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# First investigations on a *CHON* UNEX process

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**Abstract:** This paper presents first investigations on a novel An(III), Ln(III), Cs(I) and Sr(II) co-extraction conceptual process using a *CHON* solvent composed of the calixarene crown-ether MAXCalix and the diglycolamide TODGA in a 1-octanol/kerosene diluent. The co-extraction is followed by a sequential stripping of (1) Cs(I) and Sr(II), (2) An(III) and (3) Ln(III).

**Keywords:** An(III) and Ln(III) co-extraction; Cs and Sr co-extraction; MAXCalix; nuclear fuel recycling; TODGA.

## 1 Introduction

Irradiated nuclear fuel is either reprocessed or is to be directly disposed of in a deep geological repository (DGR). In the former case, the liquid waste remaining after reprocessing (HLLW, high-level liquid waste) is vitrified and is also to be disposed of in such a repository. These wastes produce significant heat due to radioactive decay. The thermal power (which governs the packing density in a DGR) is initially dominated by  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , followed by  $^{241}\text{Am}$  and Pu isotopes. Their removal from the waste prior to disposal would thus increase the storage capacity of a DGR [1].

Pu can be separated by the commercially applied PUREX process; it can be recycled as nuclear fuel. Am could also be recycled; however, processes for its separation are so far only developed at the laboratory scale [2, 3]. Finally, Cs and Sr could be separated followed by interim storage, e.g. by single processes such as SREX [4] and CSSX [5–7] or combined processes [8–10]. Some processes also intend recovering all these elements, either step-by-step (ARTIST [11]) or

altogether (UNEX [12], CRAMEX [13]). In this latter processes, extractant and diluent wastes would represent a quite large volume of secondary waste to be disposed of as they are not fully combustible.

Instead, we propose a *CHON* UNEX process, i.e. with a solvent composed of molecules containing C, H, O and N atoms only, making them combustible to gaseous wastes only [14]. The concept merges existing processes to co-extract all desired elements, followed by selective stripping steps.

*N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA, Figure 1 left) [15] is used to co-extract An(III) and Ln(III) from HLLW [16]. A solvent comprising 0.2 mol/L TODGA + 5%<sub>vol.</sub> 1-octanol in kerosene extracts An(III) and Ln(III) over a wide range of nitric acid concentrations (>0.15 mol/L  $\text{HNO}_3$ ) [17] and has been used successfully in laboratory-scale process tests for actinide separation [18, 19]. This solvent also extracts Sr(II) from approx. 3 mol/L  $\text{HNO}_3$  [18, 20]. As for Cs(I), 1,3-alt-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arenebenzocrown-6 (MAXCalix, Figure 1 right), designed for the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process [7], is used. Consequently, a solvent containing both TODGA and MAXCalix in 1-octanol-modified kerosene is proposed for a *CHON* UNEX process.

## 2 Conceptual flowsheet

Figure 2 shows a conceptual flowsheet. HLLW (containing approx. 3–4 mol/L  $\text{HNO}_3$ ) is fed to the extraction section (EX), where An(III), Ln(III), Cs(I) and Sr(II) are co-extracted. In a scrubbing section (SC), some partially co-extracted fission products (Zr(IV), Mo(VI), Pd(II)) are removed from the solvent, as demonstrated earlier [18, 21, 22]. Cs(I) and Sr(II) are stripped from the solvent in the Cs, Sr stripping section (BX). A small fraction of An(III) and Ln(III) is inevitably co-stripped, which needs to be re-extracted (RX) into the solvent.

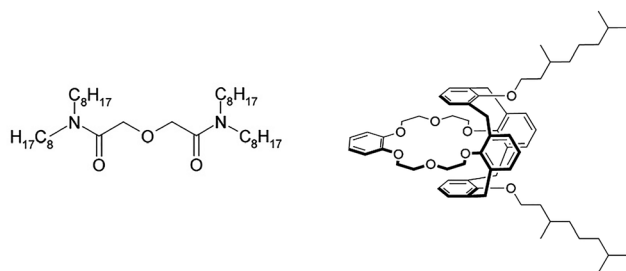
The solvent, now containing only An(III) and Ln(III), is routed to consecutive stripping steps. Selective complexing agents would be used to strip Am(III) and Cm(III) [18, 19] or only Am(III) [23]. Finally, the remaining Ln(III) (or Cm(III) and Ln(III)) would be stripped using dilute nitric acid [21, 22] or a specific stripping agent [18]. The latter steps are not shown in Figure 2.

Results reported in this communication show the feasibility of the co-extraction of An(III), Ln(III), Cs(I) and

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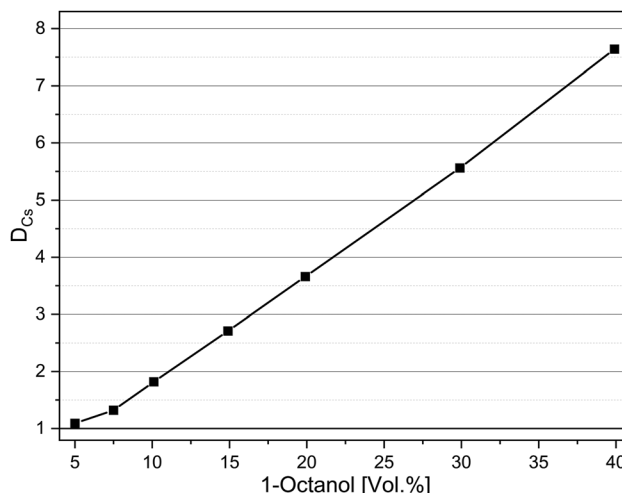


**Figure 1:** TODGA (left) and MAXCalix (right).

Sr(II) based on the simultaneous use of MAXCalix and TODGA in a kerosene/1-octanol diluent (experimental details, see Supplementary Information). Specific focus has been drawn towards the determination of suitable conditions for the extraction and stripping stages that in turn determine the conditions for the scrubbing and re-extraction stages. These latter stages will be studied in more details in the near future.

### 3 Results

With the solvent comprising 0.2 mol/L TODGA + 5 %<sub>vol.</sub> 1-octanol in kerosene, Sr(II) is extracted ( $D_{Sr} > 1$ ) from 1 to 5 mol/L  $\text{HNO}_3$  (Figure SI 1). Adding 0.02 mol/L MAXCalix (this concentration being close to its solubility limit in kerosene containing 5 %<sub>vol.</sub> 1-octanol) to this solvent results in Cs(I) distribution ratios only slightly greater than 1 (Figure SI 2), which is not sufficient for an efficient Cs(I) extraction. Figure 3 shows that increasing the 1-octanol volume fraction significantly enhances Cs(I) extraction, e.g.  $D_{Cs} = 5.6$  at 2.5 mol/L  $\text{HNO}_3$  and 30 %<sub>vol.</sub> 1-octanol (vs.  $D_{Cs} = 1.6$  at 2.5 mol/L  $\text{HNO}_3$  and 5 %<sub>vol.</sub> 1-octanol). This increase is consistent with a previous study showing a correlation between Cs extraction

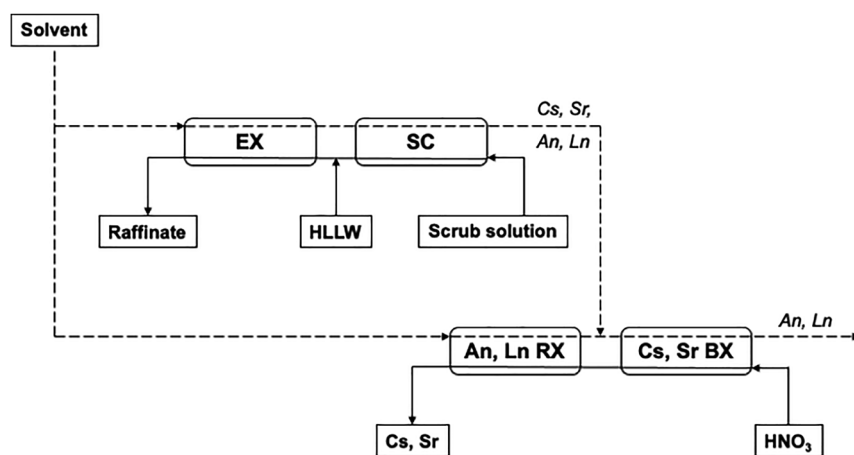


**Figure 3:** Cs(I) distribution ratio versus the 1-octanol volume fraction. Organic phase, 0.02 mol/L MAXCalix + 0.05 mol/L TODGA + 1-octanol in kerosene. Aqueous phase,  $^{137}\text{Cs(I)}$  (2 kBq/mL) in 2.5 mol/L  $\text{HNO}_3$ , A/O = 1,  $T = (293 \pm 1)$  K.

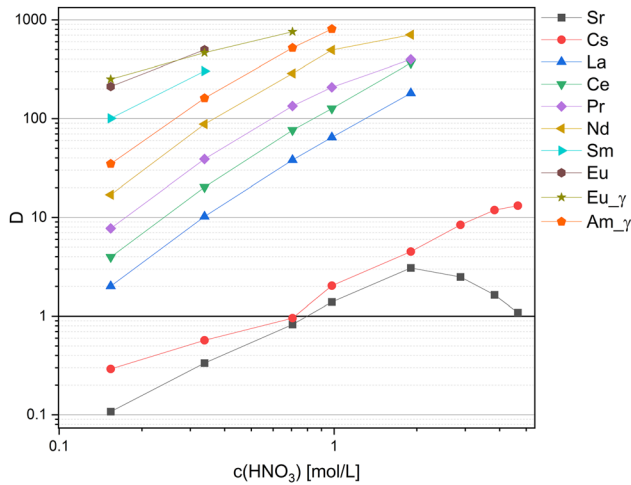
and increasing the dielectric constant of the diluent [24]. However, increasing the 1-octanol volume fraction suppresses Sr(II) extraction to distribution ratios close to 1 (Figure SI 3).

To counter-act, the TODGA concentration is increased to 0.3 mol/L (Figure SI 3). In this case, the co-extraction of An(III), Ln(III), Y(III), Cs(I) and Sr(II) from 1 to 4 mol/L  $\text{HNO}_3$  is feasible (Figure 4). According to Figure 4, Sr(II) and Cs(I) can be stripped ( $D < 1$ ) from the loaded solvent using diluted  $\text{HNO}_3$  ( $c(\text{HNO}_3) < 0.3$  mol/L) while Am(III), Y(III) and Ln(III) remain in the solvent ( $D > 1$ ).

A more detailed study was performed to assess that the nitric acid and other cations extracted by the solvent do not prevent an efficient stripping. An organic phase consisting in 0.02 mol/L MAXCalix + 0.3 mol/L TODGA + 30%<sub>vol.</sub> 1-octanol

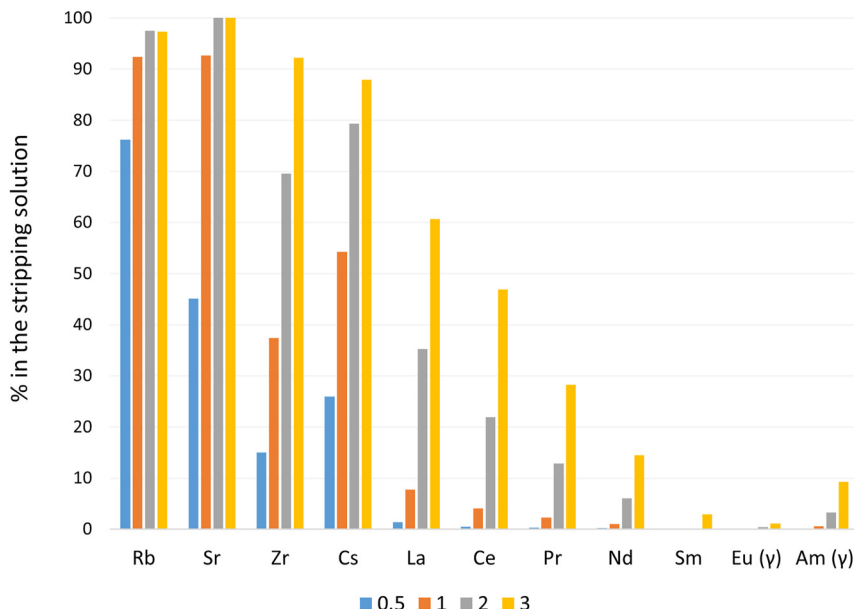


**Figure 2:** Scheme of the CHON UNEX process. HLLW = high-level liquid waste, EX = extraction section, SC = scrubbing section, RX = re-extraction section, BX = back-extraction (stripping) section. Dotted lines, organic phases. Solid lines, aqueous phases.



**Figure 4:** Distribution ratios of Cs(I), Sr(II), Y(III), Ln(III) and Am(III) into a TODGA + MAXCalix solvent. Organic phase, 0.02 mol/L MAXCalix + 0.3 mol/L TODGA + 30%<sub>vol.</sub> 1-octanol in kerosene. Aqueous phase, Cs(I), Sr(II), Ln(III), Y(III) ( $2 \times 10^{-5}$  mol/L each),  $^{241}\text{Am(III)}$  and  $^{154}\text{Eu(III)}$  (2 kBq/mL each) in  $\text{HNO}_3$ ,  $A/O = 1$ ,  $T = (293 \pm 1)$  K.

in kerosene was loaded by a contact to a HLLW simulate solution (composition, see Table SI 1). HEDTA and oxalic acid were added to the feed solution to prevent the co-extraction of some fission products such as Mo(VI) and Pd(II) [25]. The respective extraction distribution data are reported in Table SI 2. The loaded organic phase was then stripped into 1 mmol/L  $\text{HNO}_3$  at several aqueous to organic phase ratios ( $A/O$ ). Results displayed in Figure 5 show that both Cs(I) and Sr(II) are selectively stripped at  $A/O = 1$  and  $A/O = 2$ . An  $A/O$  of 0.5 is not sufficient for the stripping while an  $A/O \geq 3$  will



**Figure 5:** %Mass of extracted cations recovered in the stripping solution at several  $A/O$  ratios. Organic phase, 0.02 mol/L MAXCalix + 0.3 mol/L TODGA + 30%<sub>vol.</sub> 1-octanol in kerosene loaded by an extraction from a HLLW simulate solution (see Tables SI 1 and SI 2). Stripping solution, 1 mmol/L  $\text{HNO}_3$ .  $T = (293 \pm 1)$  K.

co-strip light lanthanides. The co-extracted fission products Rb(I) and Zr(IV) (see Table SI 2) can be stripped along with Cs(I) and Sr(II) at  $A/O = 2$ .

## 4 Conclusions

This study proved the feasibility of An(III), Ln(III), Sr(II) and Cs(I) co-extraction in the range 1–4 mol/L  $\text{HNO}_3$  by a solvent comprising 0.02 mol/L MAXCalix, 0.3 mol/L TODGA and 30%<sub>vol.</sub> 1-octanol in kerosene. Sr(II) and Cs(I) could be selectively stripped into diluted  $\text{HNO}_3$  (e.g. 1 mmol/L) while Am(III) and Ln(III) remain in the solvent, to be further separated in consecutive steps as described in the literature.

This conceptual process is an important first step towards a *CHON* UNEX process to remove all high-heat emitters from HLLW prior to its vitrification while enabling the recycling of Am(III). These results are the basis for a future development of a novel process addressing innovative nuclear fuel cycles.

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**Conflict of interest statement:** The authors report there are no competing interests to declare.

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**Supplementary Material:** This article contains supplementary material (<https://doi.org/10.1515/ract-2023-0151>).

## First investigations on a *CHON UNEX* process

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### — *Supplemental Information* —

#### Experimental methods

The extractants MAXCalix ( $M = 954$  g/mol) and TODGA ( $M = 580$  g/mol) were respectively purchased from Marshallton Research Laboratories (US) and Technocomm Limited (UK) and used without further purification. Nitric acid concentration was adjusted by dilution with ultrapure water (Millipore, Billerica; USA; 18.2 M $\Omega$ ). Kerosene and 1-octanol diluents were purchased from Fluka. A mixture of all stable lanthanides and yttrium was prepared in 1 mol/L nitric acid from Ln(NO<sub>3</sub>)<sub>3</sub> or Ln<sub>2</sub>O<sub>3</sub> powders.

All extraction experiments were performed as described in reference<sup>14</sup> at an organic to aqueous phase ratio of 1 and a temperature of (293±1) K. The kinetics of the equilibrium was checked, and it was found that it is reached within less than 10 minutes. The mixing time was thus set at 30 minutes, followed by 2 minutes of centrifugation. Results were analysed either by ICP-MS (inactive Cs(I), Ln(III) and Sr(II), 2×10<sup>-5</sup> mol/L each) or by  $\gamma$ -counting for the samples that contained <sup>154</sup>Eu(III), <sup>137</sup>Cs(I) and <sup>241</sup>Am(III) radiotracers (2 kBq/mL each).

Results are displayed as distribution ratios  $D_{\text{Cation}}$ , i. e. the ratio of the concentration of a species in the organic phase to that in the aqueous phase. A distribution ratio greater than 1 indicates an actual possibility for extraction, and smaller than 1 for stripping.



### Sr(II) extraction into TODGA + 5% vol. 1-octanol in kerosene

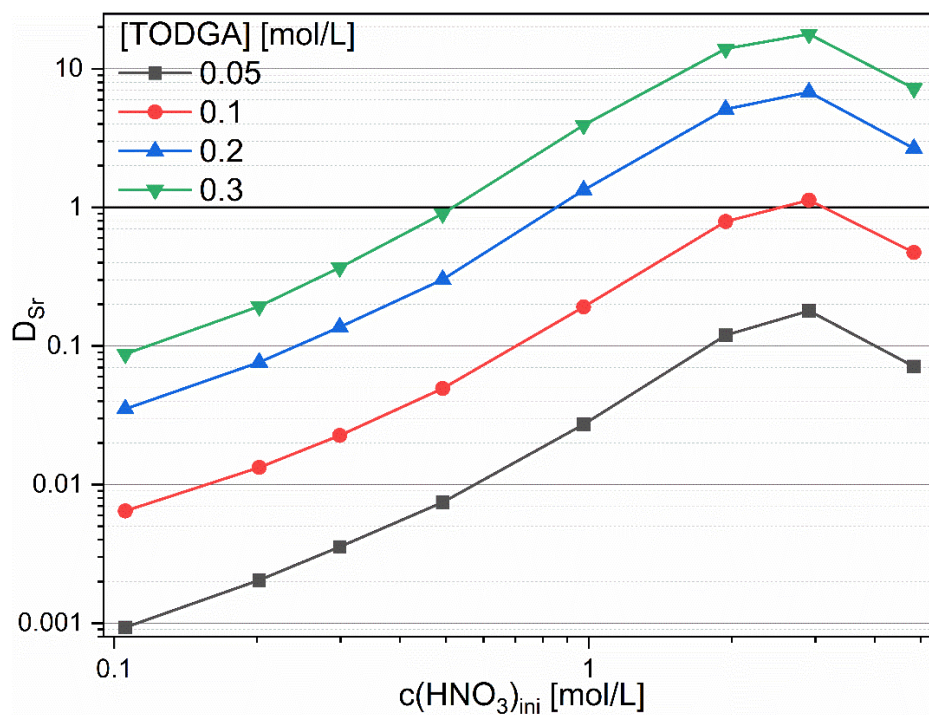


Figure SI 1. Extraction of Sr(II) into TODGA. Organic phase, TODGA + 5%vol. 1-octanol in kerosene. Aqueous phase,  $10^{-4}$  mol/L  $Sr(NO_3)_2$  in  $HNO_3$ . A/O = 1,  $T = (293 \pm 1)$  K.

### Cs(I) extraction into MAXCalix + TODGA + 5% vol. 1-octanol in kerosene

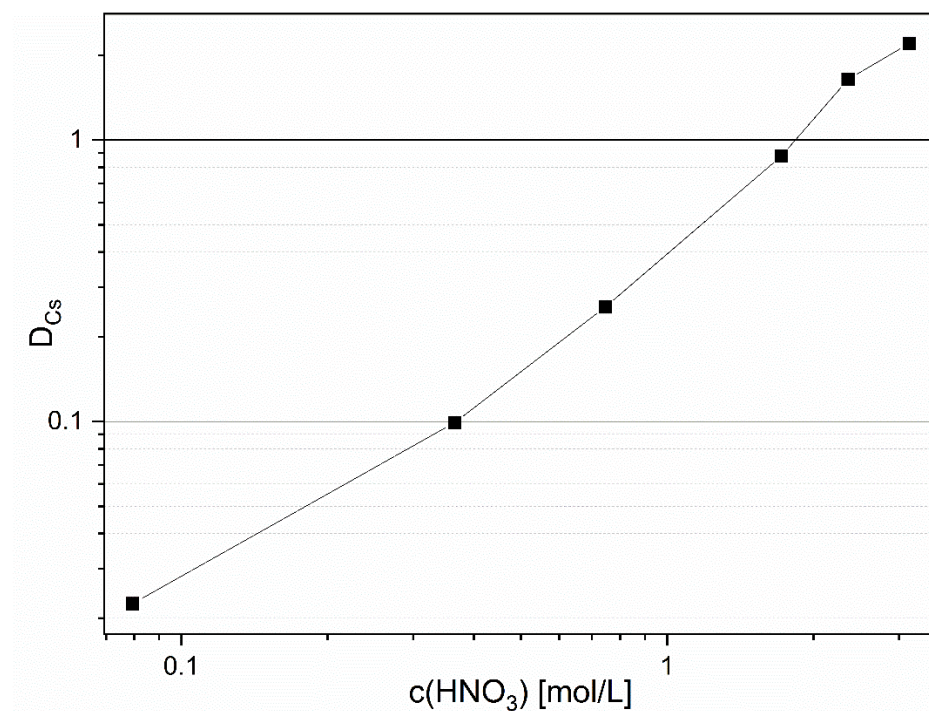


Figure SI 2. Extraction of Cs(I) into MAXCalix + TODGA. Organic phase, 0.02 mol/L MAXCalix + 0.2 mol/L TODGA + 5%vol. 1-octanol in kerosene. Aqueous phase,  $^{137}Cs(I)$  (2 kBq/mL) in  $HNO_3$ . A/O = 1,  $T = (293 \pm 1)$  K.

**Sr(II) extraction into TODGA + 25 or 30% vol. 1-octanol in kerosene**

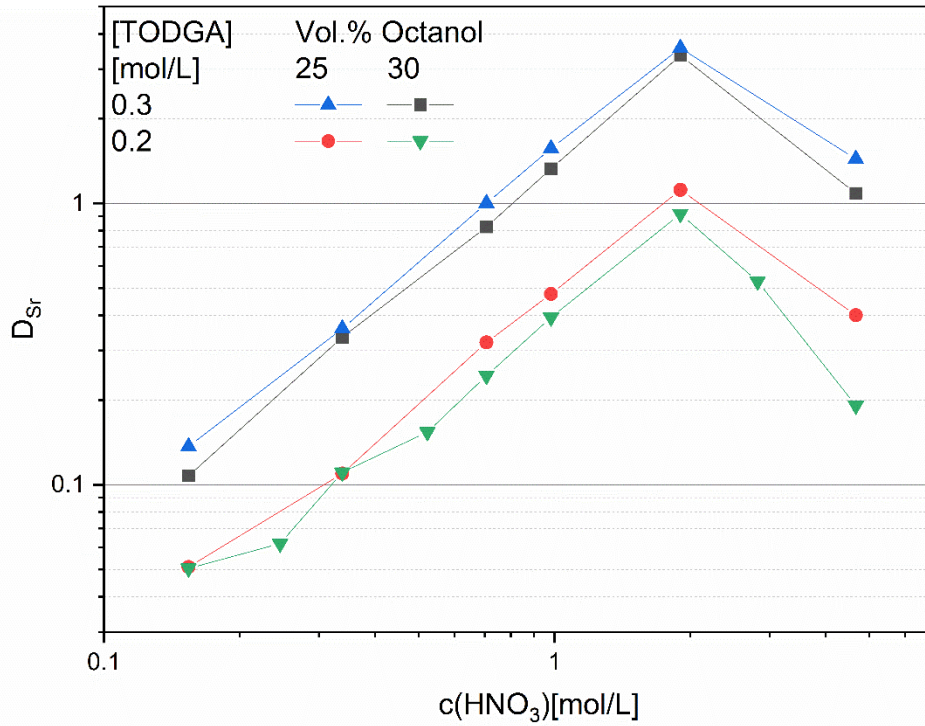


Figure SI 3. Extraction of Sr(II) into 0.2 or 0.3 mol/L TODGA + 25%<sub>vol.</sub> or 30%<sub>vol.</sub> 1-octanol in kerosene. Aqueous phase, 10<sup>-4</sup> mol/L Sr(NO<sub>3</sub>)<sub>2</sub> in HNO<sub>3</sub>. A/O = 1, T = (293±1) K.

**Stripping study**

Table SI 1. Composition of the HLLW simulate solution. Concentrations, mg/L unless stated otherwise.

Element	Concentration	Element	Concentration	Element	Concentration
Cr	133	Ru	342	La	310
Mn	25.3	Rh	39.8	Ce	494
Fe	1560	Pd	275	Pr	308
Ni	102	Ag	14.0	Nd	1110
Se	80.7	Cd	22.2	Sm	190
Rb	115	Sn	4.20	Eu	45.5
Sr	392	Sb	17.3	Gd	94.3
Y	118	Te	129	Tb	15.7
Zr	965	Cs	927	Dy	25.5
Mo	855	Ba	442	Am-241	2 kBq/mL
Eu-154	2 kBq/mL	HEDTA	0.02 mol/L	Oxalic acid	0.2 mol/L
HNO <sub>3</sub>	4 mol/L				

Table SI 2. Distribution ratios for the extraction from HLLW simulate solution. Organic phase, 0.02 mol/L MAXCalix + 0.3 mol/L TODGA + 30%vol. 1-octanol in kerosene. Aqueous phase, HLLW simulate (4 mol/L HNO<sub>3</sub> + HEDTA 0.02 mol/L + oxalic acid 0.2 mol/L).  $A/O = 1$ ,  $T = (293 \pm 1)$  K.

Extracted	D	Non-extracted	D
La	161	Ru	0.76
Ce	524	Mn	0.34
Other Ln	>3000	Sb	0.30
Y	>3000	Cd	0.24
Am (Gamma)	>3000	Ba	0.22
Eu (Gamma)	>3000	Fe	0.20
Rb	1.46	Mo	0.19
Sr	1.22	Ni	0.053
Zr	8.82	Cr	0.037
Cs	10.2	Rh, Te, Pd	<0.001
		Ag, Sn	Below limit