



Chromatographic separation of cesium by a macroporous silica-based supramolecular recognition agent impregnated material

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ABSTRACT

A novel macroporous silica-based supramolecular recognition compound 1,3-[(2,4-diethyl heptylethoxy)oxy]-2,4-crown-6-Calix[4]arene (Calix[4]arene-R14) polymeric composite (Calix[4] + Oct)/SiO₂-P was prepared. It was synthesized by impregnating and immobilizing a mixture of Calix[4]arene-R14 and *n*-octanol into the pores of the macroporous SiO₂-P particles. The adsorption of Cs(I) and some typical fission and non-fission products (FPs) contained in high level liquid waste (HLLW) such as Na(I), K(I), Cs(I), Rb(I), Sr(II), and Ba(II) onto (Calix[4] + Oct)/SiO₂-P was investigated by examining the influence of contact time and the HNO₃ concentration at 298 K. It was found that with an increase in the concentration of HNO₃, the adsorption of Cs(I) onto (Calix[4] + Oct)/SiO₂-P increased from 0.324 M to 4.0 M HNO₃ and then decreased to 7.0 M HNO₃. At the optimum HNO₃ concentration of 4.0 M HNO₃, (Calix[4] + Oct)/SiO₂-P showed excellent adsorption ability and high selectivity for Cs(I) over all of the tested elements except Rb(I). The chromatographic separation of Cs(I) from a simulated HLLW containing ~5.0 mM of the tested elements was performed by (Calix[4] + Oct)/SiO₂-P packed column at 298 K. Na(I), K(I), Sr(II), and Ba(II) showed no adsorption and were eluted into effluent along with 4.0 M HNO₃. Cs(I) and Rb(I) adsorbed by (Calix[4] + Oct)/SiO₂-P could be effectively eluted with water and separated from the others. It is demonstrated that (Calix[4] + Oct)/SiO₂-P is promising to apply in the separation of Cs(I), one of the heat emitting nuclides, from an acidic HLLW by extraction chromatography.

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1. Introduction

Two isotopes of cesium, Cs-135 and Cs-137 with the half-lives of 2×10^6 yr and 30 yr, are produced in reprocessing of nuclear spent fuel (NSF). Cs-135 has a long-term adverse impact on environment because of its mobility in final repository. Cs-137 is one of the main heat emitting nuclides and is harmful to the vitrification of high level liquid waste (HLLW) in final geological disposal. On the other hand, elimination of Cs-135 and Cs-137 is meaningful for significantly reducing the need of cooling fission products containing solutions and the time of vitrified waste storage before its disposal in geological formation. Moreover, Cs-137 can also be used as the source of β -radiation and energy generator. So, effective separation and recovery of cesium from HLLW are valuable.

The liquid–liquid solvent extraction is one of the main separation technologies. Some partitioning processes such as the universal solvent extraction [1–3], cesium separation by calix-crown extraction process [4], and fission product extraction [5,6], etc. were reported to separate the long-lived minor actinides (MAs), Sr(II),

and Cs(I) from HLLW. The extraction of Cs(I) resulted from the use of a new kind of supramolecular recognition agent, Calix[4]arene-crown. It showed excellent extraction ability and high selectivity for Cs(I).

It is well known that in solvent extraction process, many instruments and equipments are required for the multi-stage extraction, stripping and solvent washing processes. This makes the possibility of contaminating these equipments in the radioactive operation higher. Therefore, the separation technique utilizing the minimal organic solvent and compact equipment is expected for the HLLW partitioning. Extraction chromatography as an alternative separation method seems to be promising. Recently, a new kind of extraction resin, the macroporous silica-based chelating agent impregnated polymeric composite, has been developed. Compared to the conventional polymeric matrix resins, the macroporous silica-based types of extraction resin shows rapid adsorption–elution kinetics, high mechanical strength, and significantly low pressure loss in a packed column.

The Calix[4]crown compounds are generally composed of a calixarene and a crown ether moiety bonded together by the phenolic oxygens of the calixarene and a polyether chain [7,8]. The macrocyclic ring in calyx[4]arenes acts as a molecular backbone to ligate functional groups. There are many examples where the ring itself engages in binding such as with its p-basic phenolic cavities to

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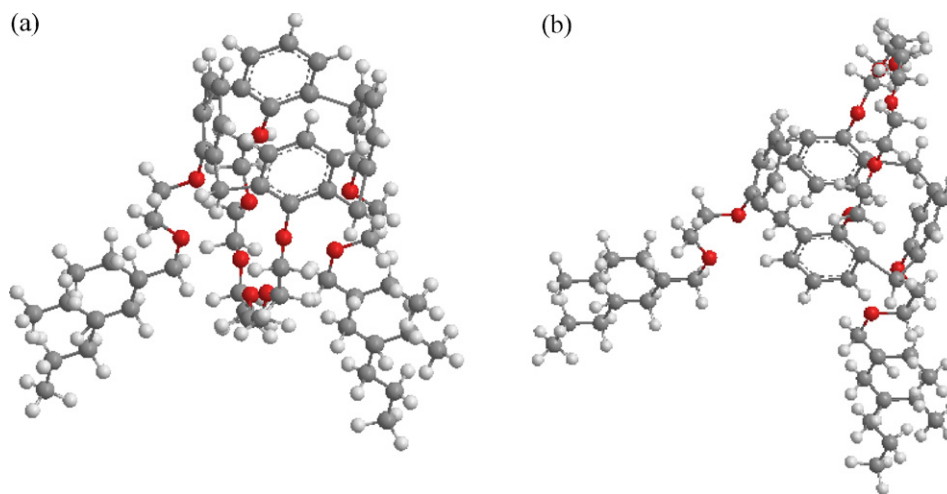


Fig. 1. Molecular structures of *trans*- and *cis*-Calix[4]arene-R14.

alkali metals cations with the phenolic oxygen atoms or to organic molecules by CH– π or π – π -stacking interactions. The investigations carried out recently showed that Calix[4]crown has the excellent selectivity for alkali and alkaline-earth metal ions [9–12]. Although the crown ether complexes with metal ions, the Calix[4]crown can assume various conformations, e.g., cone, partial cone, 1,2-alternate, and 1,3-alternate, etc., that play a crucial role on the selectivity for different metal ions. Especially, some derivatives of 1,3-alternate Calix[4]crown-6 ether synthesized have been shown to possess high selectivity for Cs(I) and to form a 1:1 type of the complex, rendering them suitable for the removal of Cs(I) from nuclear waste [13,14]. The Cs/Na and Cs/K selectivity ratios for some of these calixarenes exceed 10^4 and 10^2 as measured by liquid–liquid solvent extraction.

1,3-[(2,4-Diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) was a novel supramolecular recognition agent. It was found that in high HNO_3 concentration medium, *trans*-Calix[4]arene-R14 showed excellent supramolecular recog-

nitration ability for Cs(I) greater than that of *cis*-Calix[4]arene-R14. The structure of *trans*- and *cis*-Calix[4]arene-R14 are shown in Fig. 1.

Based on the MAREC (minor actinides recovery from HLLW by extraction chromatography) process and some investigations [15–20], an advanced partitioning technology entitled SPEC (strontium/cesium partitioning from HLW by extraction chromatography) process as shown in Fig. 2 has been developed recently to recover two heat emitting nuclides, Cs(I) and Sr(II), from an acidic HLLW [21,22]. Two supramolecular recognition agents, *trans*-Calix[4]arene-R14 and 4,4',(5')-di(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6), were used. Cs(I) was separated in the first column packed with a macroporous silica-based Calix[4]arene-R14 impregnated polymeric composite, Calix[4]arene-R14/SiO₂-P. Sr(II) was then partitioned in the second one packed with another macroporous silica-based DtBuCH18C6 impregnated polymeric composite, DtBuCH18C6/SiO₂-P [23]. However, it was found that in the separation of Cs(I), because of low affinity of Calix[4]arene-R14,

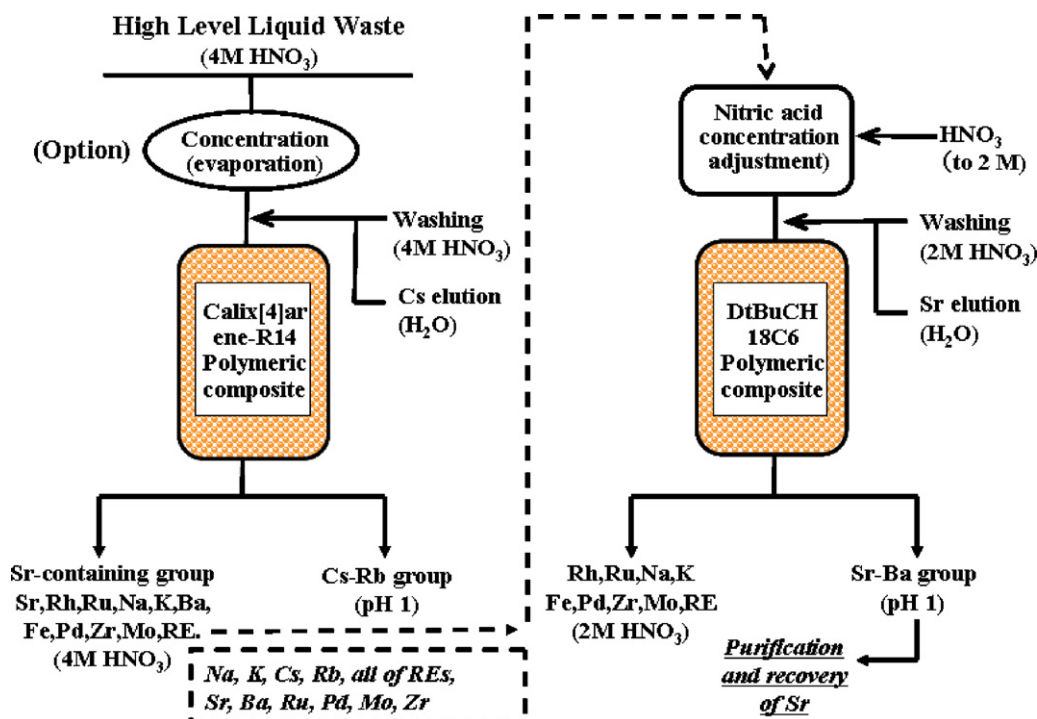


Fig. 2. An advanced SPEC process for heat generator partitioning from an acidic HLW utilizing two novel macroporous silica-based composites by extraction chromatography.

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