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Identification of optimized conditions for effecter fission product masking/ scrubbing

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Summary

Deliverable D1.2, Identification of optimised conditions for effective fission product masking/ scrubbing, reports experimental conditions suitable for scrubbing fission and corrosion products such as Tc, Sr, Zr, Mo, Pd from TODGA and mTDDGA solvents.

Approval

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CONTENT

EXECUTIVE SUMMARY

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BEHAVIOUR OF TECHNETIUM IN TODGA SYSTEMS

INTRODUCTION

The long-lived fission product technetium-99 — together with some d-block metals in particular Zr, Pd, Ru and Mo, as well as with Y and the early-middle lanthanides (Ln) — belongs to major fission products (FP) in spent nuclear fuel (SNF) that interfere selective group extraction of actinides in the EURO-GANEX process.[1–2] Polyaminocarboxylic ligands (CDTA, DTPA) used as masking agents for the cationic FP make possible efficient actinide/FP separation in the extraction step,[3] except for technetium present in the HNO_3 solutions of SNF as Tc(VII) – the pertechnetate anion, TcO_4^-. In the first cycle of the GANEX process TcO_4^- is partly co-extracted with uranium from the SNF solution to the organic phase by DEHiBA (*N*,*N*-di-2-ethylhexyl-isobutyramide) in the form of a mixed $[UO_2(DEHiBA)_2(NO_3)(TcO_4)]$ complex,[4] but most Tc remains in the aqueous raffinate. Selective co-extraction of U(VI) and Tc(VII) in a similar system (after reducing Pu and Np by acetohydroxamic acid) was also studied.[5] A recent "hot test" of the EURO-GANEX process has shown that approximately 75% of the total amount of Tc was routed to the first cycle raffinate (which is the feed of the second cycle) and then to the organic phase (0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in Exxsol D80) loaded with actinides and Ln, but the further fate of Tc in the second cycle of the EURO-GANEX process remained unknown.[2] In an earlier version of the second GANEX cycle, the actinides, Ln, Tc and some other FP were co-extracted into an organic solvent containing DMDOHEMA and HDEHP. In one of the following stages Tc is stripped by citric acid at pH of 2.7,[6] but such complicated and pH-sensitive stripping section had to be simplified.

Attempts to reduce technetium and obtain non-extractable hydrophilic complexes of its low-valent forms, well separated from the actinides were rather unsuccessful except from the work by Czerwinski et al.[7] who used acetohydroxamic acid (AHA) both as the reducing and complexing agent for Tc. However, because of a very slow kinetics of both Tc(VII) reduction and formation of a hydrophilic Tc(II)-nitrosyl-AHA complex, $[Tc^{II}(NO)(AHA)_2H_2O]^+$, the authors had to use a very high temperature and a high AHA concentration to accelerate the process, but these harsh conditions seem to be hardly acceptable in solvent extraction processes with highly radioactive material on technological scale.

The present study reports an attempt to optimise the actinide/Tc separation in the second cycle of the EURO-GANEX process where AHA is already used in the actinide stripping section as the reducing agent for plutonium and neptunium present in the organic phase containing TODGA (*N,N,N′,N′*-tetra-n-octyl diglycolamide) in kerosene diluent.[1–2] The scope of the research has been limited to the Am(III)/Tc separation and to a solvent containing TODGA only. The other extractant, DMDOHEMA (*N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexyloxy-ethyl) malonamide, is considered a phase modifier increasing the loading capacity for Pu(IV).[2, 8]

TOWARDS EFFECTIVE Tc SCRUBBING

The initial part of this study was related to the behaviour of Tc(VII) in solvent extraction systems with 0.2 mol/L TODGA in the organic phase. A significant increase of the distribution ratio of TcO_4^-, $D_{Tc(VII)}$, with increasing aqueous phase HNO_3 concentration a constant concentration of NO_3^-ions, and a strong decrease of $D_{Tc(VII)}$ with increasing concentration of only HNO_3 has been observed (Figure 1). These dependences have been interpreted as the effects of: (i) TcO_4^- extraction from the acidic media as an ion pair with the protonated form of the extractant, $(TODGA)H^+$, the concentration of the latter being increased with increasing concentration of the acid; and (ii) competition between the TcO_4^- and NO_3^- anions for the $(TODGA)H^+$ cation, resulting in the significant drop of the $D_{Tc(VII)}$ value observed with the increase of HNO_3 (both H^+ and NO_3^-) concentration.

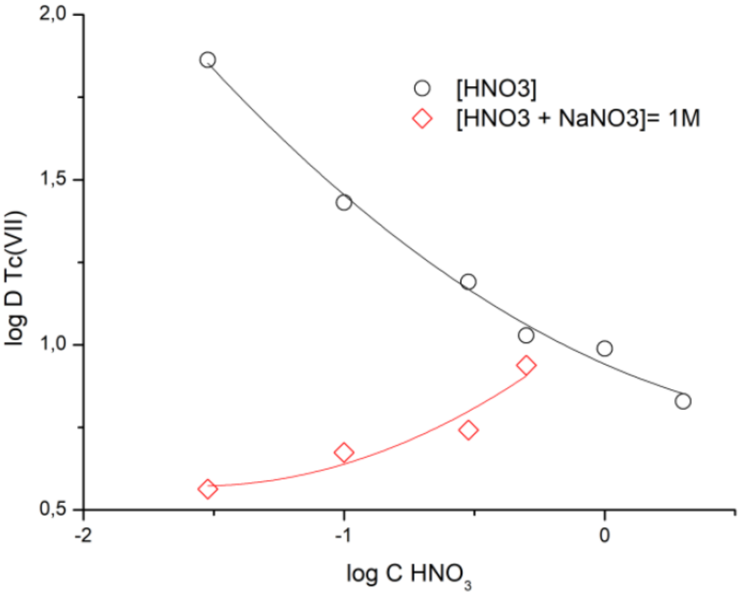


Figure 1. Effect of HNO_3 concentration on the distribution ratio of $^{99m}TcO_4^-$ in the two-phase systems: aqueous phase, ○ — 0.03–2.0 mol/L HNO_3; (ii) ◊ — 1.0 mol/L $(H,Na)NO_3$ (0.03–0.50 mol/L HNO_3); organic phase, 0.2 mol/L TODGA in kerosene; $T = 25$ °C.

None of the applied approaches resulted in reaching $D_{Tc(VII)} < 1$ required for effective separation of TcO_4^- from the actinides in the studied solvent extraction system with TODGA. Values of $D_{Tc} < 1$ have only been obtained after reducing the ^{99m}Tc tracer with $SnCl_2$. The presence of 0.05 mol/L DTPA and an increase in the pH of the aqueous phase caused their further decrease (Figure 2).

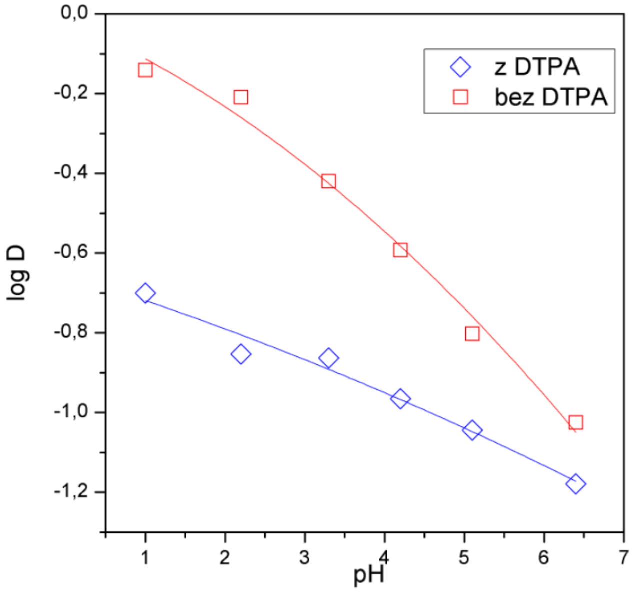


Figure 2. Effect of the aqueous phase pH on the distribution ratio of ^{99m}Tc tracer reduced with $SnCl_2$.Aaqueous phase, 1.0 mol/L $(H,Na)NO_3$ (pH = 1.0–6.4) containing 0.05 mol/L DTPA [◊] or without DTPA [□]; organic phase, 0.2 mol/L TODGA in kerosene; *T* = 25 °C.

Further work was directed on reducing Tc(VII) with acetohydroxamic acid proposed as the reducing agent for Pu and Np in the EURO-GANEX process.[1–2] First results, obtained after reducing trace amounts of ^{99m}Tc (equilibrium after 40 min shaking at 1400 rpm) resulted in a very small effect of 0.2 mol/L AHA. The desired value of $D_{Tc} < 1$ was obtained only in 0.1 mol/L HNO_3 in the presence of both reducing (AHA) and stripping (DTPA) agents (Figure 3). An increase in the AHA concentration up to 3 mol/L did not significantly affect the D_{Tc} value, and in all tested systems at 0.5 mol/L HNO_3 $D_{Tc} > 1$ was obtained.

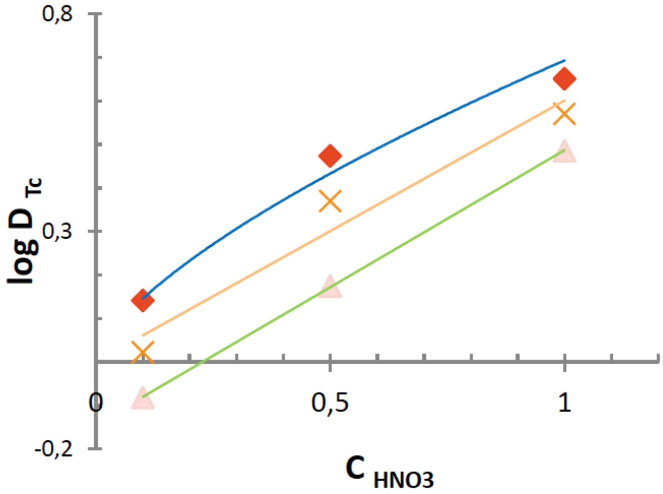


Figure 3. Effects of AHA, DTPA, and of HNO_3 concentrations on the distribution ratio of ^{99m}Tc. Aqueous phase, diamonds —HNO_3; X — HNO_3 + 0.2 mol/L AHA; triangles — HNO_3 + 0.2 mol/L AHA + 0.05 mol/L DTPA. Organic phase, 0.2 mol/L TODGA in kerosene. *T* = 25 °C.

Preliminary experiments with mg amounts of Tc-99 carried out under the conditions reported in reference[7] confirmed that Tc(VII) undergoes reductive nitrosylation by AHA, forming the Tc(II)-nitrosyl-AHA complex. This complex can be examined by UV-vis spectroscopy (peak at 434 nm, Figure 4). The reaction was very slow at ambient temperature, its equilibrium being reached after approximately two weeks. The hydrophilic complex turned out to be stable for months in aqueous solutions.

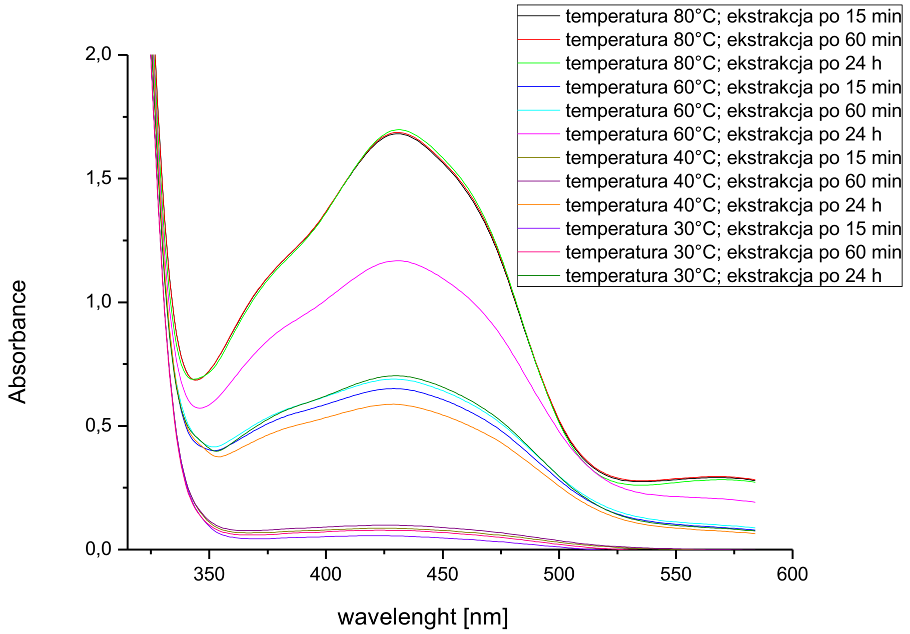


Figure 4. UV-vis spectra of the aqueous phase (1.0 mmol/L ^{99}Tc in 1 mol/L HNO_3 + 2 mol/L AHA) after heating the solutions for 60 min at various temperatures and cooling (from 15 min to 24 h) before extraction at 25 °C.

Further studies concerned the separation of such reduced ^{99}Tc from Am(III) in the system modelling the second cycle of the EURO-GANEX process. The aqueous phase (1 mol/L HNO_3 + 4 mol/L AHA) containing 180 mg/L ^{99}Tc, spiked with ^{99m}Tc and ^{241}Am radiotracers was heated to 95 °C for 15 minutes, cooled to room temperature for 15 min and shaken for 30 minutes at 25 °C with 1400 rpm with an equal volume of the organic phase (0.2 mol/L TODGA + 5 vol% octanol in kerosene). These conditions will further be called 'standard'. The distribution ratios of Am(III) and Tc were equal to: $D_{\mathrm{Am}} = 235$ and $D_{\mathrm{Tc}} = 0.0022$, resulting in a high separation factor, $SF_{\mathrm{Am/Tc}} = 1.1 \cdot 10^5$. Distribution ratios determined in a similar system but without the reduction step with AHA were equal to $D_{\mathrm{Am}} = 249$ and $\mathrm{D}_{\mathrm{Tc}} = 4.22$, the latter value indicating significant extraction of pertechnetate anions.

These results show that 4 mol/L acetohydroxamic acid in 1 mol/L HNO_3 aqueous solution, heated to 95 °C, relatively quickly reduces mg amounts of Tc(VII) to Tc(II). Subsequent solvent extraction by 0.2 mol/L TODGA + 5 vol% octanol in kerosene at ambient temperature effectively extracts Am(III) from this aqueous phase while the Tc(II) remains in the aqueous phase in the form of the strong nitrosyl-AHA complex. However, the concentration of AHA applied (4 mol/L) is much greater than 1 mol/L AHA suggested for the reduction of plutonium and neptunium in the EURO-GANEX process.[1–2] Furthermore, a temperature of 95 °C may be too high for a technological process.

In order to ease these harsh conditions, the effect of the following parameters on the D_{Tc} values (at 100 mg/L Tc-99) was investigated: AHA concentration in the aqueous phase (1 mol/L HNO_3), temperature and time of heating, time period between heating and extraction, as well as temperature and time of extraction. A very strong effect of the AHA concentration has been found under standard conditions. The D_{Tc} value increases from 0.0022 at 4 mol/L AHA, through 0.0065 and 0.0183 at 3 mol/L and 2 mol/L AHA, respectively, to an unacceptable value of 1.25 at 1 mol/L AHA. The effects of the time and temperature of heating the aqueous phase, time period between heating and extraction, and the temperature and time of the extraction allow to accept heating at 60–80 °C. 15 min heating at 80 °C with 15 min break and 30 min extraction at 25 °C for 4 mol/L AHA gives D_{Tc} = 0.053, but 60 min heating at 60 °C is required (for the same other conditions) to achieve a sufficiently low value of D_{Tc} = 0.037. For 2 mol/L AHA the same 60 min heating at 80 °C is required (for otherwise same conditions) to achieve D_{Tc} = 0.012, but the same heating time at 60 °C requires up to 24 h break to achieve D_{Tc} = 0.034 (Figure 5).

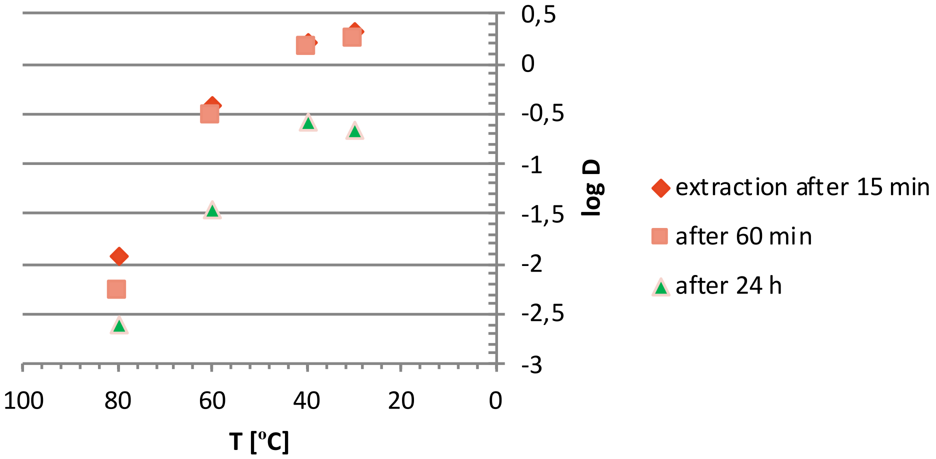


Figure 5. Distribution ratios of ^{99}Tc (1.0 mmol/L) in the system: 1 mol/L HNO_3 + 2 mol/L AHA vs standard organic phase as a function of the temperature of heating (for 60 min) of samples of the aqueous phase and of their cooling time (from 15 min to 24 h) before extraction at 25 °C.

A limitation of the developed solvent extraction method is inability to separate technetium from neptunium and plutonium both in the first GANEX cycle and at an early stage of the second cycle of EURO-GANEX. This is due to the fact that also Np and Pu present in SNF solutions in HNO_3 are reduced by AHA (even more easily than Tc^{VII}), and their strong hydrophilic AHA complexes formed[9–11] remain in the aqueous phase along with the reduced technetium. Therefore, the developed method of separating Am(III) from Tc seems to be applicable only to systems from which Np and Pu have already been removed, in particular to the raffinate from (advanced) PUREX processes. The possibility of using the developed method in the EURO-GANEX process is presented in the below conclusions.

CONCLUSIONS

The presented results indicate for the decisive effect of time on the distribution ratios of Tc at given other parameters (AHA concentration and temperature) of the tested systems. Unfortunately, the low D_{Tc} values (though still non-equilibrium ones) specified in this report for a wide range of the parameters tested, are unattainable in fast counter-current processes carried out in batteries of centrifuge contactors at ambient temperatures. Therefore, the separation of Tc using the developed method in the EURO-GANEX process is possible either in the counter-current process (perhaps in a battery of mixer-settlers) at an elevated temperature in the last (Ln stripping) section of the second cycle of EURO-GANEX,[2] or in a single reduction/separation process applied to the final spent solvent fraction (containing about 9 mg/L uranium[2]). The wide range of the determined parameters (AHA concentration, temperature and time) affecting the process of technetium(VII) reduction at various stages of the extractive separation would help in selecting their optimum values for each case.

This suggestion is possible, based on the analysis of the flow-sheet of run 2 of the EURO-GANEX (actinides stripping) given in reference.[2] The feed was a solvent (0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in kerosene) loaded with 10 g/L Pu and with much less amounts of other actinides as well as of numerous fission products, including Tc(VII), 2.4 mg/L. The authors have not reported the distribution of many fission products, also Tc, between the final fractions of the counter-current process (the concentrations being “either below detection limit or inconsistent”[2]). Using their data and the $D_{Tc(VII)}$ values determined or extrapolated for various concentrations of HNO_3 in the 0.2 mol/L TODGA system (Figure 1), we have concluded that under the conditions existing in all the stages of the flow-sheet[2] Tc(VII) is not reduced and remains in the spent solvent. at a concentration of about 1.2 mg/L. Tc should easily be removed from the spent solvent after its reduction by AHA at an elevated temperature.

The proposed method can also be used for the removal of technetium from the loaded solvent obtained in the first cycle of the GANEX process. According to the test with the genuine SNF of a fast reactor, that solvent contained Tc (2.8 mg/L) and this amount contaminated the final uranium product.[2]

BEHAVIOUR OF FISSION PRODUCTS IN MODIFIED DGA SYSTEMS

INTRODUCTION

The family of the diglycolamides (DGAs) is well known to extract trivalent actinides (An(III)) and lanthanides (Ln(III)) efficiently due to the tridentate coordination through hard-donor oxygen atoms. The most important and up to date most intensely studied member of this class of ligands is TODGA *(N,N,N',N'*-tetraoctyl diglycolamide), which was already applied in several cold and hot solvent extraction processes for the treatment of minor actinide containing high-level waste.[12] A modified DGA was recently proposed by the TWENTE group, in which of one or two methyl groups to the central methylene carbon atoms of the TODGA molecule leads to a reduction of the extraction efficiency for An(III) and Ln(III). The reduction in extraction efficiency leads to overall reduced distribution ratios of all tested metal ions, including some unwanted fission product such as Sr(II). The reduced Sr(II) extraction is beneficial as a co-extraction in a solvent extraction process could be avoided, while an efficient extraction of the desired An(III) and Ln(III) is still achieved. Furthermore, this might be a benefit, as the stripping behaviour might be improved, even at moderate nitric acid concentrations. The extraction mechanism and complexation of An(III) and Ln(III) was studied by solvent extraction and TRLFS.[13]

The EURO-grouped actinide extraction process has been developed to co-separate transuranic actinide elements from spent nuclear fuel, based on an organic solvent composed of two extractants, a DGA (TODGA) and a malonamide (DMDOHEMA). This process was recently tested in both spiked and hot tests.[2] Within GENIORS a new approach was studied, aiming to further simplify this process, since two different molecules in the organic phase complicates the process and makes the solvent regeneration more difficult. A modified DGA (mTDDGA, Figure 6) was proposed to cope with high Pu(IV) loading.[14] First batch tests showed that mTDDGA extracts some un-wanted fission products to a lesser extent compared to TODGA. This is promising as the scrubbing can probably be simplified.

The present study focuses on a systematic investigation on the extraction behaviour of the different diastereomeric forms of mTDDGA. Beside the extraction of actinides and lanthanides also the non-lanthanide fission products were in the focus of this research.

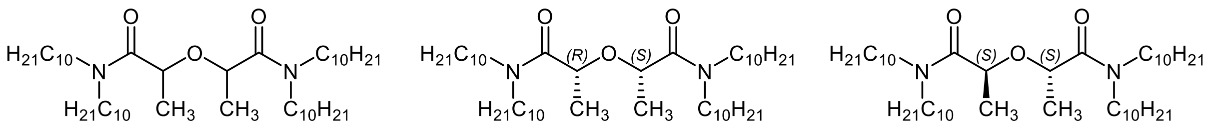
MTDDGA, A PROMISING EXTRACTANT FOR EURO-GANEX (2ND CYCLE)

Three different batches of mTDDGA with different diastereomeric excesses have been obtained from TWENTE (Figure 6):

1) RE1822 mixture of diastereomers (1:3.5 = trans:cis)

2) RE1822 lower (major) diastereomer (cis isomer, *RS)*

3) RE1822 upper diastereomer (trans isomer, *SS)*



mTDDGA
mixture of diastereomers
(1:3.5 = trans:cis)

mTDDGA
cis diastereomer

mTDDGA
trans diastereomer

Figure 6. Chemical structures of the used mTDDGA diastereomers.

In a first set of experiments 0.1 mol/L of each mTDDGA was tested in Exxsol-D80. Exxsol-D80 was chosen as the diluent as mTDDGA is foreseen to be used in a new GANEX process, which will probably be tested at NNL where Exxsol-D80 is the preferred diluent. A concentration of 0.1 mol/L of each mTDDGA was chosen for two reasons. Firstly, the available amount of the pure diastereomers was low. Secondly, we wanted to be able to compare the results directly to the results of the extraction of the pure Me_2-TODGA (TWE-14) diastereomers.[15]

As known from a recent scoping study,[14] we expected significant extraction only at higher nitric acid concentrations. Therefore, we used aqueous phases composed of 1–6 mol/L HNO_3 nitric acid containing trace amounts of inactive metals (10^{-5} mol/L each) and spiked with radioactive tracers. The composition is shown in Table 1.

Table 1. Composition of aqueous phases.

Component	Concentration	Component	Concentration	Component	Concentration
Fe	1.8E–05 mol/L	La	1.1E–05 mol/L	Tb	0.9E–05 mol/L
Sr	1.3E–05 mol/L	Ce	1.2E–05 mol/L	Dy	1.2E–05 mol/L
Zr	1.2E–05 mol/L	Pr	1.1E–05 mol/L	Ho	1.2E–05 mol/L
Mo	1.1E–05 mol/L	Nd	1.1E–05 mol/L	Er	0.9E–05 mol/L
Ru	0.9E–05 mol/L	Sm	1.1E–05 mol/L	Tm	0.9E–05 mol/L
Pd	0.7E–05 mol/L	Eu	1.2E–05 mol/L	Yb	1.0E–05 mol/L
Y	1.2E–05 mol/L	Gd	1.1E–05 mol/L	Lu	0.9E–05 mol/L
Tc-99	3.0 MBq/L	Np-237 (V)	2.2 MBq/L	Am-241	3.0 MBq/L
Eu-152	5.6 MBq/L	Pu-239	6.6 MBq/L	Cm-244	3.0 MBq/L
HNO_3	1–6 mol/L				

Phases were contacted for 30 minutes, which is expected to be sufficient to attain equilibrium. Figure 7 shows distribution ratios of Np-237, Pu-239, and Am-241 as a function of the nitric acid concentration. For Am-241 a clear difference in the extraction is observed with the cis *(RS)* isomer extracting the best. The trans isomer *(SS)* extracts significantly less and for the mixture distribution ratios in between are measured, as expected. Pu extraction however differs, as the difference in extraction between the different diastereomers is rather small. The Np extraction is hard to get a clear picture of, as the distribution ratios are generally quite low and Np is only extracted at the highest HNO_3 concentrations.

Figure 8 shows the distribution ratios of Am-241 and Cm-244 as a function of the nitric acid concentration. Here, the same principal trend is observed, with the cis *(RS)* isomer extracting the best, the trans isomer *(SS)* extracting significantly less and intermediate distribution ratios for the mixture. Interestingly, an inversion of selectivity is observed, similar to the same phenomenon that had been observed with the different diastereomers of Me_2-TODGA (TWE-14).[15] The cis *(RS)* isomer and the mixture show a preference for Cm over Am extraction, while the trans isomer *(SS)* shows the opposite selectivity.

Figure 9 shows an overview of distribution ratios of all metal ions for different diastereomers of mTDDGA and nitric acid concentrations. Most metal ions show the same trends in nitric acid concentration (increasing distribution ratios with increasing nitric acid concentration) and order of diastereomers (cis > mixture > trans). The Ln extraction pattern shows a maximum for the extraction of Er, which is comparable to Me_2-TODGA (TWE-14).[15]

Ru and Sr distribution ratios were low under all conditions. Tc extraction doesn't follow the trend in nitric acid concentration, which could be explained by its extraction as anion. It follows the order of diastereomers (cis > mixture > trans).

Fe, Pd, and Mo extraction don't follow the trends. Their distribution ratios are nearly independent of the HNO_3 concentration, and they follow a different order of diastereomers: trans > cis > mixture. Even though it could be possible that the trans isomer extracts these metal ions better, the order of diastereomers doesn't make much sense, as the mixture of diastereomers should show an intermediate behaviour in any case. Therefore, the Fe, Pd, and Mo extraction is currently not understood and further experiments are needed to understand their behaviour.

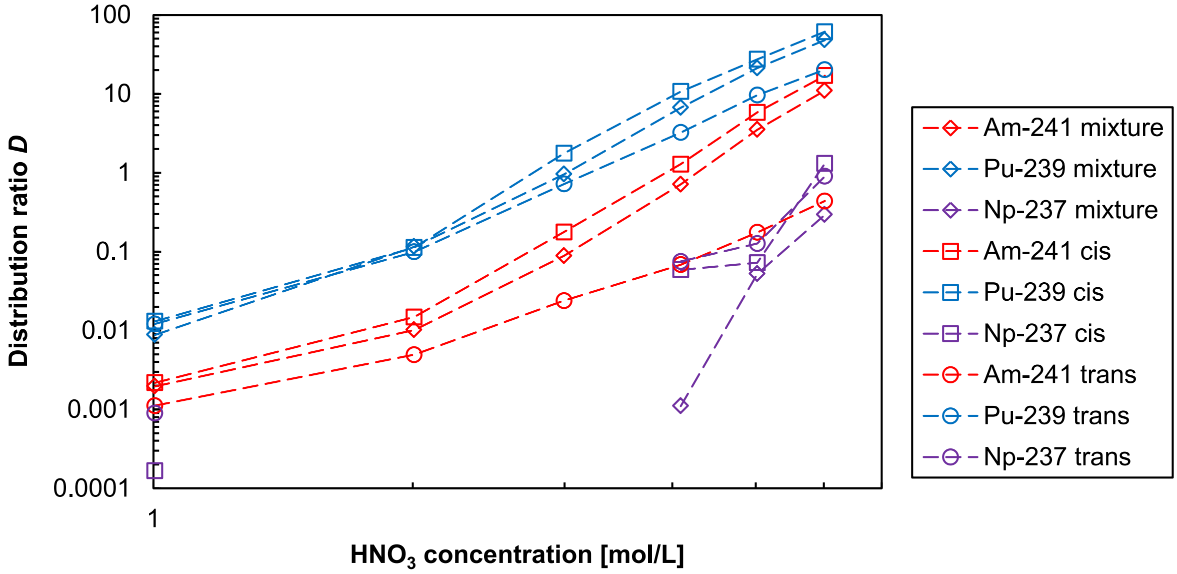


Figure 7. Distribution ratios of Np-237, Pu-239, and Am-241 as a function of the nitric acid concentration. Organic phase, 0.1 mol/L mTDDGA (different diastereomers) in Exxsol-D80. Aqueous phase, 1–6 mol/L HNO$_3$ containing trace amounts of inactive metals (10^{-5} mol/L each) and spiked with radioactive tracers (cf. Table 1). 22°C, 30 min. shaking time.

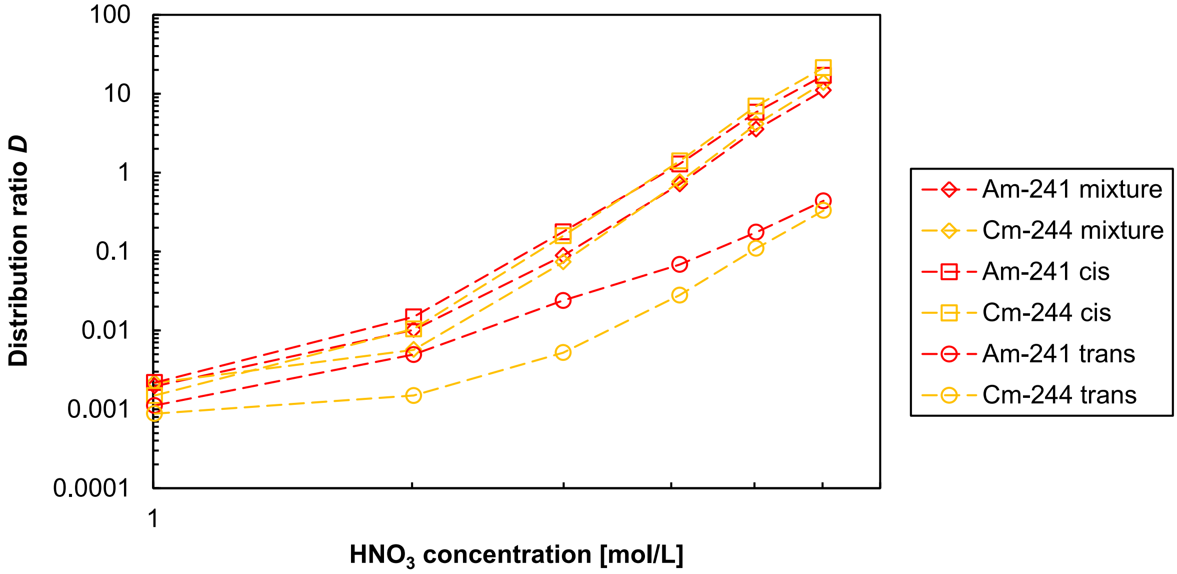


Figure 8. Distribution ratios of Am-241 and Cm-244 as a function of the nitric acid concentration. Organic phase, 0.1 mol/L mTDDGA (different diastereomers) in Exxsol-D80. Aqueous phase, 1–6 mol/L HNO$_3$ containing trace amounts of inactive metals (10^{-5} mol/L each) and spiked with radioactive tracers (cf. Table 1). 22°C, 30 min. shaking time.

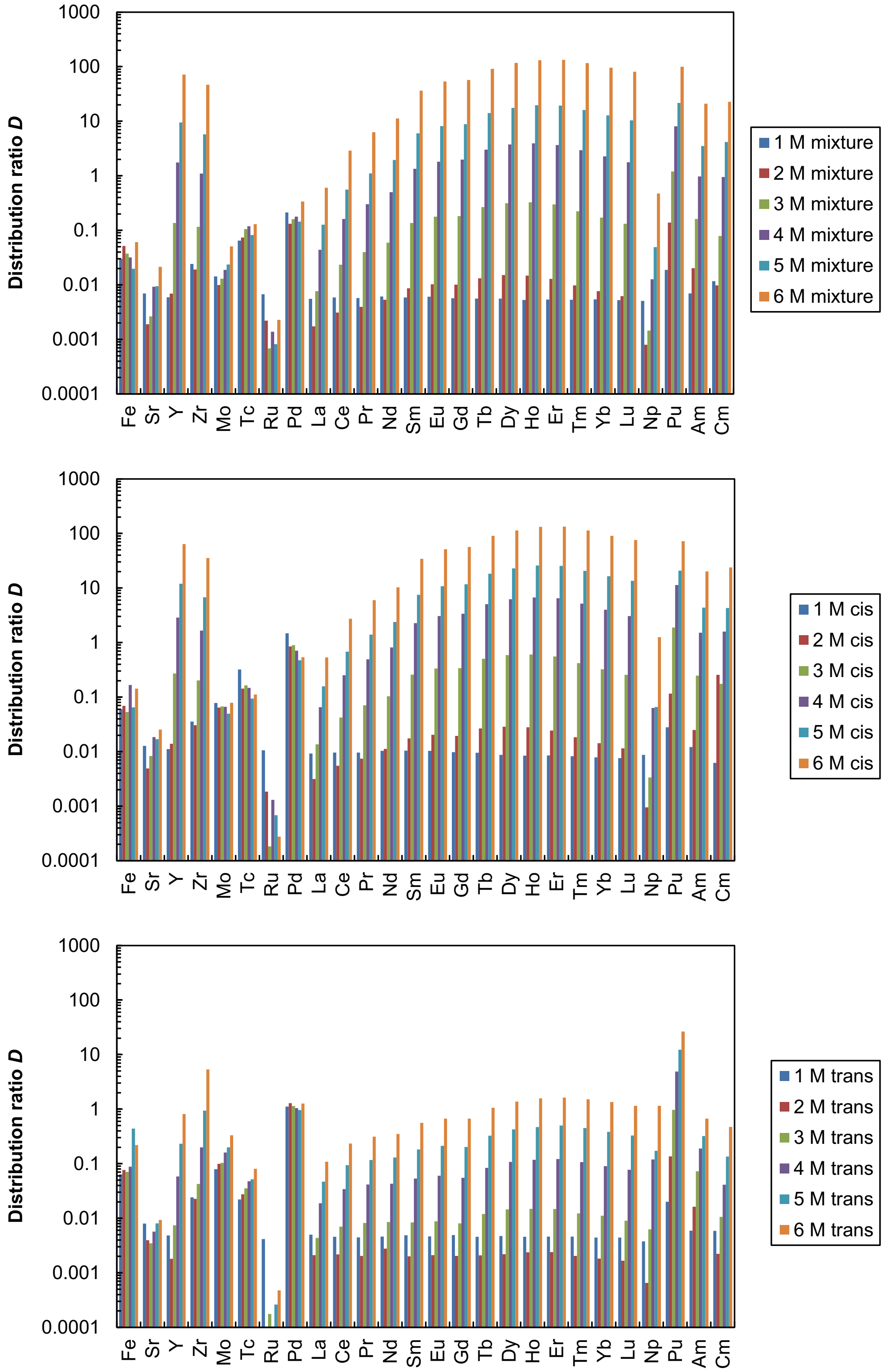


Figure 9. Distribution ratios of all metal ions for different diastereomers of mTDDGA and nitric acid concentrations. Organic phase, 0.1 mol/L mTDDGA (different diastereomers) in Exxsol-D80. Aqueous phase, 1–6 mol/L HNO_3 containing trace amounts of inactive metals (10^{-5} mol/L each) and spiked with radioactive tracers (cf. Table 1). 22°C, 30 min. shaking time.

CONCLUSIONS

Replacing the EURO-GANEX solvent (0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in Exxsol D80)[1–2] with a solvent comprising 0.5 mol/L *(R,S)*-mTDDGA in Exxsol D80[14] offers several advantages with respect to the routing of non-Ln fission products while maintaining excellent extraction properties for TRU and Ln: Distribution ratios for Sr, Zr and Mo are significantly lower compared to those determined the reference solvent. This in turn will allow to simplify the scrubbing section of a EURO-GANEX process.

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