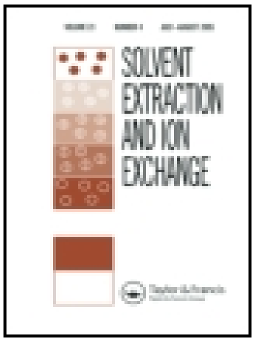

Solvent Extraction and Ion Exchange

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Batch Tests for Optimisation of Solvent Composition and Process Flexibility of the CHALMEX FS-13 Process

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ABSTRACT

Studies have been performed with the purpose of determining the optimal solvent composition of a Chalmers grouped actinide extraction (CHALMEX) solvent for the selective co-extraction of transuranic elements in a novel Grouped ActiNide EXtraction (GANEX) process. The solvent is composed of 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine ($CyMe_4$-BTBP) and tri-*n*-butyl phosphate (TBP) in phenyl trifluoromethyl sulfone (FS-13). The performance of the system has been shown to significantly depend on the ratios of the two extracting agents and the diluent to one another. Furthermore, the performance of the determined optimal solvent (10 mM $CyMe_4$-BTBP in 30% v/v TBP and 70% v/v FS-13) on various simulated PUREX raffinate solutions was tested. It was found that the solvent extracts all transuranic elements with high efficiency and good selectivity with regard to most other elements (fission products/activation products) present in the simulated PUREX raffinate solutions. Moreover, the solvent was found to extract a significant amount of acid. Palladium, silver, and cadmium were co-extracted along with the TRU-radionuclides, which has also been observed in other similar CHALMEX systems. The extraction of plutonium and uranium was preserved for all tested simulated PUREX raffinate solutions compared to experiments using trace amounts.

KEYWORDS
GANEX; CHALMEX; recycling; nuclear waste; actinides

Introduction

Several of the advanced nuclear power systems, often referred to as Generation IV (GEN IV) systems, are comprised of fast neutron reactors, fuel recycling, and novel fuel fabrication closing the fuel cycle and making it more sustainable.[1,2] By irradiating long-lived actinides in a fast reactor, one can transmute these into considerably less radiotoxic elements and isotopes, while also significantly reducing the lifetime of the final highly active waste. Through this process, not only the amount and volume of long-lived, highly radioactive waste is minimised, the need for uranium mining is also significantly

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decreased.[3,4] The latter has a huge environmental footprint on non-radioactive indicators, such as atmospheric pollution, greenhouse gases, and water consumption.

The focus within EU research over the past decade with respect to separation processes has been the development of several Grouped ActiNide EXtraction (GANEX) processes for the co-extraction of all transuranic elements from spent nuclear fuel.[5–11] These processes all include a primary cycle for the bulk extraction of uranium,[12] followed by a second cycle for transuranic element extraction.[13] Three different second-cycle GANEX processes are currently being investigated: CEA-GANEX,[13] EURO-GANEX,[10] and Chalmers-GANEX (CHALMEX).[14–18] The former two are based on the principle of extracting actinides and lanthanides together, for a subsequent selective stripping of the actinides. The latter, the CHALMEX process, differs by selectively co-extracting the actinides from spent nuclear fuel, thus potentially reducing the number of process steps.[17,18] A bis-triazinyl-bi-pyridine molecule has been developed for extracting trivalent and pentavalent actinides: 6,6′′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine (CyMe$_4$-BTBP, Figure 1a) with a good An(III)/Ln(III) selectivity.[19] A separation factor of over 100 was achieved for the separation of americium from europium. In addition, CyMe$_4$-BTBP has good radiolytic and hydrolytic stability.[19–25]

Tri-*n*-butyl phosphate (TBP, Figure 1b) is combined with CyMe$_4$-BTBP to extract the tetra- and hexavalent actinides. The chemistry of TBP is well known from its extensive use in current reprocessing routes (PUREX process). It specifically extracts plutonium (Pu(IV)) and uranium (U(IV,VI)), with generally low distribution ratios for fission products.[26–29] TBP has been demonstrated thermally stable,[30,31] although the small amounts of radiolytic and hydrolytic degradation products have proven challenging. Attempts have been made to replace the use of TBP with other extracting agents that follow the CHON principle, such as di(2-ethylhexyl)butyramide (DEHBA) and di(2-ethylhexyl)iso-butyramide (DEHiBA). These efforts were abandoned due to low D(Pu)-values for the CHALMEX system. This can be compensated for

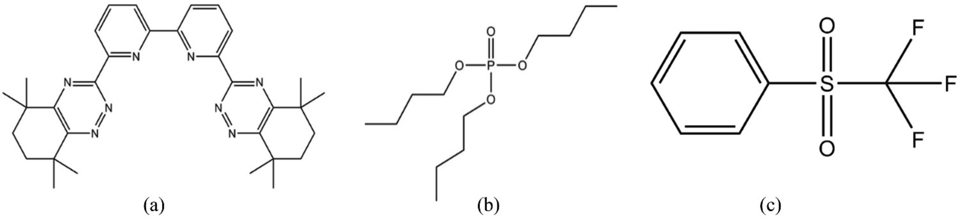

Figure 1. Molecular structure of a) CyMe$_4$-BTBP (6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8--tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine), b) TBP (tri-*n*-butyl phosphate), and c) FS-13 (phenyl trifluoromethyl sulfone).

by increasing the CyMe$_4$-BTBP concentration, but this will also increase D(Eu), yielding poor SF(Am/Eu).[16,32–34] On the other hand, TBP can handle large concentrations of plutonium, allowing a low enough CyMe$_4$-BTBP concentration to ensure D(Eu) below 1. By combining TBP and CyMe$_4$-BTBP in a suitable diluent, the need for redox control of the process is significantly reduced, if not eliminated.[18]

Several studies have been performed to decide on a diluent for the CHALMEX solvent.[18,35–38] The most recently used diluent is phenyl trifluoromethyl sulfone (FS-13), shown in Figure 1c. It has high thermal-, hydrolytic-, and radiolytic stability and yields a high solubility of CyMe$_4$-BTBP.[39–41] The actinide distribution ratios are maintained at gamma doses of up to approximately 160 kGy, and the CHALMEX FS-13 solvent was shown to have higher radiolytic stability compared to the CHALMEX cyclohexanone solvent.[39,42] FS-13 itself does not extract any metals, although the solvent as a whole (CyMe$_4$-BTBP, TBP, and FS-13) yields good separation factors for uranium, plutonium, and americium towards the lanthanides (i.e., europium), with extraction equilibrium reached within 20 minutes.[14,17] More problematic is the low extraction of neptunium(V,VI) ($SF_{\mathrm{Np/Eu}} = 4.1$, $D(\mathrm{Np}) = 1.2$) and the high extraction of curium ($SF_{\mathrm{Am/Cm}} = 1.7$, $D(\mathrm{Cm}) = 17$), cadmium ($D > 1000$) and silver ($D > 30$).[14] Curium extraction and incorporation in MOX-fuel is unwanted because of the significant shielding the fuel factory will require due to the neutron emission of curium. Despite low distribution ratios of both zirconium ($D \sim 0.65$) and molybdenum ($D \sim 0.20$), they are also of concern due to their high concentration in spent nuclear fuel.[14,17]

In previous work, a solvent using a composition of 30% v/v TBP and 70% v/v FS-13 has been used, based on the TBP concentrations used in the PUREX process. CyMe$_4$-BTBP concentrations have been varied between 10 and 50 mM corresponding to an extraction capacity of 1–100 g/L cations. In this paper, the optimisation of the extractant concentrations in the CHALMEX FS-13 solvent is presented. Furthermore, the performance of the optimised solvent on various simulated PUREX raffinate solutions is described. TBP is known to extract nitrates, as do a previous CHALMEX solvent using cyclohexanone as a diluent.[33] As the currently investigated CHALMEX solvent is now comprised of a different diluent, this work presents a study on the new solvent's nitric acid extraction. Understanding these aspects of the CHALMEX process is of scientific interest due to the importance for later process development.

Materials and methods

Materials

CyMe$_4$-BTBP was supplied by Karlsruhe Institute of Technology, Karlsruhe, Germany, and FS-13 by Marshallton Labs, King, NC, USA. Nitric acid (65%

suprapur) was bought from Merck, and TBP (97%) from Aldrich. The radiotracers used in the solvent composition experiments have the following origins:

- ^{241}Am (extracted from ^{238,239,240,241}Pu source)
- ^{239}Np silica column (produced in-house from ^{243}Am stock)
- ^{238}Pu (AEA Technology Inc., Harwell, UK)
- $^{238,\ 239,\ 240,\ 241}$Pu (Studsvik, Studsvik, Sweden)
- ^{237}Np (AEA Technology Inc., Harwell, UK)
- ^{152}Eu (IFE, Kjeller, Norway)

The radiotracers used for the simulated PUREX raffinate testing were obtained from:

- ^{244} Cm: Oak Ridge National Laboratory, Oak Ridge, TN, USA
- ^{241}Am: Isotopendienst M. Blaseg GmbH, Waldburg, Germany
- ^{239}Pu: Forschungszentrum Jülich laboratory stock solution
- ^{nat}U: Forschungszentrum Jülich laboratory stock solution
- ^{237}Np: Forschungszentrum Jülich laboratory stock solution
- ^{152}Eu: Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany

Batch solvent extraction studies and analytical procedures

TBP volume ratios from 10% v/v to 50% v/v were investigated, using a fixed CyMe$_4$-BTBP concentration of 10 mM. Later, the ligand concentration was varied for different fixed TBP volume ratio systems. A minimum of 300 µL of both organic and aqueous phase (4 M HNO$_3$) was contacted in a mechanical shaker (IKA, Vibrax, VXR 1500 rpm), at 25°C. An organic-to-aqueous phase ratio of 1 was maintained in all experiments. The contacting time was 60 minutes, as this has previously been verified as sufficient time to reach equilibrium in the studied system.[15] Trace amounts of ^{241}Am(III), ^{152}Eu(III), ^{237}Np(V) or ^{239}Np(V, VI), and ^{238}Pu(IV) or ^{238,239,240,241}Pu(IV) were added to the respective aqueous phases prior to contacting. The extraction of americium and europium was investigated in one system, while neptunium and plutonium were investigated in individual systems. The samples were centrifuged for a minimum of 5 minutes (Wifug, LABOR- 50 M, 4500 rpm). A 100 µL aliquot was taken from each phase for analysis. Am/Eu radioactivities in each phase were analysed using a high purity germanium detector (HPGe) (Canberra, Gamma Analyst GEM 23195), while Pu and Np radioactivities were analysed on a liquid scintillation counter (Wallac 1414 WinSpectral). All experiments were performed in triplicate.

Solvent performance using simulated PUREX raffinates and analytical procedures

The experiments were performed as described above, although trace amounts of ^{241}Am(III), ^{152}Eu(III), ^{237}Np(V), ^{244} Cm, ^{239}Pu, and ^{nat}U were added to the raffinate together instead of being investigated in isolated systems. The phases were contacted in an IKA, Vibrax, VXR shaker (2200 rpm). The samples were centrifuged for 5 minutes after contacting (Hettich EBA 8S). Aliquots of 200 µL from each phase were sampled for HPGe (Eurisys EGC35-195-R germanium coaxial N-type detector) analysis (Am/Eu activities), 20 µL for ICP-MS analysis (Perkin Elmer NexION 2000, all elements) and 10 µL for alpha spectrometry (Ortec Octête-pc eight chamber alpha measurement system equipped with PIPS detectors) (Am/Pu/Np/Cm). To enable dissolution of the organic phase for ICP-MS analysis, a surfactant (10% *EcoSurf*) was added in the dilution stage. A sample of each of the original aqueous solutions was also analysed by ICP-MS for mass balance calculations. Six different simulated PUREX raffinates that were available in laboratory stock from previous flow sheet tests were used, and their composition and acidity are listed in Table 1.

Acid extraction

Equal volumes of the pre-equilibrated solvent and nitric acid of varying concentrations were contacted in a mechanical shaker (IKA, VIBRAX, VXR 2200 rpm) for 15 minutes at 20°C. The solvent was subsequently contacted with the same amount of MQ water for the same amount of time. An aliquot of the water was then titrated with 0.1 M NaOH, using a Metrohm 905 Titrando titrating machine, as was the initial aqueous phase. An aliquot of the organic solvent was added to MQ water and stirred on high speed for at least 5 minutes before being titrated for mass-balance calculations.

[,]Results and discussion

Solvent optimisation: TBP and CyMe$_4$-BTBP

The extraction of americium, europium, neptunium, and plutonium was studied as a function of the TBP/FS-13 volume ratio with a constant concentration of 10 mM CyMe$_4$-BTBP. The range of TBP ratios correspond to concentrations 0 M to 1.79 M. Figure 2 shows that the extraction of americium(III) increases with increasing TBP volume ratio up to 30% v/v TBP. The distribution ratios then remain fairly constant at values of around 30. As the trivalent Am and Eu are extracted by CyMe$_4$-BTBP and not by TBP,[15,17] this is believed to be due a better solubility of the Am/Eu complexes in the TBP/FS-13 mixture compared to pure FS-13. Ekberg et al.,[43] found that both the stability and the solubility of such complexes increases with

Table 1. The composition and acid concentration of the various simulated spent nuclear fuel solutions, measured by ICP-MS.

ICP-MS (mg/L)						
Element	HAW CEA ($3.2\ M\ HNO_3$)	HAW CEA ($4.3\ M\ HNO_3$)	ALSEP ($2.9\ M\ HNO_3$)	SANEX ($4.5\ M\ HNO_3$)	HAW-ITU ($3.3\ M\ HNO_3$)	HAW-ITU ($3.7\ M\ HNO_3$)
Se	9.7	10.0	-	6.3	-	-
Rb	54.4	60.1	79.9	47.6	50.3	43.4
Sr	142.4	154.6	184.2	129.5	82.6	69.3
Y	74.6	81.0	109.5	68.6	60	50.9
Zr	676.1	736.0	629.8	488.7	464.3	380.2
Mo	548.0	599.2	384.6	501.7	377.8	325.4
Ru	320.3	346.3	271.5	290.7	353	95.9
Rh	62.2	68.6	0.9	55.9	66	17.8
Pd	86.9	192.7	5.4	159.5	157.3	150.8
Ag	6.8	10.4	-	6.7	2.8	4.1
Cd	14.1	15.8	-	14.8	16.3	13.9
Sn	9.8	8.5	11.2	0.1	3.6	3.8
Sb	3.3	3.4	-	2.1	0.5	1.2
Te	88.7	97.1	61.5	82.1	80	66.5
Cs	452.8	481.0	630.7	413.4	215.9	181.3
Ba	225.0	247.8	-	209.4	421.3	351.7
La	197.3	213.2	293.3	183.5	195.5	163
Ce	474.3	514.7	561.2	432.6	283.8	236.4
Pr	184.8	203.0	182.4	168.4	168.6	141.6
Nd	592.2	661.0	974.4	543.6	728.6	610.7
Sm	122.1	132.9	193.3	108.7	86.5	72.4
Eu	28.1	31.8	41.1	25.2	17.4	14.8
Gd	21.1	23.9	40.3	19.9	66	55.2
Na	1237.5	1661.9	-	1126.5	-	-
Cu	16.5	21.0	-	14.6	-	-
Ni	38.4	37.1	-	33.8	-	-
Fe	1545.0	1545.0	6.2	1375.4	-	-
Al	4.7	5.0	-	5	2.2	2.6
Cr	76.7	80.3	-	69.4	-	-

decreasing charge density of the solvent. Increasing the ratio of TBP to FS-13 in the solvent can therefore account for an increase in Am distribution ratio with increasing TBP ratio. Wisnubroto et al.,[44] theorised that the activity of uncomplexed CMPO is reduced by hydrogen bonds with TBP through H^+ or H_2O. $CyMe_4$-BTBP contains N-donor atoms available for such hydrogen bonds. This theory explains the role that not only increased TBP fraction plays on the solubility of $CyMe_4$-BTBP, but also that of acid extraction.

The europium(III) extraction shows a similar trend to the americium extraction, with an increase up to 30% v/v TBP. Europium distribution ratios remain below 1 for all investigated TBP/FS-13 ratios, showing the high selectivity of $CyMe_4$-BTBP for trivalent actinides over lanthanides. Separation factors of up to 97 were found. Plutonium(IV) extraction slightly increased with increasing TBP concentration, as would be expected from the well-known PUREX chemistry,[28] from distribution ratios of around 4 for 5% v/v TBP up to $D = 60$ for 50% v/v TBP. The distribution ratio Pu of 2.26 for 0% v/v TBP also confirms that plutonium is extracted by $CyMe_4$-BTBP as reported earlier.[15] Due to the significant increase in both americium and plutonium extraction above 30% v/v TBP, while higher TBP concentrations do not yield

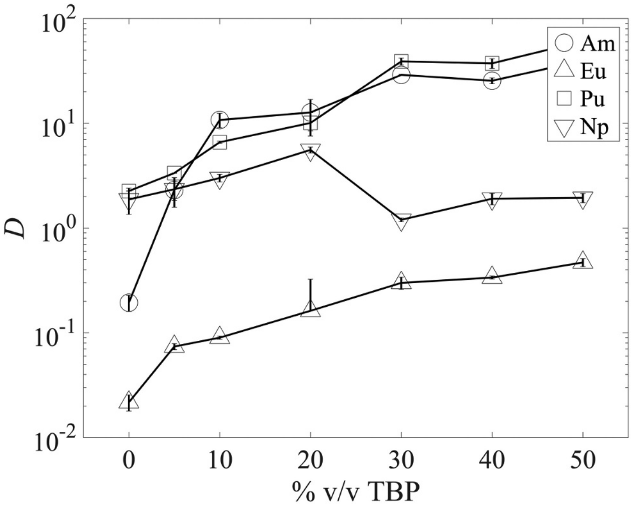

Figure 2. Distribution ratios, (*D*), of trace amounts of Am, Eu, Pu, and Np as a function of the TBP/FS-13 volume ratio and an addition of 10 mM $CyMe_4$-BTBP. The aqueous phase was 4 M HNO_3 with addition of trace amounts of the radionuclides. Am/Eu were investigated in one system, all other radionuclides were investigated in isolation. Data for 30% v/v (all radionuclides) was reproduced from Halleröd.[13]

further improvement, 30% v/v TBP was chosen as the optimal TBP volume ratio.

Neptunium(V,VI) extraction did not show a clear trend as a function of the TBP/FS-13 volume fraction. Distribution ratios were generally between 1.2 and 5.5, but were lower for the higher TBP volume fractions, which would not be expected from PUREX chemistry. The decrease in neptunium extraction could be due to a change in its oxidation state, as the pentavalent oxidation state is known to be less extractable with TBP compared to the tetra-, and hexavalent oxidation states.[45] The $P = O$ group of the TBP molecule is a potential reducing agent, and so it is possible that TBP acts as a reducing agent for any Np(VI) present in the system. Another possibility is the reducing effect by TBP by-products or degradation products, such as dibutyl phosphate, monobutyl phosphate, or ethyl hexyl phosphate.[46–48] Furthermore, the extraction of neptunium has been shown to be highly dependent on the nitric- and nitrous-acid concentrations, and small variations can impact the neptunium's distribution.[45,49] In the mixed $CyMe_4$-BTBP/TBP system, neptunium is mainly extracted by $CyMe_4$-BTBP and not TBP,[18] due to the dominant Np(V) oxidation state under the applied experimental conditions. Further speciation studies would thus be needed to fully understand the extraction behaviour of neptunium in the studied system.

Figure 3 shows the Pu, Np, Am, and Eu distribution ratios as a function of the $CyMe_4$-BTBP concentrations (up to 100 mM) in 15% v/v (Figure 3a), 30% v/v (Figure 3b) and 50% v/v (Figure 3c) TBP in FS-13. In all systems,

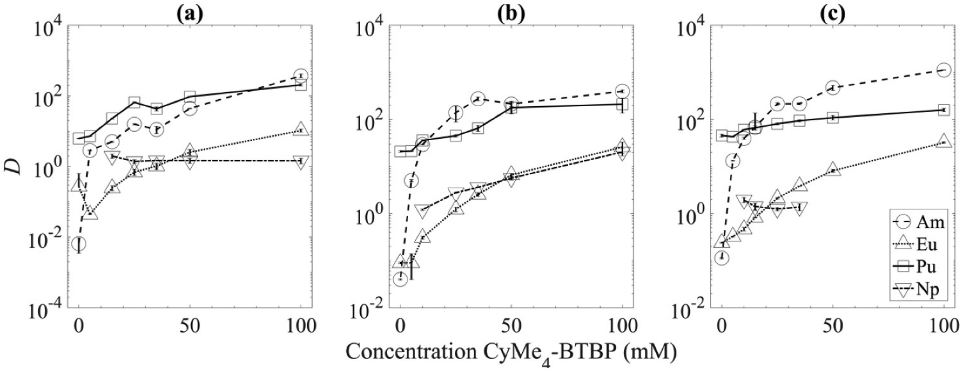

Figure 3. Distribution ratios (*D*) for Pu, Np, Am, and Eu as a function of the CyMe$_4$-BTBP concentration in **(a)** 15% v/v TBP and 85% v/v FS-13; **(b)** 30% v/v TBP and 70% v/v FS-13; **(c)** 50% v/v TBP and 50% v/v FS-13. The aqueous phase was 4 M HNO_3 with addition of trace amounts of the radionuclides for all the investigated systems. Am/Eu were investigated in one system, all other radionuclides were investigated in isolation. Data points for 10-, 25-, 35-, 50-, and 100 mM CyMe$_4$-BTBP in system (a) with 30% v/v TBP and 70% v/v FS-13 were reproduced from Halleröd.[13].

increasing the CyMe$_4$-BTBP concentration enhances the extraction of all the investigated elements (Np, Pu, Am, and Eu). Interestingly, the separation of neptunium and europium is inverted for higher CyMe$_4$-BTBP concentrations: europium is more efficiently extracted than neptunium. This behaviour appears to occur at lower CyMe$_4$-BTBP concentrations for increasing TBP fractions. As neptunium is one of the target nuclides for the extraction process, it is beneficial to keep the separation factor between neptunium and europium as high as possible. The highest separation factor between neptunium and europium is consistently seen at 10 mM CyMe$_4$-BTBP concentration, irrespective of TBP concentration. Therefore, 10 mM CyMe$_4$-BTBP concentration was chosen for further studies.

A slope analysis was performed on the distribution data in Figure 2, based on extraction as a function of % v/v TBP, and the slopes and R^2 values can be seen in Table 2. A 1:1 relationship is seen for Am:TBP complex, and similar trends are seen for the Eu:TBP ratio. Surprisingly, the ratio between *D*(Pu) and TBP concentration is found to be 1.27. In the PUREX process, TBP is known to extract plutonium as a 2:1 complex. Earlier work has shown that CyMe$_4$-BTBP also extracts plutonium independently of TBP, but the slope found here for TBP extraction may suggest a parallel adduct formation with nitric acid, as

Table 2. The slope and consequent R^2 for americium, europium plutonium, and neptunium extracted by 10 mM CyMe$_4$-BTBP and varying ratios of TBP/FS-13 from nitric acid media.

	Am	Eu	Pu	Np
Slope	1.12	0.83	1.27	0.62/0.98
R^2	0.92	0.95	0.94	0.94/0.84

proposed by Ochin et al.[15,50] Two slopes were also distinguished for the neptunium extraction: before and after the suspected reduction. The slopes (0.62 and 0.98, respectively), suggest the opposite, however: an oxidation of Np(V) to Np(VI). A slope of 0.62 indicates a low dependency of extraction on TBP, which would be expected by Np(V), while at higher TBP ratios (30% v/v and above) an increase in TBP dependency is seen, which suggests a greater proportion of Np exists as Np(VI) and is extracted by TBP. These results confirm earlier statements that further investigations into the extraction of Np in the current system is required.

Slope analysis for the extraction of actinides by CyMe$_4$-BTBP has earlier been published by our group for systems with 30% v/v TBP.[15] We showed that americium, curium, and europium are all extracted as 2:1 complexes with CyMe$_4$-BTBP, while plutonium is extracted as a 1:1 complex. Here, we see that in systems with lower TBP fractions (15% v/v), the same complex formation is seen with slopes of 2.20, 1.82, and 1.08 for americium, europium, and plutonium, respectively (Table 3). At 50% v/v TBP, however, a decrease in CyMe$_4$-BTBP:TBP ratio is seen for americium, europium, and plutonium, with slopes of 1.49, 1.59, and 0.42 respectively. This can be explained by the higher concentration of TBP, which also extracts these elements. However, it is more likely that the reduced slope is due to the complete extraction of the radiotracers at such high concentrations. In contrast to earlier reported neptunium trends here, neptunium is found to be independent of the CyMe$_4$-BTBP concentration, once again suggesting either Np(IV) or Np(VI) as the main oxidation state.

Acid extraction

A range of studies have shown that TBP extracts nitric acid.[28,50–53] Depending on the system, both increasing and decreasing distribution ratios for acid extraction are seen by TBP for acid concentrations above 1 M.[52,54,55] In Figure 4 it is seen that $D(HNO_3)$ increases up until 4 M HNO_3, after which it decreases again. Further extraction experiments showed no acid extraction by the pure FS-13 diluent. Although acid extraction by the CyMe$_4$-BTBP ligand is not unlikely due to its four N-donors, the low concentration of CyMe$_4$-BTBP (10 mM) suggests that the bulk extraction of acid rather occurs

Table 3. The slope and R^2 for the extraction of americium, europium, plutonium, and neptunium as a function CyMe$_4$-BTBP concentration in systems with 15% v/v and 50% v/v TBP.

		Am	Eu	Pu	Np
15% v/v TBP	Slope	2.20	1.82	1.08	−0.13
	R^2	0.91	0.99	0.88	0.41
50% v/v TBP	Slope	1.49	1.59	0.42	−0.09
	R^2	0.99	0.96	0.99	0.13

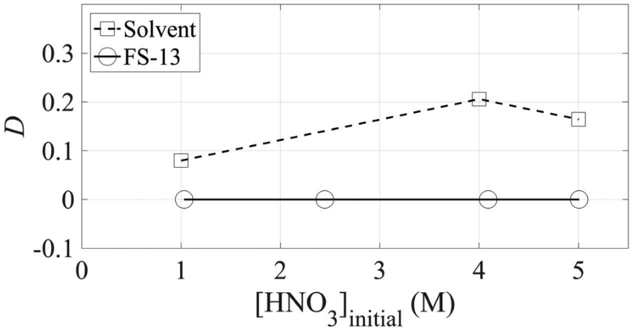

Figure 4. Distribution ratio (*D*) of HNO_3 extraction by preequilibrated organic solvent (10 mM CyMe$_4$-BTBP) in 30% v/v TBP and 70% v/v FS-13 as a function of initial nitric acid concentration.

by TBP. Similar trends for acid extraction by TBP are reported by Ochkin et al.[50] The high extraction of nitric acid by the solvent demonstrates the need for an acid scrub step in the CHALMEX process.

Performance of the optimised solvent on various simulated PUREX raffinates

Loading effects are not unanticipated in the current system due to the low concentration of CyMe$_4$-BTBP (10 mM). 30% v/v TBP corresponds to a concentration 1.07 M. In conventional PUREX raffinates, a plutonium inventory of 1 g/L (0.004 M) is typically expected. In Gen IV reactor systems, a plutonium inventory of 20 g/L (0.08 M) or even higher is predicted. By assuming the conservative 2:1 complex formation between TBP and plutonium, TBP is still present in high enough concentrations to sufficiently extract plutonium. Americium will be present in far lower concentrations compared to plutonium, namely 1 g/L (0.004 M). With a 2:1 complex with CyMe$_4$-BTBP, this will be borderline what the solvent can extract, especially since plutonium is also extracted by the BTBP ligand. Nonetheless, it is of significance to establish if the solvent preferentially extracts the actinides, or if the actinide extraction competes with other elements. Furthermore, in these experiments only trace amounts of the actinides are used, and so loading effects by the actinides cannot occur.

Figure 5 shows the distribution ratios of Am, Cm, Eu, Np, Pu, and U for different simulated PUREX raffinate compositions and acid concentrations, extracted by the optimised solvent of 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13. A significant reduction of the americium and curium extraction, in particular, compared to previously published results for isolated systems is seen.[17] This reduction in extraction with certain feed solution is probably caused by loading effects of the solvent, especially due to a reduction in free CyMe$_4$-BTBP concentration. The three feed solutions showing the highest americium and curium extraction (ALSEP 2.9 M, HAW-ITU 3.3 M,

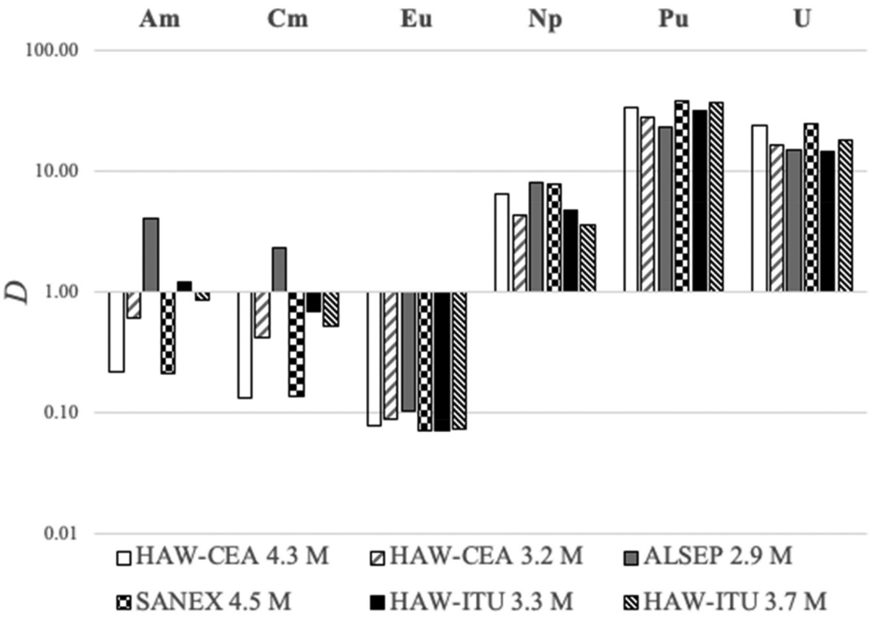

Figure 5. Distribution ratios (*D*) for Am, Cm, Eu, Np, Pu, and U extraction from various simulated PUREX raffinate solutions and different acid concentrations. Trace amounts of the radionuclides were added to each of the simulated PUREX raffinates prior to contacting with the organic phase. The organic phase was 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13.

and HAW-ITU 3.7 M) have a significantly lower metal content in total, compared to the other feed solution. The extraction of both uranium and plutonium is maintained at acceptably high levels (D(U,Pu) > 10), but it is reduced compared to non-metal-loaded systems. Little disparity is seen for the neptunium extraction.

The extraction of fission products presented in Figure 6 shows that the solvent co-extracts cadmium, palladium, and silver, causing further loading of the solvent. The ALSEP raffinate gives the best minor-actinide extraction of all raffinates, which is attributed to the lack of both silver and cadmium in the ALSEP raffinate. Despite the presence of silver and cadmium in both the ITU raffinates, the concentrations were low (Table 1) and were significantly less than the total capacity of CyMe$_4$-BTBP. The palladium concentration is below 1.90 mM for all the investigated raffinates. This suggests that the minor-actinide extraction is restrained by the preferential extraction of other elements in addition to cadmium, palladium, and silver.

Europium extraction is typically used as an analogue for all the lanthanides. The extractability of lanthanides follows the trend reported for CyMe$_4$-BTBP by Geist et al.,[21] with the highest extraction of Eu. None of the lanthanides are of concern, based on their low distribution ratios ($D < 0.1$), also confirming the use of europium as a representative analogue for the lanthanides. Molybdenum and

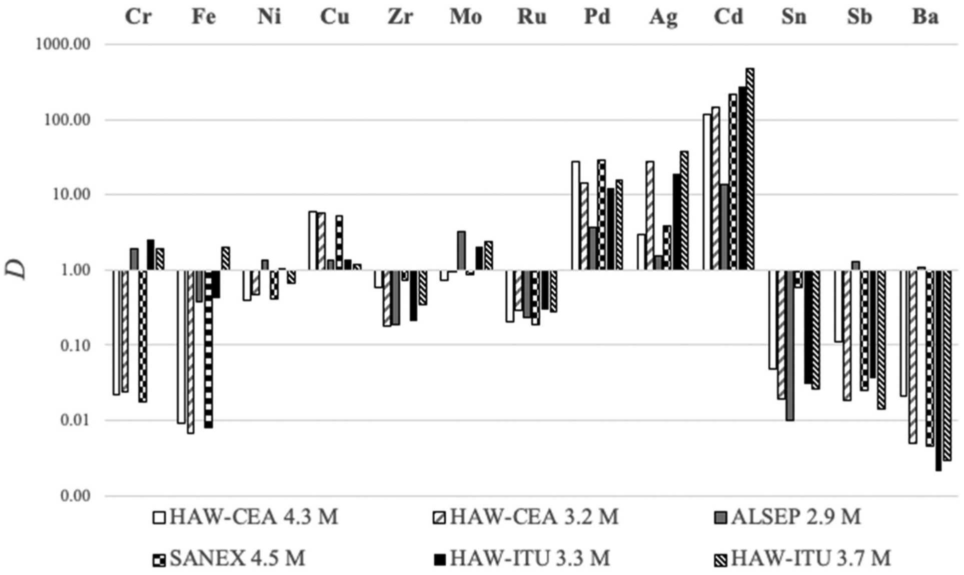

Figure 6. All distribution ratios (*D*) > 0.1 for the fission product extraction by 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13 from different simulated PUREX raffinate solutions and acid concentrations.

zirconium, however, are present in high concentrations in the raffinates, and even at low distribution ratios, a significant amount of these elements is extracted by the solvent.

Molybdenum concentrations ranged from 3.4–6.2 mM in the various raffinates and Mo had an average extraction percentage over 50%. Molybdenum typically exists as MoO_4^{2-} in spent nuclear fuel solution, and is extracted by TBP at higher TBP fractions.[31,56,57] Goletskii et. al.,[58] have shown that TBP only extracts Mo to a significant degree at fractions above 50% v/v in nonpolar diluents. It has also been demonstrated that Mo-extractability is highly dependent on nitric acid concentration, where low acid concentrations favours higher molybdenum extraction up until 4 M HNO_3, after which the distribution ratios increase again, and so it is reasonable to assume that Mo is extracted by CyMe$_4$-BTBP.[59] Complementary experiments with 30% v/v TBP and 70% v/v FS-13 in the absence of CyMe$_4$-BTBP confirmed that Mo is not extracted by TBP in the CHALMEX FS-13 solvent (*D* (Mo) = 0.04), but is rather extracted by CyMe$_4$-BTBP. The extraction of Mo is nonetheless of concern due to the possibility of Mo accumulation downstream in the process. The same concerns apply to zirconium extraction. Zirconium exists as zirconium(IV) in spent fuel raffinates[31] and is extracted by TBP, which was also confirmed by complementary experiments. Although the distribution ratio of zirconium is lower than that of molybdenum (*D*(Zr) ranges from 0.18 to 0.74), its concentration range in the raffinates is 4.2–8.1 mM. With an extraction percentage range of about 14% to 37%, a significant amount of zirconium can follow the stream of uranium and the transuranic elements.

Previous studies performed on a different CHALMEX solvent, showed that most of the elements of major concern mentioned here are extracted by CyMe$_4$-BTBP.[60] A possible strategy to avoid solvent loading with unwanted fission and corrosion products would be complexing these elements in the aqueous phase to suppress their extraction by CyMe$_4$-BTBP. The use of appropriate masking agents would therefore increase the free CyMe$_4$-BTBP concentration and advance the minor-actinide extraction. Two such complexing agents were shown to be effective in complexing several of the problematic fission products for an earlier CHALMEX solvent: bimet and mannitol.[60] However, experimental confirmation for the effects for the current CHALMEX solvent is needed.

Conclusions

The optimised CHALMEX FS-13 solvent was developed based on maximising americium and plutonium extraction, in addition to keeping the separation factor between neptunium and europium at its maximum. The optimised solvent is composed of 10 mM CyMe$_4$-BTBP in 30% v/v TBP and 70% v/v FS-13 when extracting trace amounts of radionuclides. It was also shown that the solvent co-extracts certain fission and corrosion products (Ag, Cd, Pd, Mo, and Zr) causing significant loading of the solvent, especially CyMe$_4$-BTBP, thereby decreasing the extraction efficiency for trivalent actinides. It is deemed likely that the increase in BTBP concentration combined with suppression of the aforementioned elements will increase the trivalent actinide extraction.

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