provided by the Tanaka Noble Metal Co. Inc., Japan. The concentrations of all the tested elements were about 5.0×10^{-3} M.

A macrocyclic derivative of crown ethers, 4,4′,(5′)-di (*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) with a purity greater than 97% was provided by Eichrom Technologies Inc., the United States of America. A macrocyclic supramolecular recognition agent, 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) with a purity greater than 97% and a molecular weight of 1023, was provided by the Innovation & Chimie Fine, France. It is a colorless solid and is easy to dissolve in organic solvent like dichloromethane and acetone at room temperature. The Kanto Chemical Co., INC, Japan provided tri-*n*-butyl phosphate (TBP) with a purity more than 98%, which was used specially as a molecular modifier of Calix[4]arene-R14. *n*-Octanol was used to modify DtBuCH18C6. The purpose is to significantly reduce the bleeding of the silica-based DtBuCH18C6 polymeric adsorbent.

The novel macroporous inorganic/organic polymeric composite, (Calix[4]arene-R14 + M)/ SiO_2-P, was synthesized in our laboratory. The silica-based SiO_2-P particles support employed were prepared as described previously (20,21). A symbol "P" in the SiO_2-P particles means the styrene-divinylbenzene copolymer, which was prepared through a series of polymerization reactions taking place inside the macroporous SiO_2-substrate.

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

Synthesis of the Macroporous Silica-Based Polymeric Composite

The macroporous silica-based (Calix[4]arene-R14 + M)/SiO_2-P or (DtBu CH18C6 + M)/SiO_2-P polymeric composites used was prepared by impregnating the supramolecular compound Calix[4]arene-R14 or DtBuCH18C6 into the macroporous SiO_2-P particles support with a mean diameter ~50 μm, which was synthesized the polymerization reaction between the macroporous SiO_2 microball and an organic mixture consisted of m/p-divinylbenzene, diotylphthatate, methylbenzoate, α,α-azobisisobutyronitrile, m/p-formylstyrene, and 1,1-azobis-cyclohexane-1-carbonitrile by a vacuum sucking technique developed recently. The impregnation and immobilization of Calix[4]arene-R14 or DtBuCH18C6 into the SiO_2-P particles was based on the intermolecular interaction between Calix[4]arene-R14 or DtBuCH18C6 molecule with polymeric compounds contained in the SiO_2-P particles.

The styrene-divinylbenzene copolymer of high molecular weight inside the macropores of the SiO_2-P particles is a kind of non-polar compound. It has very low reactivity with other organic compounds. Therefore, prior to synthesis of polymeric material, the macroporous SiO_2-P particles used were pretreated actively by methanol and acetone respectively for several times at room temperature to increase significantly its affinity. After shaking mechanically for 60 min and filtering through a membrane quartz-filter of 0.45 μm pore, the resultant product was then dried in vacuum drying oven at 323 K for 24 h.

The synthesis procedure of (DtBuCH18C6 + M)/SiO_2-P was described as follows: a mixture of DtBuCH18C6 and its modifier *n*-octanol (noted as M) dissolved by dichloromethane and the given amount of the activated SiO_2-P particles were mixed into a 500 mL of conical flask. Then it was stirred mechanically for 100 min at room temperature. The organic compound of small molecular weight *n*-octanol (TBP, *n*-butanol, or dodecane) was used as the molecular modifier being capable of improving significantly the affinity of DtBuCH18C6 for copolymer inside the SiO_2-P particles. Then, it was moved into a silicon-oil bath and further stirred at ~323 K for 200 min. The purpose was to impregnate and immobilize DtBuCH18C6 and its molecular modifier into the pores of the SiO_2-P particles. The operation temperature in the synthesis process was kept using an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co. Ltd., Japan). The impregnation of DtBuCH18C6 and its molecular modifier into the pores of SiO_2-P particles was continued until almost all of organic solvent was evaporated. Following drying in a vacuum drying oven at 323 K overnight, a novel kind of silica-based macroporous inorganic/organic polymeric composite, a colorless (DtBuCH18C6 + M)/SiO_2-P, was obtained.

It was then characterized by TG-DSC, elementary analysis, and others, respectively.

Similar to the synthesis of (DtBuCH18C6 + M)/SiO_2-P, another macroporous silica-based supramolecular recognition polymeric composite, (Calix[4]arene-R14 + M)/SiO_2-P, was prepared by impregnation and immobilization of Calix[4]arene-R14 molecule and its modifier TBP (*n*-octanol, *n*-butanol, or dodecane) into the pores of ~50 µm of the activated SiO_2-P particles using the vacuum sucking technique at 323 K. The schematic diagram of (DtBuCH18C6 + M)/SiO_2-P synthesis is shown in Fig. 1. The related structure and physical properties are listed in Table 1. The SEM photos of SiO_2-P, (DtBuCH18C6 + M)/SiO_2-P, and (Calix[4]arene- R14 + M)/SiO_2-P are shown in Fig. 2.

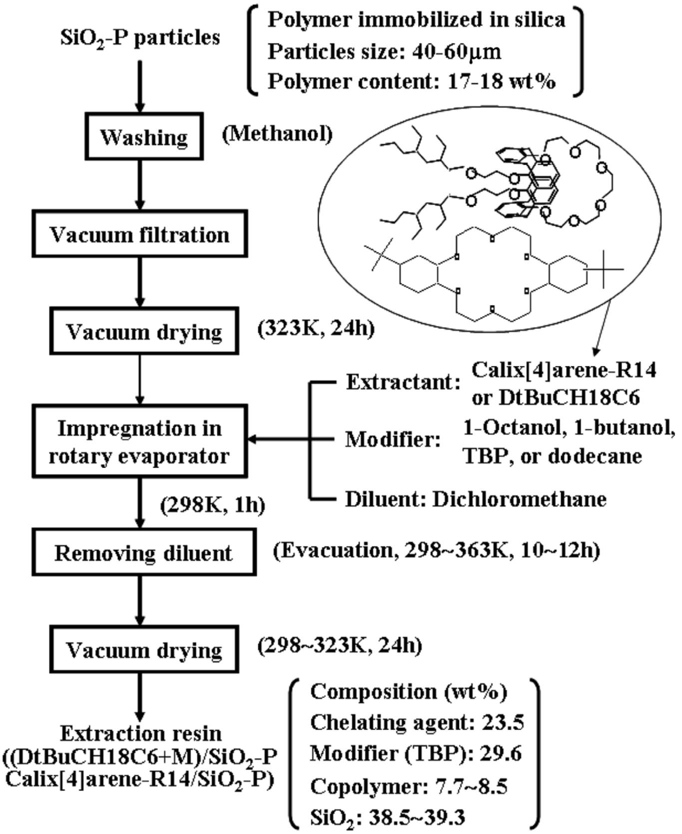
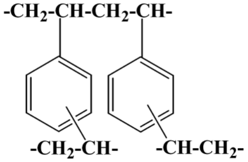


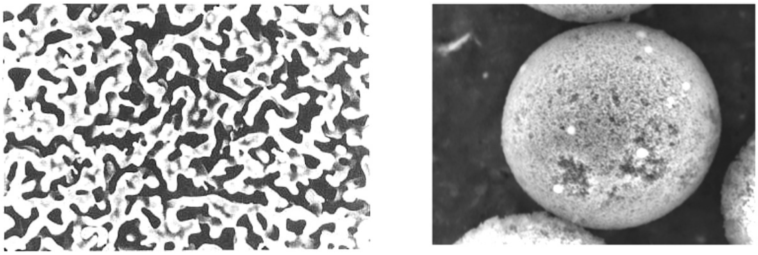
Figure 1. Synthesis of the novel macroporous silica-based Calix[4]arene-R14 or DtBuCH18C6 impregnated polymeric composite modified by a water-soluble reagent 1-octanol (TBP, 1-butanol, or dodecane).

Table 1. Structure and physical properties of the more novel silica-based macroporous Calix[4]arene-R14 or DtBuCH18C6 impregnated polymeric composites

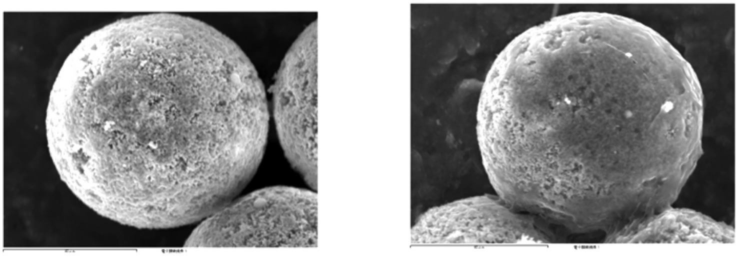
Macroporous organic/Inorganic polymeric composite	(DtBuCH18C6 + M)/SiO_2-P or (Calix[4]arene-R14 + M)/SiO_2-P
Chelating functional group	1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]are (Calix[4]arene-R14) or 4,4′,(5′)-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6)
Pore fraction	0.69
Mean pore size	0.6 μm
Bead diameter	40–60 μm
Molecular modifier	1-Octanol (TBP, 1-butanol, or dodecane).
Support of polymeric material	Macroporous SiO_2 particles modified by following inert copolymer-containing compound 
Appearance	Colorless powdered micro-ball
Affinity for water or acidic solution	Good

Adsorption of Metals onto (Calix[4]arene-R14 + M)/SiO_2-P

The adsorption of the tested metals towards (Calix[4]arene-R14 + M)/SiO_2-P performed by batch experiment was carried out at 298 K, which was controlled by a TAITEC MM-10 Model thermostated water bath. A 5 mL of HNO_3 solution containing the tested metals such as Na(I), K(I), Rb(I), Cs(I), Sr(II), and La(III) as an aqueous phase and the weighed amount of (Calix[4] arene-R14 + M)/SiO_2-P as a solid phase were mixed into a 50 mL of ground glass-stopped flask, and shaken mechanically at 120 rpm for a designed contact time. The HNO_3 concentration in aqueous phase was in the range of 1.0–6.0 M. The concentration of the tested metals and the ratio of the solid phase to the aqueous phase were $\sim 5.0 \times 10^{-3}$ M and 0.25 g/5 mL. After the phase separation through a membrane filter with ~0.45 μm pores, the concentrations of various metals in the aqueous phase were measured using a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, Inc., the United States of America) and a Varian



(a) Inner micrograph of SiO_2-P support (b) SEM micrograph of SiO_2-P support



(c) SEM of (DtBuCH18C6+M)/SiO_2-P (d) SEM of (Calix[4]arene-R14+M)/SiO_2-P

Figure 2. The micrograph of the macroporous SiO_2-P particles support, the novel silica-based (DtBuCH18C6 + M)/SiO_2-P and (Calix[4]arene-R14 + M)/SiO_2-P polymeric composites.

AA 240 FS Model atomic adsorption spectroscopy (Varian, Inc., the United States of American). The distribution coefficient (K_d) of the tested metals towards (Calix[4]arene-R14 + M)/SiO_2-P polymeric material was calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} (mL/g) \tag{1}$$

Where, C_o and C_e represent the initial and equilibrium concentration of metal in aqueous phase, respectively. W and V denote the weight of dry (Calix[4]arene-R14 + M)/SiO_2-P and the volume of the aqueous phase used in the experiments.

Partitioning of Cs(I) by Extraction Chromatography

The partitioning performance test carried out in the present work was focused on the resultant non-adsorption group obtained in the first column in the MAREC process, wherein all of the long-lived minor actinides were already separated beforehand by two columns both packed with CMPO/SiO_2-P polymeric composite. In the non-adsorption group, heat generators Cs(I) and Sr(II) and other fission products (FPs) only are contained.

Chromatographic separation experiment of Cs(I) by (Calix[4]arene-R14 + M)/SiO_2-P from other FPs was carried out using a Pyrex-glass column with 10 mm in inner-diameter and 320 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 the head and the end of the column used was adjusted with a mobile plug. The mass, density, and volume of the adsorbent in the column was about 14.2 g, 0.62 g/mL, and 22.8 mL. No significant pressure drop was found through the adsorption column due to the silica-based support, which is obviously different from the conventional polymer-based one. Prior to the separation experiment a given quantity of dry (Calix[4]arene-R14 + M)/SiO_2-P pre-equilibrated with a 4.0 M HNO_3 solution was packed into the column. A constant temperature used in the adsorption and elution cycle was kept at 298 K by the circulation of the thermostated water through an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co. Ltd., Japan). The flow rate was controlled to 1.0 mL/min. The HNO_3 concentration used in feed solution was 4.0 M HNO_3.

Following a known quantity of solution containing 5.0×10^{-3} M of Ru(III), Rh(III), Ba(II), Na(I), K(I), Rb(I), Sr(II), Cs(I), Mo(VI), Zr(IV), Pd(II), and 4.0 M HNO_3, which were used as feed solution in the alkali metals and fission products effect experiment, or 5.0×10^{-3} M of La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III), Yb(III), Lu(III), Cs(I), and 4.0 M HNO_3 used as feed solution in the rare earths effect experiment passed through the column, the given volumes of 4.0 M HNO_3 and H_2O as eluents were subsequently pumped down-flow through the column. An EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co. Ltd., Japan) was used to collect effluent fractions in 5 mL or 10 mL aliquots. The concentrations of the tested metal ions in effluent were analyzed using the Varian 700-ES ICP-OES, Agilent 7500 series ICP-MS, or Varian AA 240 FS Model atomic adsorption spectroscopy mentioned above. The corresponding pH value in fraction effluent was measured using an AUT-301 Model titrator/pH meter (TOA Electronics Ltd., Japan).

Partitioning of Sr(II) by Extraction Chromatography

Prior to the partitioning experiment the HNO_3 concentration in the resultant effluent containing Sr(II) and other tested metals was conditioned to 2.0 M HNO_3 with the concentrated nitric acid. Then the weighed amount of the (DtBuCH18C6 + M)/SiO_2-P polymeric composite equilibrated with 2.0 M HNO_3 was packed into the Pyrex glass column with 10 mm in inner-diameter and 200 mm in length with the same method described above. The flow rate, the concentrations of the tested metal ions, and other experimental conditions were the same with that of the Cs(I) separation procedure.

When a 2.0 M HNO_3 feed solution containing 5.0×10^{-3} M of Rh(III), Zr(IV), Na(I), K(I), Cs(I), Sr(II), Ba(II), Ru(III), Mo(VI), and Pd(II), which were used as feed solution in the fission products effect experiment, or 5.0×10^{-3} M of La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III), Sr(II), and Lu(III) employed as feed solution in the rare earths effect experiment passed through the column, the given volumes of 2.0 M HNO_3 and H_2O as eluents were subsequently pumped down-flow through the loaded (DtBuCH18C6 + M)/SiO_2-P. 5 mL aliquot of effluent fraction was collected. The concentrations of the tested metals in the effluent were analyzed by the ICP-OES, ICP-MS, or atomic adsorption spectroscopy mentioned above. The pH value in effluent was also measured.

RESULTS AND DISCUSSION

Adsorption Behavior of (Calix[4]arene-R14 + M)/SiO_2-P

Our previous results showed that Calix[4]arene-R14 had supramolecular recognition ability for alkali metal Cs(I) (22). To understand the adsorption property of the novel macroporous silica- based (Calix[4]arene-R14 + M)/SiO_2-P polymeric composite, the static-state adsorption behavior of a few representative elements Na(I), K(I), Rb(I), Cs(I), Sr(II), and La(III) towards (Calix[4]arene-R14 + M)/SiO_2-P was investigated at 298 K. It was performed at the HNO_3 concentration range of 1.0–6.0 M, shaking speed of 120 rpm, phase ratio of 0.25 g/5 mL, and contact time of 180 min. The results are shown in Fig. 3.

As can be seen, with an increase in the HNO_3 concentration, heat generator Cs(I) showed obvious adsorption towards (Calix[4]arene-R14 + M)/SiO_2-P. The Cs(I) adsorption increased quickly from 1.0 M to 3.0 M HNO_3, slowly increased to 4.0 M HNO_3, and then decreased to 6.0 M HNO_3. The optimum adsorption acidity was 4.0 M HNO_3. The effective adsorption of (Calix[4]arene-R14 + M)/SiO_2-P for Cs(I) resulted from the better matching of size between the calixarene cavity and Cs(I) ion as well as π-bonding interactions with the arene group. This made the molecular recognition of Calix[4]arene-R14 for Cs(I) easy. On

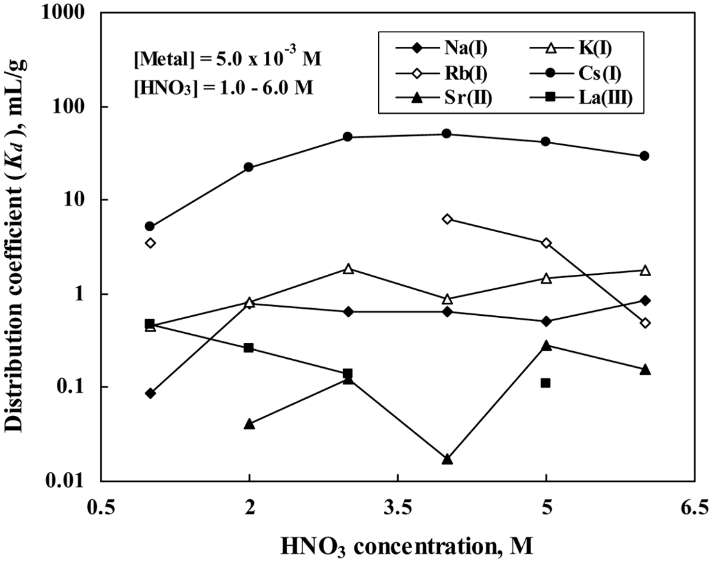


Figure 3. Adsorption of Na(I), K(I), Rb(I), Cs(I), Sr(II), and La(III) onto (Calix[4]arene-R14 + M)/SiO$_2$-P in a HNO$_3$ range of 1.0–6.0 M. [Metal] = 5.0 × 10^{-3} M, phase ratio: 0.25 g/5 mL, and shaking speed: 120 rpm.

the other hand, Sr(II), Na(I), K(I), and La(III) showed almost no adsorption onto Calix[4]arene-R14/SiO$_2$-P except a weak adsorption of Rb(I). Their distribution coefficients (K_d) were always below 1.8 mL/g except 6.3 mL/g for Rb(I). Such a low adsorption in the distribution coefficients was of great benefit to elimination of Cs(I) from Na(I), K(I), Sr(II), and La(III). So, in the 4.0 M HNO$_3$ solution, Cs(I), one of the alkali metals comparatively difficult to form the complex usually, was capable of recognizing effectively and complexed by the supramolecular compound Calix[4]arene-R14.

Chromatographic Partitioning of Cs(I)

To investigate the separation feasibility of Cs(I) from a simulated acidic HLW, the effect of alkali metals, rare earths and other typical FP elements such as Na(I), K(I), Rb(I), Sr(II), Ru(III), Rh(III), Mo(VI), Zr(IV), Ba(II), Pd(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III), Yb(III), and Lu(III) on chromatographic partitioning of Cs(I) by the novel silica-based (Calix[4]arene-R14 + M)/SiO$_2$-P polymeric composite was investigated at 298 K. The feed solution was composed of 5.0×10^{-3} M of the tested metals and 4.0 M HNO_3. The adsorption column used in the experiment was 10 mm in inner diameter and 320 mm in length. The flow rate was controlled to 1.0 mL/min. The elution curves by 4.0 M HNO_3 and water as well as the corresponding pH values in effluent are shown in Figs. 4 and 5, respectively.

Figure 4 shows the effect of Na(I), K(I), and some typical fission products such as Ru(III), Rb(I), Rh(III), Mo(VI), Zr(IV), Sr(II), Ba(II), and Pd(II) etc. on the chromatographic separation of Cs(I) by (Calix[4] arene-R14 + M)/SiO_2-P packed column.

It was found that the tested Na(I), K(I) Ru(III), Rb(I), Rh(III), Mo(VI), Zr(IV), Sr(II), Ba(II), and Pd(II) showed almost no adsorption towards (Calix[4]arene-R14 + M)/SiO_2-P and quickly leaked out column along with 4.0 M HNO_3. The effective elution might result from the poor complexation of these metal ions with Calix[4]arene-R14. The reason was due to the unmatchable size between the calixarene cavity with the tested metals as well as π-bonding interactions with the arene groups and structural reorganization of the molecule. Subsequently, with a supplement of water to the adsorption column, Rb(I) and Cs(I) adsorbed by (Calix[4] arene-R14 + M)/SiO_2-P were eluted out. The elution was contributed to the quick decomposition of the complexes of Cs(I) and Rb(I) with Calix[4]arene-R14 with a decrease in the concentration of NO_3^- in the

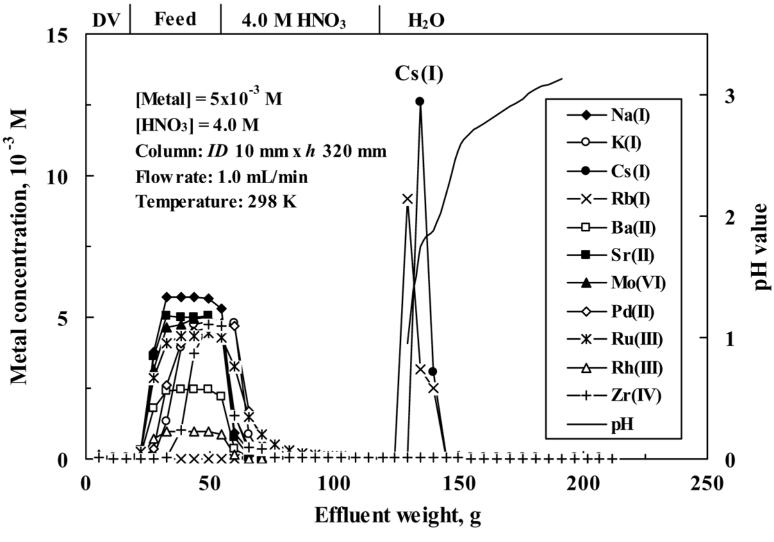


Figure 4. Partitioning of Cs(I) from a 4.0 M HNO_3 solution containing 5.0×10^{-3} M of Na(I), K(I), Rb(I), and some typical fission products by (Calix[4]arene-R14 + M)/SiO_2-P packed column utilizing water as an eluent at 298 K.

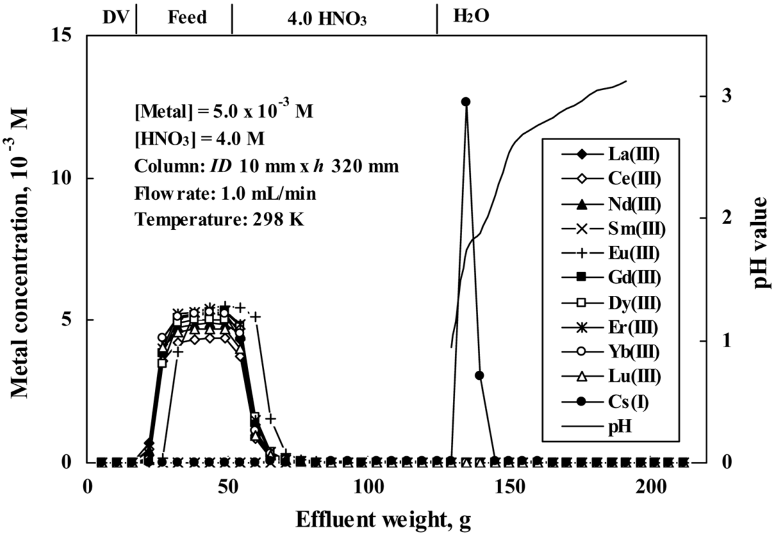


Figure 5. Effect of RE(III) elements on partitioning of Cs(I) from a 4.0 M HNO_3 solution by $(Calix[4]arene\text{-}R14 + M)/SiO_2\text{-}P$ packed column utilizing water as an eluent at 298 K.

resin bed. The elution process was presented as follows:

$$[M \cdot (Calix[4]arene - R14 + M)/SiO_2 - P]NO_{3(resin)} \longleftrightarrow M^+_{(aq)} + NO^-_{3(aq)} + (Calix[4]arene - R14 + M)/SiO_2 - P_{(resin)} (M = Cs(I) \text{ and } Rb(I)) \tag{2}$$

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

The resulting elution curves were sharp, narrow, and no elution tail. This revealed that their elution from the loaded $(Calix[4]arene\text{-}R14 + M)/SiO_2\text{-}P$ with water was efficient. The recovery percentage was calculated to be 100.5% for Cs(I) and in a range of 99.2–100.6% for others.

The adsorption of Rb(I) onto $(Calix[4]arene\text{-}R14 + M)/SiO_2\text{-}P$ indicated that Rb(I) had an adverse impact on the separation of Cs(I). The further separation of Cs(I) and Rb(I) in next step is necessary.

On the other hand, with the supply of water to the adsorption column, the pH value in the effluent was found to increase rapidly from 0 to 0.94 and then to 1.77. Such a quick change in the pH value reflected that Cs(I) and Rb(I) were desorbed from the loaded (Calix[4]arene-R14 + M)/SiO_2-P. Then, following shortly a slow change from pH 1.77

to pH 1.86, the pH value increased quickly again and finally reached to 3.42. The fact that in the elution process with water, the pH value in the effluent was below pH 3.5 showed that in the adsorption stage of alkali metals towards (Calix[4]arene-R14 + M)/SiO_2-P, a part of HNO_3 molecule was adsorbed simultaneously by (Calix[4]arene-R14 + M)/SiO_2-P.

Since the divalent metal Sr(II) contained in feed solution showed no adsorption, Sr(II) had no adverse impact on the separation of Cs(I) by (Calix[4]arene-R14 + M)/SiO_2-P. This made the chromatographic separation of heat generator Cs(I) from Sr(II) in this step possible and feasible.

Figure 5 shows the effect of rare earths such as La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III), Yb(III), and Lu(III) on the chromatographic separation of Cs(I) by (Calix[4]arene-R14 + M)/ SiO_2-P.

As can be seen, in the experimental conditions, the tested RE(III) elements showed no adsorption onto (Calix[4]arene-R14 + M)/SiO_2-P. They could be eluted facilely and flowed into the effluent along with 4.0 M HNO_3. This might be due to unmatchable size between RE(III) with calixarene cavity of Calix[4]arene-R14 as well as π-bonding interactions with the arene groups.

As a supply of water to the column, the concentration of Cs(I) in effluent rapidly increased and then decreased. The resultant elution curve of Cs(I) was sharp and showed no elution tail. This implied that Cs(I) adsorbed towards (Calix[4]arene-R14 + M)/SiO_2-P was effectively eluted by water. The elution effect was assigned to the quick decomposition of the complex of Cs(I) with Calix[4]arene-R14 with a decrease in the concentration of NO_3^- in the resin bed. This results in the elution of Cs(I) are agreement with that of the results showing in Fig. 4.

Based on the results and discussion above, the tested rare earths had no adverse impact for the effective separation of Cs(I) from an acidic simulated HLW, i.e., the impact of rare earths on the partitioning of Cs(I) is negligible. The recovery percentage was calculated to be 99.5% for Cs(I) and in a range of 99.1–101.3% for REs(III).

The pH value in effluent was measured. It was found that the change in pH value was very similar to than the change in Fig. 4, i.e., the pH value in effluent increase quickly from 0 to 0.95 and 1.76. Then, after a slow change from pH 1.76 to pH 1.87, the pH value increased again and finally reached to 3.43. The change in pH value in a range of 0.95–1.87 corresponded to the elution of Cs(I) and Rb(I). It was showed that the quick decomposition of the complex of Cs(I) and Calix[4]arene-R14 with a decrease in the concentration of NO_3^- in the resin bed.

According to the above results, it was found that by using the macroporous silica-based polymeric composite (Calix[4]arene-R14 + M)/SiO_2-P packed column, all of the tested elements contained in the simulated HLW of 4.0 HNO_3 were separated into following two groups:

1. Na(I), K(I), La(III), Ce(III), Nd(III), Sm(III), Rh(III), Ru(III), Pd(II), Zr(IV), Sr(II), Mo(VI), Ba(II), Eu(III), Gd(III), Dy(III), Er(III), Yb(III), and Lu(III) (Sr-containing group), and
2. Cs(I) and Rb(I) (Cs-group).

The heat emitting nuclide Sr(II) flowed into the first group along with 4.0 HNO_3 and other fission products since it showed no adsorption onto (Calix[4]arene-R14 + M)/SiO_2-P. It can be further separated in the next step.

These results indicated that in 4.0 M HNO_3, the novel macroporous silica-based polymeric (Calix[4]arene-R14 + M)/SiO_2-P composite had superior selectivity and excellent recognition ability for Cs(I). The application of (Calix[4]arene-R14 + M)/SiO_2-P in Cs(I) partitioning from HLW is promising.

Chromatographic Partitioning of Sr(II)

The results obtained in our research group showed that in the adsorption of Sr(II) onto (DtBuCH18C6 + M)/SiO_2-P, the optimum adsorption acidity was 2.0 M HNO_3 (23,24). So, to further separate effectively Sr(II) from the Sr-containing group obtained in the first column packed with (Calix[4]arene-R14 + M)/SiO_2-P, prior to separation the HNO_3 concentration in the Sr-containing group was conditioned to 2.0 M.

The effect of some representative elements such as Rh(III), Zr(IV), Sr(II), Ba(II), Ru(III), Na(I), K(I), Cs(I), Mo(VI), Pd(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III), and Lu(III) on chromatographic partitioning of Sr(II) by the macroporous silica-based (DtBuCH18C6 + M)/SiO_2-P polymeric composite was investigated. The elution curves by 2.0 M HNO_3 and water as well as the corresponding pH values in the effluent are shown in Figs. 6 and 7, respectively.

Figure 6 shows the effect of Rh(III), Zr(IV), Na(I), K(I), Cs(I), Ba(II), Ru(III), Mo(VI), and Pd(II), etc. on the separation of Sr(II) by (DtBuCH18C6 + M)/SiO_2-P packed column from 2.0 M HNO_3 at 298 K. As can be seen, the tested metals Rh(III), Zr(IV), Na(I), K(I), Cs(I), Ru(III), and Mo(VI) had almost no adsorption onto (DtBu CH18C6 + M)/SiO_2-P and quickly flowed into the effluent along with 2.0 M HNO_3. The elution resulted from the unmatchable size between the cavity of DtBuCH18C6 with the tested metals. This made the effective complexation of these metal ions with oxygen inside DtBuCH18C6 molecule poor.

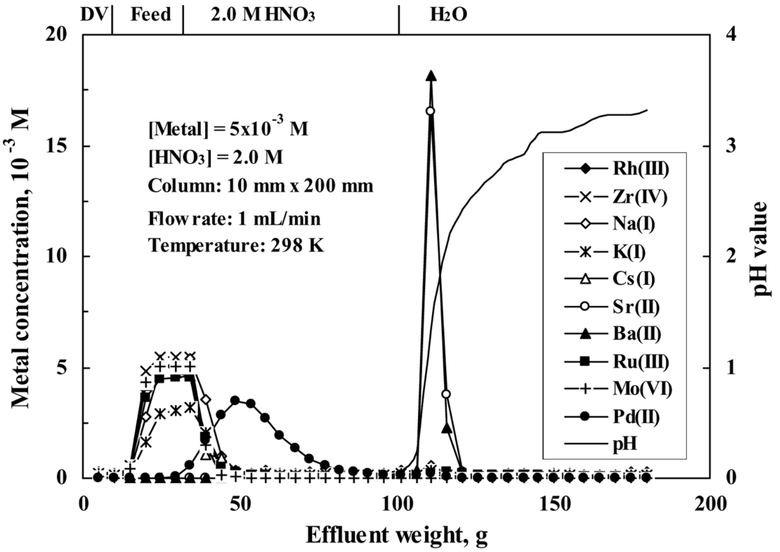


Figure 6. Partitioning of Sr(II) from a 2.0 M HNO_3 solution containing 5.0×10^{-3} M of Rh(III), Zr(IV), Na(I), K(I), Cs(I), Sr(II), Ba(II), Ru(III), Mo(VI), and Pd(II) by (DtBuCH18C6 + M)/SiO_2-P packed column utilizing water as an eluent at 298 K.

On the other hand, the elution curve of Pd(II) was wide and low. This was due to the weak adsorption of Pd(II) towards (DtBuCH18C6 + M)/SiO_2-P since the complexation of Pd(II) with DtBuCH18C6 was weak. Moreover, because the chemical stability of the complex of Pd(II) and DtBuCH18C6 in 2.0 M HNO_3 was not high, so, the elution of Pd(II) was assigned to the slow decomposition of the complex of Pd(II) with DtBuCH18C6 with a supply of 2.0 M HNO_3 to the column.

With a supplement of H_2O to the (DtBuCH18C6 + M)/SiO_2-P packed column, the divalent metals Sr(II) and Ba(II) were eluted out. The elution effect was contributed to the quick decomposition of the complexes of Sr(II) and Ba(II) with DtBuCH18C6 with an quick decrease in the concentration of NO_3^- in the resin bed. The elution process was presented as follows:

$$\begin{aligned}&[(\mathrm{DtBuCH18C6}+\mathrm{M})/\mathrm{SiO_2}-\mathrm{P}]\cdot\mathrm{Sr(NO_3)}_{2(\mathrm{resin})}\longleftrightarrow\mathrm{M}^{2+}_{(\mathrm{aq})}+2\mathrm{NO}^-_{3(\mathrm{aq})}\\&\quad+(\mathrm{DtBuCH18C6}+\mathrm{M})/\mathrm{SiO_2}-\mathrm{P}_{(\mathrm{resin})}(\mathrm{M}=\mathrm{Sr(II)\ and\ Ba(II)})\end{aligned} \tag{3}$$

The resultant elution curves of Sr(II) and Ba(II) were sharp, narrow, and had no elution tail. This confirmed that their elution from the loaded

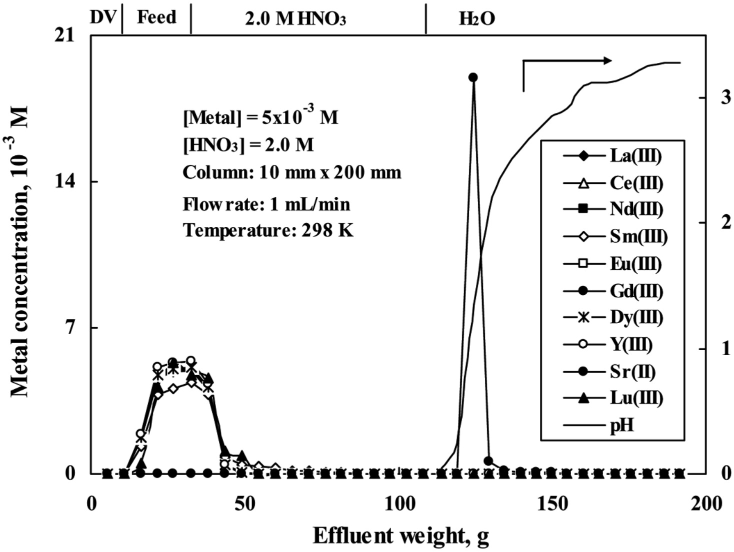


Figure 7. Partitioning of Sr(II) from a 2.0 M HNO_3 solution containing 5.0×10^{-3} M of RE(III) by (DtBuCH18C6 + M)/SiO_2-P packed column utilizing water as an eluent at 298 K.

(DtBuCH18C6 + M)/SiO_2-P with water was efficient. The recovery percentage was calculated to be 99.5% for Sr(II) and in a range of 99.3–100.3% for others.

The adsorption of Ba(II) onto (DtBuCH18C6 + M)/SiO_2-P showed that in 2.0 M HNO_3, Ba(II) had an adverse impact on the separation of Sr(II). The separation of Sr(II) from Ba(II) as a further step is necessary.

The pH value in the effluent was determined. It was found that it increased rapidly from 0 to pH 2.1 and then to pH 2.6. Such a quick change in pH value reflected that Sr(II) and Ba(II) were desorbed from the loaded (DtBuCH18C6 + M)/SiO_2-P. Then, with a supply of H_2O to the adsorption column, the pH value increased gradually to pH 3.12 and finally reached to pH 3.32. The change in pH value in a range of 0.05–2.42 corresponded to the elution of Sr(II) and Ba(II). The fact that in the elution process with water, the pH value in the effluent was below pH 4 showed that in the adsorption stage of the tested metals towards (DtBuCH18C6 + M)/SiO_2-P, a part of the HNO_3 molecule was adsorbed simultaneously by (DtBuCH18C6 + M)/SiO_2-P.

Figure 7 shows the effect of rare earths La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III), and Lu(III) on the separation of Sr(II) by (DtBuCH18C6 + M)/SiO_2-P.

The tested RE(III) elements showed no adsorption onto (DtBu CH18C6 + M)/SiO_2-P. They was eluted effectively and flowed into the effluent along with 2.0 M HNO_3. This might be due to the unmatchable size between RE(III) with the cavity of DtBuCH18C6.

As water was supplied to the column, the concentration of Sr(II) in the effluent rapidly increased and then decreased. The resultant elution curve was sharp, narrow, and had no elution tail. This showed that Sr(II) adsorbed towards (DtBuCH18C6 + M)/SiO_2-P was effectively eluted by water. The elution effect was also assigned to the quick decomposition of the complex of Sr(II) with DtBuCH18C6 with a decrease in the concentration of NO_3^- in the resin bed. This results in the elution of Sr(II) are agreement with that of the results showing in Fig. 6.

The recovery percentage was calculated to be 99.6% for Sr(II) and in a range of 99.3–101.5% for REs(III). The tested RE(III) elements had no adverse impact for the effective separation of Sr(II) from an acidic simulated HLW, i.e., the impact of REs(III) on partitioning of Sr(II) is negligible.

The change in pH value in the effluent was similar to that of the change showing in Fig. 6.

According to the results and discussion above, it was found that in 2.0 HNO_3, by the use of the macroporous silica-based polymeric (DtBuCH18C6 + M)/SiO_2-P composite packed column, all of the tested elements contained in the simulated HLW were effectively separated into two groups:

1. Rh(III), Zr(IV), Ru(III), Na(I), K(I), Cs(I), Mo(VI), Pd(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III), and Lu(III) (non-adsorption group), and
2. Sr(II) and Ba(II) (Sr-group). Only Ba(II) showed an adverse impact on the separation of Sr(II).

An Advanced SPEC Process

In terms of the Cs(I) and Sr(II) separation results obtained in the present work and the previous results (22,23), an advanced chromatographic partitioning technique entitled SPEC (Strontium/Cesium Partitioning from HLW by Extraction Chromatography) process was proposed. The concept flow sheet is illustrated in Fig. 8. In the main separation engineering, it consisted of two main separation columns packed with (Calix[4]arene-R14 + M)/SiO_2-P for Cs(I) removal in the first column and (DtBuCH18C6 + M)/SiO_2-P for Sr(II) removal in the second one.

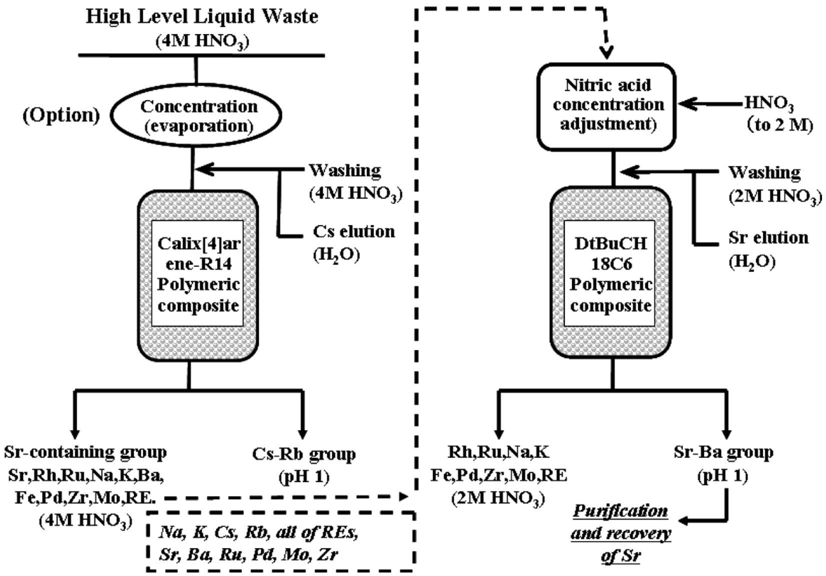


Figure 8. An advanced SPEC process for Cs/Sr partitioning from an acidic HLW by extraction chromatography utilizing two novel macroporous silica-based polymeric composites.

In comparison with the conventional liquid-liquid solvent extraction technique, the SPEC process has following advantages:

1. Cs(I) including Cs-135 with a half life of 30-year and Cs-137 with a half life of 2×10^6-year was capable of separating efficiently in the first column packed with (Calix[4]arene-R14 + M)/SiO_2-P by eluting with water only. Due to the excellent recognition ability of (Calix[4]arene-R14 + M)/SiO_2-P for Cs(I), almost all of the specific fission products such as the tested rare earths, alkali metals Na(I) and K(I), alkaline earths Ba(II) and Sr(II), noble metals Pd(II), Ru(III), and Rh(III) as well as Zr(IV) and Mo(VI) etc. showed no adverse impact on the Cs(I) partitioning from HLW except Rb(I).
2. Sr(II) with a half-life of 28-year was separated and recovered by (DtBuCH18C6 + M)/SiO_2-P utilizing water as an eluent. Almost all of the tested elements showed no adverse impact on the Sr(II) partitioning from HLW except Ba(II), which is easily separated further by a patent technique developed in our group. The third column packed with TODGA/SiO_2-P for the special separation of Sr(II) will be discarded, and
3. The purpose of the minimal utilization of the organic solvent and aqueous solution, the low waste accumulation, the compact equipment,

and the simple operation are achieved. The separation process is significantly simplified.

This makes noticeable reduction of the volume of liquid and solid wastes and the process capital in cost promising.

CONCLUSIONS

Due to the harmful of heat generators, Cs(I) and Sr(II), to the vitrified HLW in final geological disposal, their effective separation from HLW are required. For this purpose, two macroporous silica-based supramolecular Calix[4]arene-R14 and DtBuCH18C6 polymeric composites were synthesized by impregnating respectively their molecules into the pores of SiO_2-P particles support. The adsorption and elution of Cs(I), Sr(II), and more than 20 typical coexistence elements were investigated at 298 K.

It was found that by the use of (Calix[4]arene-R14 + M)/SiO_2-P packed column, Cs(I) was effectively eluted by water while the tested elements showed no adsorption and flowed into 4.0 M HNO_3 except Rb(I). By the use of (DtBuCH18C6 + M)/SiO_2-P packed column, Sr(II) was eluted by water only and flowed into the effluent along with Ba(II), while other elements showed no adsorption and flowed into 4.0 M HNO_3.

Based on the Cs(I) partitioning by (Calix[4]arene-R14 + M)/SiO_2-P in the first column and the Sr(II) separation by (DtBuCH18C6 + M)/SiO_2-P in the second one, an advanced and highly specific chromatographic partitioning technique entitled SPEC process was proposed. It was demonstrated that in HNO_3 solution, a complete partitioning of Cs(I) and Sr(II) from HLW by two kinds of silica-based impregnated polymeric composites was achieved. Application of the SPEC process in the separation of heat generators from an acidic HLW is promising.

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