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CHON AmSel: A New Extraction System for Selective Americium Partitioning Based on an Unsymmetrical Diglycolamide and a Sulfur-Free Complexant

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ABSTRACT

One of the challenges of implementing a sustainable *Partitioning and Transmutation* (P&T) strategy in the nuclear fuel cycle is the development of a solvent extraction system for the selective separation of Am. One of the latest developments is the Americium Selective (AmSel) extraction system, a two-step process based on a lipophilic diglycolamide and a hydrophilic, sulfonated bistriazinyl bipyridine. However, this process has as a drawback the presence of sulfur in the hydrophilic complexant, making it unsuitable within a CHON strategy. This study presents a sulfur-free "CHON" variant of the AmSel process, replacing TODGA with *N,N*-dipentyl-*N′,N′*-didodecyldiglycolamide (PnDdDGA), and replacing SO_3-Ph-BTBP with either 3,3′-([2,2′-bipyridine]-6,6′-diylbis(1H-1,2,3-triazole-4,1-diyl))bis(propan-1-ol) (PrOH-BPTD) or 3,3′-((1,10-Phenanthroline-2,9-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(propane-1,2-diol) (BTrzPhen-tetraol). The latter two molecules are a hydrophilic bipyridine and phenanthroline, respectively. Both the organic and aqueous phases were optimized, and extraction tests were performed with a simulated highly active raffinate solution. Efficient separation of Am(III) from Cm(III) was feasible with both ligands, with $SF_{Cm/Am}$ values of around 2.2. although the limited solubility of PrOH-BPTD requires lowering of the DGA concentration for stripping to occur. Demonstration on a simulated PUREX HAR lowered $SF_{Cm/Am}$ values to around 1.9, and showed separating Am(III) from most fission products was possible. Separating Am(III) from La(III), Ce(III), and Pr(III) was not feasible in the stripping step, and necessitated an intermediary scrubbing step for the (light) lanthanides.

KEYWORDS

P&T; nuclear fuel cycle; americium partitioning; diglycolamides; phenanthrolines

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Introduction

In order to reduce the heat load and radiotoxicity of highly active spent fuel, numerous European projects have explored new solvent extraction (SX) systems for the selective separation of minor actinides (which include Np, Am, and Cm) from PUREX raffinates.[1,2] Americium in particular produces significant decay heat, increasing the cost and complexity of spent fuel repositories if not reprocessed. One method for reducing this is the separation of Am from the raffinate, followed by "transmutation" in a fast neutron nuclear reactor, inducing fission in order to convert Am to shorter lived fission products. The reduced heat load of the resulting raffinate would allow a reduction of repository volume while maintaining sufficient heat dispersal, thus reducing construction costs, while elimination of long-lived actinides such as Am could increase public acceptance of such repositories.[3] For a transmutation strategy to be feasible, a separation of americium from both the lanthanides and curium is required; the lanthanides are neutron poisons present in significantly higher concentrations than americium, and curium complicates all downstream processes due to its intense neutron emissions. Furthermore, there is the additional requirement of using a "CHON"-system, *i.e.* the extractants and diluents used may only consist of carbon, hydrogen, oxygen, and nitrogen atoms. The CHON strategy was originally adopted to avoid the generation of solid residue when S- or P-containing organic extractants or holdback agents are burnt at their end-of-life.[4] However, this strategy remains interesting for americium-selective aqueous complexants in the AmSel process, as the presence of sulfur can end up contaminating the Am-containing fuel elements during the fuel fabrication step. Therefore, in order to minimize contamination, fully incinerable complexing agents are preferred.

The current minor actinide partitioning strategy is a combination of a modified PUREX process to handle neptunium, follow by the Americium Selective (AmSel) extraction system removing americium from resulting raffinate. This process involves an initial co-extraction of americium(III), curium(III), and lanthanide(III) ions, leaving most of the fission products (FP) in the raffinate, which is followed by a selective stripping of Am(III) to the aqueous phase.[5] The reference AmSel system uses for extraction the diglycolamide extractant *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), and for stripping the hydrophilic 3,3',3",3"'-([2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate (SO_3-Ph-BTBP) complexant in the aqueous phase, which is selective for Am(III). This results in a system with a Cm/Am separation factor (SF) of 2.5, although the system is not CHON-compliant due to the presence of sulfur in the complexing agent. More recently, CHON-alternatives have been investigated for SO_3-Ph-BTBP, though it has turned out to be difficult to synthesize complexants with high

aqueous solubility (more than a few mmol L^{-1}), good extraction performance in nitric acid, and a high selectivity.[6,7]

Diglycolamide extractants, such as *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), have already been extensively studied for application in actinide separation processes.[8–10] These emerged as highly promising extractants in the early 2000s, at a time when increasing importance was put on avoiding the use of sulfur or phosphorus in actinide partitioning processes.[11,12] Their advantages are good performance, a fairly good selectivity for An(III) and Ln(III) versus fission products, and excellent hydrolytic and radiolytic stability.[13–18] Furthermore, the relatively simple chemical structure of TODGA makes it easy to synthesize on both lab- and process-scale.[19] However, diglycolamide-type extractants also have the disadvantage of being prone to third-phase formation, necessitating the use of phase modifiers, and some co-extraction of certain fission products such as Zr, Pd, and Tc, requiring the use of masking agents.[9,10,20,21]

More recently, so-called "unsymmetrical" diglycolamides (UDGAs) have become a topic of research. UDGAs were shown to offer numerous advantages compared to their symmetrical counterparts. Initially developed in order to optimize extraction and third-phase properties, it was eventually discovered that these might also offer improvements in selectivity.[22–24] The extractant *N,N*-diisopropyl-*N',N'*-didodecyldiglycolamide (iPDdDGA) was shown to improve the Am-Cm separation factor by around 20% when used instead of TODGA, increasing $SF_{Cm/Am}$ from 4.3 to 6.8 when combined with the hydrophilic *N,N,N′,N′*-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylene-diamine (H_4TPAEN) and increasing $SF_{Cm/Am}$ from 2.5 to 3.0 when combined with SO_3-Ph-BTBP.[25,26] In a previous study, we evaluated six different UDGAs, including iPDdDGA, in combination with SO_3-Ph-BTBP.[27] This study identified *N,N*-dipentyl-*N',N'*-didodecyldiglycolamide (PnDdDGA, See Fig. 1) as the most promising extractant, showing similar performance to TODGA albeit

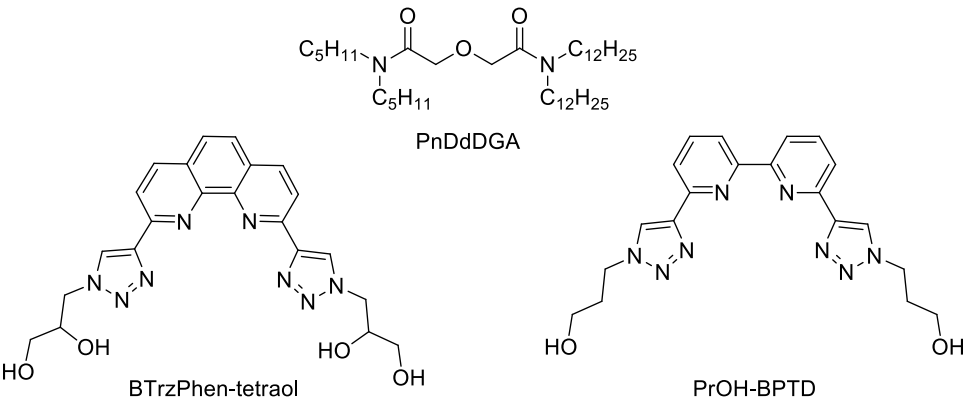

Figure 1. Structures of the ligands used in the CHON AmSel process.

with higher $SF_{Cm/Am}$ values (*ca.* 2.8). Although iPDdDGA showed the highest separation factors, it also showed excessive extraction strength, making stripping more difficult. In addition, third-phase formation was observed when the acid concentration of the aqueous phase was lowered to stripping conditions (0.5 mol L^{-1}) and the 1-octanol concentration in the solvent was below 10 vol %. Hence, PnDdDGA was selected for further development.

The objective of this study is to combine PnDdDGA with two hydrophilic CHON complexants to create a fully CHON-compliant AmSel system. The hydrophilic complexants selected for this evaluation are shown in Fig. 1; these are 3,3′-([2,2′-bipyridine]-6,6′-diylbis(1 H-1,2,3-triazole-4,1-diyl))bis(propan-1-ol) (PrOH-BPTD) and 3,3′-((1,10-Phenanthroline-2,9-diyl)bis(1 H-1,2,3-triazole-4,1-diyl))bis(propane-1,2-diol) (BTrzPhen-tetraol).[28,29] In a first stage, the composition of the organic phase will be optimized by determining which concentrations of diglycolamide and phase modifier (1-octanol) are required for the extraction step. In a second stage, the aqueous phase will be optimized by determining which concentrations of PrOH-BPTD/BTrzPhen-tetraol and nitric acid are required to obtain selective Am(III) stripping. Finally, the system will be demonstrated with a simulated PUREX raffinate, quantifying the distribution of the fission products during both extraction and stripping steps.

Experimental

Chemicals

Nitric acid solutions were prepared from 69% trace metal grade HNO_3 acquired from Fischer Chemicals (Zurich, Switzerland). Concentrations were verified through titration with a MT Titrator Excellence T5 autotitrator, using a 0.5 mol L^{-1} NaOH Titrisol standard as titrant. $Y(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%), $Ce(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%), $Pr(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%), $Nd(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%), and $Sm(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%) were obtained from Strem Chemicals (Kehl, Germany). $La(NO_3)_3{\cdot}6\,H_2O$ (purity 99.0%) was obtained from Fluka (Seelze, Germany). $Eu(NO_3)_3{\cdot}6\,H_2O$ (purity 99.99%) and $Gd(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%) were obtained from Alfa Aesar GmbH (Karlsruhe, Germany). $Dy(NO_3)_3{\cdot}6\,H_2O$ (purity 99.9%) and $Yb(NO_3)_3{\cdot}5\,H_2O$ (purity 99.9%) were obtained from Sigma-Aldrich (Steinheim, Germany). A stock solution containing 10^{-2} mol L^{-1} of each Ln(III) was prepared by weighing corresponding amounts of each lanthanide salt and dissolving in 0.1 mol L^{-1} HNO_3. All aqueous dilutions were prepared with Milli-Q grade water.

1-octanol (ACS grade) and *n*-dodecane (ReagentPlus grade) were acquired from Sigma-Aldrich (Steinheim, Germany). TODGA (purity min. 99%) was acquired from Technocomm Ltd. (Edinburgh, UK). PnDdDGA, PrOH-BPTD,

and BTrzPhen-tetraol were synthesized as described in the existing literature.[27–30]

The preparation of the simulated *Highly Active Raffinate* (sHAR) is described in our previous work.[31] Its composition is based on an in-house calculation of spent LWR UOx fuel. This fuel is assumed to have an initial ^{235}U enrichment of 4.2%, a burn-up of 50 GWd/tHM, and a cooling time of 10 years between the unloading and reprocessing of the spent fuel. This HAR simulates a PUREX raffinate that has a dissolution volume of 5000 L per metric tons of UOx fuel. Prior to use, 0.05 mol L^{-1} cyclohexyl-1,2-diamine -*N,N,N',N'*-tetraacetate (CDTA) was dissolved in the sHAR as a holdback agent for Zr(IV) and Pd(II). An exact composition of the sHAR can be found in the ESI (See Table S1).

^{152}Eu tracer (radionuclide purity > 99%) and ^{244}Cm tracer (radionuclide purity > 99.9%) solutions (1 mol L^{-1} HNO_3) were acquired from Eckert and Ziegler Nuclitec GmbH (Braunschweig, Germany). ^{241}Am radiotracer in 1 mol L^{-1} HNO_3 solution (radionuclide purity > 99%) was available from the legacy stocks of SCK CEN. Stock solutions were spiked with *ca.* 3 kBq mL^{-1} of radiotracer before extraction experiments.

Methods

Aqueous and organic phases were prepared by dissolving weighed amounts of complexant or extractant in the appropriate solvent. Aqueous phases typically contained a determined concentration of hydrophilic complexants, as well as 10 µL of Ln(III) stock solution per 1 mL of solvent (bringing the concentration to 10^{-4} mol L^{-1} of each Ln(III)) and 3 kBq mL^{-1} of each radiotracer. Organic phases typically consisted of 0.1 mol L^{-1} PnDdDGA dissolved in a solvent containing 5 vol% 1-octanol in *n*-dodecane. Organic phases were pre-equilibrated twice prior to extractions. Extractions were performed by combining 0.5 mL of aqueous and 0.5 mL of organic phase (A/O = 1) in 1.5 mL glass vials and shaking these in a TMS-200 Thermoshaker for 30 minutes at 2100 rpm. After shaking the samples were centrifuged and the phases were separated with Eppendorf Research Plus pipettes.

Samples for gamma spectrometry were prepared by diluting aliquots of 200 µL of aqueous or organic phase to 1 mL with 0.5 mol L^{-1} HNO_3 or 5 vol% 1-octanol in *n*-dodecane respectively. The samples were analyzed with a Canberra high-performance Ge detector (model: GC2520) equipped with a DSA-1000 multichannel analyzer and the raw data were analyzed with Genie2000 software. Activities were calculated based on the areas of the ^{241}Am peak at 59.5 keV, and the ^{152}Eu peak at 121.8 keV. Samples were measured until these peaks showed at least 10,000 counts, with low activity samples measured overnight.

Samples for alpha-spectrometry were prepared by diluting the samples if necessary, and pipetting aliquots of 5 µL for organic phases and 10 µL of aqueous phases onto a C-1S stainless steel planchet of 20 mm diameter. These were then dried under an IR lamp and fixed by heating to *ca*. 500°C on a Quartz Alliance (Villemer, France) epiradiator of the model 534 RB 2. The samples were measured on a Canberra Alpha Analyst spectrometer equipped with passivated implanted planar silicon (PIPS) detectors and analyzed with Apex-Alpha software. Activities were calculated from the surfaces of the ^{241}Am peaks around 5.5 MeV and ^{244}Cm peaks around 5.8 MeV.

Non-radioactive samples were analyzed with ICP-MS to determine the behavior of fission products. Samples were analyzed on a Thermo-Fisher Scientific X2 series II ICP-MS instrument. Sample preparation was performed through dilution with 2% HNO_3 solution. Organic phases were first stripped with a 0.1 mol L^{-1} glycolate solution at pH 4 (A/O = 10). Although Pd was present in the sHAR, concentrations could not be accurately measured due to interference from Y, Mo, and Zr. The maximum uncertainty on the measurements is 6% (2σ).

Distribution ratios (*D*) were calculated by taking the ratio of the (activity) concentration of a metal in organic phase over the (activity) concentration of the metal in the aqueous phase (both at equilibrium) as shown in "Eq. (1)". The separation factor (SF) of two metals was calculated as the ratio of their distribution ratios, with the higher value taken as the numerator, as shown in "Eq. (2)".

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{1}$$

$$SF = \frac{D_{M_1}}{D_{M_2}} \tag{2}$$

Results and discussion

Influence of DGA concentration

The first step of this study was an optimization of the loading step, *i.e.* the composition of the organic phase. A key parameter is the concentration of diglycolamide extractant. Higher concentrations of DGA increase extraction of Ln(III), Am(III), and Cm(III), but also extract unwanted fission products and nitric acid to a higher extent.[14,32] Furthermore, as the equilibrium is pushed more towards the formation of M-DGA complexes, stripping of Am(III) might be more difficult at higher concentrations of DGA. Most commonly, solvents containing 0.1 mol L^{-1} or 0.2 mol L^{-1} of DGA are used

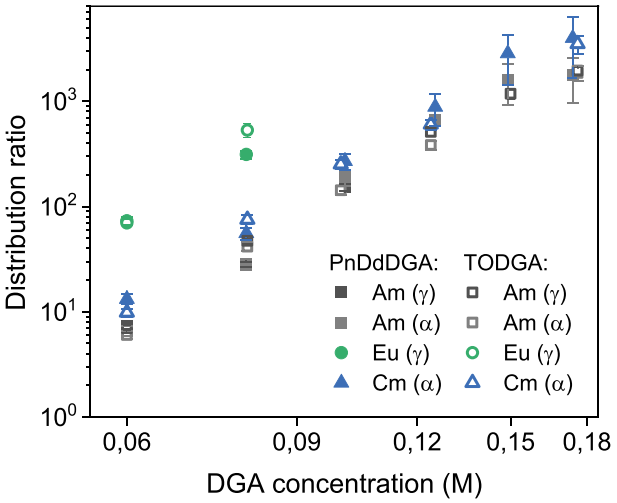

Figure 2. Influence of DGA concentration on extraction of Eu(III), Am(III), and Cm(III). Aqueous phase: sHAR (3.0 mol L^{-1} HNO_3, See Table S1) with 0.05 mol L^{-1} CDTA. Organic phase: x mol L^{-1} DGA in *n*-dodecane with 5 vol% 1-octanol, 2× pre-equilibrated (3 mol L^{-1} HNO_3). Shaking time: 30 min; A/O = 1.

in literature.[8,10] However, most data on the influence of DGA concentration on extraction was obtained with TODGA or similar symmetrical diglycolamides with four identical alkyl chains, while UDGAs remain mostly underexplored. For the diluent, *n*-dodecane was used as a representative for aliphatic diluents in general, and 1-octanol was used as phase modifier to prevent third-phase formation. Extraction experiments with varying PnDdDGA and TODGA concentrations were performed starting from a sHAR, of which the composition can be found in Table S1, to simulate a genuine PUREX raffinate, with the results presented in (Fig. 2).

Strong extraction is observed for both DGAs, with D_{Am} and D_{Cm} in excess of 10^3 at DGA concentration of 0.15 mol L^{-1} or higher. D_{Eu} values already fall above the limit of quantification (*i.e.* its concentration in the aqueous phase falls below the limit of detection) at DGA concentrations of 0.10 mol L^{-1} or higher. It can be noted that the obtained distribution ratios for TODGA and PnDdDGA show good overlap. In our previous study it was already shown that the extraction strength of TODGA and PnDdDGA is similar, these new data confirm the finding.[27] Both extraction with PnDdDGA and TODGA yield similar slopes for Am(III) (PnDdDGA: 5.6; TODGA: 5.3) and Cm(III) (PnDdDGA: 5.6; TODGA: 5.4). This implies the formation of 1:5 M:L complexes, which deviates from previous studies where the formation of a 1:3 M:L complex with both TODGA and PnDdDGA were observed.[27] However, it must be pointed out that for a slope analysis to be valid, the free ligand concentration must be used. Due to the high acid and metal concentrations in the feed solution, the free ligand concentration after extraction would have

been significantly lower than the initial DGA concentration, making the obtained slopes unreliable.

Data for the extraction of fission products with PnDdDGA and TODGA can be found in the ESI (See Tables S2 and S4). In both cases, only Y(III) and the Ln(III) are extracted throughout the whole DGA concentration range. Of the remaining fission products, only Sr(II), Mo(VI), and Ru(III) are extracted at higher concentrations of DGA. A comparison between PnDdDGA and TODGA shows slightly lower extraction of fission products for PnDdDGA, although the difference is too small to draw any definitive conclusions. A clear increase in distribution ratios is observed for both PnDdDGA and TODGA when the DGA concentration is increased. For example, for Sr(II) a distribution ratio of 0.044 is obtained during extraction with 0.125 mol L^{-1} of PnDdDGA, whereas a ratio of 0.51 is obtained during extraction with 0.175 mol L^{-1}. The increase is even more pronounced for the light Ln(III), with La(III) distribution ratios increasing from 0.43 at 0.06 mol L^{-1} PnDdDGA to 60.5 at 0.175 mol L^{-1}. Similar increases are observed for TODGA, and can be explained through the equilibrium being pushed towards complex formation when the DGA concentration is increased.[11,33] Despite the lower Ln(III) extraction at 0.06 mol L^{-1} PnDdDGA, the extraction of An(III) remains feasible with distribution ratios around 10.

Influence of 1-octanol concentration

Diglycolamide-type extractants are known to be prone to third-phase formation, a phenomenon where the organic phase splits in two when the solubility of the metal-extractant complex is exceeded.[20,34] The split results into a dense intermediary phase, rich in extractant and metal-extractant complex, and a lighter, depleted organic phase rich in diluent. Third-phase formation must be avoided in extraction processes, as it can interfere with the flow, disrupting the delicate equilibrium, and cause significant holdup of metals. To avoid third-phase formation, a phase modifier can be added to improve solubility of the metallic complexes. Some of the most common phase modifiers are TBP and long-chain alcohols such as 1-octanol.[10] The concentration of phase modifier is best kept low (with 5 vol% of 1-octanol being typically used), as the increase in viscosity of the solvent at higher modifier concentrations can negatively affect hydrodynamics, and higher concentrations of phase modifier correlate with higher extraction of acid.[10,32,35] To evaluate the influence of the phase modifier (1-octanol) concentration on the distribution ratios of radionuclides, extractions using solvents containing between 0 vol% and 10 vol% 1-octanol were performed. The experiment was performed by first equilibrating a spiked sHAR with the solvent, with the results presented in Fig. 3. Although typically third-phase formation is a phenomenon

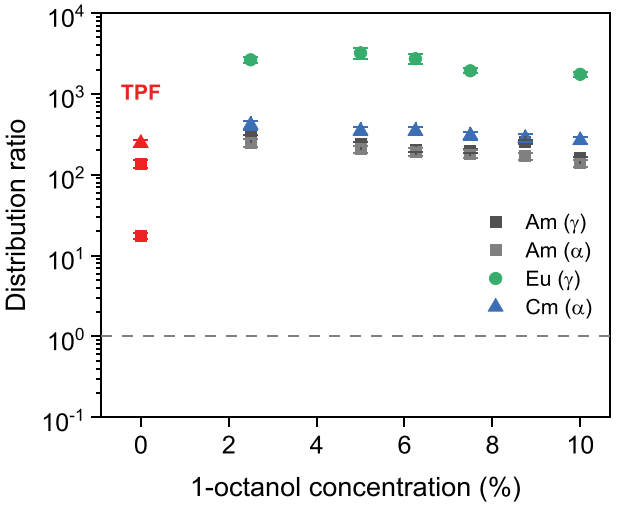

Figure 3. Influence of 1-octanol concentration on extraction of Eu(III), Am(III), and Cm(III). Aqueous phase: sHAR (3.0 mol L^{-1} HNO_3, See Table S1) with 0.05 mol L^{-1} CDTA. Organic phase: 0.1 mol L^{-1} PnDdDGA in *n*-dodecane with × vol% 1-octanol, 2× pre-equilibrated (3 mol L^{-1} HNO_3). Shaking time: 30 min; A/O = 1. At 0% (TPF), third-phase formation occurred, and the lighter organic phase was analyzed to calculate the distribution ratio.

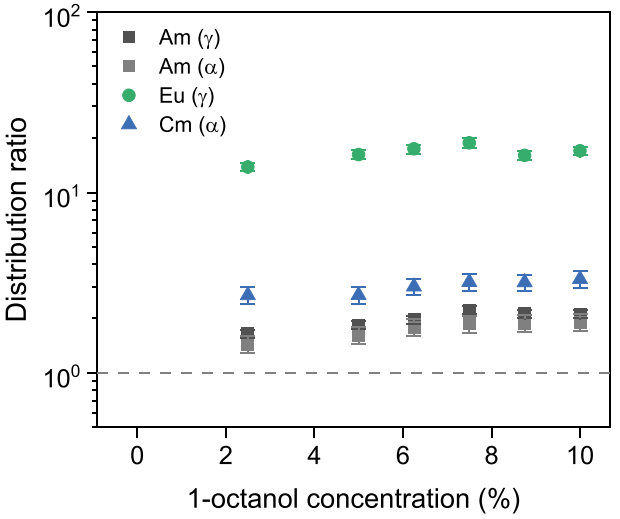

Figure 4. Influence of 1-octanol concentration on stripping of Eu(III), Am(III), and Cm(III) from loaded organic phase. Organic phase: 0.1 mol L^{-1} PnDdDGA in *n*-dodecane with × vol% 1-octanol, 2× pre-equilibrated (3 mol $L^{-1}HNO_3$), loaded from sHAR (3.0 mol L^{-1} HNO_3, See Table S1). Aqueous phase: 0.1 mol L^{-1} HNO_3. Shaking time: 30 min; A/O = 1.

expected during the loading step (where higher HNO_3 concentrations are used), our previous work has demonstrated that for certain UDGAs third-phase formation can also occur at lower nitric acid concentrations, which are typically required for stripping.[27] For this reason, the extraction

experiment was followed by contacting the loaded organic phase with a solution containing 0.1 mol L^{-1} of HNO_3, the results of which are presented in Fig. 4.

When no 1-octanol is added to the organic phase, third-phase formation is clearly observed, both visually (through the appearance of a third phase) and in the data (through a decrease in the activity ratio and activity balance calculated based on the aqueous phase and the lighter organic phase). For 1-octanol concentrations of 2.5 vol% or higher, no third-phase formation is observed, during either loading or stripping. Over this range, only marginal differences are observed in distribution ratios, with a slight decrease in D_M values observed when the phase modifier concentration is increased during extraction, and a slight increase in D_M values when the modifier concentration is increased during stripping.

The decrease in distribution ratios during extraction can be explained through the decrease of free ligand concentration at higher 1-octanol concentrations. Higher phase modifier concentrations are known to result in higher concentrations of acid in the organic phase when extractions are performed with DGA and UDGA extractants, caused by synergistic effects resulting in the formation of mixed adducts containing DGA, 1-octanol, and nitric acid.[26,32] Therefore, although the aqueous nitric acid concentration at equilibrium is constant throughout the series (as the organic phases have been twice pre-equilibrated prior to extractions), higher concentrations of acid are present in the organic phases for samples with higher 1-octanol concentrations. This decreases the free ligand concentration, leaving fewer extractant molecules available for complexing metals, and therefore slightly decreases distribution ratios. Similar observations have been made in literature for extraction of Ln(III) with TODGA in 1-alcohol/*n*-dodecane solvents, although the differences in D values were small and the observed trends appeared to be dependent on the length of the phase modifier's alkyl chain.[36]

On the other hand, when the loaded organic phases are contacted with the stripping solutions (containing 0.1 mol L^{-1} HNO_3), the equilibrium for acid extraction is displaced, leading to a partial stripping of the acid and an increase in HNO_3 concentration at equilibrium. As the organic phases with a higher phase modifier concentration also contain more acid, more acid is stripped, resulting in a relatively higher aqueous acid concentration at equilibrium, which correlates with higher distribution ratios for DGA and UDGA extractants.[26,37]

Overall, the differences observed in distribution ratios are minimal and are not expected to have a significant impact on process design. Nevertheless, the results demonstrate the feasibility of reducing 1-octanol concentration when used as a phase modifier, even when simulated raffinates are used as feed, which might benefit fluid dynamics and nitric acid management. As 1-octanol has been shown to be an important driver of acid co-extraction, limiting its concentration can contribute to minimizing or avoiding acid holdup in

a continuous process.[26,38] For this reason, we have chosen a 1-octanol concentration of 2.5 vol%, the lowest tested concentration to not show third-phase formation, for the demonstration of the extraction process with a simulated HAR.

Stripping with PrOH-BPTD

In the AmSel system, after loading the organic phase with Am(III), Cm(III), and Ln(III) at the extraction step, a second step takes place where Am(III) is selectively stripped back to the aqueous phase. In the original AmSel system, SO_3-Ph-BTBP is used as aqueous complexant to achieve this, resulting in a $SF_{Cm/Am}$ of *ca*. 2.5. In this study, the sulfonated SO_3-Ph-BTBP is replaced with the CHON-compliant PrOH-BPTD. This complexant has already been studied in combination with TODGA, and was shown to be a well-performing molecule, albeit with a slightly lower $SF_{Cm/Am}$ (2.0–2.3).[28] In this study, PrOH-BPTD will be combined with the unsymmetrical PnDdDGA in an attempt to increase the $SF_{Cm/Am}$ values, keeping TODGA as a reference. The distribution ratios for Am(III) and Cm(III) as a function of the equilibrium nitric acid concentration and at a constant concentration of PrOH-BPTD (20 mmol L^{-1}) are displayed in Fig. 5.

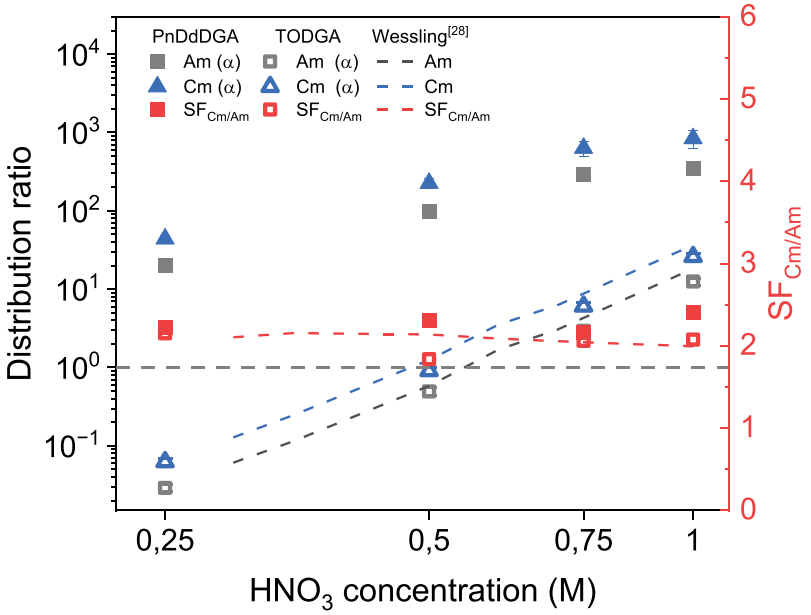

Figure 5. Influence of the HNO_3 concentration on the distribution ratios for extraction of Eu(III), Am(III), and Cm(III). Organic phase: 0.1 mol L^{-1} DGA in *n*-dodecane with 5 vol% 1-octanol, 2× pre-equilibrated (x mol L^{-1} HNO_3). Aqueous phase: 20 mmol L^{-1} PrOH-BPTD, 10^{-3} mol L^{-1} Ln(III), and 3 kBq mL^{-1} radiotracer in × mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

Comparison of the TODGA data with literature results shows an excellent agreement, and provides a reliable reference for the PnDdDGA data.[28] In the case of PnDdDGA, much higher distribution ratios are found than for TODGA (by 1–3 orders of magnitude), despite both extractants showing similar distribution ratios during the extraction step. Furthermore, different slopes can be found for the two sets of data: 4.0 ± 0.2 for TODGA and 2.2 ± 0.1 for PnDdDGA, and is likely the result of a combined effect between the extraction properties of the DGAs and the BPTD complexant. It can also be noted that the measured distribution ratios were higher than what was obtained for stripping without the presence of any hydrophilic complexant in Fig. 4. This is a result of the higher HNO_3 concentrations and lower metal concentration used in this experiment, and it must be kept in mind that in a continuous process a wide range of concentrations can be found throughout the different stages, and that stripping should be feasible throughout this range to avoid recycling of metal within the process. Comparison of the measured $SF_{Cm/Am}$ values shows a small improvement when PnDdDGA is used (2.2–2.4) instead of TODGA (1.8–2.1), bringing the former closer to the AmSel reference of 2.5.

In our previous study, several UDGAs were examined through both extraction and speciation experiments.[27] When stripping was performed with SO_3-Ph-BTBP, slightly higher distribution ratios were found for PnDdDGA than for TODGA, but the difference was too small to be statistically significant, and certainly not of the same order of magnitude as observed in this study. Furthermore, no difference in extraction mechanism was observed between TODGA and UDGAs, although these experiments were performed without the presence of hydrophilic complexant.

With the current composition of the aqueous phase, distribution ratios for Am(III) are too high to obtain stripping. The aqueous phase can be optimized by increasing the ligand concentration, decreasing the HNO_3 concentration, or both. However, the BPTD solubility decreases as the nitric acid concentration is lowered, making it difficult to obtain a sufficiently high concentration for stripping. In our study, we were only able to obtain stable PrOH-BPTD solutions up to 20 mmol L^{-1} for nitric acid concentrations of 0.5 mol L^{-1} or lower. An alternative method to decrease distribution ratios is decreasing the DGA concentration in the organic phase, as demonstrated in Fig. 2. This shows that lower concentrations of DGA (as low as 0.06 mol L^{-1}) still permit loading of An (III) and Ln(III), and do not hinder the first extraction step. The influence of the DGA concentration on the distribution ratios during the stripping step is shown in Fig. 6.

Lowering the diglycolamide concentration induces a substantial decrease in distribution ratios, and at a concentration around 0.08 mol L^{-1} PnDdDGA a region is reached where selective Am(III) stripping is possible. $SF_{Cm/Am}$ values range between 2.0 and 2.4 throughout the series, with a value of 2.2

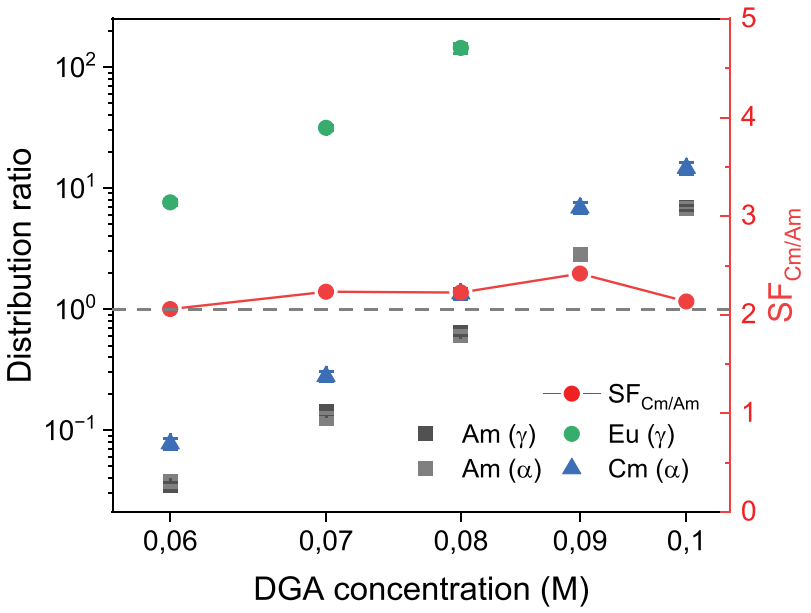

Figure 6. Influence of the PnDdDGA concentration on the distribution ratios for extraction of Eu(III), Am(III), and Cm(III). Organic phase: x mol L^{-1} PnDdDGA in *n*-dodecane with 5 vol% 1-octanol, 2× pre-equilibrated (0.25 mol L^{-1} HNO_3). Aqueous phase: 20 mmol L^{-1} PrOH-BPTD, 10^{-4} mol L^{-1} Ln(III), and 3 kBq mL^{-1} radiotracer in 0.25 mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

obtained at 0.08 mol L^{-1} PnDdDGA. Overall, this shows that selective Am(III) stripping is possible with a PnDdDGA/PrOH-BPTD system, with workable $SF_{Cm/Am}$ values that are higher when compared to corresponding values in the TODGA system, and slightly lower than the non-CHON AmSel reference.

Stripping with BTrzPhen-tetraol

A second alternative to replace SO_3-Ph-BTBP is the BTrzPhen-tetraol ligand, a phenanthroline ligand made soluble with two dihydroxypropyl groups. It was first synthesized in 2017 by Edwards *et al.*, and more recently studied in more depth by Troosters *et al.*, showing promising extraction properties and a $SF_{Cm/Am}$ value around 2.3 when combines with TODGA.[29,39] A major advantage compared to PrOH-BPTD is its higher solubility (>50 mmol L^{-1}), allowing stripping to be performed over a wider range of ligand concentrations, making optimization of the stripping step easier. In this study, we combined the BTrzPhen-tetraol ligand with PnDdDGA, and the distribution ratios of Am(III), Cm(III), and Eu(III) as a function of the ligand concentration, at a constant HNO_3 concentration of 0.25 mol L^{-1}, are shown in Fig. 7.

Distribution ratios for Am(III) and Cm(III) decrease as the ligand concentration increases, and are below 1 even at the lowest tested concentration (10 mmol L^{-1}).

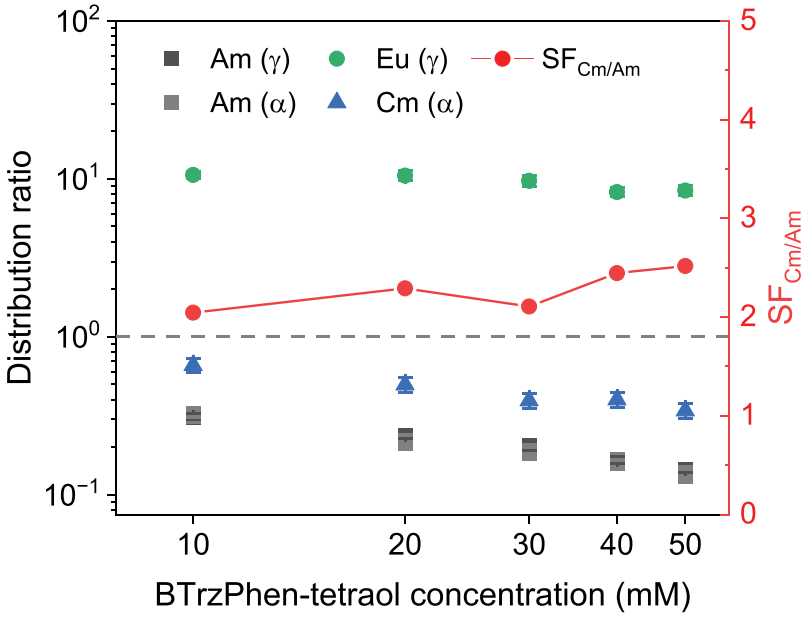

Figure 7. Influence of the BTrzPhen-tetraol concentration on the distribution ratios for extraction of Eu(III), Am(III), and Cm(III). Organic phase: 0.1 mol L^{-1} PnDdDGA in *n*-dodecane with 5 vol% 1-octanol, 2× pre-equilibrated (0.25 mol L^{-1} HNO_3). Aqueous phase: x mmol L^{-1} BTrzPhen-tetraol, 10^{-4} mol L^{-1} Ln(III), and 3 kBq mL^{-1} radiotracer in 0.25 mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

A limited effect can be observed for Eu(III), which is explained by the limited complexation of soft N-donors with the lanthanides' 4f orbital, with similar observations reported in the literature.[29,40] When compared to PrOH-BPTD, the BTrzPhen-tetraol ligand is a stronger complexant, as stripping of both Am(III) and Cm(III) is already obtained with 10 mmol L^{-1} of ligand without lowering the DGA concentration. The higher solubility of the ligand also gives more flexibility in the optimization of the aqueous phase, as well as allows the $SF_{Cm/Am}$ to be increased from 2.0 (at 10 mmol L^{-1} of ligand) to 2.5 (at 50 mmol L^{-1} of ligand). However, for stripping to be feasible at these higher ligand concentrations, the HNO_3 concentration must be increased to raise the distribution ratios until a region is reached wherein $D_{Cm} > 1$ and $D_{Am} < 1$. The distribution ratios as a function of HNO_3 concentration with a fixed ligand concentration of 40 mmol L^{-1} is plotted in Fig. 8.

Increasing the HNO_3 concentration has a strong increasing effect on all measured distribution ratios. Furthermore, $SF_{Cm/Am}$ shows a small decrease from 2.2 (at 0.25 mmol L^{-1} HNO_3) to 1.8 (at 1 mol L^{-1} HNO_3). A region where selective stripping of americium is possible (*e.g.* with $D_{Cm} > 1$ and $D_{Am} < 1$) can be found between approximately 0.32 and 0.4 mol L^{-1} HNO_3, with a $SF_{Cm/Am}$ value of 2.1 at 0.37 mol L^{-1} HNO_3. While it may be possible to improve the separation factor by increasing the ligand concentration even further, it seems unlikely for the

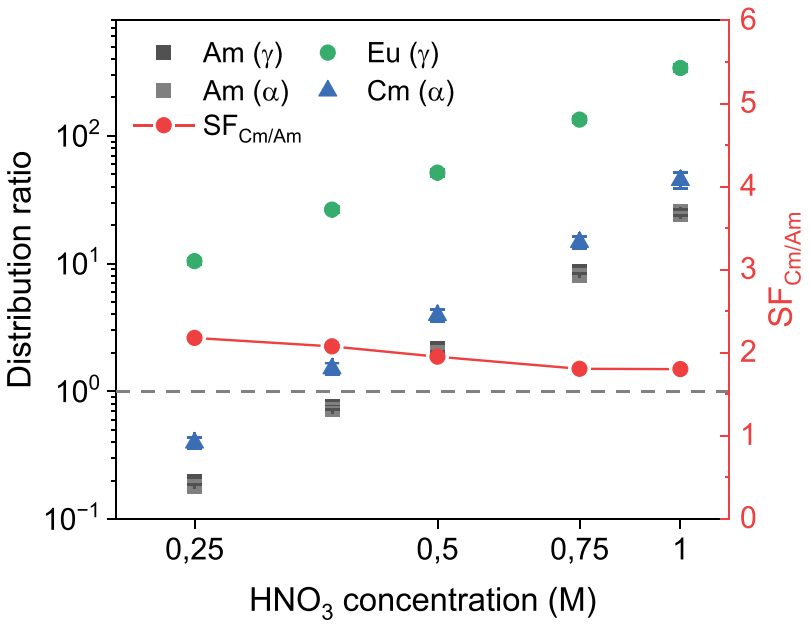

Figure 8. Influence of the HNO_3 concentration on the distribution ratios for extraction of Eu(III), Am(III), and Cm(III). Organic phase: 0.1 mol L^{-1} PnDdDGA in *n*-dodecane with 5 vol% 1-octanol, 2× pre-equilibrated (x mol L^{-1} HNO_3). Aqueous phase: 40 mmol L^{-1} BTrzPhen-tetraol, 10^{-4} mol L^{-1} Ln(III), and 3 kBq mL^{-1} radiotracer in × mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

separation factor to exceed the one found in the AmSel process (2.5). When compared to the PrOH-BPTD system, the BTrzPhen-tetraol ligand appears to yield a similar separation factor, although the higher solubility of the ligand gives more flexibility. Furthermore, higher DGA concentrations can be used due to the stronger complexation shown by the phenanthroline ligand.

Demonstration with simulated HAR

The AmSel process is intended to be implemented after a PUREX-type process, in which the major actinides (uranium and plutonium) are recovered from the spent nuclear fuel. The resulting raffinate contains not only minor actinides, but also high concentrations of fission products.[9] In order to achieve a full separation of Am(III), their behavior also needs to be taken into account. For diglycolamide-based systems, elements such as Sr, Pd, Ru, Mo, and Zr are known to exhibit a degree of co-extraction, and holdback agents are required to keep these in the aqueous raffinate.[10] Some elements, such as Sr and Mo, can be scrubbed from the organic phase with a low-acid scrub solution or an oxalic acid solution.[41] For Zr and Pd, CDTA was shown to be an effective holdback agent.[42] For Ru, no effective holdback agent has been found yet, and will either need a specialized scrubbing strategy, or it must be demonstrated that the Am-selective ligand does not strip Ru to a significant extent.

Although the original non-CHON AmSel system has already been demonstrated with a simulated HAR, no such studies have been reported yet for the two ligands covered in this work.[31] For our demonstration of the CHON AmSel system, the experiment was performed in three steps, with aliquots taken at each step for analysis in order to calculate the distribution ratios. First, the optimized organic solvent was loaded with metals by contacting it with the sHAR solution. The organic phase consisted of either 0.08 mol L^{-1} PnDdDGA (in the case of stripping with PrOH-BPTD) or 0.1 mol L^{-1} PnDdDGA (in the case of stripping with BTrzPhen-tetraol), and in both cases 2.5 vol% of 1-octanol in *n*-dodecane was used as the diluent. The composition of the sHAR can be found in the ESI (See Table S1), had a HNO_3 concentration of 3 mol L^{-1}, and had 0.05 mol L^{-1} CDTA added as a masking agent prior to extractions. After loading, the organic phases were scrubbed with a 1 mol L^{-1} HNO_3 solution to scrub excess acid and evaluate the possibility of scrubbing co-extracted fission products. The distribution ratios for the loading and scrubbing steps are presented in Fig. 9. Finally, the scrubbed organic phase was stripped with solutions containing the CHON ligand and HNO_3 concentrations varying between 0.25 and 1.0 mol L^{-1} HNO_3. In the case of PrOH-BPTD, 20 mmol L^{-1} of ligand was used for the stripping, and the results are presented in Fig. 10, whereas the higher solubility of BTrzPhen-tetraol enabled 40 mmol

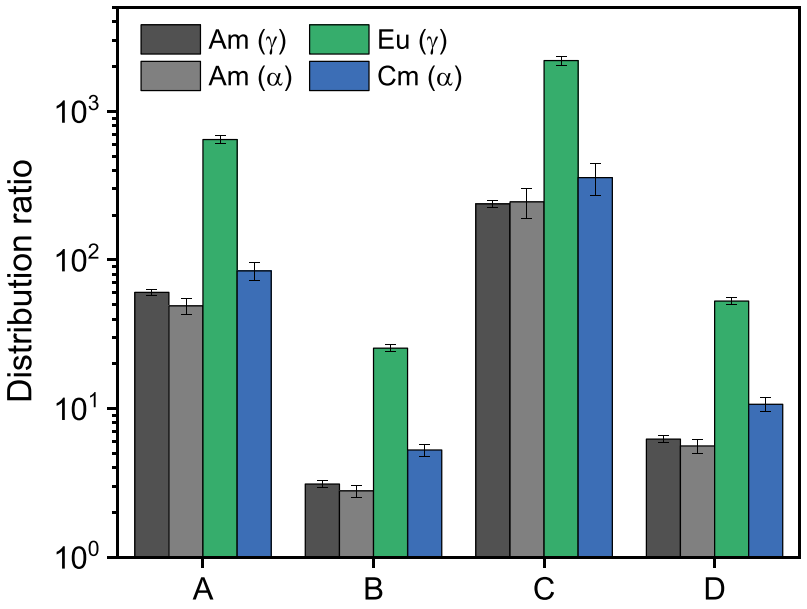

Figure 9. Distribution ratios for loading (A) and scrubbing (B) using 0.08 mol L^{-1}PnDdDGA, and loading (C) and scrubbing (D) using 0.1 mol L^{-1} PnDdDGA. Feed: sHAR (3.0 mol L^{-1} HNO_3, See Table S1) with 0.05 mol L^{-1} CDTA. Organic phase: 0.08/0.1 mol L^{-1} PnDdDGA in *n*-dodecane with 2.5 vol% 1-octanol, 2× pre-equilibrated (3 mol L^{-1} HNO_3). Scrubbing solution: 1 mol L^{-1} HNO_3. Shaking time: 30 min; A/O = 1.

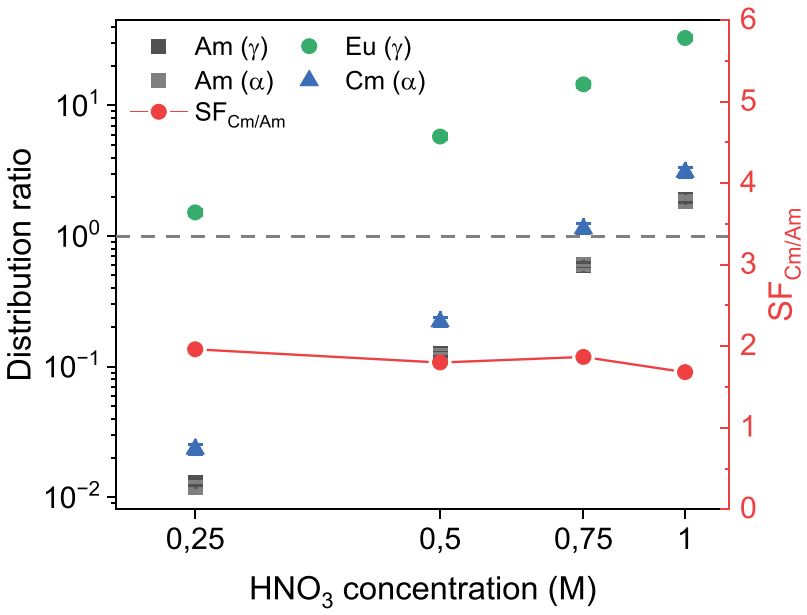

Figure 10. Distribution ratios for stripping from organic phase (loaded with sHAR (3.0 mol L^{-1} HNO_3, See Table S1) and scrubbed with 1 mol L^{-1} HNO_3) with PrOH-BPTD. Organic phase: 0.08 mol L^{-1} PnDdDGA in *n*-dodecane with 2.5 vol% 1-octanol, loaded + scrubbed. Aqueous phase: 20 mmol L^{-1} PrOH-BPTD in × mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

L^{-1} of ligand to be used, with these results presented in Fig. 11. Data for the fission product extraction during loading, scrubbing, and stripping is presented in the ESI (See Tables S4 and S5).

During the loading step, both 0.08 mol L^{-1} and 0.1 mol L^{-1} of PnDdDGA with 2.5 vol% 1-octanol show good loading of Am(III), Cm(III) and Eu(III) with no third-phase formation, reaching D_{Am} values of 64 and 240 respectively. In the scrubbing step, D_{Am} is significantly lower (3.1 and 6.2 respectively) but remain above 1 for both solvent compositions, indicating a majority of the Am(III) remains in the organic phase. Comparison with data obtained for the fission products shows that for both DGA concentrations tested, a majority of the fission products are not extracted. Only Y(III) and the Ln(III) appear to be extracted to a significant extent. For the original AmSel system, it was found that there was a significant co-extraction of Sr, and some extraction of Ru as well.[31] Similar observations were made for the EURO-GANEX solvent, where DMDOHEMA is used as a phase modifier instead of 1-octanol.[10,43] In this study, no such co-extraction was observed, which is partially explained by the lower DGA concentration used compared to the reference systems (where 0.2 mol L^{-1} of TODGA was used), but could also be indicative of improved selectivity for the PnDdDGA extractant. When scrubbing is performed, extraction efficiencies drop noticeably for the light lanthanides. At both 0.08 mol L^{-1} and 0.1 mol L^{-1} PnDdDGA, La(III) can be scrubbed with 1 mol L^{-1} HNO_3, while at the lower DGA concentration

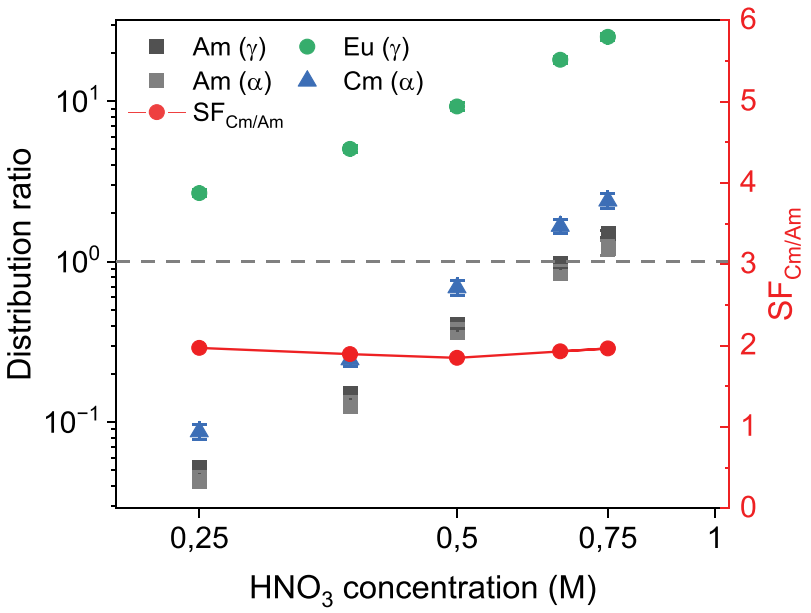

Figure 11. Distribution ratios for stripping from organic phase (loaded with sHAR (3.0 mol L^{-1} HNO_3, See Table S1) and scrubbed with 1 mol L^{-1} HNO_3) with BTrzPhen-tetraol. Organic phase: 0.1 mol L^{-1} PnDdDGA in *n*-dodecane with 2.5 vol% 1-octanol, loaded + scrubbed. Aqueous phase: 40 mmol L^{-1} BTrzPhen-tetraol in × mol L^{-1} HNO_3 solution. Shaking time: 30 min; A/O = 1.

Ce(III) can be scrubbed as well. As the Am/Ln separation is typically most difficult for the light lanthanides, this could be an effective method of removing these prior to the stripping step.

The stripping step demonstrated for both ligands the feasibility of stripping Am(III) and achieving a separation from Cm(III). In the case of PrOH-BPTD, this is achieved with a solution containing 20 mmol L^{-1} of ligand in 0.75 mol L^{-1} HNO_3, yielding a D_{Am} of 0.60, and a D_{Cm} of 1.14, resulting in a $SF_{Cm/Am}$ of *ca.* 1.9. In the case of BTrzPhen-tetraol, the separation is achieved with a solution containing 40 mmol L^{-1} of ligand in 0.66 mol L^{-1} HNO_3, yielding a D_{Am} of 0.86 and a D_{Cm} of 1.66, also combining into a $SF_{Cm/Am}$ of *ca.* 1.9. It can be noted that the distribution ratios observed in this experiment are lower than what has been observed in the earlier optimization experiments. This can be observed for both PrOH-BPTD (When comparing Fig. 10) as well as for BTrzPhen-tetraol (When comparing Figs. 11 to 8). These differences are a result of the higher metal concentrations present in the simulated HAR feed solution. The lanthanides in particular, due to their high extractability, increase competition and decrease the free ligand concentration, hence suppressing distribution ratios. The observed separation factors are slightly lower than what was observed in earlier optimization experiments, and is also a result of the higher metal concentration used in this demonstration, lowering the free ligand concentration. Comparison with fission product data (See Tables S4 and S5) shows that at these conditions, La(III), Ce(III),

and Pr(III) are stripped alongside Am(III), indicating that a full separation of Am from the lanthanides is not feasible in the stripping step. A separation could still be achieved by scrubbing the light lanthanides at a lower HNO_3 concentration, which was shown to be feasible for both La(III) and Ce(III), while Pr(III) also shows lower extraction efficiencies than Am(III) in the scrubbing step.

Conclusion

The objective of this study was to create and optimize a fully CHON-compliable AmSel system, by combining a UDGA (PnDdDGA) with new hydrophilic ligands (PrOH-BPTD and BTrzPhen-tetraol). Evaluation of the organic solvent showed 0.1 mol L^{-1} of PnDdDGA to be sufficient for quantitative extraction of An(III) and Ln(III), although lower concentrations are still feasible. Furthermore, although some phase modifier is necessary to inhibit third-phase formation, the concentration of 1-octanol in *n*-dodecane can be as low as 2.5 vol%. When PrOH-BPTD was used as the aqueous ligand, its limited solubility made it difficult to achieve stripping without lowering the DGA concentration in the organic phase. If a DGA concentration of 0.08 mol L^{-1} was used, selective stripping of Am(III) could be achieved with an aqueous phase consisting of 20 mmol L^{-1} PrOH-BPTD in 0.25 mol L^{-1} HNO_3 with $SF_{Cm/Am}$ 2.2. In the case of BTrzPhen-tetraol, solubility was not an issue, as stable solutions with at least 50 mmol L^{-1} of ligand could be prepared, and selective Am(III) stripping from 0.1 mol L^{-1} PnDdDGA was feasible with 40 mmol L^{-1} ligand in *ca*. 0.35 mol L^{-1} HNO_3, yielding a $SF_{Cm/Am}$ of 2.0–2.2. Pairing of either ligand with PnDdDGA resulted in a system that was able to selectively strip Am(III) and separate it from Cm(III) and most Ln(III), although the obtained $SF_{Cm/Am}$ values are slightly lower than in the benchmark AmSel process. Demonstration of both systems on a simulated HAR solution showed it possible to separate Am(III) from Cm(III), albeit with a slightly lower $SF_{Cm/Am}$ of 1.9. Separation from a majority of the fission products was also demonstrated, but revealed difficulties in achieving a full separation from the light Ln(III), making it necessary to introduce additional scrubbing stages or a more advanced Ln(III) management strategy. Nevertheless, these findings represent an important step towards the development of an americium extraction system that is fully compliant with the CHON-principle, and the implementation of a sustainable fuel cycle.

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Author contributions

CRediT: **Filip Kolesar:** Conceptualization, Formal analysis, Investigation, Visualization, Writing – original draft; **Karen Van Hecke:** Conceptualization, Supervision, Writing – review & editing; **Ken Verguts:** Supervision, Writing – review & editing; **Cécile Marie:** Conceptualization, Supervision, Writing – review & editing; **Laurence Berthon:** Conceptualization, Supervision, Writing – review & editing; **Thomas Sittel:** Writing – review & editing; **Thomas Cardinaels:** Funding acquisition, Supervision, Writing – review & editing; **Koen Binnemans:** Supervision, Writing – review & editing.

Disclosure statement

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