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Progress in experimental results of the combined Cs/Sr partitioning

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Authors: Ken Verguts

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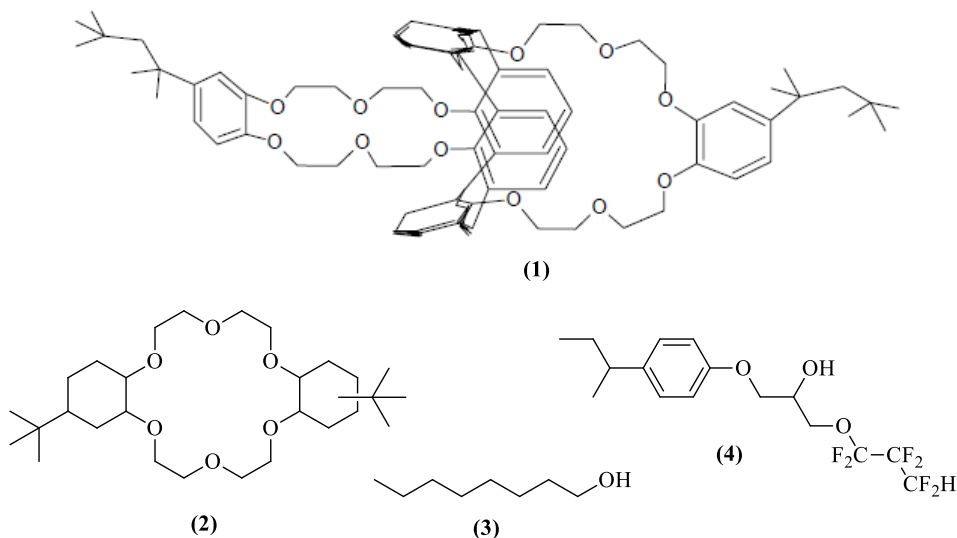
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Introduction

In deliverable 1.2.1. *Recovery of cesium and strontium isotopes - ASOF WP1*, an overview of the existing literature was given regarding the partitioning of cesium and strontium isotopes in the nuclear field. Solvent extraction on one hand, and column separations on the other hand were discussed. It can be concluded that the partitioning of Cs and Sr originating from a PUREX raffinate is quite challenging using ion exchange columns. Mainly because these solutions are very acidic ($\text{pH} < 1$) and orders of magnitude more radioactive as compared to the historic tank waste solutions. The resins *e.g.* using crystalline silicotitanate (CST) would degrade very fast due to the radiation and the heat produced. The literature also shows that the majority of the methods is not suitable for very acidic feed solutions. The most promising route towards Cs and Sr separation from the highly active, acidic PUREX raffinate is the solvent extraction route. To be compliant with all safety and environmental measures, an optimized FPEX II solvent extraction system, as developed by US DoE, is an interesting path to be studied more in depth.

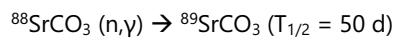
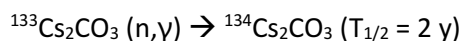
Cesium and strontium isotopes are extracted by respectively BOBCalixC6 (calix[4]arene-bis-(tert-octylbenzo-crown-6), **Error! Reference source not found. (1)**) and DtBuCH18C6 (4,4',5')- di-(t-butyl)dicyclo-hexano)-18-crown-6, **Error! Reference source not found. (2)**). To avoid third-phase formation, modifiers as n-octanol (**Error! Reference source not found. (3)**), or Cs-7SB (1-(2,2,3,3- tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol **Error! Reference source not found. (4)**), are added to the diluent.



Results

Test irradiation in BR1

Radiotracers ^{134}Cs and ^{89}Sr were produced in the research reactor BR1 at the SCK CEN site in Mol (see equations below).



Samples were prepared in sealed quartz ampoules containing 0.6 g Cs_2CO_3 (natural Cs-133) and 1.7 g SrCO_3 / $\text{Sr}(\text{NO}_3)_2$ (natural Sr-88) and were irradiated for 7 h in BR1. The final activity at the end of irradiation of ^{134}Cs was 12 MBq and 50 kBq for ^{89}Sr .

The goal of this test irradiation was to check the feasibility of in-house production and processing of radiotracers. The sealed quartz ampoule containing $^{89}\text{SrCO}_3$ / $^{89}\text{Sr}(\text{NO}_3)_2$ was placed in a flexible tubing, sealed with PEEK connectors. This flexible tubing allows one to crush the ampoule using *e.g.* a vice. The small HPLC tubing was on the one end connected to a peristaltic pump, which allows the transfer of solutions (nitric acid in this case) into the tube. Nitric acid is chosen to relate to the PUREX process, where the highly active raffinate is also present as a nitric acid solution. On the other end of the flexible tubing, a small HPLC tubing was mounted, which allows overpressure to be released. The full setup was mounted in a fume hood in the surveilled area (see figure below).

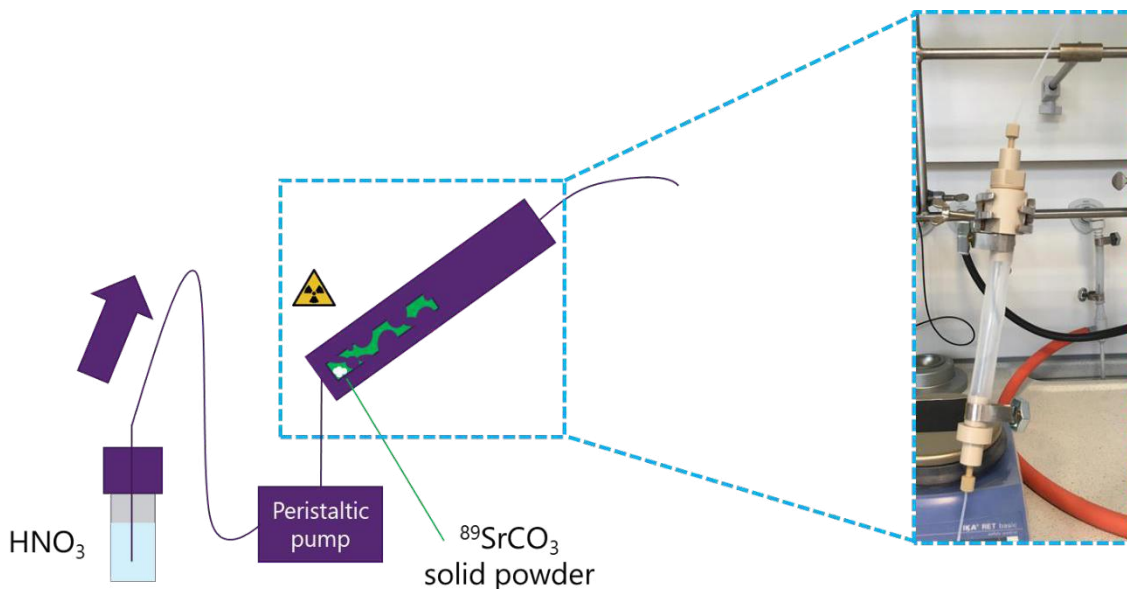
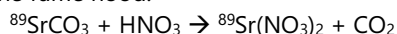


Figure 1: Schematic giving an impression of the crushing and dissolution of the activated, solid tracers.

After crushing of the quartz ampoule, $^{89}\text{SrCO}_3$ powder and quartz glass debris is present within the flexible tubing. The crushing was followed by pumping a diluted nitric acid solution into the tubing allowing nitric acid to react with $^{89}\text{SrCO}_3$, forming $^{89}\text{Sr}(\text{NO}_3)_2$ and CO_2 (see equation below). The gaseous CO_2 escapes through the opening on top. The HPLC tubing on top reduces the risk of contaminating the fume hood.



When all carbonate anions have been converted to CO_2 (absence of gas formation), the motion of the peristaltic pump is reversed, to collect the dissolved $^{89}\text{Sr}(\text{NO}_3)_2$ in its final recipient (see figure below).

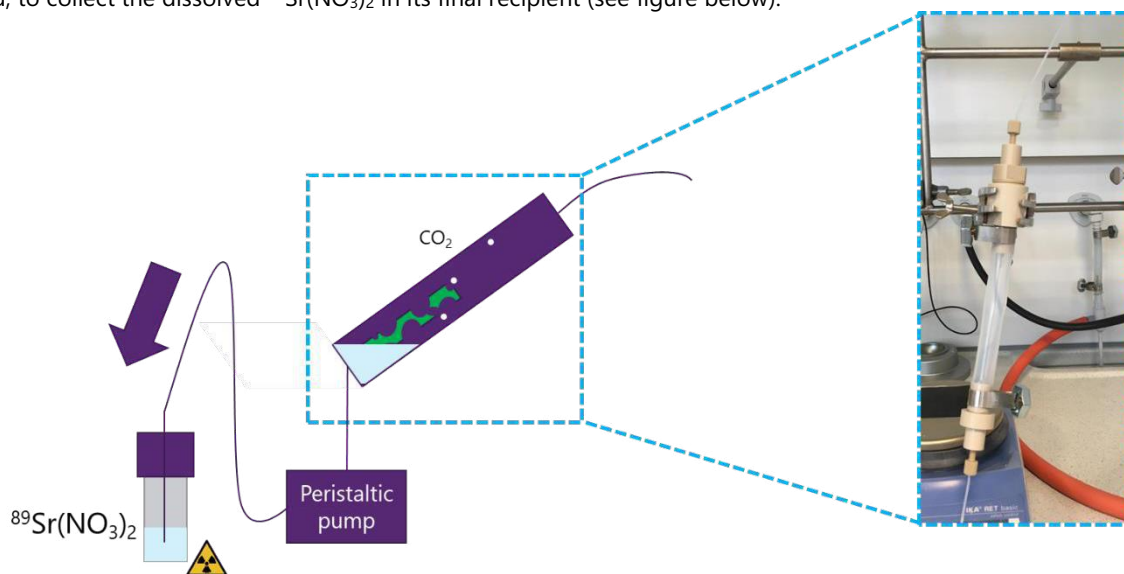


Figure 2: Schematic giving an impression of the collection of the radiotracers, dissolved in nitric acid.

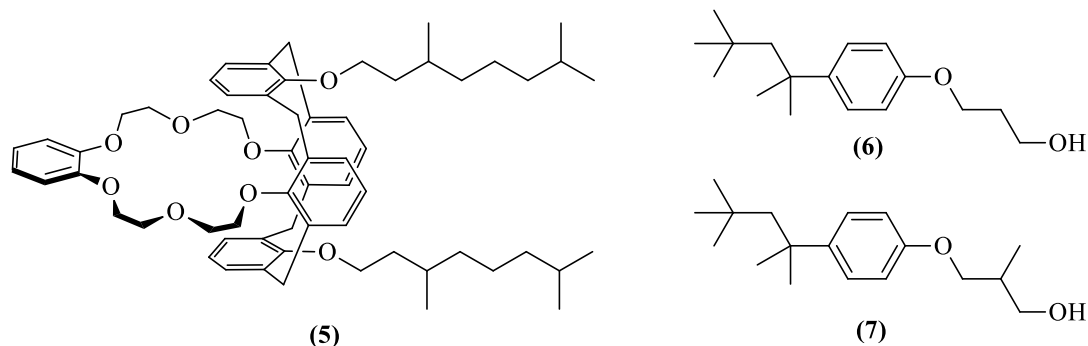
The procedure on ampoule preparation, irradiation, crushing, dissolution and collection was first executed on strontium, and later copied to cesium. However, since the ^{89}Sr activity was only 50 kBq, the irradiation had to be repeated in a high flux reactor such as BR2.

Production of ^{89}Sr in BR2

After a successful test-irradiation in BR1, ^{89}Sr was produced in BR2. Therefore 95 mg natural SrCO_3 was irradiated for 87 u to yield 18 MBq $^{89}\text{SrCO}_3$. An identical procedure as described above was followed to convert the $^{89}\text{SrCO}_3$ powder in a $^{89}\text{Sr}(\text{NO}_3)_2$ solution.

Extraction experiments

During the literature study, it was found that a more performant cesium extractant, MAXCalix – see Figure 2 (5), had been synthesized by the US DoE. A (small) sample of this molecule could be obtained from Marshallton Research Laboratories and will be used in the near future to evaluate its performance in the presence of new CHON compatible modifiers. These modifiers being 3-(4-tert-octylphenoxy)-1-propanol (abbreviated as Cs-4) and 3-(4-tert-octylphenoxy)-2-methyl-1-propanol (abbreviated as Cs-5) - (see Figure 2 (6) and (7)) were synthesized by Technocomm (UK).



However, since only a small quantity of the rare MAXCalix ligand could be acquired, first experiments are performed to study the behavior of strontium only. Therefore, DtBuCH18C6 is used as ligand in combination with the new CHON-compatible modifiers. First tests included kinetics studies, nitric acid dependency, ligand dependency, kinetics of Sr stripping and nitric acid dependency of Sr stripping.

Distribution ratios (D-value) are by definition calculated as the ratio of the concentration of an element (e.g. Sr) in the organic phase over the concentration of the same element in the aqueous phase in an equilibrium state. It can be seen that the distribution ratio is nearly unaffected by the contact time (see Figure 3) and is immediately reached from the 1st minute. Therefore, in further experiments, 1 min shaking time was chosen. Also, higher distribution ratios are observed when phases are contacted at a higher temperature (40 °C vs room temperature).

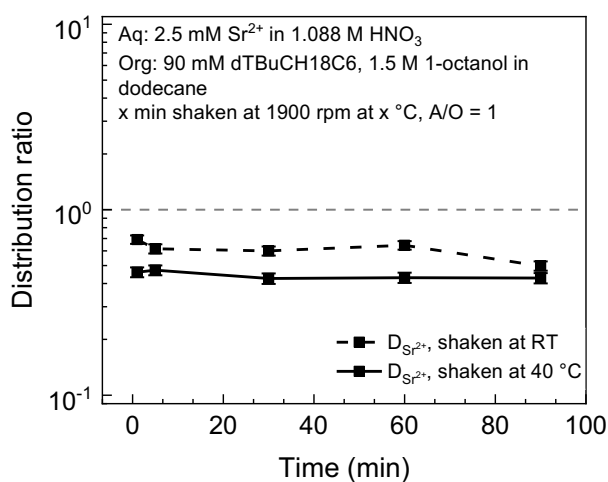


Figure 3: Kinetics experiment

Next, the proposed system is tested in different feed solutions. Several starting solutions were chosen with different nitric acid concentrations (see Figure 4). An increase in distribution ratio is observed by increasing nitric acid concentration. High distribution ratio (approx. 20) at 4.8 M HNO₃ and distribution ratio <1 below 1 M HNO₃ (Cs-4 and Cs-5) and below 1.5 M HNO₃ (1-octanol).

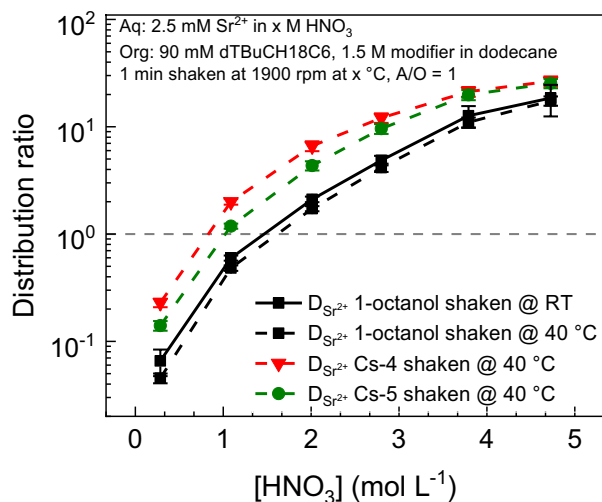


Figure 4: Nitric acid dependency

The observations in Figure 4 suggest that a system can be designed where extraction of Sr^{2+} can take place at high nitric acid concentrations (which are relevant actual spent fuel waste concentrations), followed by an effective stripping using diluted nitric acid solutions.

When assessing the influence of the DtBuCH18C6 concentration at high acidities (see Figure 5), it is found that an increasing ligand concentration leads to increasing distribution ratio for strontium. Since D-values above 20 are found at ligand concentrations of 90 mM, this concentration is chosen in the following stripping experiments.

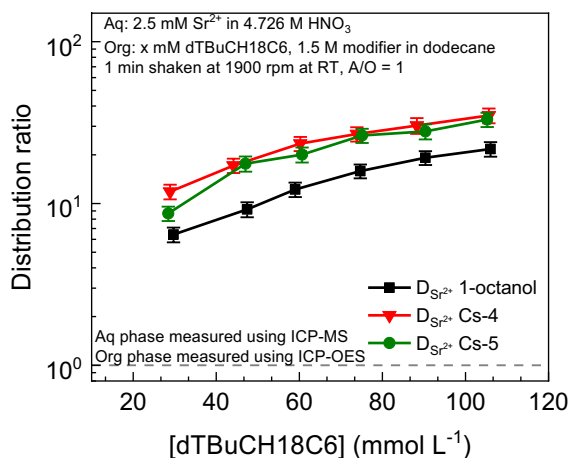


Figure 5: Ligand dependency

To decontaminate the loaded organic phase, stripping studies are necessary. Here the aim is to strip (also wrongly called 'back-extract') ions from the organic phase, back into a fresh aqueous phase. The nitric acid dependency tests described earlier already suggested that there might be a window where effective stripping is possible. In a first test, again, the kinetics of the system is evaluated (see Figure 6). For the chosen system, the D-value is somewhere between 0.1 and 0.2 at different shaking times. But more important, equilibrium is, as well as in the extraction experiments, reached within a minute.

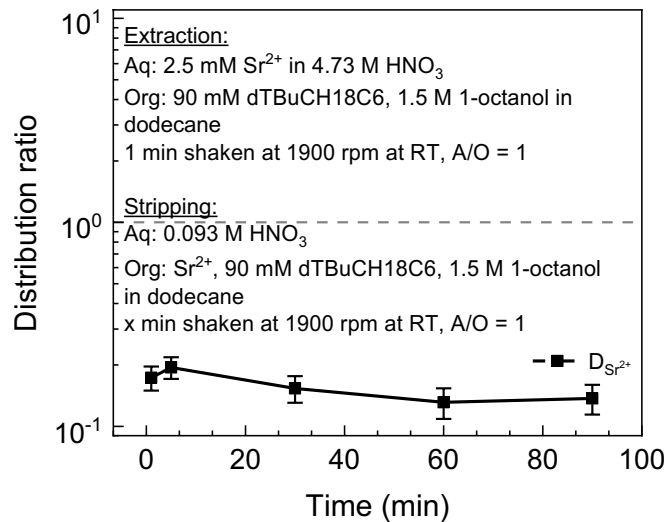


Figure 6: Kinetics experiment Sr stripping.

In a final experiment, the stripping of strontium is examined by contacting a loaded organic phase with solutions with different nitric acid concentrations (see Figure 1). The effective stripping of Sr²⁺ is confirmed below 1 M (for 1-octanol), and below approx. 0.4 M for Cs-4 and Cs-5. The lowest D-value is found when deionized water is used.

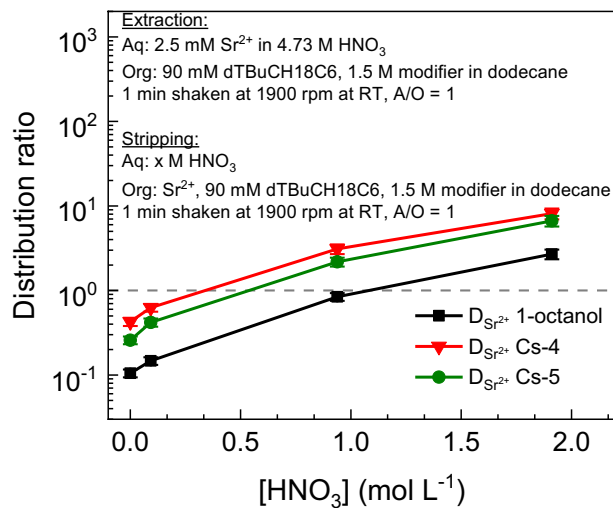


Figure 7: Nitric acid dependency on Sr stripping.

Conclusions and Outlook

In this deliverable, the progress in cesium/strontium research is described. Successful irradiations in BR1 and BR2 took place to synthesize ⁸⁹Sr and ¹³⁴Cs radioisotopes. These can be used in further partitioning research to evaluate their behaviour in specific conditions. In parallel, ligands, modifiers and equipment were synthesized / bought to allow further research. First extraction experiments were performed using the commercially available DtBuCH18C6 extractant to evaluate the feasibility of Sr partitioning. It can be concluded that a combination of 90 mM DtBuCH18C6 in 1.5 M Cs-4 (or Cs-5) in dodecane shows the best extraction properties when contacted to 2.5 mM Sr²⁺ in a 4.7 M HNO₃ solution. Moreover, effective stripping is possible when this loaded organic phase is contacted with deionized water.

In the next year, solvent extraction experiments on both Sr and Cs will be performed. Since ligands, equipment and knowhow was built-up, we foresee to finish this research in time.