Optimisation of the extraction of ^{137}Cs and ^{90}Sr from high-level liquid waste

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Abstract

It is anticipated that in the future, when nuclear waste repositories are constructed in many countries, the separation of individual components and their separate handling or burial will become urgent. This persuasion stems from options of retrievability, individual burying, and possible further use of individual radionuclides.

After the Fukushima disaster, cheap efficient processes for separating ^{137}Cs and ^{90}Sr seem to be required. This was our second motivation in addressing the issue.

The two main processes for the extraction separation of the title radionuclides are the so-called "dicarbollide process" (developed in NRI and industrially used in the Russian Federation) and the "FPEX process" (being developed in the US). The two reference processes differ in terms of used extraction agents, characteristics of extraction, and possibly in the level of chemical and radiation stability. Whereas the "dicarbollide process", using highly stable dicarbollide anion, is to be viewed as a classic, new processes use cationic organic selective ligands, i.e. special crown ethers for the extraction of ^{90}Sr and calixcrowns for ^{137}Cs extractions. The "dicarbollide process" has been studied in detail before at NRI and our institute also actively participated in the development of selective ligands for the extraction of Cs in the frame of the Japanese ARTIST Project proposed and developed by one of the authors (S.T.).

The main obstacles in both types of processes lie in the choice of suitable solvent. This report presents some results for two ecological variants of dicarbollide solvents. Further, some alcohol solvents for systems with selective ligands and the extraction of ^{137}Cs and ^{90}Sr will be compared and evaluated.

New solvents for dicarbollide process

In contrast to public opinion that a polar solvent is needed for dicarbollide extractant, two new nonpolar nontoxic and cheap solvents have been devised.

The first system is composed of dodecanenitrile + *n*-dodecane solvent. The extraction of Cs and Sr is possible with the addition of various crown ethers. The system has been described in detail in [4].

The second system, being evaluated now, is that with dioctyl sebacate and *n*-dodecane, the extraction of Cs and Sr is possible from cca. 1M HNO_3 and there is a formation of third phase at high *n*-dodecane contents.

Molecular recognition processes

After the discovery of Dozol of calixcrowns as powerful extractants of Cs [5], several calixcrowns were used for practical purposes. Two-crown calixarene, viz. calix [4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) is as a rule used in the US [2]. One-crown calixcrown was used originally [5] and also in the Chinese process – viz. 25, 27-bis(isopropoxy) calix[4] arene benzo crown-6(iPr-C[4]C-6) [6]. We also used one-crown calyx, namely 25, 27 – bis(n-octyloxo) calix[4] arene benzo crown-6, i.e. a more hydrophobic variant of Chinese reagent.

For the extraction of Sr, essentially two crown ethers were used: dicyclo-hexano-crown-6 (DCH18C6) and the more hydrophobic 4,4′,(5′)-Di-(t-butyldicyclo-hexano)-crown-6) (DtBuCH18C6). Although mostly higher D_{Sr} is achieved with DtBuCH18C6, the matter is not so simple, because the same or even lower D_{Sr} with DtBuCH18C6 have been occasionally reported [7]. Because of the much higher price of the latter reagent, we preferred to use DCH18C6 in this work.

Solvents

The studied repertoire of possible solvents for the extraction of Cs and Sr with molecular recognisers is still very narrow. In fact, only alkane Isopar and *n*-octanol were mainly used. Hence, we systematically studied some more solvents and Table 1 presents the distribution ratios of Cs and Sr from 3M HNO_3.

Table 1: Extraction of ^{137}Cs and ^{90}Sr with 0.03M calixcrown or 0.05M DC18C6 in solvent at 25±1°C, for 1-dodecanol t=30°C

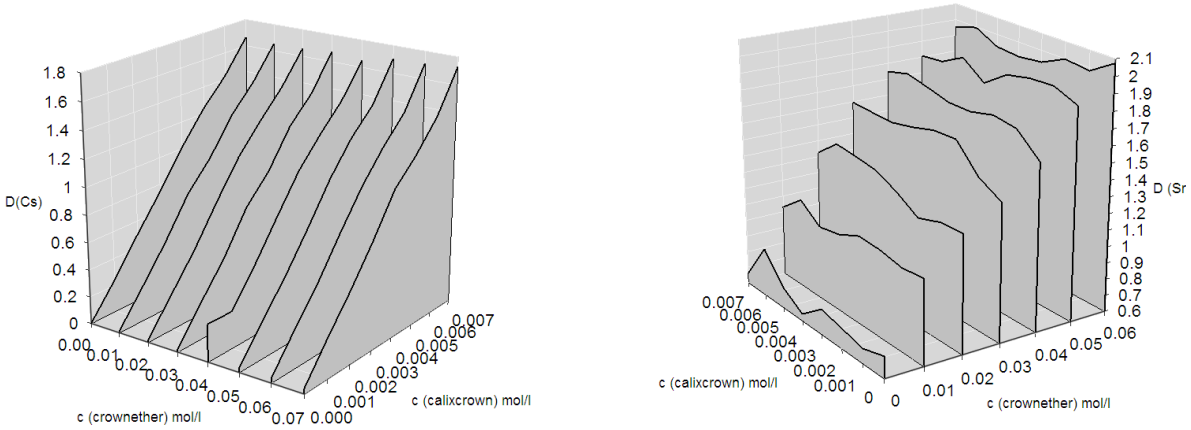
Solvent	D_{Cs}	D_{Sr}
1-octanol	23.0	1.81
2-octanol	18.5	1.19
1-decanol	19.0	1.16
1-dodecanol	12.1	0.74
cyclohexanol	36.6	3.83
2-methylcyclohexano	22.5	4.20
4-methylcyclohexano	26.9	4.01
2-methylcyclohexano	35.8	2.21
3-methylcyclohexano	41.7	3.79
4-methylcyclohexano	40.2	2.21
hexyl methyl ketone	20.0	0.64
1,2-dichloroethane	28.9	4.88
dioctyl sebacate	0.2	0.00

As can be seen from the table, the increasing molecular weight of linear alcohol leads to a decrease of both ^{137}Cs and ^{90}Sr extraction, some solvents (hexyl methyl ketone and dioctylsebacate) are a poor choice, and the best seems to be methylcyclohexanols and 1,2-dichloroethane.

Additivity of extraction

For the common extraction of both ^{137}Cs and ^{90}Sr it is necessary to ascertain that the effects of crown and calixcrown are additive, i.e. there is no synergy or antergy. This is exemplified for the system with DCH18C6 and 25, 27 – bis(n-octyloxo) calix[4] arene benzo crown – 6, respectively, as shown in Figure 1.

Figure 1: Extraction of Cs and Sr from 3M HNO_3 by mixtures of crown and calixcrown in *n*-octanol



Strip

The systems with crown and calixcrown have the big advantage over the dicarbollide systems that the strip of both ^{137}Cs and ^{90}Sr is in essence possible with diluted nitric acid or even pure water. Although the strip of Sr did not show any irregularities, the Cs strip from calixcrown reagent is often less clear, because in low acidity regions there is some increase of extraction as well documented in the literature. A practical remedy for this is to use a hydrophobic asymmetrical electrolyte, such as tri-*n*-octylammonium salt. This method has been used throughout. Whereas practically usable, the theory of strip at low acidity conditions seems to be involved and the following two figures present the theory to be developed in the future.

Figure 2: Extraction of Cs in the presence of Aliquat 336; 0.01M calixcrown in 1-octanol, 10^{-4} M HNO_3

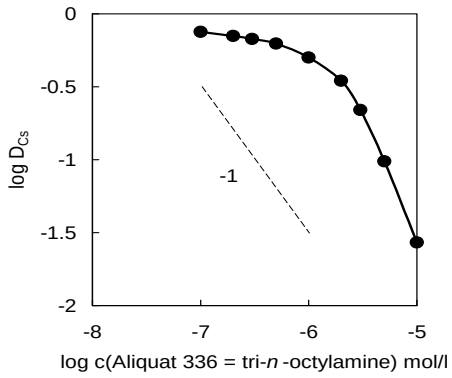
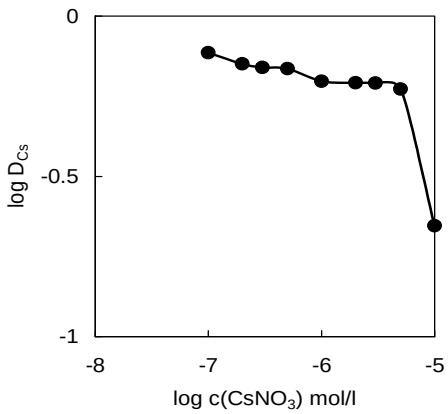


Figure 3: Extraction of Cs in dependence on its concetration; 0.01M calixcrown in 1-octanol, 10^{-4} M HNO_3



Summary

Several new systems for the extraction of ^{137}Cs and ^{90}Sr were studied. It is believed that a suitable candidate can be determined from them which will withstand criteria of effectiveness, price and ease of manipulation.

Acknowledgements

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