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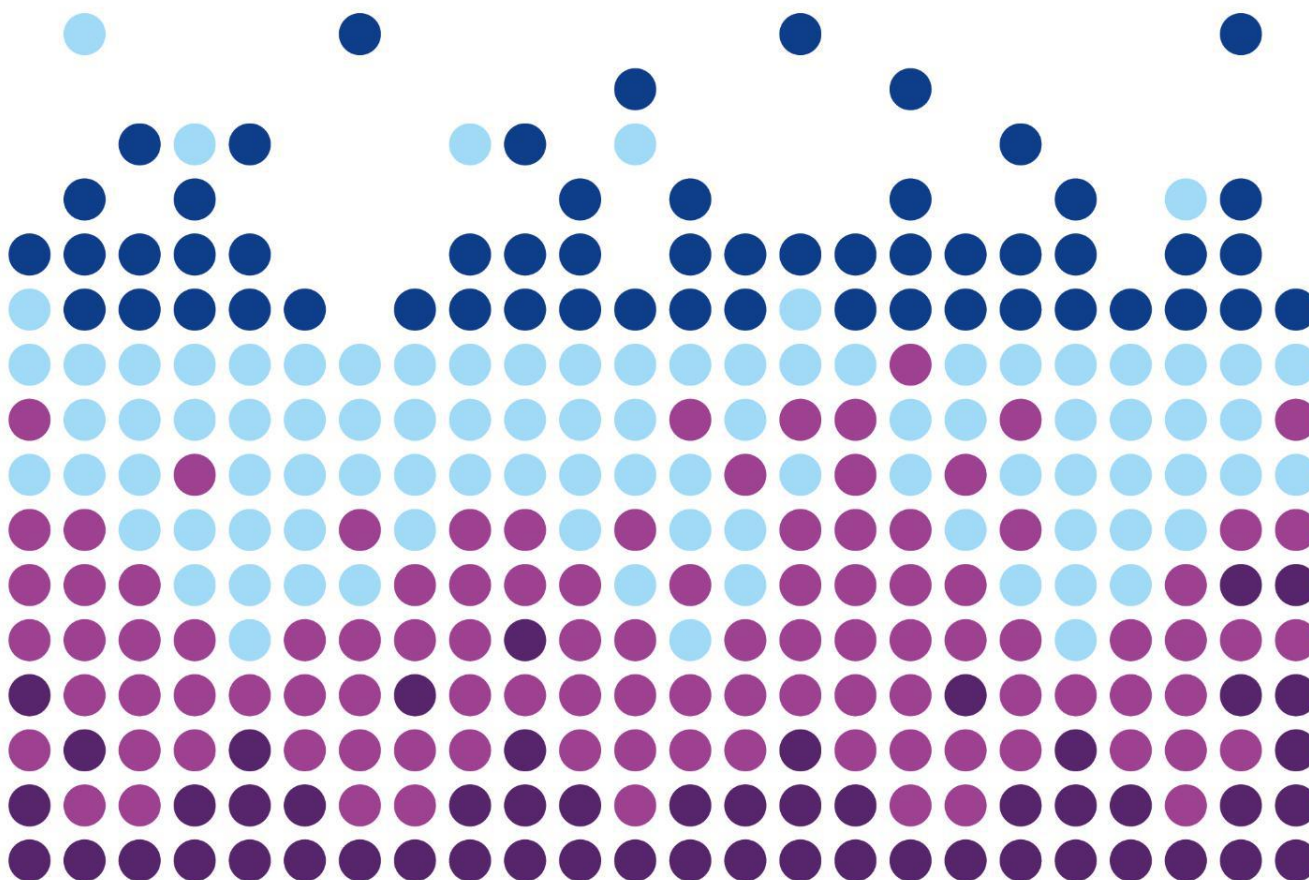
Proof of concept study on the combined Cs/Sr partitioning

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Authors: Ken Verguts

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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), *Figure 1 (1)*) and DtBuCH18C6 (4,4',(5')- di-(t-butyl)dicyclo-hexano)-18-crown-6, *Figure 1 (2)*). To avoid third-phase formation, modifiers as n-octanol (*Figure 1 (3)*), or Cs-7SB (1-(2,2,3,3- tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol *Figure 1 (4)*), are added to the diluent.

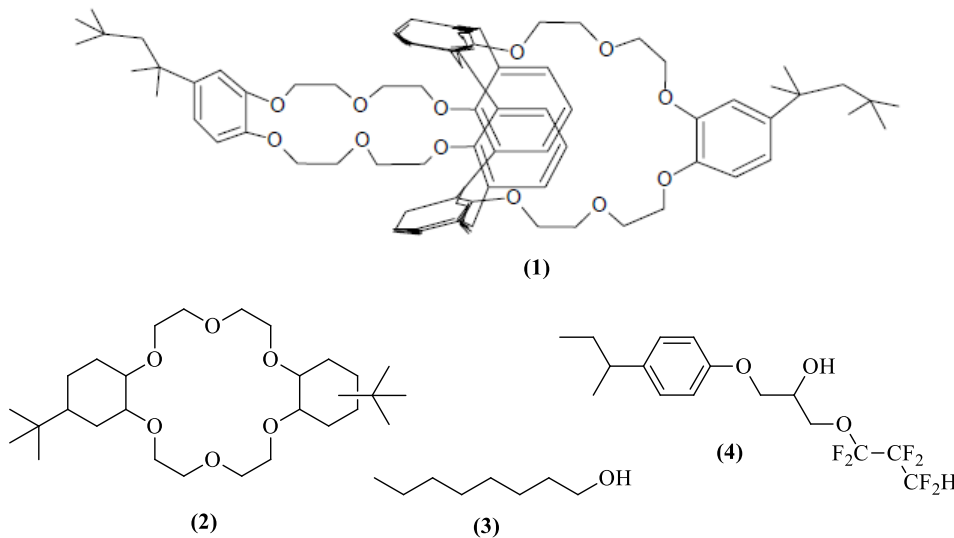
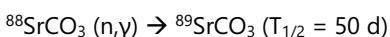
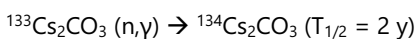


Figure 1: extractants and modifiers

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).

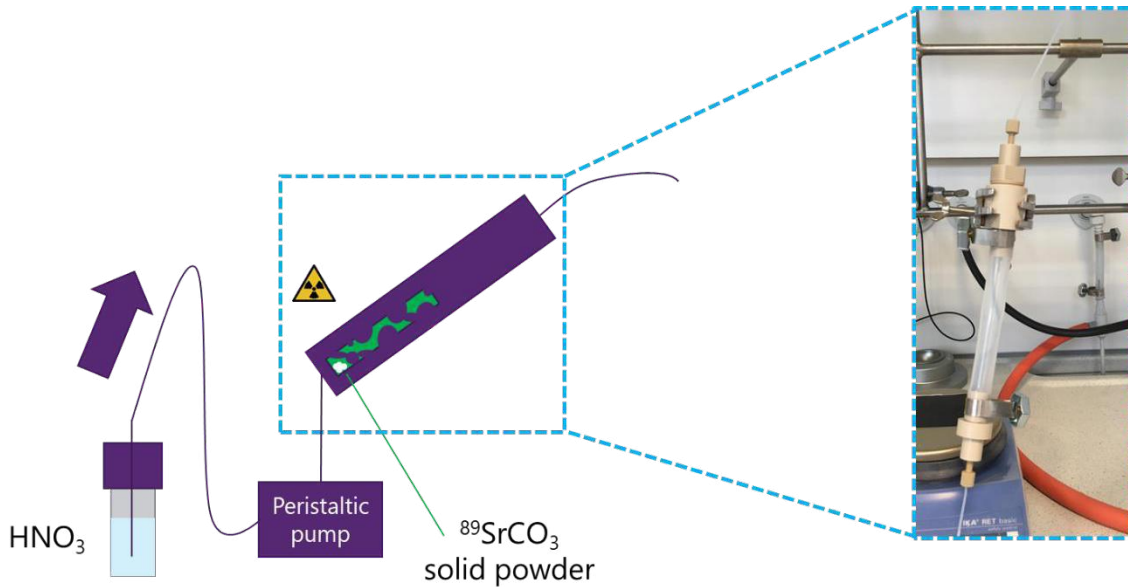
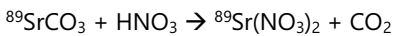


Figure 2: Schematic giving an impression of the crushing and dissolution of the activated, solid tracers.

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).

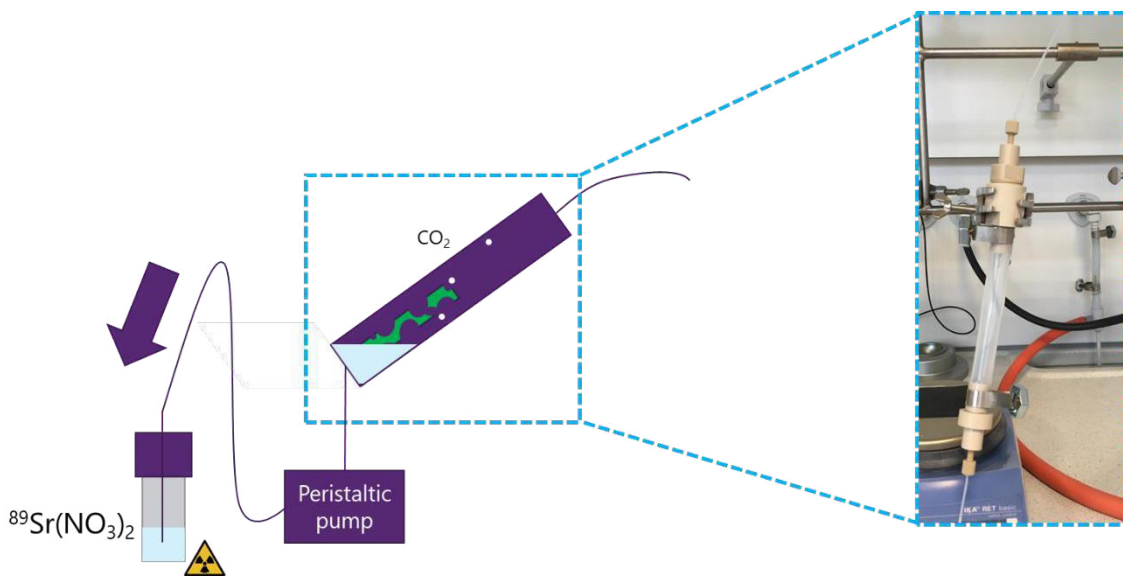


Figure 3: Schematic giving an impression of the collection of the radiotracers, dissolved in nitric acid.

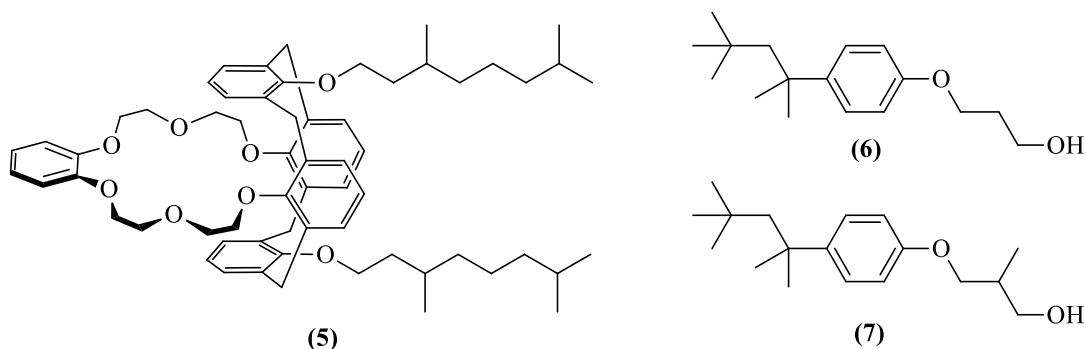
The procedure on ampoule preparation, irradiation, crushing, dissolution and collection was first executed on strontium, and later copied to cesium. However, since the ^{89}Sr activity was only 50 kBq, the irradiation had to be repeated in a high flux reactor such as BR2.

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 h 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.

Inactive extraction experiments

During the literature study, it was found that a more performant cesium extractant, MAXCalix (**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 active experiments 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, **6**) and 3-(4-tert-octylphenoxy)-2-methyl-1-propanol (abbreviated as Cs-5, **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 4*) 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).

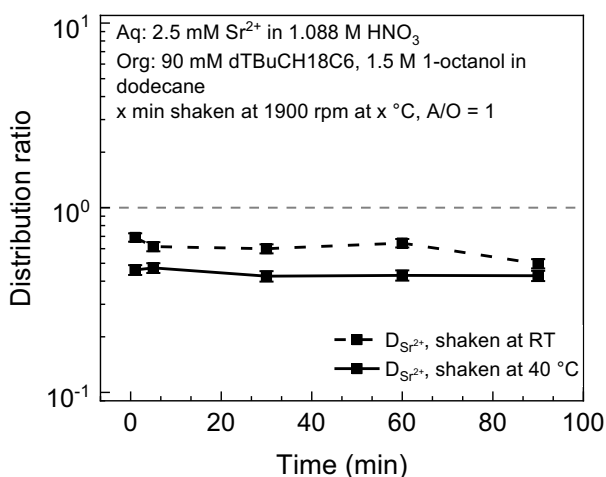


Figure 4: Kinetics experiment

Next, the proposed system is tested in different feed solutions. Several starting solutions were chosen with different nitric acid concentrations (see *Figure 5*). An increase in distribution ratio is observed by increasing nitric acid concentration. High distribution ratio (approx. 20) at 4.8 M HNO_3 and distribution ratio <1 below 1 M HNO_3 (Cs-4 and Cs-5) and below 1.5 M HNO_3 (1-octanol).

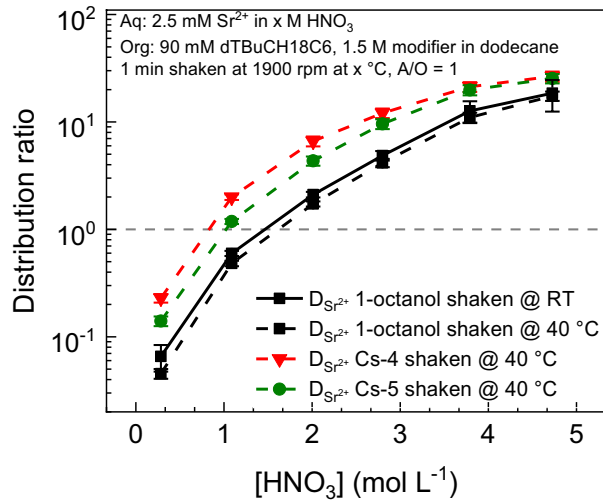


Figure 5: Nitric acid dependency

The observations in Figure 5 suggest that a system can be designed where extraction of Sr²⁺ 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 6), 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.

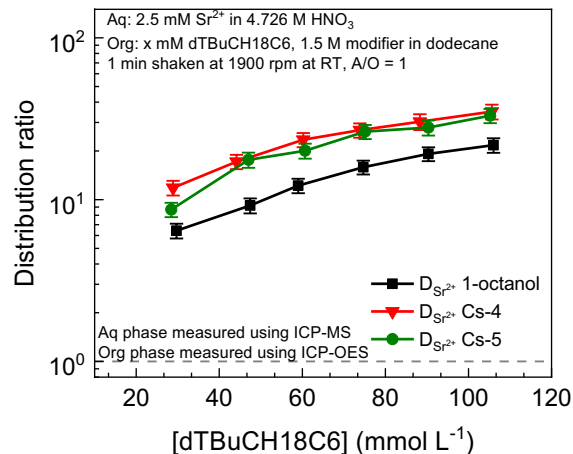


Figure 6: Ligand dependency

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 7). 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.

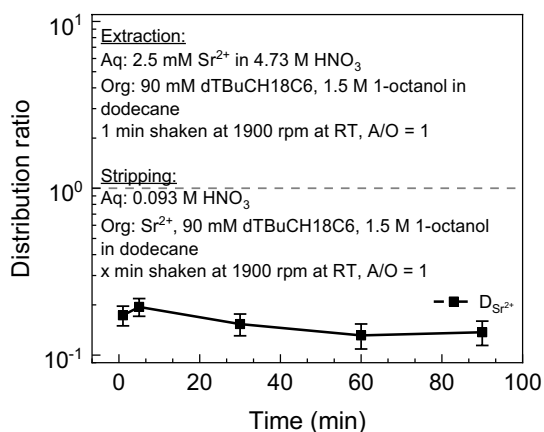


Figure 7: Kinetics experiment Sr stripping

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 7). The effective stripping of Sr^{2+} 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.

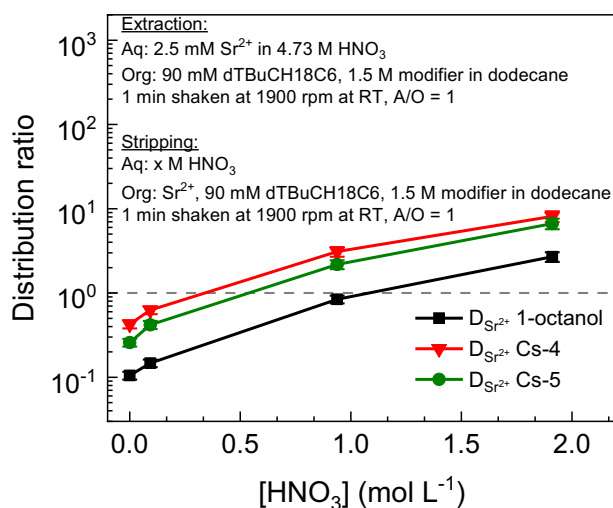


Figure 8: Nitric acid dependency on Sr stripping

Active extraction experiments

As discussed earlier, due to the limited availability of extractants, it was decided to only include cesium extraction experiments in the combined Cs/Sr system. Analyses were performed using ICP-MS (Cs^+ and Sr^{2+}) and/or gamma spectrometry (Cs^+ only). To analyse the combined Cs/Sr extractions, kinetics tests were performed first. These first tests give us an idea on 'how fast' the equilibrium of the system is reached, which will determine the overall processing time in the end. From the cold Sr tests, it was learned that the nitric acid concentration should be increased to 3-5 M HNO_3 to allow proper extraction (at lower nitric acid concentrations, Cs and Sr are stripped back to the aqueous phase (see later)).

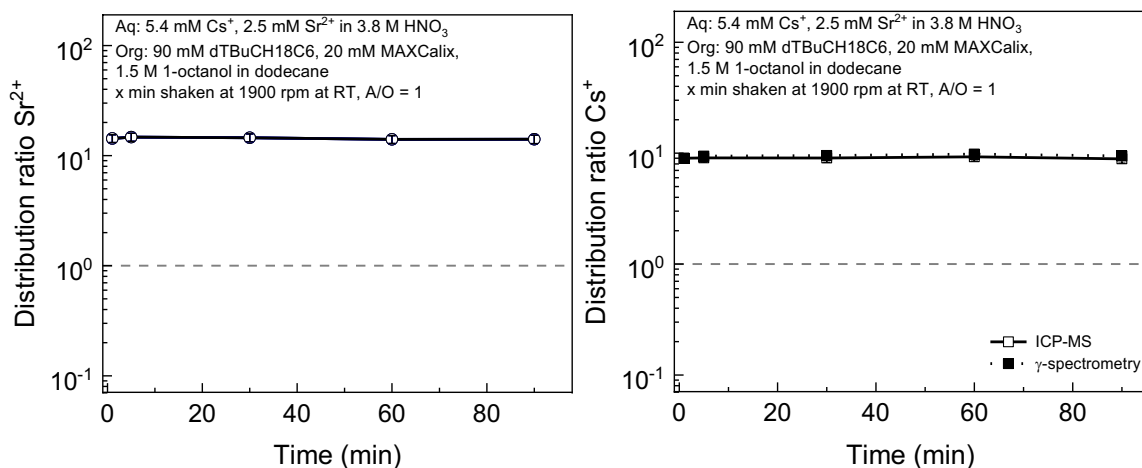


Figure 9: Kinetics test on Sr (left) and Cs (right) extraction - active experiments

In Figure 9, the distribution ratio of Sr^{2+} and Cs^+ are evaluated as a function of shaking time. Process relevant conditions were chosen. It can be observed that equilibrium is reached immediately (within the first minute). The distribution ratio is stable during all performed experiments. However, for practical reasons, 5 minutes of shaking time was chosen for all subsequent hot experiments. All experiments in the kinetics studies were performed using 1.5 M 1-octanol as phase modifier. In the following experiments also the influence of the phase-modifier is explored. These are denoted as 1-octanol (black curves), Cs-4 (red curves) and Cs-5 (blue curves).

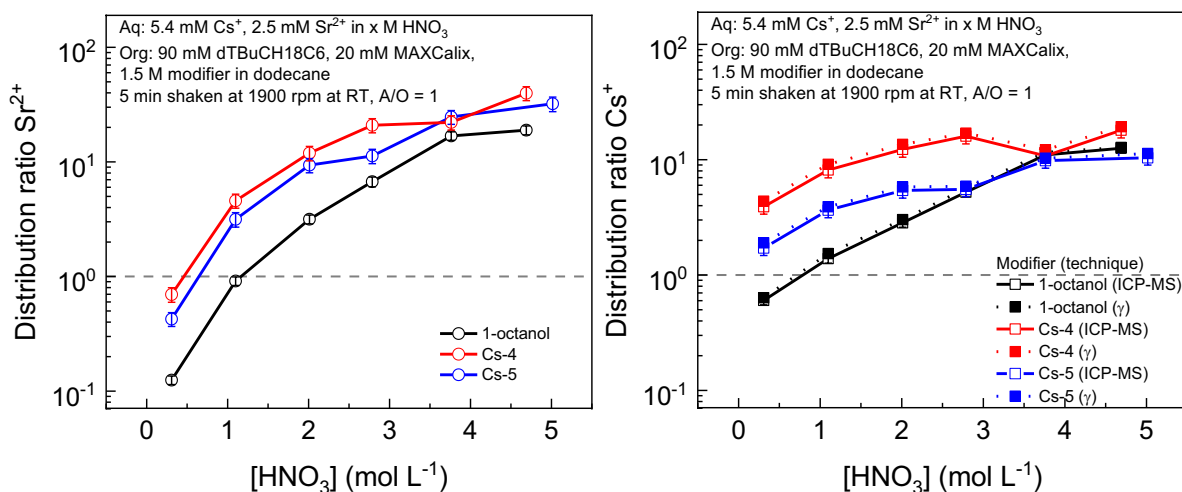


Figure 10: Nitric acid dependency on Sr (left) and Cs (right) extraction - active experiments

In the next experiment, the influence of the nitric acid concentration, together with the influence of the modifier is studied. The data is given in Figure 10 for strontium (left) and cesium (right). The distribution ratios for Sr do clearly relate to the inactive experiments where an increase in distribution ratio is observed by increasing nitric acid concentration. The ligand dTBuCH18C6 is in charge for the selective extraction of this element. It is observed that Sr^{2+} extraction happens at around 0.5 M nitric acid for Cs-4 and Cs-5, and around 1.1 M for 1-octanol. When comparing these results with the cold tests (see Figure 5), it can be seen that the presence of the MAXCalix, *i.e.* the selective cesium extractant, does not seem to affect the Sr^{2+} extraction. The highest distribution ratios are found at 4.7 - 5.0 M HNO_3 (depending on the modifier). Also, the three modifiers show a similar behavior at increasing nitric acid concentration. However, at a defined concentration, the presence of Cs-4 always gives the highest D-value, whereas the presence of 1-octanol shows the lowest D-value.

The influence of the nitric concentration on Cs^+ extraction is given in Figure 10 (right). Also for cesium, it is observed that the distribution ratio increases with increasing nitric acid concentrations. In the given conditions, only extraction ($D > 1$) was found when Cs-4 or Cs-5 was used as modifier. When 1-octanol was used as modifier, and the nitric acid concentration was below 1 M, stripping ($D < 1$) can be observed.

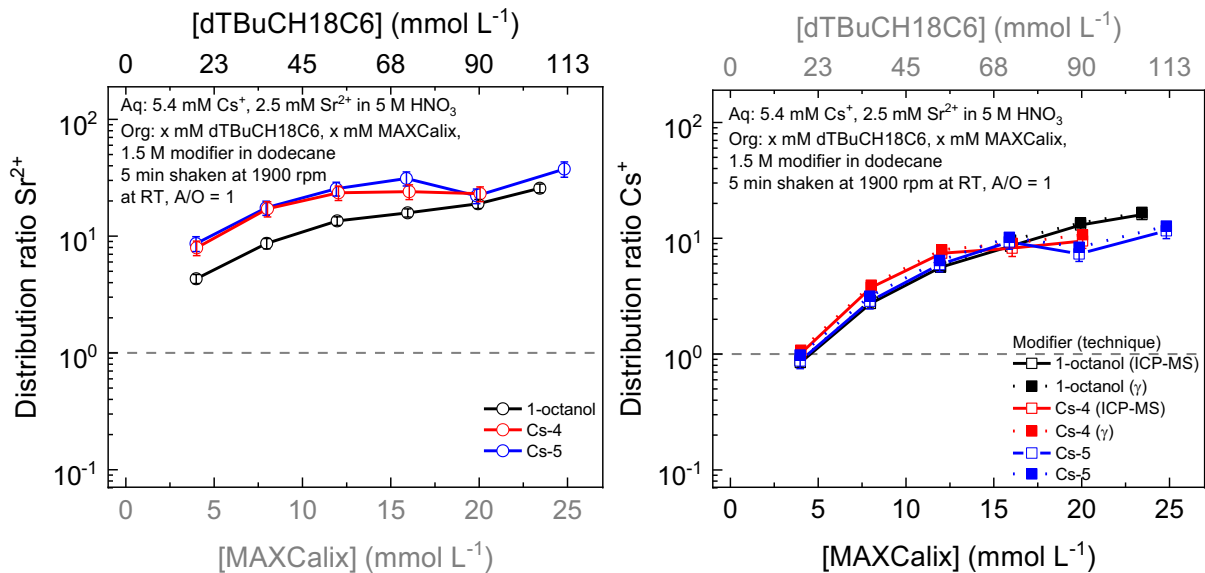


Figure 11: Ligand dependency on Sr (left) and Cs (right) extraction - active experiments

Next, the influence of the ligand's concentrations was tested on Sr and Cs extraction (see Figure 11). In this experiment both the concentration of dTBuCH18C6 (between 18 and 108 mmol L⁻¹) as well as the concentration of MAXCalix was varied (between 4 and 24 mmol L⁻¹). Strontium extraction was observed in all tested conditions. Increasing the ligand concentration results in better extraction. The higher distribution ratios are found when Cs-4 or Cs-5 was used as phase modifier. Cesium extraction was observed for MAXCalix concentrations of 5 mmol L⁻¹ and above. The influence of the phase modifier on Cs extraction is less pronounced.

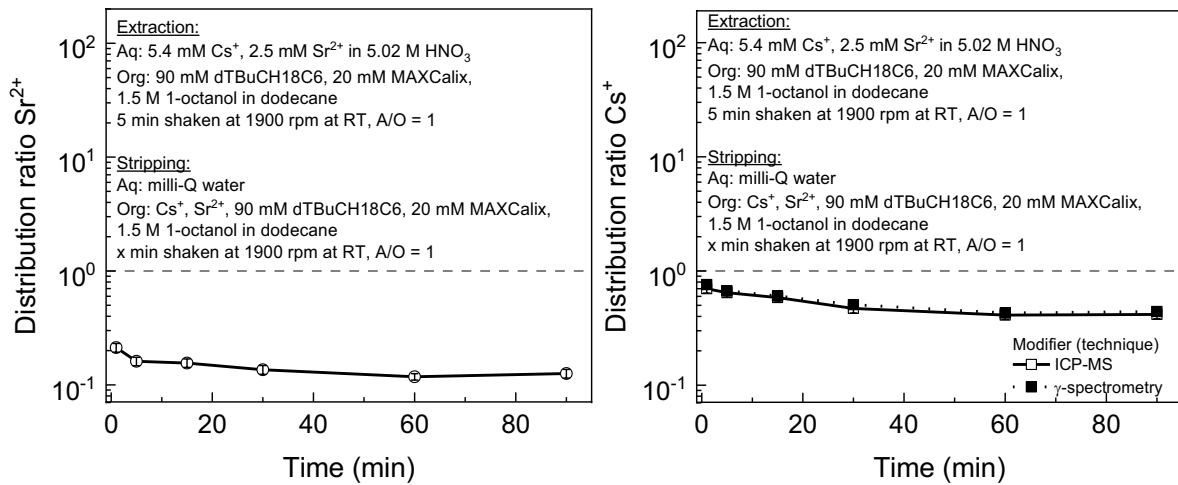


Figure 12: Kinetics experiment on Sr (left) and Cs (right) when stripping - active experiments

In the next set of experiments, co-stripping of strontium and cesium was tested. These experiments are crucial to develop a decontamination strategy. Aim is to first extract both elements to an organic phase. This loaded organic phase is contacted with a fresh aqueous phase to strip the strontium and cesium. To simplify the process, just milli-Q water was chosen as fresh aqueous phase. To test the kinetics of the system, the shaking time during stripping was varied first (see Figure 12). It is observed that both Cs and Sr are effectively stripped to this fresh aqueous phase. However, since the distribution ratio is not constant over the different shaking times, it is recommended to have a shaking time of at least 60 minutes, to make sure that the system is in equilibrium. The kinetic tests were only performed using 1-octanol as phase modifier.

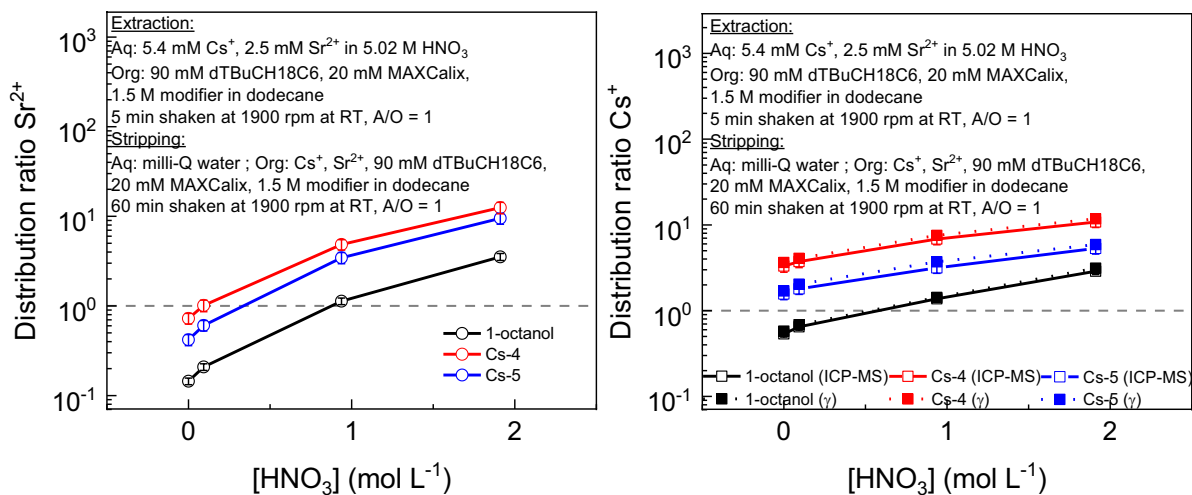


Figure 13: Nitric acid dependency on Sr (left) and Cs (right) when stripping – active experiments

In the next experiment, the influence of the concentration of nitric acid in the aqueous phase on the stripping efficiency is studied. It is observed that strontium can effectively be stripped at low nitric acid concentrations (from 0 mol L⁻¹, or just milli-Q water, until 0.9 mol L⁻¹ when 1-octanol is used as phase modifier. For Cs-4 and Cs-5, the maximum initial nitric acid concentration in the aqueous phase is best below 0.1 mol L⁻¹ and 0.4 mol L⁻¹ respectively. Experiments show that effective Cs stripping is observed for nitric acid concentrations below 0.5 mol L⁻¹ when 1-octanol is used as phase modifier.

Conclusions and outlook

In this work, the extraction of cesium and strontium was studied. Successful irradiations in BR1 and BR2 took place to synthesize ⁸⁹Sr and ¹³⁴Cs radioisotopes. An extraction system was developed using the commercially available DtBuCH18C6 extractant (selective Sr extractant), in combination with the MAXCalix extractant (selective Cs extractant). The latter extractant is not commercially available and was obtained from Marshallton research laboratories in the USA.

Extraction experiments were designed to mimic the exact concentrations of Sr²⁺ (5.4 mmol L⁻¹) and Cs⁺ (2.5 mmol L⁻¹) in an highly active raffinate (in 3-5 mol L⁻¹ HNO₃ solution). It was found that a combination of 20 mmol L⁻¹ MAXCalix and 90 mmol L⁻¹ DtBuCH18C6 in 1.5 M Cs-4 (or Cs-5) in dodecane shows the best extraction properties for both Sr²⁺ and Cs⁺.

In addition, experiments show that Sr²⁺ can be effectively stripped to a pure water phase with all tested modifiers, including 1-octanol. The Cs⁺ -ions, however, are only stripped when 1-octanol was used as modifier in the extraction stage.

To conclude, from a technical point of view, selective extraction of Sr and Cs isotopes from spent nuclear fuel is feasible. However, one of the main drawbacks is the availability of the specific Cs extractant 'MAXCalix'. In addition, together with Cs-134 and Cs-137, also the long-lived Cs-135 isotope will be co-extracted. Due to the large heat load, the final Cs/Sr waste forms need to have a small diameter and spaced appropriately to dissipate the heat.

Future experiments could be designed to first optimize the Cs stripping results. This can be done when the MAXCalix extractant is readily available to achieving more datasets showing distribution ratios below 1. Second, by using a simulated highly active raffinate (HAR), the interference and behaviour of other group I and II elements (e.g. Ba) can be studied as well.

Acknowledgements

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