# Development of a new simultaneous separation of cesium and strontium by extraction chromatograph utilization of a hybridized macroporous silica-based functional material

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## ABSTRACT

Based on the intermolecular modification of 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4] arene (Calix[4]) with 4,4′,(5′)-di(*t*-butylcyclohexano)-18-crown-6 (DBC), a hybridized macroporous silica-based supramolecular recognition material, Calix[4]@DBC/SiO$_2$-P, was prepared. The agents were impregnated and immobilized into the pores of the SiO$_2$-P particles support. The adsorption of Cs(I), Sr(II), and some typical coexistent metals onto Calix[4]@DBC/SiO$_2$-P was investigated. The influence of contact time and HNO$_3$ concentration in the range of 0.4–6.0 M was studied. Calix[4]@DBC/SiO$_2$-P exhibited high adsorption ability and selectivity for Sr(II) and Cs(I) except for Rb(I) and Ba(II). The simultaneous partitioning of Cs(I) and Sr(II) from a simulated highly active liquid waste was performed by Calix[4]@DBC/SiO$_2$-P packed column. They were effectively eluted with water and flowed into effluent along with Rb(I) and Ba(II), while others showed no adverse impact. A new separation process, GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography), for the separation of Cs(I) and Sr(II) was proposed.

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## 1. Introduction

Cs(I) and Sr(II) are called heat generators. The isotopes of Cs(I), Cs-137 with a half-life of 30-year and Sr-90 with a half-life of 28.5-year contained in highly active liquid waste (HLW), are harmful for the vitrified-HLW in final geological disposal. Another isotopes, Cs-135 with a half-life of $2 \times 10^6$-year, has the long-termed potential risk on environment due to its mobility in final repository. They are considered to be one of the most contributors of the radioactivity in HLW. It is reported that they can pose a serious radiation hazard to health and environment. To significantly decrease the adverse impact, the effective separation of Cs(I) and Sr(II) from HLW to a great extend is necessary. However, the most of the investigations on the HLW treatment have been focused on the separation of the long-lived minor actinides MAs(III) [1–8], while a little of attention to Sr(II) and Cs(I). The partitioning and recovery of Sr(II) and Cs(I) have always been one of the most challenging works these decades.

The liquid–liquid solvent extraction is one of the main technologies for the Sr(II) and Cs(I) separation [9–18]. A few partitioning processes such as the universal solvent extraction [9–11], fission

product extraction [12,13], strontium extraction [14–16], and cesium separation with calixcrown extraction [17,18] have been reported. As an alternative pathway, extraction chromatography has not been used in the separation of Sr(II) and Cs(I) from HLW. In fact, it is known that the quantity of heat generators in HLW is lower than those of other metals in HLW. This made it possible that the effective separation of heat generators by means of extraction chromatography is better than that of solvent extraction, a conventional separation technology.

The derivative of calix[4]arene-crown is a kind of the macrocyclic organic agent with a special molecular structure. It is composed of a calix[4]arene and a crown ether moiety bonded together by means of the phenolic oxygens of the calix[4]arene and a polyether chain [19,20]. It usually combines the excellent supramolecular recognition ability of the calix[4]arene with the simplicity and high selectivity character of the crown ether. Especially, one of the most effective conformations, 1,3-alternate calix[4]arene-crown shows high selectivity for Cs(I) and forms to a 1:1 type of the mononuclear complex formation [21,22]. It was reported that in liquid–liquid solvent extraction, the selectivity ratios of Cs(I) to Na(I) and K(I) for some of these calix[4]arene-crown exceed 10,000 and 100. Application of the derivative of calix[4]arene-crown is suitable for the separation of Cs(I) from highly active liquid waste.

A new kind of the macroporous silica-based calix[4]arene-crown supramolecular recognition material (SSRM) was developed recently. It had better recognition property and high selectivity for Cs(I) or Sr(II) [23,24]. The preliminary results showed that in HNO$_3$ medium, Cs(I) or Sr(II) was promising to separate alone from an acidic highly active liquid waste by the macroporous SSRM. However, the simultaneous separation of Sr(II) and Cs(I) from HLW has not been archived yet. The investigations on the adsorption/separation of Sr(II) and Cs(I) together by the macroporous SSRM has not been reported. Because the alkali metals and the alkaline earths are difficult comparatively to form the stable complex, it is promising to separate Cs(I) or Sr(II) from waste water, respectively.

To separate Cs(I) and Sr(II) simultaneously, the object of the present work is focused on (1) vacuum preparation of a new macroporous silica-based 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) and 4,4′,(5′)-di(tert-butylcyclohexano)-18-crown-6 (DBC) supramolecular recognition material, Calix[4]@DBC/SiO$_2$-P, through impregnation and immobilization of both Calix[4] and DBC into the pores of the SiO$_2$-P particles. (2) Evaluating the impact of contact time and the HNO$_3$ concentration on the adsorption of some typical fission and non-fission products such as Pd(II), Ru(III), Mo(VI), Ba(II), Sr(II), Zr(IV), La(III), Na(I), K(I), Rb(I), Cs(I), and Y(III) onto Calix[4]@DBC/SiO$_2$-P. The optimum HNO$_3$ concentration in the Cs(I) and Sr(II) adsorption was determined, and (3) simultaneous partitioning of Cs(I) and Sr(II) from a simulated HLW was performed by Calix[4]@DBC/SiO$_2$-P packed column. An advanced separation process entitled GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography) was developed.

## 2. Experimental

### 2.1. Reagents

Alkali metals nitrates M$^I$NO$_3$ (M$^I$ = Na, K, Rb, and Cs), alkaline earths nitrates M$^{II}$(NO$_3$)$_2$ (M$^{II}$ = Sr and Ba), ZrO(NO$_3$)$_2$·2H$_2$O, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, RE(NO$_3$)$_3$·nH$_2$O (RE = Y and La, n = 3 or 6) were of analytical grade. Ruthenium nitrosyl nitrate solution with 1.5 wt% of Ru(III) and palladium nitrate solution with 4.5 wt% of Pd(II) were provided by the Strem Chemicals, USA and the Tanaka Noble Metal Co. Inc., Japan, respectively. Trivalent La(III) and Y(III) were used to understand the adsorption behavior of all rare earths REs(III), Am(III), and Cm(III). The concentrations of all the tested metals were about $5.0 \times 10^{-3}$ M. The HNO$_3$ solutions of different concentrations in batch and column experiments were prepared temporarily.

1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) was synthesized quantitatively by a complicated technical route as shown in Fig. 1. Its purity was greater than 98.5%, which was determined through a high performance liquid chromatography (HPLC). 4,4′,(5′)-Di(tert-butylcyclohexano)-18-crown-6 (DBC) with a purity more than 97% was provided by the Eichrom Technologies Inc., USA. 1-Octanol was an available commercial product, which was used as the molecular modifier being capable of improving significantly the affinity of Calix[4] and DBC through intermolecular interaction force.

### 2.2. Preparation of the macroporous silica-based materials

Calix[4]@DBC/SiO$_2$-P was prepared through impregnating and immobilizing Calix[4] and DBC into the macroporous SiO$_2$-P particles. It was based on the intermolecular interaction between Calix[4], DBC and co-polymer contained in the SiO$_2$-P particles. Calix[4] is composed of a hydrophobic calix[4]arene and a hydrophilic crown ether, while DBC is a hydrophilic compound containing oxygen atoms. The united use of them in the synthesis of the materials might be beneficial to increasing the hydrophilicity of calix[4]crown while decreasing the hydrophobicity of DBC. As a result, the quantity of 1-octanol, a molecular modifier, used in the synthesis of SSRM would be decrease. On the other hand, prior to synthesis of SSRM the macroporous SiO$_2$-P particles were pretreated actively using methanol and acetone at room temperature. The synthesis of Calix[4]@DBC/SiO$_2$-P was described as follows: Calix[4], DBC, and the modifier dissolved with an organic solvent and the activated SiO$_2$-P particles were mixed into a 250 cm$^3$ of conical flask. After it was shaken for 90 min, it was then stirred in a silicon-oil bath for 180 min. The impregnation of Calix[4], DBC, and the modifier into the pores of the SiO$_2$-P particles was not continued until the solvent was evaporated. The purpose was to effectively impregnate and immobilize the agents inside the SiO$_2$-P particles at 323 K. Following drying the product at 318 K overnight, the novel material, Calix[4]@DBC/SiO$_2$-P, was got. It was characterized by XRD, $^{29}$Si CP/MAS NMR, TG-DSC, and BET. The appearance of the SiO$_2$-P particles support and the Calix[4]@DBC/SiO$_2$-P material are shown in Fig. 2.

### 2.3. Adsorption of the tested metals onto SSRMs

The adsorption of the tested elements towards Calix[4]@DBC/SiO$_2$-P was performed at 298 K, which was controlled using a TAITEC MM-10 Model thermostated water bath.

As the designed volume of HNO$_3$ solution containing the tested metals Mo(VI), Na(I), K(I), La(III), Zr(IV), Pd(II), Rb(I), Cs(I), Ru(III), Ba(II), Sr(II), and Y(III) and the given amount of Calix[4]@DBC/SiO$_2$-P were mixed into a 50 cm$^3$ of ground glass-stopped flask, it was shaken mechanically at 120 rpm. The HNO$_3$ concentration in aqueous phase was in the range of 0.4–6.0 M. The concentrations of the tested metals and the ratio of solid phase to aqueous one were around $5.0 \times 10^{-3}$ M and 0.25 g/5 cm$^3$. Following the phase separation through a membrane filter, the concentrations of the tested metals in aqueous phase were then measured using a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Inc., USA) or by a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian Inc., USA). The distribution coefficients ($K_d$) of the tested metals onto Calix[4]@DBC/SiO$_2$-P was calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (\text{cm}^3/\text{g}) \qquad (1)$$

In Eq. (1), the symbols $C_o$ and $C_e$ present the initial and equilibrium concentrations of the tested metals in aqueous phase, respectively. The symbols $W$ and $V$ denote the weight of dry Calix[4]@DBC/SiO$_2$-P and the volume of aqueous phase used in the experiments.

### 2.4. Simultaneous separation of Cs(I) and Sr(II) by extraction chromatography

The partitioning of Cs(I) and Sr(II) by the macroporous SSRM Calix[4]@DBC/SiO$_2$-P was performed using a Pyrex-glass column as shown in Fig. 3. Prior to separation performance the Calix[4]@DBC/SiO$_2$-P packed column was fully equilibrated with 3.0 M HNO$_3$. The operation temperature in the loading and elution cycles was maintained at 298 K. It was kept by the circulation of the thermostated water using an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co. Ltd., Japan). The flow rate in the column operation was 1.0 cm$^3$/min controlled by a metering pump. The concentration of HNO$_3$ in feed solution was 3.0 M HNO$_3$, which is the same with that of in genuine HLW. The tested metals were composed of $5.0 \times 10^{-3}$ M of Na(I), K(I), Rb(I), Ru(III), Mo(VI), Cs(I), Ba(II), Sr(II), La(III), Pd(II), and Y(III).
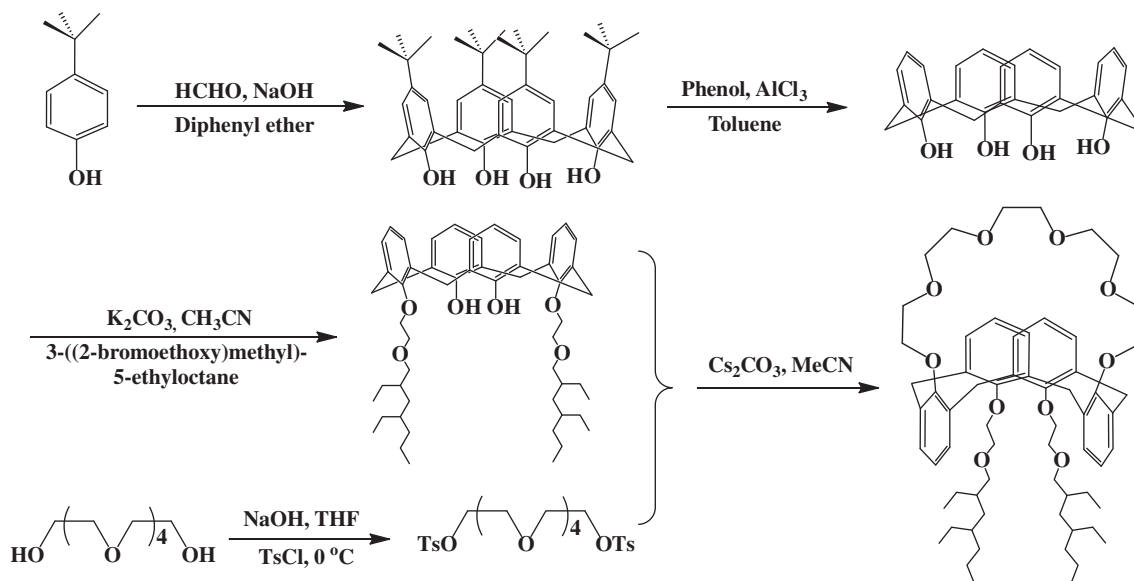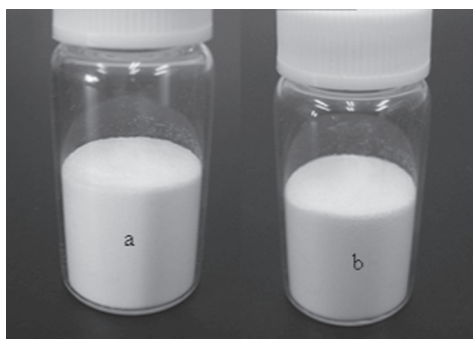
**Fig. 1.** Synthesis of 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]).



Appearance of the materials

(a) SiO$_2$-P particles, (b) Calix[4]@DBC/SiO$_2$-P

**Fig. 2.** Photos of the SiO$_2$-P particles and Calix[4]@DBC/SiO$_2$-P.
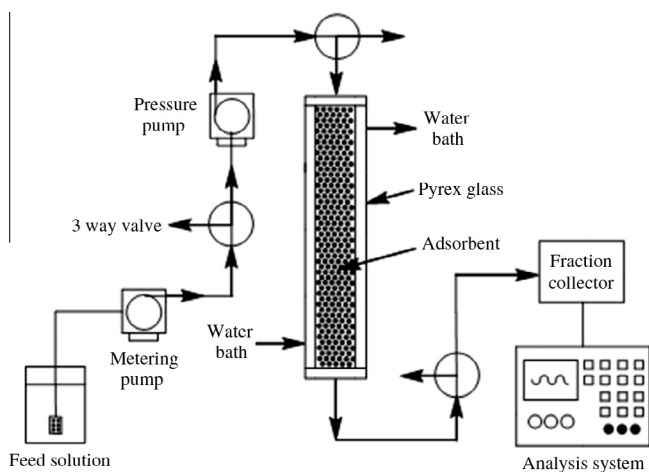


**Fig. 3.** Schematic diagram of experimental apparatus for the simultaneous separation of Cs(I) and Sr(II) by Calix[4]@DBC/SiO$_2$-P.

As feed solution mentioned above was supplied, the amount of 3.0 M HNO$_3$ and H$_2$O as eluents was subsequently pumped downflow through the adsorption column. 5 cm$^3$ aliquots of effluent fractions were collected one by one using an EYELA DC-1500 Model auto-fractional collector (Tokyo Rikakikai Co., Ltd., Japan). The concentrations of the tested metals in effluent were analyzed using the Varian 700-ES ICP-OES or the Varian AA 240 FS Model atomic adsorption spectroscopy mentioned above. The pH value in effluent was measured by a Leici pHs-3C Model meter (Shanghai Precision & Scientific Instrument Co., Ltd., China). In terms of the analysis results of effluent, the recovery percentage of the tested metal was calculated.

## 3. Results and discussion

### 3.1. Dependence of the metals adsorption on contact time

Calix[4]@DBC/SiO$_2$-P is a new kind of the hybridized material. The investigations related to Calix[4]@DBC/SiO$_2$-P have not been reported. To understand the adsorption behavior of Calix[4]@DBC/SiO$_2$-P, the static-state adsorption of some typical fission and non-fission products such as Mo(VI), La(III), Na(I), K(I), Pd(II), Rb(I), Zr(IV), Ba(II), Cs(I), Sr(II), Ru(III), and Y(III) with a change in contact time in 3.0 M HNO$_3$ was studied. The results are exhibited in Fig. 4.

Fig. 4 shows the dependence of the adsorption kinetics of the tested elements towards the Calix[4]@DBC/SiO$_2$-P functional material on contact time in 3.0 M HNO$_3$. It was found that in the tested HNO$_3$ solution, the adsorption of Calix[4]@DBC/SiO$_2$-P for Sr(II) and Cs(I) was strong. The distribution coefficients ($K_d$) of them increased with increasing contact time and then kept constant after 60 min, which reflected that the adsorption equilibrium was reached. The relevant valuable of the distribution coefficients ($K_d$) were greater than 77.1 cm$^3$/g. The strong adsorption of heat generators in 3.0 M HNO$_3$ was considered to the size matching between host and guest, i.e., the excellent match between the diameter of Cs(I) and the cavity of Calix[4] as well as the diameter of Sr(II) and the cavity of DBC comprising six oxygen atoms as shown in Fig. 5. It made the complexation of Sr(II) and Cs(I) with Calix[4]@DBC/SiO$_2$-P stronger.
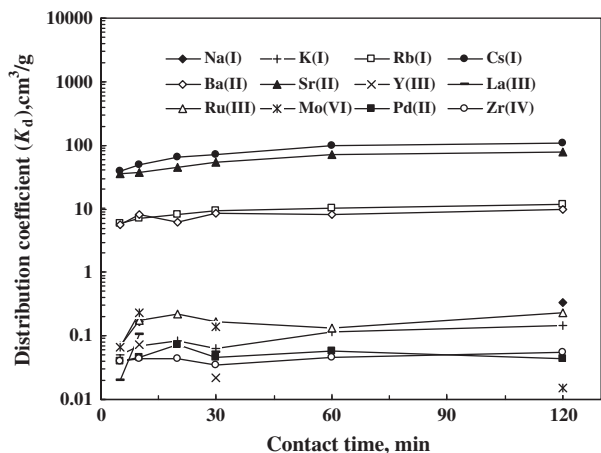
**Fig. 4.** Dependence of the tested metals adsorption onto Calix[4]@DBC/SiO₂-P on contact time in 3.0 M HNO₃ at 298 K. [Metal]: 5 mM, Phase ratio: 0.25 g/5 cm³, Shaking speed: 120 rpm.

Opposite to the adsorption of Cs(I) and Sr(II), the other tested metals Mo(VI), La(III), Pd(II), Zr(IV), Na(I), K(I), Ru(III), and Y(III) showed very weak or almost no adsorption onto Calix[4]@DBC/SiO₂-P with the exception of Rb(I) and Ba(II). The distribution coefficients ($K_d$) of them were always below 0.23 cm³/g.

On the other hand, the apparent shape and character of the adsorption curves of Cs(I) and Sr(II) were quite close to those of the typical chemical adsorption of metals [25,26]. The adsorption mechanism of Sr(II) and Cs(I) toward Calix[4]@DBC/SiO₂-P in HNO₃ medium was considered to the chemical adsorption. In other words, the complexation of Sr(II) with DBC and Cs(I) with Calix[4] might be the rate-controlling step.

It is known that the chemical properties of all the trivalent rare earths REs(III) and trivalent minor actinides MAs(III) are quite similar. The negligible adsorption of La(III) and Y(III) onto Calix[4]@DBC/SiO₂-P predicts that in 3.0 M HNO₃, all REs(III) including Y(III) and from La(III) to Lu(III) as well as MAs(III) such as Am(III) and Cm(III) might have weak or almost no adsorption onto Calix[4]@DBC/SiO₂-P. It implies that all REs(III) and MAs(III) contained in genuine HLW solution might have no adverse impact on the separation of Sr(II) and Cs(I).

The difference in the adsorption of the tested metal ions revealed that in 3.0 M HNO₃, the novel Calix[4]@DBC/SiO₂-P materials showed excellent adsorption ability and high selectivity for Sr(II) and Cs(I) over all of the tested metals with the exception of Rb(I) and Ba(II). It is beneficial to partitioning of heat generators from HLW by the porous adsorbent.
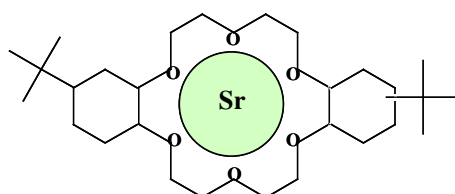
### 3.2. Dependence of the metals adsorption on the HNO₃ concentration

DBC as a derivative of crown ether comprises six oxygen atoms. It has excellent affinity for hydrogen or hydrogen-containing compound through hydrogen bonding. In addition, the Calix[4]crown is composed of a highly lipophilic calix[4]arene and a hydrophilic crown ether. Such a special structure in Calix[4]crown makes its affinity for hydrogen or hydrogen-containing compound through hydrogen bonding high. On the other hand, the HNO₃ concentration in genuine HLW is usually around 3.0 M. To evaluate the impact of the HNO₃ concentration, the adsorption of the tested metals onto Calix[4]@DBC/SiO₂-P with a change in the HNO₃ concentration was investigated. The results are illustrated in Fig. 6.

It was found that with increasing the concentration of HNO₃, both Sr(II) and Cs(I) showed strong adsorption onto Calix[4]@DBC/SiO₂-P. The Cs(I) adsorption increased from 0.4 M to 4.0 M HNO₃ and then decreased to 6.0 M HNO₃. Cs(I) showed a
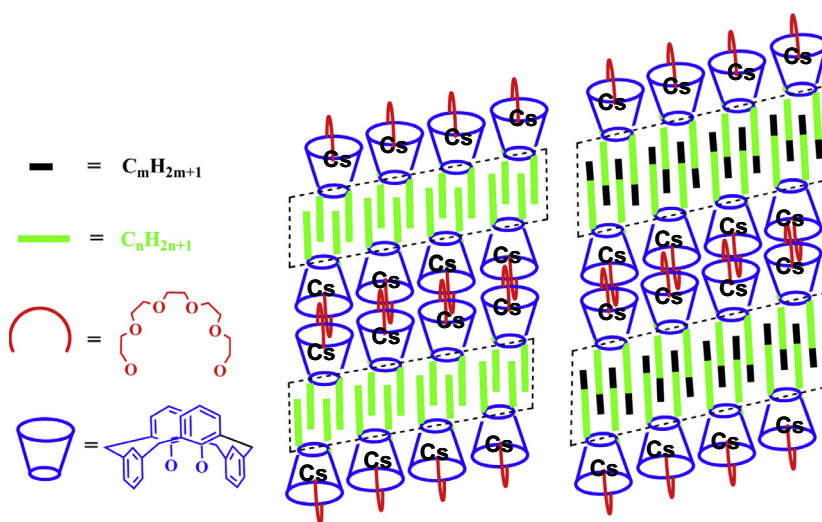


(a) Match of the Cs(I) size with cavity of Calix[4] containing π-bonding interactions.



(b) Match of the Sr(II) size with cavity of DBC.

**Fig. 5.** Supramolecular recognition of Calix[4] for Cs(I) and DBC for Sr(II).
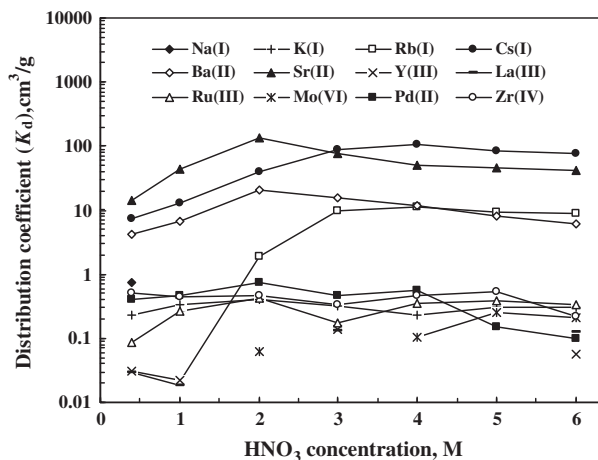
**Fig. 6.** Dependence of the tested metals adsorption onto Calix[4]@DBC/SiO$_2$-P on the HNO$_3$ concentration in the range of 0.4 M to 6.0 M at 298 K. [Metal]: 5 mM, Phase ratio: 0.25 g/5 cm$^3$, Shaking speed: 120 rpm, Contact time: 120 min.



**Fig. 7.** Relationship between ionic radius, atomic number, and the distribution coefficients ($K_d$) of 28 elements in three dimensions.

maximum adsorption at HNO$_3$ concentration of 4.0 M, while Sr(II) showed an increase from 0.4 M to 2.0 M HNO$_3$ and then a decrease to 6.0 M HNO$_3$. The maximum HNO$_3$ concentration for the adsorption of Sr(II) was 2.0 M. Obviously, the HNO$_3$ concentrations, 2.0 M HNO$_3$ and 4.0 M HNO$_3$, in the maximum adsorption of Sr(II) and Cs(I) were different. To get a satisfactory adsorption results, the reasonable way is to select 3.0 M HNO$_3$ as the optimum adsorption acidity due to the following reasons: (1) the distribution coefficients ($K_d$) of Sr(II) and Cs(I) in 3.0 M HNO$_3$ were 75.91 cm$^3$/g and 89.93 cm$^3$/g, respectively. Although such the values in the distribution coefficients in 3.0 M HNO$_3$ were lower than those of in 2.0 M HNO$_3$ and 4.0 M HNO$_3$, it was still far greater than those of other tested metals onto Calix[4]@DBC/SiO$_2$-P. It reflected that in 3.0 M HNO$_3$ medium, Calix[4]@DBC/SiO$_2$-P had strong adsorption ability and high selectivity for both Sr(II) and Cs(I). (2) 3.0 M HNO$_3$ is the full same with that of in the genuine HLW solution. If application of Calix[4]@DBC/SiO$_2$-P in simultaneous partitioning of Sr(II) and Cs(I) from the genuine HLW, it can be used directly without adjustment of the HNO$_3$ concentration, and (3) the quantity of a variety of radioactive wastes produced in the separation operation cycle would be reduced significantly. Therefore, it is more reasonable to select 3.0 M HNO$_3$ as the optimum concentration of HNO$_3$ in the adsorption and separation of both Sr(II) and Cs(I). It is of great beneficial to separation of heat generators by Calix[4]@DBC/SiO$_2$-P.

The trivalent La(III) and Y(III) exhibited almost no adsorption onto Calix[4]@DBC/SiO$_2$-P. It would be meaningful for understanding the impact of REs(III) and MAs(III) on the Cs(I) and Sr(II) adsorption. It is known that the ionic radii of the actinide elements decrease with an increase in atomic number, indicative of decreased shielding by f electrons of the outer valence electrons nuclear charge. This makes the actinide contraction and lanthanide contraction similar. Namely, the chemical properties of trivalent MAs(III) were close to those of trivalent REs(III). From this viewpoint, the long-lived minor actinides Am(III) and Cm(III) as well as 16 species of REs(III), i.e. Y(III) and from La(III) to Lu(III), would have no adsorption onto Calix[4]@DBC/SiO$_2$-P. Combination of the discussions with the adsorption of the tested metals carried out, more than 28 elements contained in an acidic HLW might have no adverse impact on the adsorption of Sr(II) and Cs(I). The relationship between ionic radius, atomic number, and the distribution coefficients ($K_d$) of these metals in 3.0 M HNO$_3$ in three dimensions is presented in Fig. 7. It is valuable for the effective elimination of Cs(I) and Sr(II) from HLW.
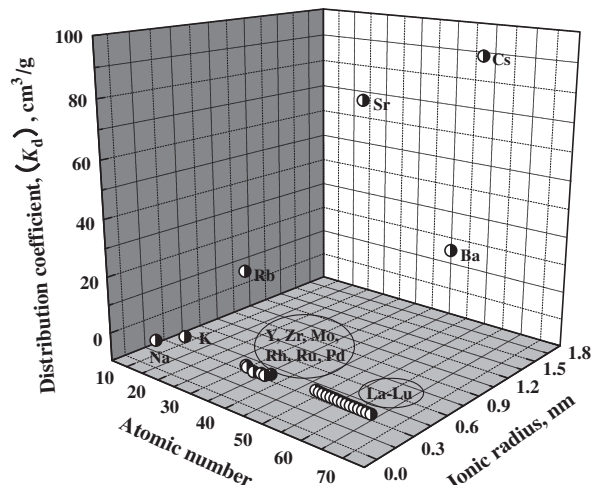
### 3.3. Chromatographic partitioning of Cs(I) and Sr(II)

To evaluate the possibility and feasibility of the simultaneous separation of heat generators, the impact of some typical fission and non-fission products on chromatographic partitioning of Cs(I) and Sr(II) was investigated. It was performed utilizing the Calix[4]@DBC/SiO$_2$-P material packed column. The elution results using 3.0 M HNO$_3$ and water are shown in Fig. 8.

Fig. 8 represents the chromatographic separation of Sr(II) and Cs(I) from a 3.0 M HNO$_3$ solution. As can be seen, with the supplement of the feed solution to the adsorption column, the tested Ru(III), Na(I), K(I), Zr(IV), Mo(VI), Pd(II), La(III), and Y(III) exhibited almost no adsorption towards Calix[4]@DBC/SiO$_2$-P and leaked out the column along with 3.0 M HNO$_3$. In terms of no adsorption of La(III) and Y(III), it is predicted that in 3.0 HNO$_3$ solution, all of REs(III) and MAs(III) in HLW would have no adsorption onto Calix[4]@DBC/SiO$_2$-P and flow into effluent along with La(III), Y(III), and 3.0 M HNO$_3$. The conclusion of REs(III) and MAs(III) showing no impact on the separation of heat generators by Calix[4]@DBC/SiO$_2$-P was verified.

Subsequently, when water as an eluent was supplied to the adsorption column, it was found that Sr(II) and Cs(I) were efficiently eluted and flowed into effluent along with Rb(I) and Ba(II). The resultant elution band appeared in elution curves of
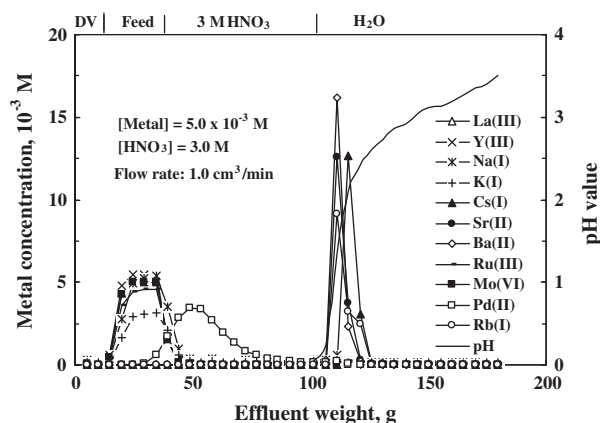


**Fig. 8.** Simultaneous partitioning of Cs(I) and Sr(II) from 3.0 M HNO$_3$ by Calix[4]@DBC/SiO$_2$-P packed column at 298 K. Column: *ID* 10 mm × *h* 320 mm, Flow rate: 1.0 cm$^3$/min.
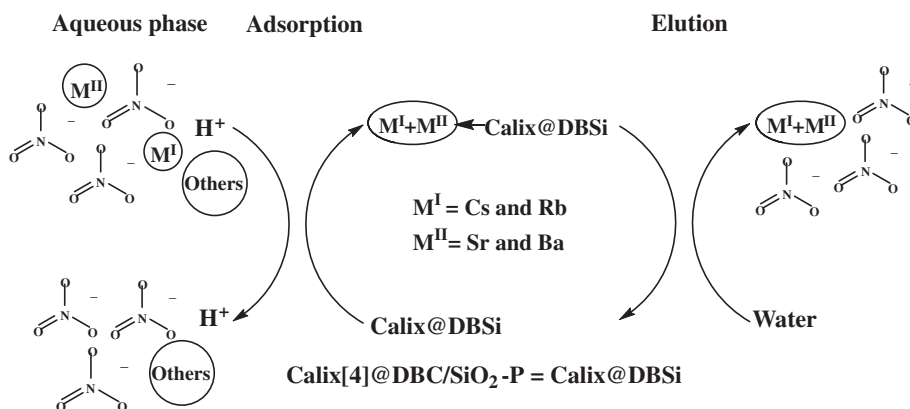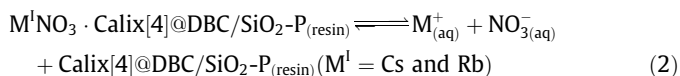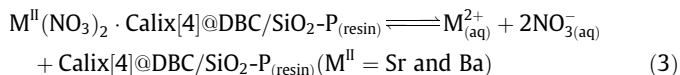
**Fig. 9.** Loading and elution mechanism of Sr(II) and Cs(I) in chromatographic partitioning by the Calix[4]@DBC/SiO$_2$-P materials.

Sr(II) and Cs(I) were sharp, narrow, and almost no elution tail. Sr(II), Ba(II), Rb(I), and Cs(I) were effectively eluted with water and separated into the same group, i.e., Cs–Sr group. The elution effect was contributed to the quick decomposition of the complexes of Cs(I) and Rb(I) with Calix[4]crown as well as of Sr(II) and Ba(II) with DBC with a quickly decrease in the concentration of NO$_3^-$ in the resin bed. The corresponding adsorption and elution mechanism of them in the loading and elution cycles is shown in Fig. 9.

To understand the complex composition of calix[4]arene-crown and Cs(I), the extraction of Cs(I) with 1,3-[(2,4-nony)oxy]-2,4-crown-6-calix[4]arene (NonCalix[4]C6) containing system was investigated [27]. It was found that in 3.0 M HNO$_3$, a stable 1:1 type of the extracted species, CsNO$_3$·NonCalix[4]C6, was formed. Consideration of the adsorption behavior of the Calix[4]@DBC/SiO$_2$-P materials, if one assumes that in HNO$_3$ solution, one Cs(I) can react with one Calix[4], then, the composition of the complex formation of Cs(I) with Calix[4]@DBC /SiO$_2$-P would be CsNO$_3$·Calix[4]@DBC/SiO$_2$-P. The elution mechanism of Cs(I) and Rb(I) in column operation was therefore presented as follows:

$$M^I NO_3 \cdot Calix[4]@DBC/SiO_2\text{-}P_{(resin)} \rightleftharpoons M^+_{(aq)} + NO^-_{3(aq)}$$
$$+ Calix[4]@DBC/SiO_2\text{-}P_{(resin)}(M^I = Cs \text{ and } Rb) \qquad (2)$$
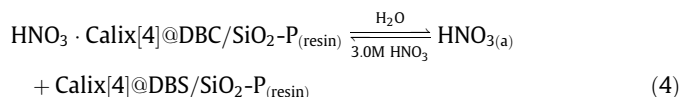
Similarly, it was found that in HNO$_3$ solution, the divalent Sr(II) was strongly adsorbed by DBC/SiO$_2$-P and formed to the complex formation, Sr(NO$_3$)$_2$·DBC/SiO$_2$-P [28]. This makes it possible that if one assumes that one Sr(II) reacts with two DBC, then, the composition of the complex formation of Sr(II) with Calix[4]@DBC/SiO$_2$-P would be Sr(NO$_3$)$_2$·Calix[4]@DBC/SiO$_2$-P. The elution mechanism of Sr(II) and Ba(II) was described as follows:

$$M^{II}(NO_3)_2 \cdot Calix[4]@DBC/SiO_2\text{-}P_{(resin)} \rightleftharpoons M^{2+}_{(aq)} + 2NO^-_{3(aq)}$$
$$+ Calix[4]@DBC/SiO_2\text{-}P_{(resin)}(M^{II} = Sr \text{ and } Ba) \qquad (3)$$

According to the mass balance, the recovery percent of the tested metals was calculated to be 99.2 for Cs(I), 99.7 % for Sr(II) and in the range of 98.7–100.5% for the others. A satisfactory partitioning and recovery of Cs(I) and Sr(II) from the tested metals was achieved. It implied that these metals were desorbed completely from the loaded Calix[4]@DBC/SiO$_2$-P materials.

To evaluate the elution of Cs(I) and Sr(II), the pH value in effluent was measured. As the loaded Calix[4]@DBC/SiO$_2$-P were eluted by water, the pH value increased rapidly from 0.24 to 2.73 and then to 3.33. It revealed that with the supply of the feed solution composed of 4.0 M HNO$_3$ and $5.0 \times 10^{-3}$ M of the tested metals to column at initial stage, besides the adsorption of Cs(I), Sr(II), and the other metals onto Calix[4]@DBC/SiO$_2$-P occurred, a portion of HNO$_3$ was simultaneously associated with Calix[4]crown and

DtBuCH18C6 through hydrogen bonding and probably formed to a 1:1 type of the complex, HNO$_3$·Calix[4]@DBC/SiO$_2$-P. The same type of the complex of HNO$_3$ with other crown ethers was reported [29–32]. Subsequently, when water as an eluent was supplied, the HNO$_3$ concentration in effluent significantly decreased. The corresponding pH value in effluent rapidly increased. It means that with washing using water, the HNO$_3$ removed to the effluent might result from the dead volume of the column and the decomposition of HNO$_3$·Calix[4]@DBC/SiO$_2$-P. For the latter, HNO$_3$ associated with Calix[4] and DBC was released and then flowed into effluent. Therefore, the low pH value smaller than 3.33 in effluent was observed. The association and disassociation of the formation of Calix[4] and DBC with HNO$_3$ were probably described as follows:

$$HNO_3 \cdot Calix[4]@DBC/SiO_2\text{-}P_{(resin)} \xrightleftharpoons[3.0M\ HNO_3]{H_2O} HNO_{3(a)}$$
$$+ Calix[4]@DBS/SiO_2\text{-}P_{(resin)} \qquad (4)$$

### 3.4. Establishment of an advanced GPSC process

On the basis of the partitioning results mentioned above, an advanced chromatographic separation process entitled GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography) has been developed. The relevant concept flow sheet for the simultaneous separation of Cs(I) and Sr(II) from a simulated HLW is illustrated in Fig. 10. It consisted of one separation column packed with Calix[4]@DBC/SiO$_2$-P.

In comparison with the conventional liquid–liquid solvent extraction and the others, the GPSC process has following advantages: (1) the separation of Cs(I) and Sr(II) was simultaneous. It was carried out in the same adsorption column packed with Calix[4]@DBC/SiO$_2$-P by eluting with water only. Due to the excellent supramolecular recognition of Calix[4]@DBC/SiO$_2$-P for Cs(I) and Sr(II), almost all of the other fission and non-fission products such as Na(I), K(I), REs(III), the long-lived minor actinides MAs(III) such as Am(III) and Cm(III), noble metals Ru(III), Pd(II), and Rh(III) as well as Zr(IV) and Mo(VI). showed no adverse impact on the Cs(I) and Sr(II) partitioning from HLW except Rb(I) and Ba(II). (2) Cs(I) and Sr(II) are usually considered to the main origin of the strong radioactivity in HLW. If both of them are separated from HLW in advance, then, the radioactivity in HLW would be reduced significantly. It is of great beneficial to the further treatment of HLW next step such as the separation of MAs(III), which is thought as the very important investigations due to the partitioning and transmutation (P/T) strategy [33–35]. While, it is also valuable for the further separation of the other long-lived nuclides such as Pd(II) and Tc(VII)
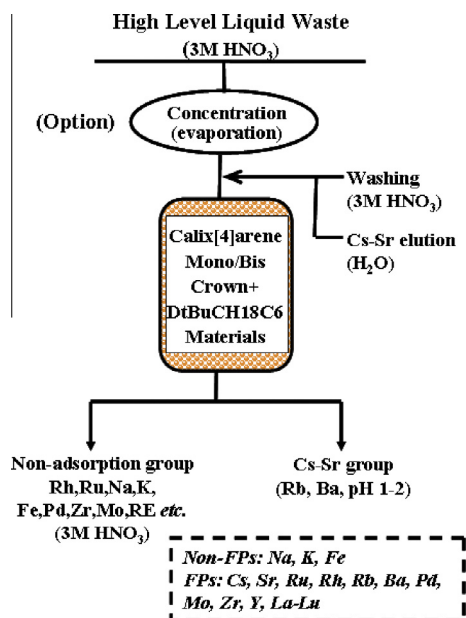
**Fig. 10.** Concept flowsheet of the GPSC process for simultaneous partitioning of cesium and strontium from HLW by extraction chromatography.

from HLW, and (3) the purposes of utilization of minimal organic solvent, the low waste accumulation, and the compacted equipments in effective treatment of HLW are probably achieved. This makes the separation performance significantly simplified. It is beneficial to significant reduction of the quantity of the radioactive wastes and the process capital in cost.

## 4. Conclusions

Cs(I) and Sr(II) are harmful for the vitrified-HLW in final geological disposal. The long- termed potential risk might result in possible release of radioactive nuclides to environment. For the purpose of effective disposal of HLW, the simultaneous separation of them from HLW is valuable. Moreover, Cs(I) and Sr(II) are the main origin of the strong radioactivity in HLW. The elimination of them together can significantly decrease the radioactivity. However, effective partitioning of Cs(I) and Sr(II) from HLW has always been one of the most challenging works. To simultaneous separation of them, a hybridized macroporous silica-based supramolecular recognition material, Calix[4]@DBC/SiO$_2$-P, was synthesized through the impregnation and immobilization techniques.

The adsorption of Calix[4]@DBC/SiO$_2$-P for some typical metals was investigated. It was evaluated by examining the effects of contact time and the HNO$_3$ concentration. Calix[4]@ DBC/SiO$_2$-P showed excellent adsorption ability and high selectivity for Cs(I) and Sr(II) over all of the tested elements except Rb(I) and Ba(II). The optimum concentration of HNO$_3$ in the adsorption of Sr(II) and Cs(I) was selected to 3.0 M. The chromatographic separation of Sr(II) and Cs(I) from a 3.0 M HNO$_3$ solution was performed by Calix[4]@DBC/SiO$_2$-P packed column. More than 28 of fission and non-fission products such as alkali metal, alkaline earths, 16 species of REs(III), Ru(III), Zr(IV), and Mo(VI). would have no adverse impact on the Sr(II) and Cs(I) separation. A satisfactorily simultaneous partitioning of Sr(II) and Cs(I) utilizing Calix[4]@DBC/SiO$_2$-P was achieved. Based on the partitioning results, an advanced chromatographic separation technology entitled GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography) process was developed.

## References

[1] C. Madic, Overview of the hydrometallurgical and pyrometallurgical process studied world-wide for the partitioning of high active nuclear wastes. International Symposium NUCEF 2001, 31 October–2 November 2001, Japan Atomic Energy Research Institute, Conf 2002–004, March 2002, Japan, 2002, p. 27.
[2] J.M. Mathur, M.S. Murali, K.L. Nash, Solvent Extr. Ion Exch. 19 (2001) 357.
[3] A. Apichaibukol, Y. Sasaki, Y. Morita, Solvent Extr. Ion Exch. 22 (2004) 997.
[4] Y. Koma, M. Watanabe, S. Nemoto, Y. Tanaka, Solvent Extr. Ion Exch. 16 (1998) 1357.
[5] A. Zhang, K. Etsushu, M. Kumagai, Y. Koma, T. Koyama, J. Radioanal. Nucl. Chem. 269 (2006) 119.
[6] A. Zhang, K. Etsushu, H. Hoshi, M. Kumagai, J. Chromatogr. A 1061 (2004) 175.
[7] A. Zhang, Y. Wei, M. Kumagai, Y. Koma, A new partitioning process for high level liquid waste by extraction chromatography using impregnated adsorbents, 2003 ANS/ENS Int. Winter Meeting, Global 2003, New Orleans, Louisiana, American, November 16–20, 2003.
[8] R.S. Mark, J. Foreman, J.H. Michael, G. Andreas, C. Madic, M. Weigl, Solvent Extr. Ion Exch. 23 (2005) 645.
[9] R.S. Herbst, J.D. Law, T.A. Todd, V.N. Romanovskiy, V.A. Babain, V.M. Esimantovskiy, I.V. Smirnov, B.N. Zaitsev, Solvent Extr. Ion Exch. 20 (2002) 429.
[10] V.N. Romanovskiy, I.V. Smirnov, V.A. Babain, T.A. Todd, J.D. Law, R.S. Herbst, K.N. Brewer, Solvent Extr. Ion Exch. 19 (2001) 1.
[11] J.D. Law, R.S. Herbst, T.A. Todd, V.N. Romanovskiy, V.A. Babain, V.M. Esimantovskiy, I.V. Smirnov, B.N. Zaitsev, Solvent Extr. Ion Exch. 19 (2001) 23.
[12] C.L. Riddle, J.D. Baker, J.D. Law, C.A. McGrath, D.H. Meikrantz, B.J. Mincher, D.R. Peterman, T.A. Todd, Solvent Extr. Ion Exch. 23 (2005) 449.
[13] B.J. Mincher, S.P. Mezyk, W.F. Bauer, G. Elias, C. Riddle, D.R. Peterman, Solvent Extr. Ion Exch. 25 (2005) 593.
[14] J.D. Law, D.J. Wood, R.S. Herbst, Sep. Sci. Technol. 32 (1997) 223.
[15] D.J. Wood, J.D. Law, Sep. Sci. Technol. 32 (1997) 241.
[16] E.P. Horwitz, L.D. Mark, D.E. Fisher, Solvent Extr. Ion Exch. 9 (1991) 1.
[17] N. Simon, B. Tournois, S. Eymard, G. Volle, P. Rivalier, J. Leybros, J.Y. Lanoe, N.R. Tronche, G. Ferlay, J.F. Dozol, Cs selective extraction from high level liquid waste with crown calixarene: Where are today? Int. Con. Atalante 2004, Advances for Future Nuclear Fuel Cycles, Nimes, France, June 21–25, 2004, p. 1.
[18] 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, in: Proceedings of Global 2003, New Orleans, the United States of, America, 2003, p. 565.
[19] Z. Asfari, S. Wenger, J. Vicens, J. Incl. Phenom. Macro. 19 (1994) 137.
[20] H. Ji, G.M. Dabestani, R.L. Brown, J. Chem. Soc. Perkin Trans. 2 (2001) 585.
[21] R.A. Sachleben, A. Urvoas, J.C. Bryan, T.J. Haverlock, B.H. Hay, B.A. Moyer, Chem. Commun. 17 (1999) 1751.
[22] P.V. Bonnesen, L.H. Delmau, T.J. Haverlock, B.A. Moyer, Alkaline-side extraction of cesium from Savannah River tank waste using a calixarene-crown ether extractant. Chemical and Analytical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., Report ORNL/TM-13704, December, 1998.
[23] A. Zhang, Q. Hu, Z. Chai, AIChE J. 56 (2010) 2632.
[24] A. Zhang, W. Wang, Z. Chai, M. Kumagai, J. Sep. Sci. 31 (2008) 3148.
[25] J.L. Cortina, N. Miralles, Solvent Extr. Ion Exch. 15 (1997) 1067.
[26] K. Takeshita, M. Kumagai, Y. Takashima, S. Matsumoto, J. Chem. Eng. Japan 27 (1994) 52.
[27] W. Zhang, A. Zhang, L. Xu, Z. Chai, J. Chem. Eng. Data 58 (2013) 167.
[28] A. Zhang, Y. Wei, M. Kumagai, T. Koyama, J. Radioanal. Nuch. Chem. 262 (2004) 739.
[29] M.N. Michael, J. Am. Chem. Soc. 105 (1983) 4906.
[30] M.L. Dietz, A.H. Bond, M. Clapper, J.W. Finch, Radiochim. Acta 85 (1999) 119.
[31] J. Kriz, J. Dybal, E. Makrlik, J. Budka, J. Phys. Chem. A 112 (2008) 10236.
[32] J. Dybal, E. Makrlik, P. Vanura, J. Budka, Monatsh. Chem. 139 (2008) 1175.
[33] E.D. Collins, J.P. Renier, Systems studies of actinide partitioning-transmutation recycle methods, in: Proc. Int. Conf. (Global 2005), 9–13 October, 2005, Japan, 2005, p .235.
[34] H. Oigawa, K. Minato, T. Kimura, Y. Morita, S. Nakayama, K. Nishihara, Present status and future perspective of research and development on partitioning and transmutation technology at JAERI, in: Proc. Int. Conf. (Global 2005), 9–13 October, 2005, Japan, 2005, p. 207.
[35] D. Warin, B. Boullis, H. Mouney, Status of French programme on partitioning and transmutation for nuclear waste management. Proc. Int. Con. (Global 2001), September 9–13, 2001, Paris, France, 2001, p. 59.