Direct selective extraction of trivalent americium from PUREX raffinate using a combination of $CyMe_4BTPhen$ and TEDGA – a feasibility study

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Keywords

Am(III) separation; Cm(III); Lanthanides; $CyMe_4BTPhen$; TEDGA; Bimet

Abstract

The direct and selective extraction of Am(III) from simulated PUREX raffinate was studied. A novel combination of the lipophilic extractant $CyMe_4BTPhen$ (2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e]-[1,2,4]triazin-3-yl)-1,10-phenanthroline) and the hydrophilic complexant TEDGA (*N*,*N*,*N'*,*N'*-tetraethyl-diglycolamide) was used to enhance the selectivity towards Am(III) extraction. Separation factors (*SF*) of up to $SF_{\mathrm{Am/Cm}} = 4.9$ were observed in tracer experiments using this combination of $CyMe_4BTPhen$ and TEDGA. Distribution ratios of stable isotopes of fission and activation products contained in a simulated PUREX raffinate solution are reported for the first time with $CyMe_4BTPhen$ and some co-extracted metal ions are identified. The metal ions partly co-extracted from the simulated PUREX raffinate solution were Cu, Pd, Cd, Ag, Ni, and to a lesser extent Sn and Mo. The co-extraction of Pd and Ag was successfully suppressed using Bimet ((2*S*,2'*S*)-4,4'-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)). The extraction was also studied as a function of the TEDGA concentration. The distribution ratios of Am and Cm can be adjusted by variation of the TEDGA concentration to yield D_{Am} values >1 and D_{Cm} values <1. Separation factors for Am(III) over Cm(III) of up to $SF_{\mathrm{Am/Cm}} = 2.4$ were observed in these experiments. For Ln(III) + Y(III) distribution ratios below 1 were observed, thus enabling a direct

extraction of Am(III) from simulated PUREX raffinate with a sufficient selectivity against trivalent lanthanides and Cm(III).

Introduction

In the field of advanced used nuclear fuel recycling strategies recent developments focussed on the separation of americium alone, instead of americium and curium, from nuclear fuel solutions. The separation of americium alone might be beneficial for the fabrication of new fast reactor fuel as curium would cause a strong neutron radiation requiring special shielding of the fabrication line.[1-3] Furthermore, the impact of Cm with regard to final repository long-term heat-load is limited, as the major curium isotope Cm-244 has a half-life of only 18 years.[4]

However, the separation of Am(III) from Cm(III) by solvent extraction techniques is a very difficult task due to their chemical similarity and only a few processes have demonstrated a successful separation, mainly based on a multi-cycle approach.[5-7] Recently, a trend can be observed for the reduction of required processes and the increased interest in potentially simpler single-cycle processes, although a more complicated chemistry and process control might be necessary.[5, 8] For the separation of americium from used nuclear fuel, several routes are followed. American researchers recently re-investigated the possibility of selectively oxidizing Am(III) to higher oxidation states and extract it away from Cm(III) using common extractants.[9-13] The French CEA has demonstrated a process using the DIAMEX (DIAmide EXtraction) extractant DMDOHEMA (*N*,*N′*-dimethyl-*N*,*N′*-dioctyl-2-hexylethoxy-malonamide) for the separation of Am(III) from Cm(III). Due to the low selectivity of the extractant ($SF_{\mathrm{Am/Cm}}$ ~ 1.6), a large number of 56 stages had to be used to successfully demonstrate the process.[14] In the LUCA (Lanthaniden Und Curium-Americium Abtrennung) process a dithiophosphinic acid with a much higher selectivity ($SF_{\mathrm{Am/Cm}}$ = 6 – 10) was used to separate Am(III) from Cm(III) and lanthanides after a separation of An(III) + Ln(III) from PUREX raffinate, and was demonstrated on the laboratory scale using spiked simulate solutions.[15]

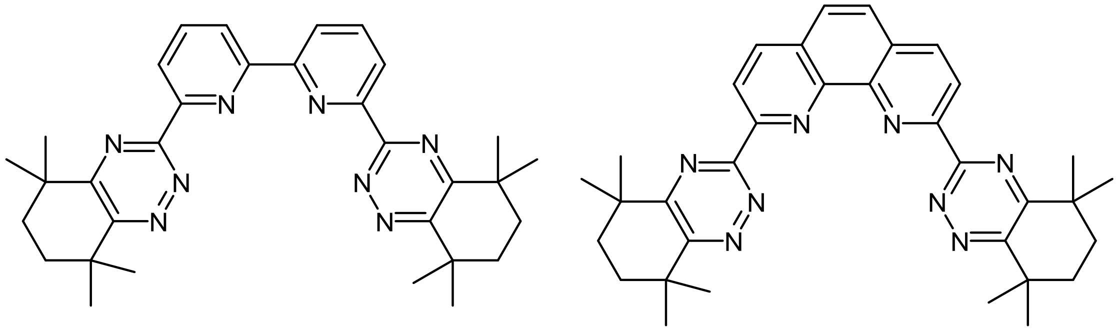
French researchers developed and hot tested the EXAm process making use of a sophisticated combination of lipophilic extractant and hydrophilic complexant. By combination of a solvent comprising DMDOHEMA (*N*,*N′*-dimethyl-*N*,*N′*-dioctyl-2-hexylethoxy-malonamide) and HDEHP (di-2-ethylhexylphosphoric acid) with the hydrophilic TEDGA (*N*,*N*,*N’*,*N’*-

tetraethyldiglycolamide (Figure 1), the selectivity of the extraction system for Am(III) over Cm(III) was increased.[16] Thereby it was possible to extract Am(III) together with some light lanthanides and fission products away from Cm(III) and heavier lanthanides. Am(III) was then selectively stripped from the loaded solvent using HEDTA in a citric acid buffered system.[17-18]

We have recently reported on the development and laboratory-scale demonstration of a "1-cycle SANEX" process.[19-21] In that process we used the highly selective soft N-donor extractant CyMe$_4$BTBP (6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2']-bipyridine (Figure 1)[22], for the direct selective extraction of Am(III) and Cm(III) from PUREX (Plutonium Uranium Reduction Extraction) raffinate. Due to slow kinetics TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) was used as a phase-transfer reagent and due to the co-extraction of Pd we had to introduce a tailored Pd stripping step using L-cysteine. We wanted to develop this process further to overcome the described drawbacks and additionally to increase the Am(III)/Cm(III) selectivity of the system to make the process selective for Am(III) only.

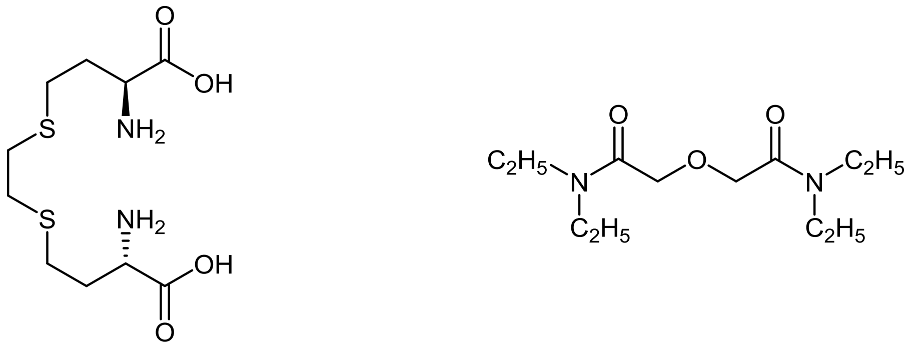
Therefore, we investigated the new extractant CyMe$_4$BTPhen (2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-[1,2,4]-triazin-3-yl)-1,10-phenanthroline (Figure 1) in 1-octanol, which still shows a high selectivity for Am(III) and Cm(III) over trivalent lanthanides but was shown to have faster extraction kinetics compared to CyMe$_4$BTBP.[23-26] Furthermore, a slightly increased selectivity of CyMe$_4$BTPhen for Am(III) over Cm(III) was observed when linked to silica-coated magnetic nanoparticles.[27] Then, we made use of the hydrophilic TEDGA to increase the selectivity of the system for Am(III) extraction over Cm(III), as CyMe$_4$BTPhen shows a slight preference for Am(III) while diglycolamides show a slight preference for Cm(III).[16] And finally we tried to overcome an expected Pd co-extraction by using the new masking agent Bimet ((2*S*,2′*S*)-4,4′-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)), introduced by Aneheim and Foreman et al. in a system using CyMe$_4$BTBP.[28-29]

This paper describes first experiments and results using this approach to develop a system for the direct selective extraction of Am(III) only from simulated PUREX raffinate ("1-cycle SAmEX").



$CyMe_4BTBP$
6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-[2,2']-bipyridine

$CyMe_4BTPhen$
2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-1,10-phenanthroline



BIMET
(2*S*,2'*S*)-4,4'-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)

TEDGA
N,*N*,*N'*,*N'*-tetraethyl-diglycolamide

Figure 1. Chemical structures of $CyMe_4BTBP$, $CyMe_4BTPhen$, Bimet and TEDGA.

Experimental

All chemicals used were of analytical grade. $CyMe_4BTPhen$ (purity >98%) and TEDGA were purchased from Technocomm Ltd., Wellbrae House, Wellbrae, Falkland KY15 7AY, United Kingdom. Bimet was kindly provided by Mark Foreman, Department of Chemical and Biological Engineering, Chalmers University of Technology, Gothenburg, Sweden. For all aqueous dilutions ultra-pure water (18.2 MΩ·cm) was used. Nitric acid was purchased from Merck KGA, Darmstadt, Germany. Radionuclide stock solutions (^{152}Eu, ^{241}Am, ^{244}Cm) were prepared from radiotracers purchased from Isotopendienst M. Blaseg GmbH, Waldberg, Germany, Oak Ridge National Laboratory, USA, and Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany.

For the extraction experiments, weighed amounts of the ligand/complexing agent were diluted in test tubes with the desired solvent in the desired concentration.

Batch experiments were performed in 2 mL glass vials. 500 µL of the aqueous phase were spiked with 10 µL tracer solution and contacted with 500 µL of the desired organic phase. The vials were shaken for one hour to reach equilibrium in a temperature controlled aluminum block shaker at 22 ± 1°C. This shaking time was found to be sufficient to reach the chemical equilibrium. The vials were centrifuged for effective phase separation and the phases were separated by hand using pipettes. 300 µL aliquots of each phase were taken for gamma-ray spectroscopy and 10 µL for alpha and ICP-MS preparation, respectively.

The γ-lines of ^{241}Am (59.5 keV) and ^{152}Eu (121.8 keV) were measured using a 300 µL sample volume in a 2 mL borosilicate glass placed close to a high-purity germanium coaxial N-type detector system (type: EGC 35-195-R), purchased from Eurisys Mesures, Lingolsheim, France, equipped with the spectrometer system obtained from EG & G Ortec, Munich, Germany. Analyses of the spectra were performed with the GammaVision® software (version 5.20).

Alpha spectroscopy of ^{241}Am and ^{244}Cm was done using PIPS-detectors and the Alpha Spektrometer Octête™ PC purchased from EG & G Ortec, Munich, Germany. Sample preparation was done by homogenizing the 10 µL alpha-spectroscopy sample in 100 µL of a mixture of Zapon varnish and acetone (1:100 v/v). This mixture was distributed over a stainless steel plate obtained from Berthold, Bad Wildbad, Germany. The sample was dried under a heating lamp and annealed into the stainless steel plate by a gas-flame burner.

Concentrations of inactive elements were determined in-house by ICP-MS. Aliquots of the individual phases were diluted to a concentration of the stable elements to a range of 1 to 100 ppb and measured by ICP-MS using an Elan 6100 DRC, purchased from Perkin Elmer Sciex, Roggau-Jügesheim, Germany, equipped with the Elan software (version 3.4). The organic phases were mixed with the non-ionic surfactant TRITON-X-100 obtained from BASF, Ludwigshafen, Germany, and diluted to an adequate concentration.

Distribution ratios *D* were calculated as the ratio between the radioactivity or concentration in the organic phase and the one in the aqueous phase. The maximum and minimum distribution ratios arising from the detection limits in the aqueous and organic phases were 1000 and 0.001 for gamma-ray spectroscopy and ICP-MS measurements, respectively, and 350 and 0.003 for alpha spectroscopy. Calculated distribution ratios above the limits were set to the upper detection limits, and distribution ratios below the limits were set to the lower detection limit. The separation factor between two metal ions $SF_{\mathrm{M1/M2}}$ was calculated as the ratio of two distribution ratios of the two metal ions: $SF_{\mathrm{M1/M2}} = D_{\mathrm{M1}}/D_{\mathrm{M2}}$. Distribution ratios between 0.01 and 100 typically exhibit an uncertainty of ±5%, while lower/higher values exhibit larger uncertainties. Due to a high salt content the uncertainty of distribution ratios and separation factors calculated from alpha spectroscopy can be higher. The given uncertainty can be applied to all data presented in the paper, including the tables and figures.

The synthetic PUREX raffinate solutions (HAR), which were used in the extraction experiments, were produced following a specific dissolution strategy using mainly metal nitrate salts and oxides. The solutions simulate PUREX raffinate solutions after reprocessing of a zirconia cladded UO_2-type fuel initially containing 3-5% ^{235}U with a burn-up of 33 GWd/t, a cooling time of 150 days and dissolution in 5000 L/t fuel with the cladding remaining undissolved.[30-31] The solutions contain 29 different inactive elements in nominal concentrations, which differ over a wide range of concentrations. The compositions of the PUREX raffinate solutions at different nitric acid concentrations are shown in Table 1. High concentrations of iron are due to the use of ferrous sulfamate for the reduction of plutonium.

Table 1. Composition of the simulated PUREX raffinate solutions used in this study (HAR).

HNO_3 [mol/L]	1.1	2.0	3.1	4.3	HNO_3 [mol/L]	1.1	2.0	3.1	4.3
Element	[mg/L]	[mg/L]	[mg/L]	[mg/L]	Element	[mg/L]	[mg/L]	[mg/L]	[mg/L]
Se	31	29	32	27	Cd	24	25	26	28
Fe	2570	2305	2149	2215	Sn	1	2	14	12
Cr	115	109	105	108	Sb	4	7	6	5
Ni	49	63	87	47	Te	81	129	122	131
Cu	25	25	23	27	Cs	618	623	590	641
Rb	73	71	72	78	Ba	294	301	277	308
Sr	222	218	206	227	La	300	298	282	308
Y	117	110	107	114	Ce	703	709	662	719
Zr	682	984	956	1006	Pr	274	269	257	281
Mo	104	729	696	747	Nd	810	821	746	840
Ru	414	423	393	421	Sm	165	161	153	168
Rh	102	104	98	104	Eu	47	46	43	47
Pd	112	226	108	231	Gd	50	52	48	55
Ag	19	21	17	22					

Results and discussion

In this feasibility study a potential “1-cycle SAmEX” system was studied by combination of the highly selective extractant $CyMe_4BTPhen$ and the hydrophilic complexant TEDGA. TEDGA was introduced to this system to increase the selectivity of the system towards americium(III) against curium(III).

Extraction experiments using $CyMe_4BTPhen$ alone

Figure 2 shows the ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) distribution ratios for extraction with $CyMe_4BTPhen$ alone as a function of the nitric acid concentration. As reported earlier, the ligand dissolved in 1-octanol is very efficient in extracting An(III) and only low concentrations are needed for an effective extraction.[23-24] The distribution ratios increased with increasing acidity and very high distribution ratios were reached for An(III) at nitric acid concentrations >0.1 mol/L. Separation factors $SF_{\mathrm{Am/Cm}}$ were not calculated for nitric acid concentrations above 0.1 mol/L, as both the distribution ratios of Am(III) and Cm(III) exceeded the detection limits in the aqueous phase samples. At nitric acid concentrations below 0.1 mol/L, the Am(III)/Cm(III) separation factor was 1.8. The Am(III)/Eu(III) separation factors, $SF_{\mathrm{Am/Eu}} = 80 – 160$, are in good agreement with the results of Lewis et al.[23-24] showing the potential of CyMe$_4$BTPhen for the selective separation of trivalent actinides from lanthanides. Therefore, CyMe$_4$BTPhen in 1-octanol was further studied for the selective extraction of Am(III).

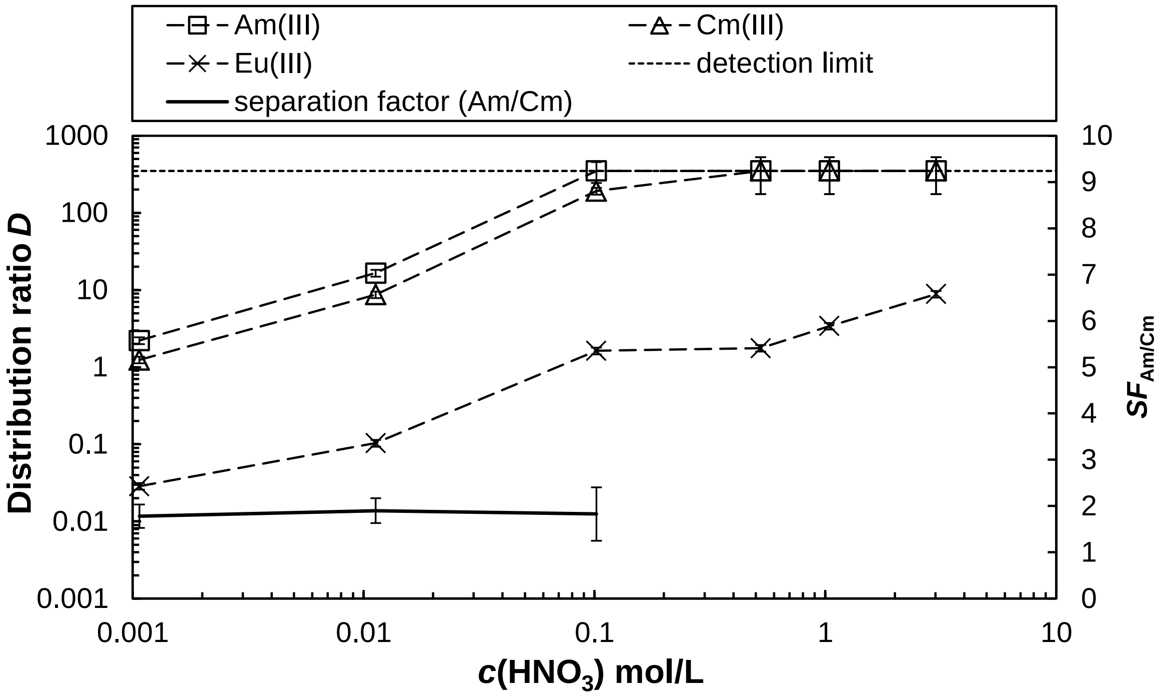


Figure 2. Extraction of ^{152}Eu(III), ^{241}Am(III) and ^{244}Cm(III) with CyMe$_4$BTPhen as a function of the nitric acid concentration.

Organic phase: 0.01 mol/L CyMe$_4$BTPhen in 1-octanol

Aqueous phase: nitric acid, ^{152}Eu(III), ^{241}Am(III), ^{244}Cm(III) tracer, mixing time: 60 min; *T* = 22°C ± 1°C.

Extraction experiments using CyMe$_4$BTPhen and TEDGA

As demonstrated in the EXAm process[17-18] and studied in detail by Chapron et al.[16] the selectivity of an extraction system can be increased by appropriate combination of lipophilic and hydrophilic ligands.[32] CyMe$_4$BTPhen shows a higher affinity for Am(III), while diglycolamides show a higher affinity for Cm(III).[33] Therefore, we tested the combination of CyMe$_4$BTPhen with the hydrophilic TEDGA to increase the selectivity towards Am(III) extraction.

The influence of TEDGA on the selectivity of the extraction system was studied by adding TEDGA to the aqueous phase and extracting Am, Cm and Eu with CyMe$_4$BTPhen. Figure 3 shows the distribution ratios of Am, Cm and Eu as a function of the initial nitric acid concentration with 0.01 mol/L TEDGA added. The distribution ratios of all trivalent metal ions were decreased by a factor of approx. 10 compared to the experiments without addition of TEDGA (Figure 2), due to the metal ion complexation with TEDGA. The Am/Cm separation factor increased from $SF_{\mathrm{Am/Cm}}$ = 1.8 in the system without TEDGA to $SF_{\mathrm{Am/Cm}}$ =

2.3 – 4.9 in the system with addition of TEDGA. The highest selectivity was observed between 0.03 and 0.5 mol/L HNO_3 ($SF_{Am/Cm}$ ~ 5). At higher acidities the separation factor decreased, but values of 2.4 were still observed showing the higher selectivity of the combined system in comparison to $CyMe_4BTPhen$ alone.

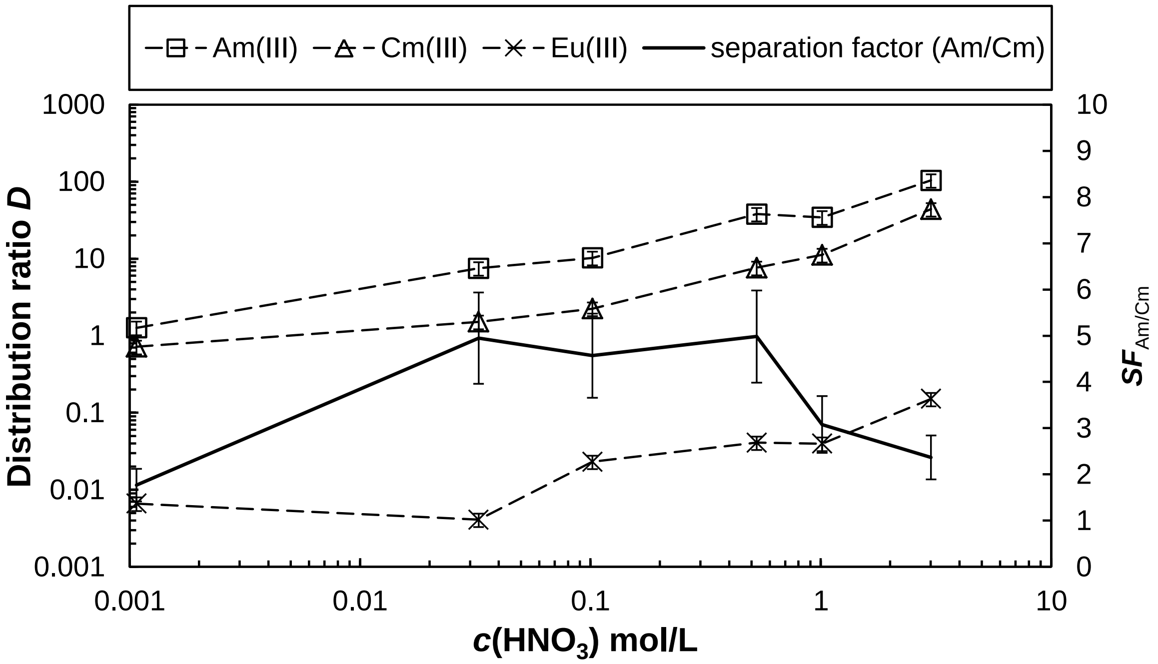


Figure 3. Extraction of ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) with $CyMe_4BTPhen$ as a function of the nitric acid concentration; the influence of TEDGA.

Organic phase: 0.01 mol/L $CyMe_4BTPhen$ in 1-octanol

Aqueous phase: 0.01 mol/L TEDGA, nitric acid in different concentrations, ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) tracer, mixing time: 60 min; T = 22°C ± 1°C.

The influence of the TEDGA concentration was further studied. Due to the high extraction efficiency of $CyMe_4BTPhen$, the concentration of TEDGA had to be increased to further reduce the distribution ratios, as it would be desired to extract only Am(III) from highly acidic PUREX raffinate directly, and keep Cm(III) in the aqueous phase. Therefore, the TEDGA concentration was varied between 0.001 mol/L and 0.1 mol/L in 1 mol/L HNO_3. Results are shown in Figure 4.

Distribution ratios of Am(III), Cm(III), and Eu(III) decreased linearly in the double logarithmic plot with increasing TEDGA concentration (except when detection limits were reached). Distribution ratios of the trivalent actinides varied in these experiments over a wide range between 0.02 and 200 using different concentrations of TEDGA. The slopes for Am(III) and Cm(III) in Figure 4 were -2.6 and -2.7, respectively. The selectivity of the system remained relatively constant with Am/Cm separation factors of $SF_{\mathrm{Am/Cm}}$ = 2.0 – 3.4 over the tested range of TEDGA concentrations. The relatively high jump in the $SF_{\mathrm{Am/Cm}}$ at 0.05 mol/L TEDGA is caused by the cumulated uncertainty of two alpha spectroscopy measurements (which have a higher uncertainty). Therefore, it can be concluded that the distribution ratios can be tuned to a desired value using an appropriate concentration of TEDGA.

The slope of approximately –3 suggests the formation of 1:3 complexes of Am(III) and Cm(III) with the diglycolamide. The formation of 1:3 complexes with the lipophilic TODGA (*N*,*N*,*N'*,*N'*-tetraoctyl-diglycolamide) has been observed in Cm(III) complexes by TRLFS (time-resolved laser induced fluorescence spectroscopy) and through slope analysis with Am(III), Cm(III), and Eu(III), previously.[34] The complex stoichiometry of lanthanide-TEDGA complexes has also been studied extensively by French researchers in the EXAm system (TEDGA – DMDOHEMA – HDEHP). They found that TEDGA forms complexes with different metal:ligand ratios for lighter lanthanides (preferentially 1:1 or 1:2) and for heavier lanthanides (1:3) in the EXAm system.[16, 35-36] They concluded that 1:1 and 1:2 complexes were extracted in this process (HDEHP and DMDOHEMA), while the 1:3 complexes were not extracted.

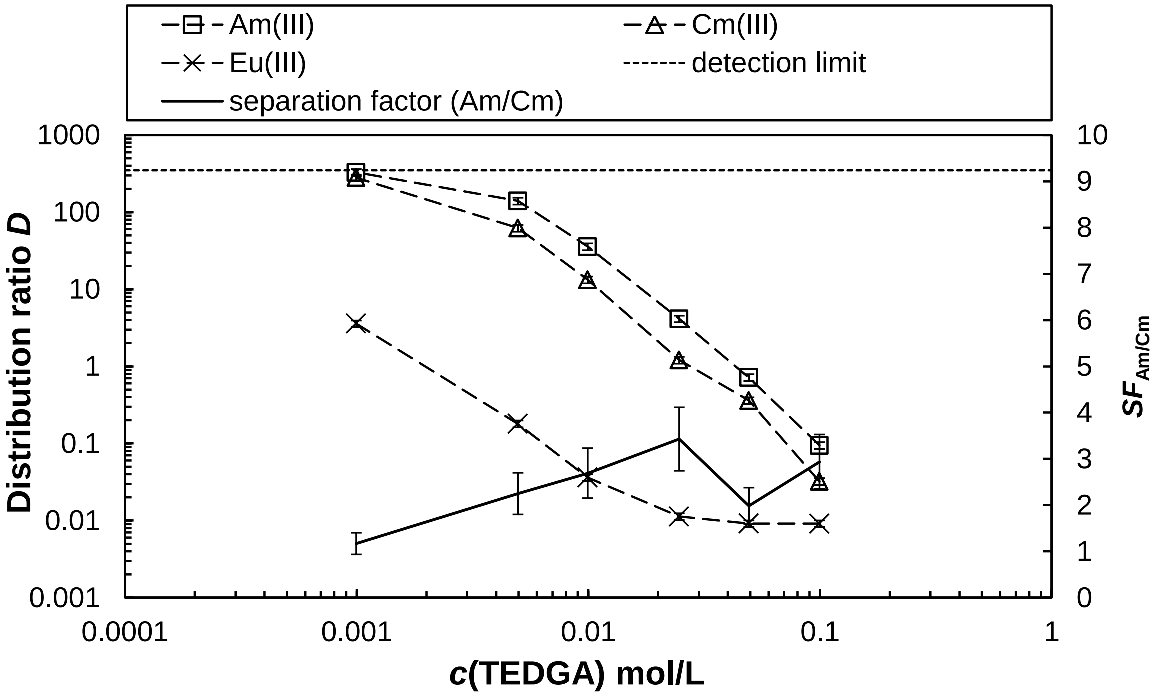


Figure 4. Extraction of ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) with CyMe$_4$BTPhen as a function of the TEDGA concentration.

Organic phase: 0.01 mol/L CyMe$_4$BTPhen in 1-octanol.

Aqueous phase: c(HNO$_3$) = 1 mol/L. variable TEDGA concentration, ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) tracer, mixing time: 60 min; T = 22°C ± 1°C.

Experiments using simulated PUREX raffinate

As this feasibility study aims to investigate the possibility of selectively extracting Am(III) alone from PUREX raffinate, we used simulated PUREX raffinate solutions to study the system under more realistic conditions. Instead of tracer experiments with 10^{-7} mol/L trace elements, the extraction system was tested with a solution containing approx. 30 elements in nominal concentrations at high acidity. Therefore, loading of extractant and hydrophilic complexant have to be taken into account, due to a possible co-extraction of fission and activation products. The selective extraction of Am(III) from Ln(III) and other fission and activation products contained in simulated HAR solutions is a very important step in a process development study. The compositions of the used simulated PUREX raffinate solutions and their elemental concentrations at four different nitric acid concentrations are given in Table 1 above (Experimental Section). As mentioned previously, the extractant used here is related to CyMe$_4$BTBP which was used in the 1-cycle SANEX process. Therefore, a similar co-extraction of fission products as observed in that process is expected.[19, 21]

Results of extraction experiments using only 0.01 mol/L CyMe$_4$BTPhen in 1-octanol are shown in Table 2. To the best of our knowledge distribution ratios of all the fission and activation products present in used nuclear fuel have not been reported before. Only distribution ratios of lanthanides(III) have been reported.[23, 37-38] Higginson et al. reported on the application of CyMe$_4$BTPhen as extractant in a liquid-liquid extraction process for nuclear forensics application from chloride media[39] and in an immobilized form as Me$_4$BTPhen for the same application.[40] They found Cd(II) to be co-extracted by CyMe$_4$BTPhen, but didn't test all the fission and activation products present in used nuclear fuel. As shown in Table 2, CyMe$_4$BTPhen has similar extraction properties as observed for CyMe$_4$BTBP in the 1-cycle SANEX process:[19-21] Cu, Pd, Cd were well extracted at any acidity and Ag and Sn were extracted from the lower concentration HNO_3. In the experiment using the HAR with 1.1 mol/L HNO_3 a small precipitation was observed at the phase boundary after mixing. Increasing distribution ratios were observed for Ni and Mo with increasing nitric acid concentration with the highest distribution ratios being 1.3 and 0.83, respectively. In the counter current flow extraction of the 1-cycle SANEX process Cu, Ni and Cd were extracted and remained in the org. phase during the whole test, including the An(III) stripping section.[21] Therefore, a clean product was obtained although the used solvent had been contaminated with these metal ions and a special solvent clean-up would be required. The same behavior is expected in the CyMe$_4$BTPhen system.

Am(III) and Cm(III) distribution ratios were lower compared to the tracer experiments, presumably due to a lower free ligand concentration through loading by co-extraction of other metal ions, and hardly exceeded $D_{\mathrm{Am}} = 1$. The Am/Cm separation factor was in the range 1.3 – 2.0. Masking of some co-extracted problem elements would reduce the overall loading of the extractant and increase the distribution ratios of the desired An(III) but maybe also other unwanted metal ions. Distribution ratios of Sb, Zr and Sn were slightly increased only in the simulated HAR solution at 1.1 mol/L HNO_3, which could be explained by the precipitation observed in this experiment.

Therefore, the main problematic elements remaining to be dealt with were Pd and Ag.

Table 2. Extraction of An(III) and fission products from simulated PUREX raffinate with $CyMe_4BTPhen$.
Organic phase: 0.01 mol/L $CyMe_4BTPhen$ in 1-octanol
Aqueous phase: HAR elements, nitric acid in different concentrations, $^{241}Am(III)$, $^{244}Cm(III)$ and $^{152}Eu(III)$ tracer, mixing time: 60 min; $T = 22°C \pm 1°C$.

	Distribution ratios/$SF_{Am/Cm}$			
	HAR	HAR	HAR	HAR
HNO_3 [mol/L]	1.1*	2.0	3.1	4.3
Am-241	0.84	0.79	1.12	0.96
Cm-244	0.59	0.61	0.73	0.49
Eu-152	0.14	0.05	0.04	0.01
$SF_{Am/Cm}$	*1.4*	*1.3*	*1.5*	*2.0*
Cu	1302	596	553	666
Pd	9.1	18	9.2	21
Cd	5.1	3.0	3.7	4.6
Ag	4.9	1.1	0.74	0.99
Sn	2.0	0.17	< 0.02	< 0.02
Ni	0.73	0.74	1.2	1.3
Mo	0.40	0.51	0.77	0.84
Sb	0.34	< 0.1	< 0.1	< 0.1
Zr	0.19	< 0.1	< 0.1	< 0.1
Sm	0.13	< 0.1	< 0.1	< 0.1
Gd, Ba, Ru, Rb, Nd, Cr	< 0.1	< 0.1	< 0.1	< 0.1
Pr, Te, Y, Rh, Sr, Ce, Fe, La, Cs	< 0.02	< 0.02	< 0.02	< 0.02

*precipitation at phase boundary

Aneheim and Foreman et al. reported on the masking effect of Bimet in the so-called CHALMEX process, a process aiming at a group actinide extraction using $CyMe_4BTBP$ and TBP in cyclohexanone. In their approach the co-extraction of Pd and some other metal ions was observed and the co-extraction of Pd was overcome using the Bimet complexant as a masking agent.[28-29]

Consequently, the four simulated HAR solutions of different nitric acid concentrations were mixed with 0.01 mol/L TEDGA and 0.01 mol/L Bimet. Afterwards, they were contacted with the solvent for 60 minutes and the distribution ratios were determined. The results are shown in Table 3. The Am and Cm distribution ratios were still lower than in the tracer experiments due to partial loading of the extractant by HAR elements, but substantially higher compared to Table 2. The separation factor $SF_{\mathrm{Am/Cm}}$ was lower compared to the tracer experiments, as an Am/Cm separation factor between 1.8 – 2.2 was observed which was only slightly higher than the separation factor observed using CyMe$_4$BTPhen only (Table 2). Therefore, it is assumed that TEDGA, which increased the $SF_{\mathrm{Am/Cm}}$ in tracer experiments, was fully consumed for the complexation of fission/activation products and lanthanides.

The An(III) distribution ratios decreased with increasing acidity as an increased co-extracted of fission and activation products was observed (Table 3). The results show that the masking of Pd with Bimet worked very well. Only trace amounts of Pd were measured in the organic phase, the distribution ratio was below 0.02. The extraction of silver was also suppressed and the remaining co-extracted elements were Cu, Cd, Ni and Mo. As described previously, it is expected that Cu, Cd, and Ni will remain in the organic phase during an americium stripping step so that molybdenum is the only remaining problematic element. Due to the overall lower loading in the experiments presented in Table 3 higher Mo distribution ratios were observed compared to Table 2. To cope with the Mo co-extraction, a scrubbing section with lower nitric acid concentration could be used, as Mo distribution ratios decreased with decreasing acidity.

Table 3. Extraction of An(III) and fission products from simulated PUREX raffinate with $CyMe_4BTPhen$.
Organic phase: 0.01 mol/L $CyMe_4BTPhen$ in 1-octanol
Aqueous phase: HAR elements, c(TEDGA) = 0.01 mol/L, c(Bimet) = 0.01 mol/L, nitric acid in different concentrations, ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) tracer, mixing time: 60 min; T = 22°C ± 1°C.

Distribution ratios/$SF_{\text{Am/Cm}}$				
	HAR	HAR	HAR	HAR
HNO_3 [mol/L]	1.1*	2.0	3.1	4.3
Am-241	60	47	22	26
Cm-244	29	23	12	12
Eu-152	0.41	0.23	0.07	0.07
$SF_{Am/Cm}$	*2.1*	*2.0*	*1.8*	*2.2*
Cu	535	207	859	>1000
Cd	4.9	4.2	5.8	6.6
Ni	0.72	2.3	3.5	3.3
Mo	0.35	1.0	1.7	1.9
Sm	0.37	0.29	0.26	0.17
Ru	0.08	0.14	0.22	0.21
Gd	0.27	0.14	0.10	0.06
Nd	0.24	0.13	0.13	0.06
Pr	0.18	0.04	0.03	0.02
Sn	1.1	0.02	0.01	0.01
Zr, Ag, Ce, Sb	<0.1	<0.1	<0.1	<0.1
Y, Sr, Rh, La, Ba, Rb, Te, Cr, Cs, Pd, Fe	<0.02	<0.02	<0.02	<0.02

*small amounts of precipitation at phase boundary

As discussed previously, the increased separation factor between americium(III) and curium(III) by TEDGA in tracer experiments was reduced using simulated HAR solutions, but was still higher than in experiments without TEDGA addition. For an efficient process application the distribution ratio of americium should ideally be above 1, while the distribution ratios of curium and lanthanides should be below 1. Therefore, and to test the loading effect of TEDGA, the concentration of TEDGA was varied between 0.01 mol/L and 0.1 mol/L. Figure 5 shows Am(III), Cm(III), and Eu(III) distribution ratios as a function of the TEDGA concentration for the HAR solution with 3 mol/L HNO_3, while the distribution ratios of all metal ions are given in Table 4. The distribution ratios obtained for americium and curium shown in Figure 5 were very similar at 0.01 moL/L and 0.02 mol/L TEDGA. At 0.04 mol/L TEDGA and higher concentrations a decrease in D_{Am} and D_{Cm} was observed. Presumably, up to 0.04 mol/L TEDGA were needed for the complexation of fission and activation products. Then, at higher concentrations of TEDGA the free concentration increased, causing decreasing distribution ratios of Am and Cm. The $SF_{\mathrm{Am/Cm}}$ was still lower compared to the tracer experiments and remained relatively constant over the whole range of TEDGA concentrations ($SF_{\mathrm{Am/Cm}} = 1.6 – 2.4$). Interestingly, the distribution ratio of europium and the other lanthanides was much less affected by variation of the TEDGA concentration compared to the tracer experiments. Consequently, the separation factor of Am(III) vs. Ln(III) strongly decreased towards higher TEDGA concentrations and reached a minimum value of $SF_{\mathrm{Am/Sm}} = 2.4$ at 0.1 mol/L TEDGA. The highest distribution ratios are observed for Sm, as a maximum is observed in the distribution ratios for extraction with $\mathrm{CyMe_4BTPhen}$ across the lanthanide series.[23] At low TEDGA concentration, the extraction of lanthanides is dominated by $\mathrm{CyMe_4BTPhen}$ due to the complexation of metal ions with TEDGA in the aqueous phase. However, distribution ratios are still lower in comparison to tracer experiments with $\mathrm{CyMe_4TBPhen}$ alone, due to partial loading of the solvent, but higher compared to experiments with HAR solution without addition of TEDGA. Above 0.04 mol/L TEDGA, an excess of TEDGA is achieved. After this point a further addition of TEDGA shows decreasing distribution ratios for americium and curium (Figure 5). The maximum in distribution ratios of the lanthanides slightly shifts, as a superposition of the complexation with $\mathrm{CyMe_4BTPhen}$ and TEDGA is observed. $\mathrm{CyMe_4BTPhen}$ shows a preference for intermediate lanthanides (maximum for Sm),[23] while diglycolamides mainly show a preference for heavier lanthanides.[34]

Between 0.06 and 0.08 mol/L TEDGA conditions were found where D_{Am} was above 1 while D_{Cm} was below 1, allowing for a counter-current process operation where Am(III) would be extracted and separated from Cm(III). Taking the observed slopes in that region into account, the aimed separation of americium seems to be possible at c(TEDGA) = 0.075 mol/L. The majority of the other fission and corrosion products will not be extracted under these conditions. Only slightly increased distribution ratios were observed for molybdenum, due to the decreased loading of the extractant, but Mo can be scrubbed from the loaded solvent in later stages using lower $\mathrm{HNO_3}$ concentrations. The problem elements Cu, Cd and Ni were still well extracted and are believed to remain in the organic phase under Am(III) stripping conditions, allowing for a recovery of Am(III) alone.

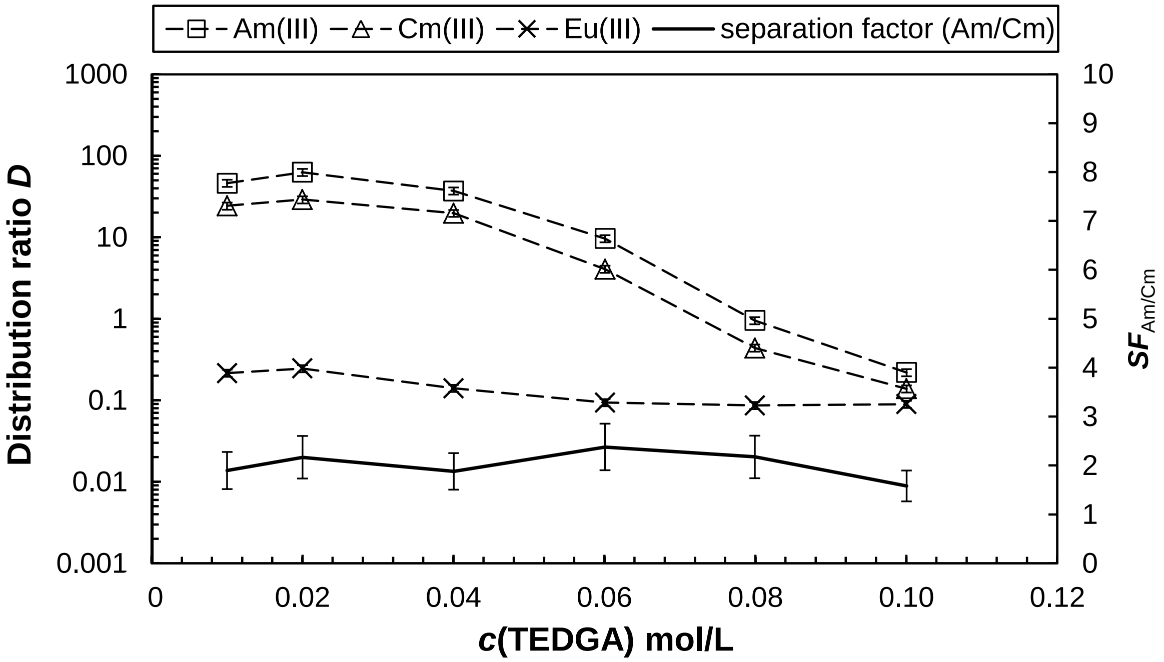


Figure 5. Extraction of ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) with CyMe$_4$BTPhen. Influence of TEDGA and Bimet as a function of the TEDGA concentration.

Organic phase: 0.01 mol/L CyMe$_4$BTPhen in 1-octanol

Aqueous phase: HAR elements, *c*(Bimet) = 0.01 mol/L, *c*(HNO$_3$) = 3.1 mol/L, variable TEDGA concentration, ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) tracer, mixing time: 60 min; *T* = 22°C ± 1°C.

Table 4. Extraction of An(III) and fission products from simulated PUREX raffinate with CyMe$_4$BTPhen. Influence of TEDGA and Bimet as a function of the TEDGA concentration.

Organic phase: 0.01 mol/L CyMe$_4$BTPhen in 1-octanol

Aqueous phase: HAR elements, c(Bimet) = 0.010 mol/L, c(HNO$_3$) = 3.1 mol/L, variable TEDGA concentration, ^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) tracer, mixing time: 60 min; T = 22°C ± 1°C.

Distribution ratios/$SF_{Am/Cm}$						
	c(TEDGA) [mol/L]	c(TEDGA) [mol/L]	c(TEDGA) [mol/L]	c(TEDGA) [mol/L]	c(TEDGA) [mol/L]	c(TEDGA) [mol/L]
	0.01	0.02	0.04	0.06	0.08	0.10
Am-241	46	63	37	9.6	0.95	0.22
Cm-244	24	29	20	4.1	0.44	0.14
Eu-152	0.21	0.25	0.14	0.09	0.09	0.09
$SF_{Am/Cm}$	*1.9*	*2.2*	*1.9*	*2.4*	*2.2*	*1.6*
Cu	>100	>100	>100	>100	>100	>100
Ni	>100	>100	>100	>100	>100	>100
Cd	3.7	2.8	3.1	1.8	3	2.5
Mo	1	1.2	1.7	3.4	1.5	1.2
Sm	0.21	0.25	0.17	0.19	0.1	0.09
Ru	0.19	0.19	0.2	0.42	0.22	0.21
La	<0.02	<0.02	<0.02	0.09	0.09	0.12
Ce	<0.02	<0.02	<0.02	0.11	0.09	0.11
Pr	<0.02	0.03	0.04	0.13	0.10	0.10
Nd	0.06	0.07	0.07	0.14	0.09	0.09
Sm	0.21	0.25	0.17	0.19	0.10	0.09
Gd	0.06	0.08	0.07	0.08	0.09	0.09
Zr, Gd, Nd, Fe, Ag, Pr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Rh, Ce, Sn, Te, Y, Rb, Cs, Cr, Ba, Sr, Sb, Pd	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

Conclusions

A series of batch experiments was performed to study the selective extraction of americium(III) from HAR solution using the extractant CyMe$_4$BTPhen in 1-octanol. In combination with the water soluble complexant TEDGA, an increased Am/Cm selectivity was observed in tracer experiments with separation factors up to $SF_{Am/Cm}$ = 4.9. The Am/Cm separation factors for extraction from simulated HAR solutions were lower compared to the tracer experiments, but conditions were elaborated where distribution ratios of americium and curium where $D_{\mathrm{Am}} > 1$ and $D_{\mathrm{Cm}} < 1$ by adjusting the TEDGA concentration. Co-extracted elements from simulated HAR solutions were Cu, Pd, Cd, Ag and to a lesser extent Sn, Ni, and Mo. The co-extraction of Pd and Ag was successfully suppressed by the use of Bimet. Cu, Cd and Ni are expected to remain in the organic phase, comparable to the 1-cycle SANEX process. All lanthanides, which are approximately 1/3 of the fission product elements contained in HAR solutions, were not extracted with distribution ratios well below 1. During the experiments with simulated HAR solutions no third phase formation was observed even though the concentration of the extractant was low. The only remaining co-extracted element possibly causing an americium product contamination was molybdenum. Molybdenum could probably be scrubbed from the loaded solvent using lower nitric acid concentrations. A direct extraction and selective separation of Am(III) from PUREX raffinate solutions seems to be possible with the developed system of $\mathrm{CyMe_4BTPhen}$ extractant, TEDGA complexant, and Bimet masking agent. Further process development will be conducted to study the applicability of the system in a counter-current separation process.

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