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Adsorption of cesium and some typical coexistent elements onto a modified macroporous silica-based supramolecular recognition material

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ABSTRACT

To find an effective method in separation of Cs(I), an advanced macroporous silica-based supramolecular recognition composite, (Calix[4] + MODB)/SiO_2-P, was synthesized. It was done by impregnation and immobilization of 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) and methyloctyl-2-di-methy-lbutanemide (MODB) into the pores of the SiO_2-P particles. MODB was used to modify Calix[4]arene-R14. The adsorption of some typical fission products such as Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) contained in highly active liquid waste (HLW) onto (Calix[4] + MODB)/SiO_2-P was investigated. It was performed by examining the effects of contact time, the concentration of HNO_3 in the range of 0.3–7.0 M, and operation temperature on the adsorption of the tested metals. (Calix[4] + MODB)/SiO_2-P showed strong adsorption ability and excellent selectivity for Cs(I) over all the tested metals. The separation of Cs(I) from a simulated HLW containing 5.0 mM of the tested elements was performed by (Calix[4] + MODB)/SiO_2-P packed column at 298 K. Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) showed no adsorption and were eluted into effluent along with 3.0 M HNO_3. Cs(I) adsorbed by (Calix[4] + MODB)/SiO_2-P was effectively eluted with water and then separated from the others. The results demonstrated that in 3.0 M HNO_3, (Calix[4] + MODB)/SiO_2-P is promising to apply in separation of Cs(I), one of the heat generators, from HLW in the SPEC (*S*trontium/Cesium *P*artitioning from HLW by *E*xtraction *C*hromatography) process developed recently.

1. Introduction

Cs-135 and Cs-137 are isotopes of cesium contained in highly active liquid waste (HLW). It is produced in reprocessing of nuclear spent fuel generated through uranium fission occurred in nuclear reactor. It is reported that Cs can pose a serious radiation hazard to health and environment. For instance, Cs-135 with a half-life of 2×10^6 yr might has long-termed adverse impact on environment because of its mobility in final repository. Cs-137 with a half-life of 30 yr is one of the heat emitting nuclides (HEN) and is probably harmful to the vitrified HLW in final geological disposal. It has potential risk to environment of underground water. On the other hand, Cs-137 is a β-emitter, it is used as the resource of β-radiation and energy generator. Consideration of the environment protection and resource reuse, effective partitioning and recovery of Cs from HLW is valuable. However, its separation has always been one of the most challenging works in chemical engineering.

In addition to Cs-137, Sr-90 is the other HEN contained in HLW. The separation method of them usually has liquid–liquid solvent extraction, adsorption, ion exchange, liquid membrane extraction, and ionic liquid [1,2]. The current attention has been focused on the liquid–liquid solvent extraction. Based on some selective extractants, a few partitioning processes such as universal solvent extraction [3–5], cesium separation by calix-crown extraction [6,7], and fission product extraction [8,9], *etc.* have been proposed to partition Cs(I) from a simulated or genuine HLW. In these extractants, some supramolecular recognition agents such as calix[4]arene-bis(*t*-octylbenzo-crown-6) (BOB CalixC6), 4,4′,(5′)-di(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), and 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14), *etc.* showed high extraction ability and selectivity for Cs(I) or Sr(II) [10–13]. It is said that in the countercurrent extraction, it might generate a variety of organic wastes because of the hydrolytic and radiolytic degradation of extractants and diluents. This probably increases the number of the instruments and equipments used in the multi-stage extraction, striping, and washing processes. Therefore, a minimal use of organic solvents and compact equipments in separation process is required. Recently, a macroporous silica-based chelating agent impregnated polymeric composite has been developed [14]. In comparison with the conventional polymeric matrix resins, the silica-based type of the adsorbent shows rapid adsorption and elution kinetics, high mechanical strength, better resistant ability against HNO_3,

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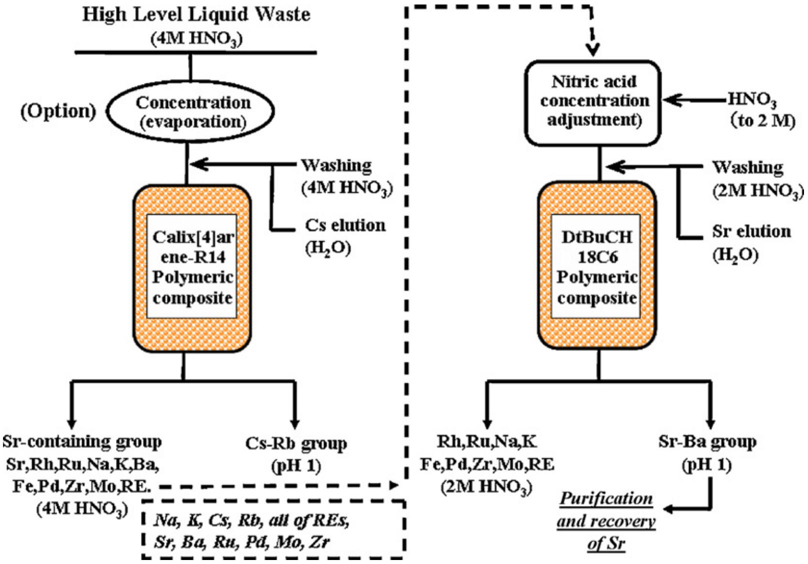


Fig. 1. An advanced SPEC process for Cs/Sr partitioning from HLW by extraction chromatography utilizing two novel macroporous silica-based polymeric composites.

temperature, and γ-irradiation as well as significantly low pressure loss in packed column [15,16].

Based on the MAREC (*M*inor *A*ctinides *R*ecovery from HLW by *E*xtraction *C*hromatography) process and some fundamental investigations [17–19], an advanced partitioning technology entitled SPEC (*S*trontium/Cesium *P*artitioning from HLW by *E*xtraction *C*hromatography) process as shown in Fig. 1 has been developed [20]. It was specially used to separate and recover both Cs(I) and Sr(II) by two adsorption columns. Cs(I) was separated in the first column packed with Calix[4]arene-R14/SiO_2-P, a macroporous silica-based supramolecular recognition composite [21,22]. Sr(II) was then partitioned in the second one packed with the other silica-based supramolecular recognition composite, DtBuCH18C6/SiO_2-P [23,24]. However, it was found that the optimum concentration of HNO_3 in separation of Cs(I) was 4.0 M. It is higher than that of 3.0 M HNO_3 in genuine HLW. It implies that prior to separation of Cs(I), the acidity in HLW must be adjusted to 4.0 M by the concentrated nitric acid. Obviously, this can cause an increase in volume of the radioactive wastes. It is opposite to our final target that is significant reduction of the quantity of the radioactive wastes in the SPEC process.

To find a specific material for the effective separation of Cs(I), the objective of the present work has been focused on (1) synthesis of an improved macroporous silica-based composite, (Calix[4] + MODB)/SiO_2-P, by molecular modification of Calix[4]arene-R14 with methyloctyl-2-dimethylbutanamide (MODB). (2) Investigation of the adsorption behavior of Cs(I) and some typical coexistent fission products Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) onto the (Calix[4] + MODB)/SiO_2-P composite. It was performed through examining the effect of contact time, the HNO_3 concentration in the range of 0.3–7.0 M, and temperature, and (3) separation of Cs(I) from a 3.0 M HNO_3 solution containing ∼5.0 mM of the tested metals by (Calix[4] + MODB)/SiO_2-P packed column utilizing 3.0 M HNO_3 and water as eluents. The possibility and feasibility of the Cs(I) separation by extraction chromatography were evaluated.

2. Experimental

2.1. Reagents

$RE(NO_3)_3{\cdot}6H_2O$ (RE = La and Y), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $ZrO(NO_3)_2{\cdot}H_2O$, and $CsNO_3$ used were of analytical grade. Both ruthenium nitrosyl nitrate solution with 1.5 wt% of Ru(III) and rhodium nitrosyl nitrate solution with 1.6 wt% of Rh(III) were 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. Both La(III) and Y(III) were used to understand the adsorption and separation behavior of all the trivalent rare earths REs(III) and minor actinides MAs(III) because of their similarity in the chemical properties. The concentrations of all of the tested elements used were about 5.0×10^{-3} M (M = mol/dm^3). The HNO_3 solutions of different concentrations were freshly prepared by the concentrated nitric acid.

1,3-[(2,4-Diethyl heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) with a purity greater than 97% is a kind of the macrocycle supramolecular recognition agent. It was provided by the Innovation & Chimie Fine, France. Methyloctyl-2-dimethylbutanamide (MODB) with a purity more than 99% was provided by the Shanghai Chemical Reagent Co., China. It was used as a molecular modifier of Calix[4]arene-R14.

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

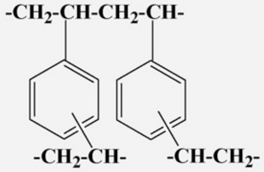
The macroporous silica-based polymeric composite material, (Calix[4] + MODB)/SiO_2-P, was synthesized. The silica-based SiO_2-P particles support was prepared as described previously [23,25]. A symbol P in the SiO_2-P refers to the styrene-divinylbenzene copolymer, which was prepared by the polymerization reaction inside the macroporous SiO_2 substrate.

2.2. Preparation of (Calix[4] + MODB)/SiO_2-P

Prior to preparation of the (Calix[4] + MODB)/SiO_2-P composite, the SiO_2-P particles were treated by the use of methanol and acetone. The purpose is to improve the surface activity of the silica-based support. The treatment process by acetone was described as follows: the quantity of the SiO_2-P particles and the given amount of acetone were mixed into 300 cm^3 of conical flask and then shaken mechanically at 120 rpm for ca. 60 min. Following separation, it was dried in a vacuum drying oven at 313–323 K for 24 h. The similar operation procedure was repeated at least three times. It was then treated again with methanol by the identical method. The synthesis of (Calix[4] + MODB)/SiO_2-P was described as follows.

The quantity of the Calix[4]arene-R14 compound weighted in advance and the calculated amount of MODB were dissolved com-

Table 1
Physical and chemical parameters of the novel silica-based Calix[4]arene-R14 impregnated polymeric composite modified with MODB.

Silica-based polymeric composite	(Calix[4] + MODB)/SiO_2-P
Supramolecular recognition agent	1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14)
Pore fraction	0.69
Mean pore size	0.6 μm
Bead diameter	40–60 μm
Specific surface area	3.66 m^2/g
Integrated pore volume	1.1 cm^3/g
Molecular modifier	Methyloctyl-2-dimethylbutanamide (MODB)
Copolymer inside SiO_2-P support	Macroporous SiO_2 particles modified by following inert copolymer-containing compound 
Appearance	Colorless powdered micro-ball
Affinity for water or acidic solution	Good

pletely with 150 cm^3 of dichloromethane in a 300 cm^3 of glass conical flask, then, a given quantity of the macroporous SiO_2-P particles was added under shaking. Following the resultant mixture was stirred mechanically for ca. 90 min, it was moved into a silicon-oil bath controlled by an EYELA OHB-2000 Model (Tokyo Rikakikai Co. Ltd., Japan) temperature controller and stirred continuously for ca. 300 min at 323 K. The purpose was to impregnate and immobilize the Calix[4]arene-R14 and MODB molecules into the pores of the SiO_2-P particles. After drying in a vacuum drying oven at 318 K for overnight, a colorless macroporous silica-based polymeric composite, (Calix[4] + MODB)/SiO_2-P, was obtained. It was characterized by elementary analysis, TG-DSC, and FT-TR, respectively. The synthesis of the schematic diagram of (Calix[4] + MODB)/SiO_2-P and the composite mechanism are shown in Figs. 2 and 3. The physical and chemical parameters are listed in Table 1.

2.3. Adsorption of the tested metals onto (Calix[4] + MODB)/SiO_2-P

The adsorption evaluation of the tested elements onto the novel (Calix[4] + MODB)/SiO_2-P polymeric composite was performed using a TAITEC MM-10 Model auto-thermostated water bath shaker. The operation temperature was controlled in the range of 293–333 K. When a 5 cm^3 of HNO_3 solution containing ~5.0×10^{-3} M of Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) as an aqueous phase and the weighed quantity of (Calix[4] + MODB)/SiO_2-P as a solid phase were mixed into a 50 cm^3 of ground glass-stopped flask, it was then mechanically shaken at

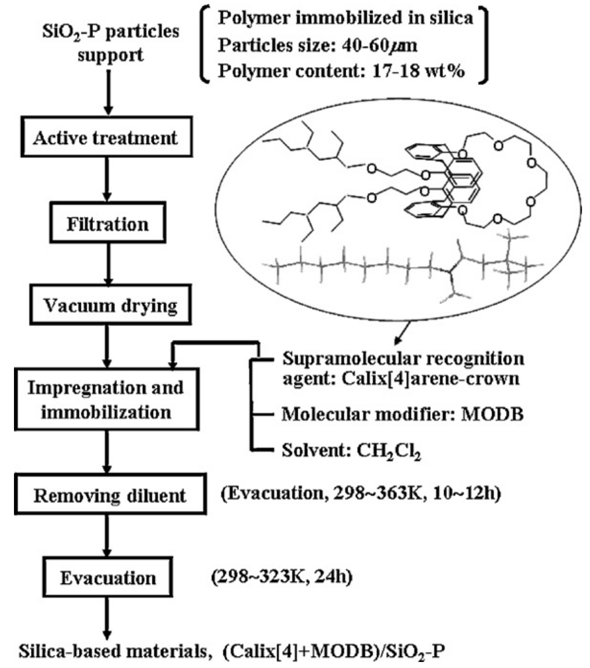


Fig. 2. Schematic diagram of synthesizing the (Calix[4] + MODB)/SiO_2-P composite.

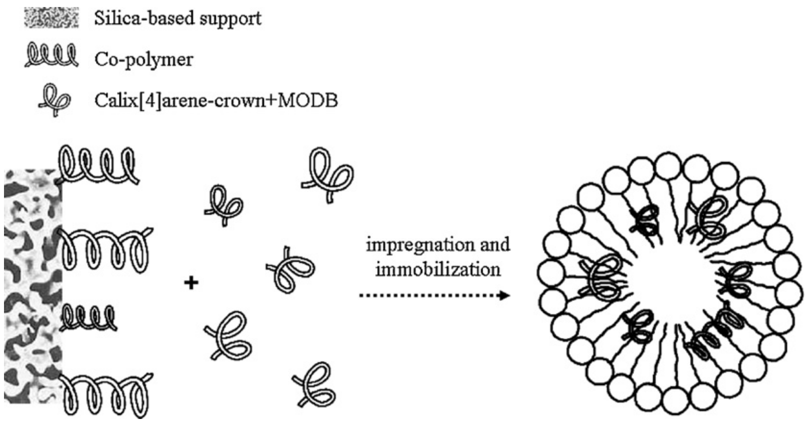


Fig. 3. Synthesis mechanism of (Calix[4] + MODB)/SiO_2-P through impregnation and immobilization.

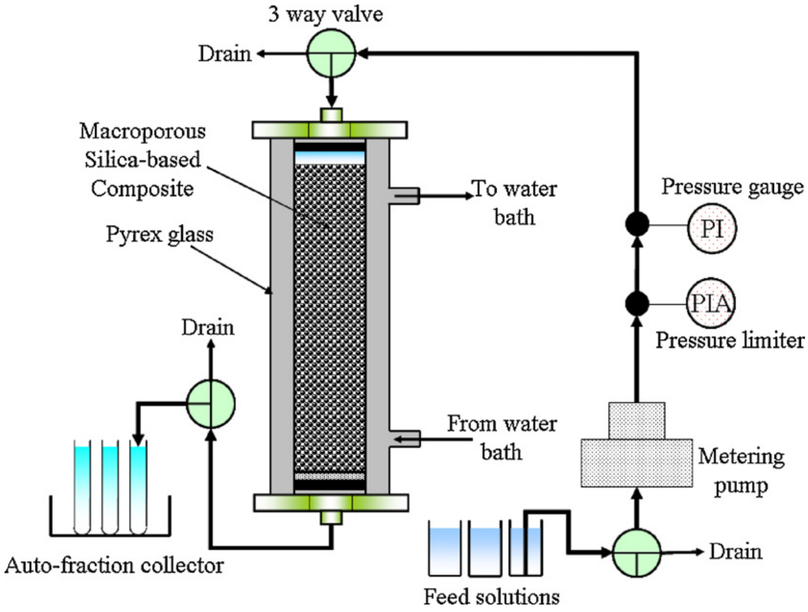


Fig. 4. Apparatus for Cs(I) partitioning from a HNO_3 solution containing fission products by extraction chromatography.

120 rpm at the designed contact time under the given temperature. The concentration of HNO_3 in aqueous phase was investigated in the range of 0.3–7.0 M. After the phase separation through a membrane filter with a mean pores of 0.45 μm, the concentrations of the tested metals in aqueous phase were determined utilizing a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian, Inc., the United States of America) except the content of Cs(I) that was analyzed using a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian, Inc., the United States of America). The distribution coefficients of the tested elements onto the (Calix[4] + MODB)/SiO_2-P composite in HNO_3 medium were calculated as follows:

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

where C_0 and C_e show the initial and equilibrium concentrations of the tested metals in aqueous phase, respectively. W and V represent the weight of dry (Calix[4] + MODB)/SiO_2-P composite materials and the volume of the aqueous phase used in the experiments.

2.4. Chromatographic partitioning of the tested elements

Prior to the separation performance, the macroporous silica-based (Calix[4] + MODB)/SiO_2-P polymeric composite was packed into a Pyrex glass column with a dimension of 10 mm in inner-diameter and 300 mm in length under 0.25–0.35 MPa of N_2 gas pressure. It was then equilibrated by 3.0 M HNO_3 solution. The column operation temperature, 298 K, used in the loading and elution cycle was controlled and maintained 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 cm^3/min by combination of a NPG-50UL Model pressure gage (Nihon Seimitsu Kagaku Co. Ltd., Japan) with a 2GN15K Model pressure limiter (Oriental Motor Co. Ltd., Japan). The concentration of HNO_3 in feed solution was 3.0 M. The schematic diagram of column partitioning of Cs(I) from a simulated HLW is illustrated in Fig. 4.

Following a 3.0 M HNO_3 solution containing 5.0×10^{-3} M of Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) as feed solution passed through the column packed with the (Calix[4] + MODB)/SiO_2-P composite, the given volumes of 3.0 M HNO_3 and distilled water as eluents were then pumped down-flow through the adsorption column. 5 cm^3 aliquots of effluent fraction were collected using an EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co. Ltd., Japan). The concentrations of the tested metals in effluent were analyzed by the ICP-OES and/or the atomic adsorption spectroscopy as mentioned above. The pH value in effluent was measured using a digital pHs 3C Model pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd., China).

3. Results and discussion

3.1. Dependence of the adsorption of (Calix[4] + MODB)/SiO_2-P on contact time

The supramolecular recognition agent calix-crown is composed of two functional groups, a lipophilic calix[4]arene and a hydrophilic crown ether. The function of the crown ether having six O atoms acts as a chelating agent with metal ions through the chemical complexation. The crucial role of the calix[4]arene with a cavity is to increase the selectivity of calix[4]crown for metal ions or organic compounds through molecular recognition [26]. The complexation of calix[4]crown with metal is different from that of the conventional complexing agent with metal. It is considered to result from the matched size of the calixarene cavity and the radius of metal ions, π-bonding interactions with the arene groups, and structural reorganization of the molecule [27,28]. It is known that Cs(I) is a kind of metal which is comparatively difficult to form the stable complex with the conventional chelating agents. The supramolecular structure of calix[4]crown makes utilization of calix[4]crown to complex Cs(I) possible. The recognition ability of calix[4]crown for Cs(I) might depend on the effective complexation of Cs(I) with the hydrophilic crown ether and the high selectivity of calix[4]arene for Cs(I), i.e., the well matched size between lipophilic calixarene cavity and Cs(I) ion radius.

It was found that with the exception of Rb(I), almost all of alkali metals and alkaline earths such as Na(I), K(I), Sr(II), and Ba(II), *etc.* had no adverse impact on the adsorption of Cs(I) onto (Calix[4] + MODB)/SiO_2-P [29]. This is of great beneficial to the effective elimination of Cs(I) by the use of the macroporous silica-based calix[4]crown impregnated composite. Actually, it is reported that there is about 30 elements contained in HLW. They might have adverse impact on the effective elimination of Cs(I).

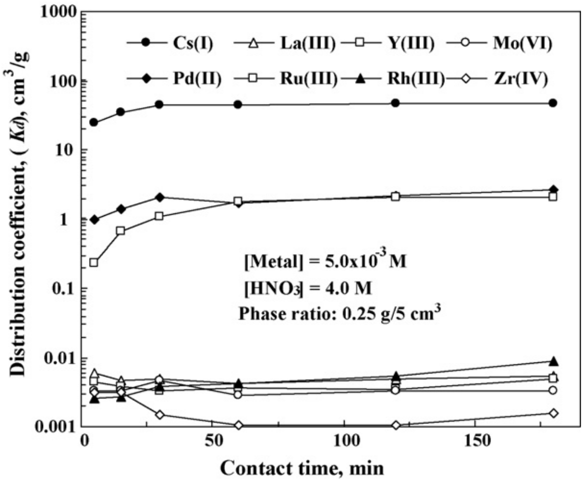


Fig. 5. Dependence of the distribution coefficient (K_d) of the tested metals onto (Calix[4] + MODB)/SiO$_2$-P with an increase in contact time in 4.0 M HNO$_3$ at 298 K. Phase ratio: 0.25 g/5 cm^3, metal content: ~5.0 × 10^{-3} M, shaking speed: 120 rpm.

The effect of the these elements such as 16 species of rare earths (REs(III)) including Y(III) and La(III) to Lu(III), two minor actinides (MAs(III), MA = Am and Cm), noble metals, and the other elements on the adsorption of Cs(I) has not been reported yet.

To understand the adsorption property of (Calix[4] + MODB)/SiO$_2$-P, some representative fission products such as Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), Cs(I), and Zr(IV) were selected as the tested metals in aqueous phase. Both La(III) and Y(III) were used to understand the behavior of all of REs(III) and MAs(III) due to their similarity in chemical properties. The adsorption of the tested metals onto (Calix[4] + MODB)/SiO$_2$-P with a change in contact time in 4.0 HNO$_3$ was investigated at 298 K. It was performed at phase ratio of 0.25 g/5 cm^3, metal concentration of 5.0 × 10^{-3} M, and shaking speed of 180 rpm. The relevant results are shown in Fig. 5.

Fig. 5 shows the dependence of the tested metals adsorption onto (Calix[4] + MODB)/SiO$_2$-P on contact time in 4.0 M HNO$_3$ solution at 298 K. As can be seen, with increasing contact time, the tested Mo(VI), Pd(II), La(III), Y(III), Ru(III), Rh(III), and Zr(IV) showed weak or almost no adsorption onto the (Calix[4] + MODB)/SiO$_2$-P polymeric composite. The distribution coefficient (K_d) at contact time of 180 min was always less than 8.74 × 10^{-3} cm^3/g for Mo(VI), La(III), Y(III), Rh(III), and Zr(IV) and 2.03 cm^3/g for Pd(II) and Ru(III). Such a low value in the distribution coefficient was ascribed to the weak complexation of the tested metals with Calix[4]arene-R14 inside (Calix[4] + MODB)/SiO$_2$-P. It might result from the unmatched size between the cavity of Calix[4]arene-R14 molecule with the radius of the tested metal ions.

Contrary to the above tested elements, the adsorption of Cs(I) onto the (Calix[4] + MODB)/SiO$_2$-P polymeric composite obviously increased with an increase in contact time and basically reached equilibrium within 30 min. The distribution coefficient (K_d) of Cs(I) was 24.42 cm^3/g at 5 min, 43.96 cm^3/g at 30 min, 46.09 cm^3/g at 120 min, and 46.85 cm^3/g at 180 min. It revealed that in 4.0 M HNO$_3$, Cs(I), one of the main heat emitting nuclides, had quick adsorption kinetics onto the (Calix[4] + MODB)/SiO$_2$-P composite. It resulted from the effective complexation of Cs(I) with the macrocyclic compound Calix[4]arene-R14 inside (Calix[4] + MODB)/SiO$_2$-P. On the other hand, the apparent shape and character of the dynamic-state adsorption curve of Cs(I) was in accordance with that of the chemical adsorption of metal ion. Therefore, the adsorption mechanism of Cs(I) onto the (Calix[4] + MODB)/SiO$_2$-P composite material in 4.0 M HNO$_3$ was considered to be the chemical adsorption, i.e., the chemical complexation of Cs(I) ion with Calix[4]arene-R14 molecule might be the rate-controlling step.

Based on the above discussion, it was found that in 4.0 M HNO$_3$, the adsorption ability of the tested metals was different. The novel macroporous silica-based (Calix[4] + MODB)/SiO$_2$-P polymeric composite had excellent adsorption ability and high selectivity for Cs(I) over all of the tested elements, which showed weak or almost no adsorption. Namely, the tested fission products had no adverse impact on the adsorption of Cs(I) onto (Calix[4] + MODB)/SiO$_2$-P. It is of great beneficial to effective separation of Cs(I) from HLW utilization of (Calix[4] + MODB)/SiO$_2$-P through column chromatograph.

No adsorption of La(III) and Y(III) onto (Calix[4] + MODB)/SiO$_2$-P is valuable. It implies that all of the trivalent RE(III) elements might have no adsorption onto (Calix[4] + MODB)/SiO$_2$-P due to the lanthanide contraction. Moreover, based on the chemical similarity of lanthanide contraction and actinide contraction, the chemical properties of the trivalent minor actinides MA(III) such as Am(III) and Cm(III) are usually very close to those of the RE(III) elements. So, it is predicted that in HNO$_3$ solution, they might show no adsorption onto (Calix[4] + MODB)/SiO$_2$-P, i.e., 16 species of REs(III) and 2 species of MAs(III) might has no adverse impact on the adsorption of Cs(I).

It is known that in acidic HLW solution generated in reprocessing of MOX nuclear spent fuel, the contents of all of the REs(III), MAs(III), and heat emitting nuclides are around 1.9%, 0.4%, and less that 0.1%, respectively. To separate one of the heat emitting nuclides, Cs, it is required that the adverse impact of REs(III) and MAs(III) on the Cs adsorption must be reduced to a great extent. On the basis of no adsorption of REs(III) and MAs(III) onto (Calix[4] + MODB)/SiO$_2$-P, the macroporous silica-based supramolecular recognition composite is meaningful for effective partitioning of Cs from HLW by column chromatography.

3.2. Dependence of the tested elements adsorption on HNO$_3$ concentration

Nitric acid is almost sole medium employed in reprocessing process of nuclear spent fuel. It is reported that in a genuine HLW produced, the concentration of HNO$_3$ is usually around 3.0 M. In addition, the calix[4]crown is composed of a calix[4]arene and a 18-crown-6 moiety bonded together by the phenolic oxygen of the calix[4]arene and a polyether chain. Due to the affinity of oxygen atom contained in 18-crown-6, HNO$_3$ is considered to probably have obvious effect on the complexation of Calix[4]arene-R14 with the tested metals. It might result from the protonation of Calix[4]arene-R14 with HNO$_3$ molecule. This makes it possible that in the adsorption process, the complexation of the tested metals with (Calix[4] + MODB)/SiO$_2$-P as well as the association of (Calix[4] + MODB)/SiO$_2$-P with HNO$_3$ molecule by intermolecular interaction force may be two competition reactions.

To evaluate the effect of the HNO$_3$ concentration, the adsorption behavior of the tested metals such as Cs(I), Ru(III), Rh(III), Mo(VI), Pd(II), La(III), Y(III), and Zr(IV) onto (Calix[4] + MODB)/SiO$_2$-P was investigated at 298 K. It was operated at metal concentration of ~5.0 × 10^{-3} M, phase ratio of 0.25 g/5 cm^3, contact time of 120 min, and the HNO$_3$ concentration range of 0.3–7.0 M. The relevant results are illustrated in Fig. 6.

Fig. 6 shows the adsorption properties of the tested fission and non-fission products onto the macroporous silica-based (Calix[4] + MODB)/SiO$_2$-P supramolecular recognition composite in the HNO$_3$ concentration range of 0.3–7.0 M at 298 K. As ca be seen, with an increase in the HNO$_3$ concentration, the adsorption of Cs(I) onto the (Calix[4] + MODB)/SiO$_2$-P material obviously increased from 0.3–3.0 M HNO$_3$ and then decreased to 7.0 M HNO$_3$. The distribution coefficient (K_d) of Cs(I) was 0.8132 cm^3/g in 0.3 M HNO$_3$, 5.486 cm^3/g in 1.0 M HNO$_3$, 39.56 cm^3/g in 3.0 M HNO$_3$, 22.98 cm^3/g in 5.0 M HNO$_3$, and 10.53 cm^3/g in 7.0 M HNO$_3$. The

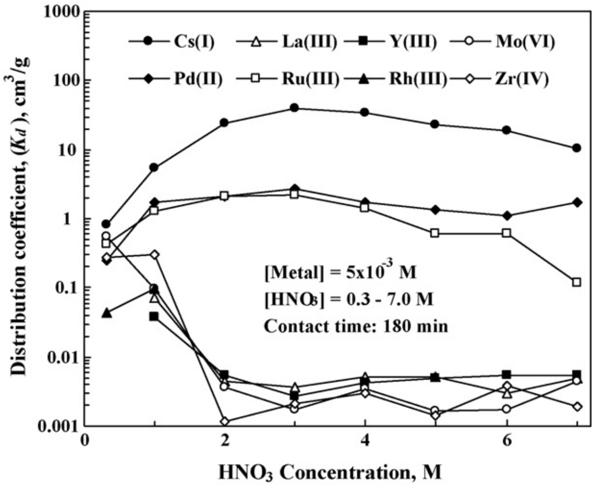


Fig. 6. Dependence of the distribution coefficient (K_d) of the tested elements onto (Calix[4] + MODB)/SiO_2-P with an increase in the HNO_3 concentration from 0.3 M to 7.0 M at 298 K. Metal content: $\sim 5.0 \times 10^{-3}$ M, phase ratio: 0.25 g/5 cm^5, contact time: 180 min.

maximum adsorption acidity of Cs(I) onto (Calix[4] + MODB)/SiO_2-P was therefore determined at 3.0 M HNO_3, which was very close to the HNO_3 concentration in genuine HLW. This is beneficial of application of the (Calix[4] + MODB)/SiO_2-P composite in HLW separation. Meanwhile, the other tested metals showed weak or almost no adsorption and their distribution coefficients (K_d) were waylays below 1.6 cm^3/g. It is reflected that in 3.0 M HNO_3, the novel macroporous silica-based polymeric composite (Calix[4] + MODB)/SiO_2-P had strong adsorption ability and high selectivity for Cs(I) over all of the tested elements. It makes effective separation of Cs(I) from an acidic HLW containing the tested fission products Ru(III), Rh(III), Mo(VI), Pd(II), La(III), Y(III), and Zr(IV) possible.

Some alkali metals and alkaline earths are also fission and non-fission products contained in HLW. For example, Na(I) was introduced into HLW by addition of $NaNO_2$ in valent adjustment of Np. The preliminary investigation of the adsorption of Na(I), K(I), Rb(I), Sr(II) and Ba(II) showed that in HNO_3 solution, the (Calix[4] + MODB)/SiO_2-P composite had high adsorption ability and selectivity for Cs(I) over the others except Rb(I) [29]. Combination of the adsorption of tested metals onto (Calix[4] + MODB)/SiO_2-P, it is clear that in 3.0 M HNO_3, almost 26 species of elements including alkali metals except Rb(I), alkaline earths Sr(II) and Ba(II), all of trivalent REs(III), trivalent minor actinides Am(III) and Cm(III), and the tested metals in the experiments might have adverse impact on the adsorption of the (Calix[4] + MODB)/SiO_2-P composite.

Compared with the adsorption behavior of Cs(I) in different HNO_3 concentration range, the increase of the adsorption of Cs(I) with an increase in the HNO_3 concentration from 0.3 M to 3.0 M was considered to result from the effective complexation of (Calix[4] + MODB)/SiO_2-P for Cs(I). The relevant adsorption reaction was described as follows:

$$Cs^+ + NO_3{}^- + (Calix[4] + MODB)/SiO_2\text{-}P \overset{0.3\text{–}3.0\,M\,HNO_3}{\rightleftharpoons} CsNO_3 \cdot (Calix[4] + MODB)/SiO_2\text{-}P \quad (2)$$

In excess of 3.0 M HNO_3, the adsorption of (Calix[4] + MODB)/SiO_2-P for Cs(I) decreased. It was caused probably by the protonation of Calix[4]arene-R14 molecule through association of oxygen atom in 18-crown-6 with HNO_3 via hydrogen bonding. The possible mechanism was represented as follows:

$$HNO_3 + (Calix[4] + MODB)/SiO_2\text{-}P \overset{3.0\text{–}7.0\,M\,HNO_3}{\rightleftharpoons} HNO_3 \cdot (Calix[4] + MODB)/SiO_2\text{-}P \quad (3)$$

In comparison with Eqs. (2) and (3), the adsorption of Cs(I) onto (Calix[4] + MODB)/SiO_2-P at low concentration of HNO_3 increased obviously with an increase in the HNO_3 concentration. Namely, Eq. (2) might be dominant in the HNO_3 concentration from 0.3 M to 3.0 M. In this case, monovalent Cs(I) was able to be strongly complexed with the supramolecular recognition agent Calix[4]arene-R14 inside (Calix[4] + MODB)/SiO_2-P, and form to a stable complex formation, $CsNO_3$·(Calix[4] + MODB)/SiO_2-P. However, in excess of 3.0 M HNO_3, the adsorption of Cs(I) onto the (Calix[4] + MODB)/SiO_2-P composite gradually decreased. Eq. (3) was hence considered to be the dominant reaction due to the protonation of Calix[4]arene-R14 with HNO_3 through hydrogen bonding. It probably made the available concentration of Calix[4]arene-R14 inside the (Calix[4] + MODB)/SiO_2-P composite being capable of complexing Cs(I) significantly lower. The 3.0 M HNO_3 was therefore determined to be the optimum adsorption acidity.

The recognition property of Calix[4]arene-R14 for Cs(I) results from two functional groups, a hydrophilic 18-crown-6 and a lipophilic calix[4]arene. It was found that in an acidic solution, almost all of the derivatives of the macrocyclic crown ethers such as dicyclohexano-18-crown-6 (DC18C6) and DtBuCH18C6, *etc.* are usually able to associate with HNO_3, HCl, HCN, and the others through hydrogen bonding and form to the stable complex [30–32]. This phenomenon was consistent with the results observed in the experimental conditions. Therefore, the decrease in the distribution coefficient (K_d) of Cs(I) onto the (Calix[4] + MODB)/SiO_2-P composite in excess of 3.0 M HNO_3 was ascribed to the effective association of 18-crown-6 inside the Calix[4]arene-R14 molecule with HNO_3. However, the detailed composition and structure of the associated complex of HNO_3 and Calix[4]arene-R14 have not been investigated. The relevant investigation is being carried out.

3.3. Dependence of the tested elements adsorption on temperature

To understand the temperature effect, the adsorption behavior of Ru(III), Pd(II), and Cs(I) onto the (Calix[4] + MODB)/SiO_2-P polymeric composite in 3.0 M HNO_3 was investigated. The experimental temperature was controlled in the range of 293–333 K utilizing the TAITEC MM-10 Model auto-thermostatted water bath shaker. It was carried out at phase ratio of 0.25 g/5 cm^3, the metal concentration of 5.0×10^{-3} M, and contact time of 120 min. The corresponding results are depicted in Fig. 7.

Fig. 7 shows the effect of the operation temperature on the adsorption of the tested Ru(III), Pd(II), and Cs(I) towards the macroporous silica-based (Calix[4] + MODB)/SiO_2-P polymeric composite. Obviously, their distribution coefficient (K_d) decreased with an increase in temperature, reflecting that the adsorption of the tested metals onto (Calix[4] + MODB)/SiO_2-P was exothermic. Therefore, increasing temperature is not of great beneficial to the adsorption of (Calix[4] + MODB)/SiO_2-P for Ru(III), Pd(II), Zr(IV), and Cs(I).

3.4. Chromatographic partitioning of Cs(I)

The separation of Cs(I) from a 3.0 M HNO_3 solution was performed utilizing the (Calix[4] + MODB)/SiO_2-P polymeric composite packed column at 298 K. The column dimensions used were 10 mm in inner-diameter and 300 mm in length. To effectively adsorb the tested elements, the silica-based adsorbent was

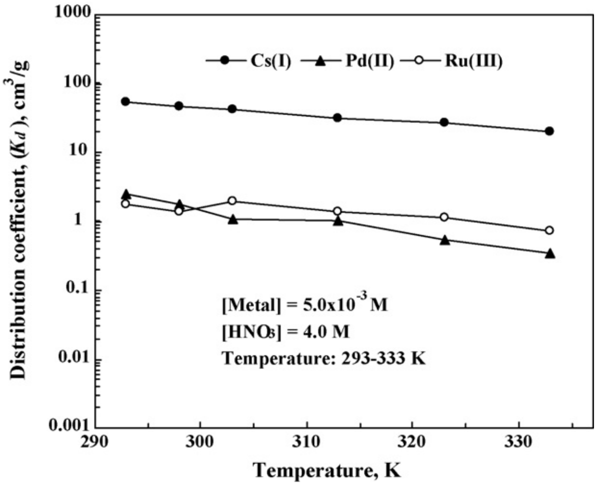


Fig. 7. Dependence of the distribution coefficient (K_d) of Pd(II), Ru(III), and Cs(I) onto (Calix[4] + MODB)/SiO_2-P with a change in temperature in the range of 293–333 K in 4.0 M HNO_3. Metal content: ~5.0×10^{-3} M, phase ratio: 0.25 g/5 cm^5, contact time: 180 min.

pre-equilibrated using a 3.0 M HNO_3 prior to experiment. The concentrations of the tested Ru(III), La(III), Y(III), Rh(III), Mo(VI), Pd(II), Cs(I), and Zr(IV) in feed solution were around 5.0×10^{-3} M. The flow rate was controlled to 1.0 cm^3/min using a NPG-50UL Model pressure gage and a 2GN15K Model pressure limiter. Following the sample was collected, the pH value in corresponding effluent was determined. The mass balance before and after the separation was calculated. The relevant partitioning results utilizing 3.0 M HNO_3 and water as eluents are illustrated in Fig. 8.

As feed solution was supplied to the column, the tested elements Ru(III), La(III), Y(III), Rh(III), Mo(VI), Pd(II), and Zr(IV) showed almost no adsorption and quickly leaked out the column along with 3.0 M HNO_3. Such the easy adsorption behavior of these tested metals in the column separation operation is quite similar to those of in the batch experiments. It was considered to result from the weak complexation of the supermolecular recognition compound Calix[4]arene-R14 with these metals. Meanwhile, Cs(I) was adsorbed by (Calix[4] + MODB)/SiO_2-P and did not appear in effluent.

Based on the separation behavior of La(III) and Y(III), it is predicted that in 3.0 HNO_3 solution, all of trivalent REs(III) such as Y(III), and from La(III) to Lu(III), and trivalent MAs (III) such as Am(III), Cm(III), *etc.* usually contained in the acidic HLW have no adsorption onto (Calix[4] + MODB)/SiO_2-P, and can flow into effluent along with La(III), Y(III), and 3.0 M HNO_3. Namely, these metals may have no adverse impact on the separation of Cs(I) from HLW.

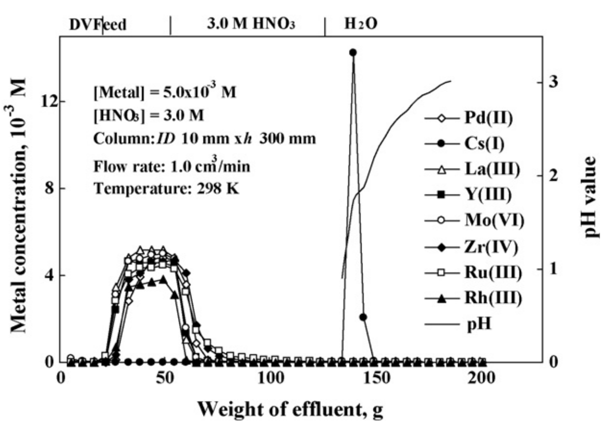


Fig. 8. Chromatographic separation of Cs(I) from a 3.0 M HNO_3 containing some typical fission products by (Calix[4] + MODB)/SiO_2-P packed column at 298 K. Column: *ID* 10 mm × *h* 300 mm, flow rate: 1.0 cm^3/min.

Subsequently, with a supply of water to the adsorption column in the form of continuous way, Cs(I) adsorbed onto the (Calix[4] + MODB)/SiO_2-P composite was eluted efficiently. The elution band observed was narrow, sharp, and showed almost no elution tailing in elution curves, reflecting that Cs(I) was eluted from the loaded (Calix[4] + MODB)/SiO_2-P polymeric composite, then quickly leaked out the adsorption column, and flowed into effluent. It indicated that the silica-based polymeric adsorption composite materials had rapid elution kinetics for Cs(I). The satisfactory elution of Cs(I) in the experiment was ascribed to the quick decomposition of the complex of Cs(I) and (Calix[4] + MODB)/SiO_2-P with a rapid decrease in the NO_3^- concentration in the resin bed. The elution equation was probably described as follows:

$$[\mathrm{Cs(Calix[4]+MODB)/SiO_2\text{-}P]NO_3} \overset{\mathrm{H_2O}}{\rightleftharpoons} \mathrm{Cs^+ + NO_3^- + (Calix[4] + MODB)/SiO_2\text{-}P} \qquad (4)$$

In terms of the mass balance, the recovery percent of the tested metals was calculated to be 99.2% for Cs(I) and in the range of 98.3–102.5% for the others. A satisfactory partitioning and recovery of Cs(I) from the tested metals was achieved.

The pH value in effluent was measured by pH-meter. As the loaded (Calix[4] + MODB)/SiO_2-P composite was eluted by 3.0 M HNO_3 and then by water, the pH value was found to increase from 0.91 to around 2.19 and then gradually to 3.02. The fact that in the elution process of Cs(I) with water, the pH value in effluent was below 3.5 showed that in the adsorption of the tested metals onto (Calix[4] + MODB)/SiO_2-P, a part of HNO_3 in feed solution composed of 3.0 M HNO_3 and 5.0×10^{-3} M of metal ions was simultaneously associated by the (Calix[4] + MODB)/SiO_2-P composite and probably formed to 1:1 type of the complex, HNO_3·(Calix[4] + MODB)/SiO_2-P, which might result in a comparatively slow increase in pH value in effluent. The elution of the loaded (Calix[4] + MODB)/SiO_2-P by water decreased the stability of HNO_3·(Calix[4] + MODB)/SiO_2-P and then released the HNO_3 molecule into effluent from the associated complex. So, the pH value less than 3.5 in the elution process of Cs(I) was observed. The association and disassociation of the complex formation of Calix[4]arene-R14 with HNO_3 were probably described as follows:

$$\mathrm{HNO_3 \cdot (Calix[4] + MODB)/SiO_2\text{-}P} \underset{3.0\,\mathrm{M\,HNO_3}}{\overset{\mathrm{H_2O}}{\rightleftharpoons}} \mathrm{HNO_3 + (Calix[4] + MODB)/SiO_2\text{-}P} \qquad (5)$$

In comparison with the adsorption of the (Calix[4] + MODB)/SiO_2-P composite material for some typical alkali and alkaline-earth metals [29], it was found that in 3.0 M HNO_3, almost 27 of the typical fission and non-fission products such as Na(I), K(I), Sr(II), Ba(II), Y(III), from La(III) to Lu(III), Am(III), Cm(III), Mo(VI), Pd(II), Ru(III), Rh(III), and Zr(IV) showed no adsorption onto (Calix[4] + MODB)/SiO_2-P with the exception of Rb(I). Recently, the preliminary research was found that U(VI), Pu(III), and Np(V) also had almost no adsorption onto (Calix[4] + MODB)/SiO_2-P. It reveals these metals have no adverse impact on the loading and elution of Cs(I) from HLW. As a result, the actual application of the silica-based (Calix[4] + MODB)/SiO_2-P composite material in effective partitioning of Cs(I), one of the main emitting heat nuclides, from HLW in the SPEC process by extraction chromatography is promising.

On the other hand, another emitting heat nuclide, Sr(II), was demonstrated to be separated effectively from a 2.0 M HNO_3 effluent containing Cs(I). It was achieved by utilizing the macroporous silica-based N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) or DtBuCH18C6 impregnated composite, DtBuCH18C6/SiO_2-P or TODGA/SiO_2-P [33]. Compared to TODGA/SiO_2-P, DtBuCH18C6/SiO_2-P showed better separation property for Sr(II). Therefore, using two novel macroporous silica-based (Calix[4] + MODB)/SiO_2-P and DtBuCH18C6/SiO_2-P composites in the SPEC process to partition Cs(I) and Sr(II) from HLW solution is feasible. The relevant verification of Cs(I) and Sr(I) separation from a genuine HLW by the hot experiment is currently being carried out.

4. Conclusions

For the purpose of safe treatment and disposal of the hazardous highly active liquid waste, effective partitioning of the heat generators, Cs(I) and Sr(II), from HLW has always been one of the most challenging works. Based on the SPEC process developed recently, an advanced separation technology of Cs(I) and Sr(II) by extraction chromatography has been established. Under the framework of the SPEC process, a novel macroporous silica-based supramolecular recognition polymeric material containing Calix[4]arene-R14 was demonstrated to be promising for selectively complexing Cs(I). However, the lipophilic calix[4]arene and hydrophilic crown ether inside Calix[4]arene-R14 molecule made synthesis of the composite unsatisfactory. In addition, the optimum concentration of HNO_3, 4.0 M, in the separation of Cs(I) in the SPEC process was higher than that of 3.0 M in genuine HLW. To overcome the disadvantages, an improved macroporous silica-based supramolecular recognition composite, (Calix[4] + MODB)/SiO_2-P, was synthesized by molecular modification of Calix[4]arene-R14 with MODB.

The adsorption of some typical fission products Ru(III), La(III), Y(III), Rh(III), Mo(VI), Cs(I), Pd(II), and Zr(IV) onto (Calix[4] + MODB)/SiO_2-P was investigated. It was found that in 3.0 M HNO_3, (Calix[4] + MODB)/SiO_2-P had high adsorption ability and excellent selectivity for Cs(I) over all of the tested elements. A target of the optimum HNO_3 concentration close to that in genuine HLW in the adsorption of Cs(I) was achieved. The chromatographic partitioning of Cs(I) from a 3.0 M HNO_3 containing $\sim 5.0 \times 10^{-3}$ M of the tested elements was performed. It was conducted by (Calix[4] + Oct)/SiO_2-P packed column by using 3.0 M HNO_3 and water as eluents. Cs(I) adsorbed by (Calix[4] + Oct)/SiO_2-P was effectively eluted out by water. A satisfactory separation of Cs(I) from the tested elements by extraction chromatography was achieved.

The experimental results demonstrated that in 3.0 M HNO_3, the macroporous silica-based polymeric composite, (Calix[4] + MODB)/SiO_2-P, is promising to application in partitioning of Cs(I) in the SPEC process. It is of great beneficial to the significant reduction of potential risk of radioactive wastes to environment.

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References

[1] N.M. Hassan, K.A. Wusu, Cesium removal from Hanford Tank Waste solutions using resorcinol-formaldehyde resin, Solvent Extr. Ion Exch. 23 (2005) 375–389.

[2] C. Madic, Overview of the hydrometallurgical and pyrometallurgical processes studied world-wide for the partitioning of high active nuclear wastes, in: International Symposium NUCEF 2001, Japan Atomic Energy Research Institute, Tokai, Japan, 2001, pp. 27–37.

[3] R.S. Herbst, J.D. Law, T.A. Todd, V.N. Romanovskiy, V.A. Babain, V.M. Esimantovskiy, I.V. Smirnov, B.N. Zaitsev, Universal solvent extraction (UNEX) flowsheet testing for the removal of cesium, strontium, and actinides elements from radioactive, acidic dissolved waste, Solvent Extr. Ion Exch. 20 (2002) 429–445.

[4] V.N. Romanovskiy, I.V. Smirnov, V.A. Babain, T.A. Todd, J.D. Law, R.S. Herbst, K.N. Brewer, The universal solvent extraction (UNEX) process. I. Development of the UNEX process solvent for the separation of cesium, strontium, and the actinides from acidic radioactive waste, Solvent Extr. Ion Exch. 19 (2001) 1–21.

[5] J.D. Law, R.S. Herbst, T.A. Todd, V.N. Romanovskiy, V.A. Babain, V.M. Esimantovskiy, I.V. Smirnov, B.N. Zaitsev, The universal solvent extraction (UNEX) process. II. Flowsheet development and demonstration of the UNEX process for the separation of cesium, strontium, and actinides from actual acidic radioactive waste, Solvent Extr. Ion Exch. 19 (2001) 23–36.

[6] N. Simon, S. Eymard, B. Tournois, J.F. Dozol, Cs selective extraction from high level liquid wastes with crown calixarenes: where are we today, in: The Atalante-2004 International Conference, June 21–24, 2004, Atalante-2004, France, 2004, pp. 1–57.

[7] P. Baron, M. Lecomte, B. Boullis, N. Simon, D. Warin, Separation of the Long Lived Radionuclides: Current Status and Future R&D Program in France, November 16–20, New Orleans, Global-2003, 2003, pp. 508–511.

[8] C.L. Riddle, J.D. Baker, J.D. Law, C.A. McGrath, D.H. Meikrantz, B.J. Mincher, D.R. Peterman, T.A. Todd, Fission product extraction (FPEX): development of a novel solvent for the simultaneous separation of strontium and cesium from acidic solutions, Solvent Extr. Ion Exch. 23 (2005) 449–461.

[9] B.J. Mincher, S.P. Mezyk, W.F. Bauer, G. Elias, C. Riddle, D.R. Peterman, FPEX γ-radiolysis in the presence of nitric acid, Solvent Extr. Ion Exch. 25 (2005) 593–601.

[10] L.H. Delmau, T.J. Lefranc, P.V. Bonnesen, J.C. Bryan, D.J. Presley, B.A. Moyer, Fundamental studies regarding synergism between calix[4]arene-bis(tert-octylbenzo-crown-6) and alcohol modifiers in the solvent extraction of cesium nitrate, Solvent Extr. Ion Exch. 23 (2005) 23–58.

[11] N.L. Engle, P.V. Bonnesen, B.A. Tomkins, T.J. Haverlock, B.A. Moyer, Synthesis and properties of calix[4]arene-bis[4-(2-ethylhexyl)bemzo-crown-6], a cesium extractant with improved solubility, Solvent Extr. Ion Exch. 22 (2004) 611–636.

[12] H. Ji, R. Dabestani, G.M. Brown, R.L. Hettich, Synthesis and sensing behavior of cyanoanthracene modified 1,3-alternate calyx[4]benzocrown-6: a new class of Cs^+ selective optical sensors, J. Chem. Soc., Perkin Trans. 2 (2001) 585–591.

[13] R.A. Sachleben, A. Urvoas, J.C. Bryan, T.J. Haverlock, B.P. Hay, B.A. Moyer, Dideoxygenated calix[4]arene crown-6 ethers enhanced selectivity for caesium over potassium and rubidium, Chem. Commun. 17 (1999) 1751–1752.

[14] A. Zhang, Y.-Z. Wei, M. Kumagai, Properties and mechanism of molybdenum and zirconium adsorption by a macroporous silica-based extraction resin in the MAREC process, Solvent Extr. Ion Exch. 21 (2003) 591–611.

[15] A. Zhang, E. Kuraoka, M. Kumagai, Removal of Pd(II), Zr(IV), Sr(II), Fe(III), and Mo(VI) from simulated high level liquid waste by extraction chromatography utilizing the macroporous silica-based polymeric materials, Sep. Purif. Technol. 50 (2006) 35–44.

[16] A. Zhang, E. Kuraoka, H. Hoshi, M. Kumagai, Synthesis of two novel macroporous silica-based impregnated polymeric composites and their application in high level activity liquid waste partitioning by extraction chromatography, J. Chromatogr. A 1061 (2004) 175–182.

[17] Y.-Z. Wei, A. Zhang, M. Kumagai, M. Watanabe, N. Hayashi, Development of the MAREC process for HLLW partitioning using a novel silica-based CMPO extraction resin, in: The 11th International Conference on Nuclear Engineering, Shinjuku, Tokyo, Japan, April 20–23, 2003 (No. 03-209, CD-ROM-ICONE-11-36084).

[18] A. Zhang, Y.-Z. Wei, M. Kumagai, Y. Koma, A new partitioning process for high level liquid waste by extraction chromatography using impregnated adsorbents, in: 2003 ANS/ENS Int. Winter Meeting, Global 2003, New Orleans, Louisiana, American, November 16–20, 2003.

[19] Y.-Z. Wei, A. Zhang, M. Kumagai, M. Watanabe, N. Hayashi, Development of the MAREC process for HLLW partitioning using a novel silica-based CMPO extraction resin, J. Nucl. Sci. Technol. 41 (2004) 315–322.

[20] A. Zhang, Q. Hu, Z. Chai, SPEC: a new process for strontium and cesium partitioning utilizing two macroporous silica-based supramolecular recognition agents impregnated polymeric composites, Sep. Sci. Technol. 44 (2009) 2146–2168.

[21] A. Zhang, E. Kuraoka, H. Hoshi, M. Kumagai, Development of the chromatographic partitioning of cesium and strontium utilizing two macroporous silica-based calix[4]arene-crown and amide impregnated polymeric composites: PREC partitioning process, J. Chromatogr. A 1157 (2007) 85–95.

[22] A. Zhang, Y.-Z. Wei, H. Hoshi, M. Kumagai, Y. Koma, M. Kamiya, Partitioning of cesium from a simulated high level liquid waste by extraction chromatography utilizing a macroporous silica-based supermolecular calix[4]arene-crown impregnated polymeric composite, Solvent Extr. Ion Exch. 25 (2007) 389–405.

[23] A. Zhang, Y.-Z. Wei, M. Kumagai, Synthesis of a novel silica-based macroporous polymeric adsorption material containing 4,4′,(5′)-di(tert-butylcyclohexano)-18-crown-6 functional group and its adsorption mechanism for strontium, React. Funct. Polym. 61 (2004) 191–202.

[24] A. Zhang, C. Xiao, E. Kuraoka, M. Kumagai, Preparation of a novel silica-based DtBuCH18C6 impregnated polymeric composite modified by tri-*n*-butyl phosphate and its application in chromatographic partitioning of stron-

tium from high level liquid waste, Ind. Eng. Chem. Res. 46 (2007) 2164–2171.

[25] Y.-Z. Wei, M. Kumagai, Y. Takashima, G. Modolo, R. Odoj, Studies on the separation of minor actinide from high-level wastes by extraction chromatography using novel silica-based extraction resins, Nucl. Technol. 132 (2000) 413–423.

[26] Z. Asfari, S. Wenger, J. Vicens, Calixcrowns and related molecules, J. Inclusion Phenom. Mol. Recognit. Chem. 19 (1994) 137–148.

[27] R. Ludwing, N.T.K. Dzung, Calixarene-based molecules for cation recognition, Sensors 2 (2002) 397–416.

[28] Z. Asfieri, V. Bohmer, J. Harrowfield, J. Vicens, M. Saadioui, Calixarenes 2001: Molecular Dynamics of Cation Complexation and Extraction, 3300 AA Dordrecht, Kluwer Academic Publishers, The Netherlands, 2001, pp. 312–333.

[29] A. Zhang, C. Xiao, W. Xie, Z. Chai, Chromatographic separation of cesium by a macroporous silica-based supramolecular recognition agent impregnated material, Sep. Purif. Technol. 66 (2009) 541–548.

[30] J. Kriz, J. Dybal, E. Makrlik, J. Budka, Interaction of hydronium ion with dibenzo-18-crown-6: NMR, IR, and theoretical study, J. Phys. Chem. A 112 (2008) 10236–10243.

[31] J. Dybal, E. Makrlik, P. Vanura, J. Budka, Protonation of 25,27-bis(1-octyloxy)calix[4]arene-crown-6 in the 1,3-*alternate* conformation, Monatsh. Chem. 139 (2008) 1175–1178.

[32] M.N. Michael, The ionic hydrogen bond. 2. Intramolecular and partial bonds. Protonation of polyethers, crown ethers, and diketones, J. Am. Chem. Soc. 105 (1983) 4906–4911.

[33] A. Zhang, Y.-Z. Wei, H. Hoshi, M. Kumagai, Chromatographic separation of strontium(II) from a nitric acid solution containing some typically simulated elements by a novel silica-based TODGA impregnated polymeric composite in MAREC process, Solvent Extr. Ion Exch. 23 (2005) 231–247.