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Rikard Malmbeck, Daniel Magnusson, Stephane Bourg, Michael Carrott, Andreas Geist, et al.. Homogenous Recycling of Transuranium Elements from Irradiated Fast Reactor Fuel by the EURO-GANEX Solvent Extraction Process. *Radiochimica Acta*, R Oldenbourg Verlag GMBH, 2019, 107 (9-11), pp.917-929. 10.1515/ract-2018-3089 . cea-02460444

HAL Id: cea-02460444

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Homogenous recycling of transuranium elements from irradiated fast reactor fuel by the EURO-GANEX solvent extraction process

<https://doi.org/10.1515/ract-2018-3089>

Received December 5, 2018; accepted April 25, 2019; published online May 27, 2019

Abstract: The EURO-GANEX process was developed for co-separating transuranium elements from irradiated nuclear fuels. A hot flow-sheet trial was performed in a counter-current centrifugal contactor setup, using a genuine high active feed solution. Irradiated mixed (carbide, nitride) $U_{80}Pu_{20}$ fast reactor fuel containing 20% Pu was thermally treated to oxidise it to the oxide form which was then dissolved in HNO_3 . From this solution uranium was separated to >99.9% in a primary solvent extraction cycle using 1.0 mol/L DEHiBA (*N,N*-di(2-ethylhexyl)isobutyramide in TPH (hydrogenated tetrapropene) as the organic phase. The raffinate solution from this process, containing 10 g/L Pu, was further processed in a second cycle of solvent extraction. In this EURO-GANEX flow-sheet, TRU and fission product lanthanides were firstly co-extracted into a solvent composed of 0.2 mol/L TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) and 0.5 mol/L DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxy-ethyl) malonamide) dissolved in Exxsol D80, separating them from most other fission and corrosion products. Subsequently, the TRU were selectively stripped from the collected loaded solvent

using a solution containing 0.055 mol/L SO_3 -Ph-BTP (2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)pyridine tetrasodium salt) and 1 mol/L AHA (acetohydroxamic acid) in 0.5 mol/L HNO_3 ; lanthanides were finally stripped using 0.01 mol/L HNO_3 . Approximately 99.9% of the TRU and less than 0.1% of the lanthanides were found in the product solution, which also contained the major fractions of Zr and Mo.

Keywords: Homogeneous recycling, TRU separation, solvent extraction, centrifugal contactor.

1 Introduction

Energy produced by nuclear power today means a demand of 65,000 metric tonnes natural uranium per year for nuclear fuels [1]. In turn, approximately 10,000 metric tonnes of spent nuclear fuels are discharged annually.

The fraction of uranium consumed during a once through irradiation in a reactor is in fact only approximately 0.6–0.7%, slightly dependent on fuel enrichment and burn-up of the fuel. Although large deposits of uranium exist worldwide, the sustainability of electricity generation by nuclear fission can be massively enhanced by recycling the actinides, essentially plutonium, from used nuclear fuels.

By reprocessing the irradiated nuclear fuel once and recycling recovered plutonium together with reprocessed uranium, as done in France, the natural uranium consumption is reduced by 17% [2, 3]. A further significant reduction can be achieved by multi-recycling of fuels in reactors with a fast neutron spectrum and using the depleted uranium stockpiles. No natural uranium would be required in this case [2]. Furthermore, reprocessing reduces the amount of highly radioactive waste compared to the direct disposal of used nuclear fuel. The reduction is both with respect to volume (since the major component of used nuclear fuel, uranium, is removed during reprocessing) and with respect to long term heat generation

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(since plutonium is also removed). A further reduction in heat generation would be achieved by also separating the remaining minor actinides [4], neptunium, americium and curium, which will allow for a smaller final high-level waste (HLW) repository. In summary, recycling actinides saves two resources – natural uranium and space required for final repositories.

While the PUREX (plutonium uranium reduction extraction) process for separating uranium and plutonium from nuclear fuel by solvent extraction is used on a commercial scale, innovative processes for homogenous recycling of fast reactor fuels [5], i. e. grouped separation of both the major and the minor actinides, are currently under development. To date, only one concept has been demonstrated with irradiated nuclear fuel on the lab scale [6].

Major challenges are the high Pu concentration, the high specific radioactivity of fission products and ensuring selectivity between the actinides and the fission products. Single cycle concepts exist but at this point are rather exploratory. They are usually based on TBP (tri-*n*-butyl phosphate) extraction taking advantage of its capability to recover U(VI) and Pu(IV) at high loading. The co-recovery of minor actinides is incorporated by introducing a second extracting agent that shows high selectivity for the minor actinides over FPs, including chemically similar lanthanides. For example, the CHALMEX concept [7–9] uses a solvent containing CyMe₄-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) [10–11] plus TBP dissolved in a polar diluent such as cyclohexanone or FS-13 (phenyl trifluoromethyl sulfone) to directly extract only U and TRU from dissolved fuel solutions. The chemical system has promise but so far has not been tested in a counter-current flow-sheet trial.

A different approach is pursued in the US, exploiting the oxidation of Am(III) to Am(VI), making it extractable by e. g. TBP or phosphonate extracting agents [12–14]. This opens up the possibility of a single process to co-extract U, Np, Pu and Am.

The so called GANEX (grouped actinides extraction) process was initially developed at the CEA (Commissariat à l'énergie atomique et aux énergies alternatives) in France [15, 16]. It consists of two cycles; the first cycle removes the large mass of uranium and the second cycle is to recover the trans-uranium elements (TRU: Np, Pu, Am, Cm).

The first cycle process is based on a selective U(VI) extraction from an aqueous phase of approximately 5 mol/L HNO₃ into DEHiBA (*N,N*-di(2-ethylhexyl)isobutyramide, Figure 1) dissolved in TPH (hydrogenated tetrapropene), an industrial aliphatic diluent. Co-extracted Tc and Np are reduced and scrubbed by hydrazine in a scrubbing section at 1.5 mol/L HNO₃ and thereby routed together with the TRU and the fission products (FP) to the high level raffinate (HAR). U(VI) is efficiently stripped from the organic phase into 0.01 mol/L HNO₃. The first GANEX cycle has been demonstrated in the ATLANTE facility at the CEA using a high active feed solution from dissolved irradiated fuel [17].

The raffinate from the first cycle is the feed for the second GANEX cycle, where TRU (present as tri-, tetra- and hexavalent actinides) are separated and selectively recovered: TRU, lanthanides, Y, Mo, Tc, Zr and Fe are co-extracted into a solvent containing DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxy-ethyl) malonamide [18], Figure 1) and HDEHP (di(2-ethylhexyl)phosphoric acid, Figure 1) diluted in TPH. Several selective stripping stages are implemented. Firstly, Mo, Ru, Tc are stripped with 0.4 mol/L citric acid at pH of 2.7, then TRU are stripped into a solution containing 0.5 mol/L *N*-(2-hydroxyethyl)

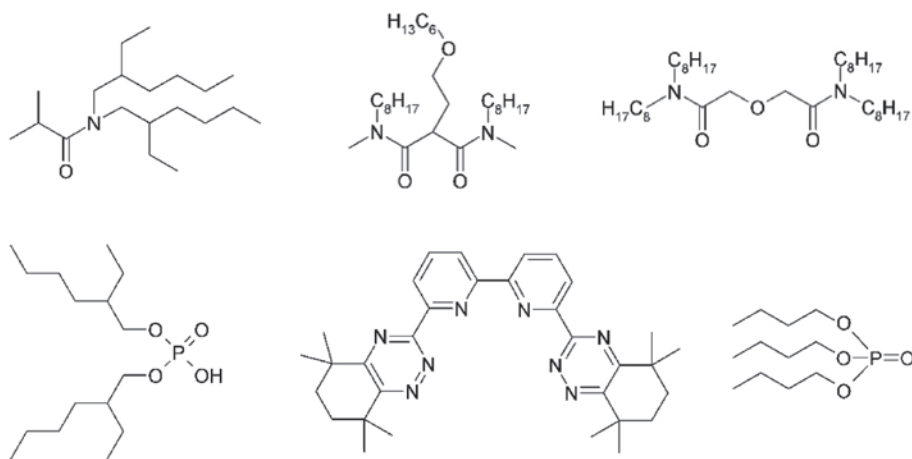


Figure 1: Extracting agents used in various GANEX flow-sheets: top, DEHiBA, DMDOHEMA, TODGA; bottom, HDEHP, CyMe₄-BTBP, TBP.

ethylenediaminetriacetic acid (HEDTA, Figure 2) and 0.5 mol/L citric acid at pH=3 with 0.1 mol/L hydroxyurea, acting as a reducing agent for neptunium(VI). Finally, Ln, Zr and Fe are recovered by 0.5 mol/L oxalic acid and 0.2 mol/L TEDGA (tetraethyl diglycolamide, Figure 2). The second GANEX cycle has also been demonstrated in the ATLANTE facility at the CEA using the high active raffinate from the first cycle test [19]. Although excellent results were obtained it was generally recognised that there is a need to simplify the rather complicated and pH sensitive stripping section.

In the framework of the EURATOM research project, ACSEPT [20], an alternative GANEX second cycle concept was developed, the EURO-GANEX process. The approach for selective TRU stripping is based on the selectivity of a novel water soluble BTP molecule for complexation with trivalent actinides compared to the trivalent lanthanides. This enables stripping at higher acidities and thereby removes the need to control pH.

The EURO-GANEX solvent is 0.2 mol/L TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide [21], Figure 1)+0.5 mol/L DMDOHEMA in Exxsol D80 (a kerosene diluent). This solvent co-extracts Np(VI), Pu(IV), Am(III), Cm(III) and Ln(III) from the GANEX first cycle raffinate [22–25] and is capable of high Pu(IV) loading capacity, up to 40 g/L depending on acidity, in contrast to many other solvents tested [26]. DMDOHEMA is expected to act primarily as a phase modifier but its role is not perfectly clear. Indeed, malonamides extract An(IV) much more efficiently than An(III) [27]. Hence, DMDOHEMA may also contribute to Pu(IV) extraction. Zr(IV) and Pd(II) are masked using CDTA (trans-1,2-cyclohexanediaminetetraacetic acid, Figure 2) [28]; co-extracted Sr(II) and Fe(III) are scrubbed using 0.5 mol/L HNO₃. TRU are stripped from

the loaded solvent using a strip solution containing SO₃-Ph-BTP (2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)pyridine tetrasodium salt, Figure 2) [29] and AHA (aceto-hydroxamic acid, Figure 2) [30] while Ln(III) are kept in the solvent by a sufficiently high concentration of HNO₃ in the strip phase. A first “Pu-active” test (i.e. using a surrogate feed solution containing a representative Pu(IV) concentration and spiked with Np and Am) proved the principle. Excellent results regarding hydrodynamics and Pu and Am recovery were obtained. However, approximately 30% of Np was routed to the raffinate and approximately 7% of Eu (representing the Ln) was routed to the TRU product [31]. A slightly modified flow-sheet was later developed at NNL (National Nuclear Laboratory, UK), producing separate Np+Pu and Am+Cm product solutions for potential applications in the heterogeneous recycling of actinides [32].

Based on the experience gained with the Pu-active test [31], the EURO-GANEX process was finally “hot tested” using genuine dissolved spent fuel as the feed solution. This solution was obtained by performing a GANEX first cycle run on a feed solution prepared by dissolving irradiated fast reactor fuel. This paper is a full report on the development and execution of the hot test. It reports on the adapted first and second cycle flow-sheets, feed solution preparation and results from the hot first and second cycle process tests. For further experimental details see Annex – Experimental.

2 Fuel dissolution

Fast reactor (FR) fuel (U₈₀Pu₂₀) with stainless steel cladding taken from a selection of mixed FR fuels of (U,Pu)N,

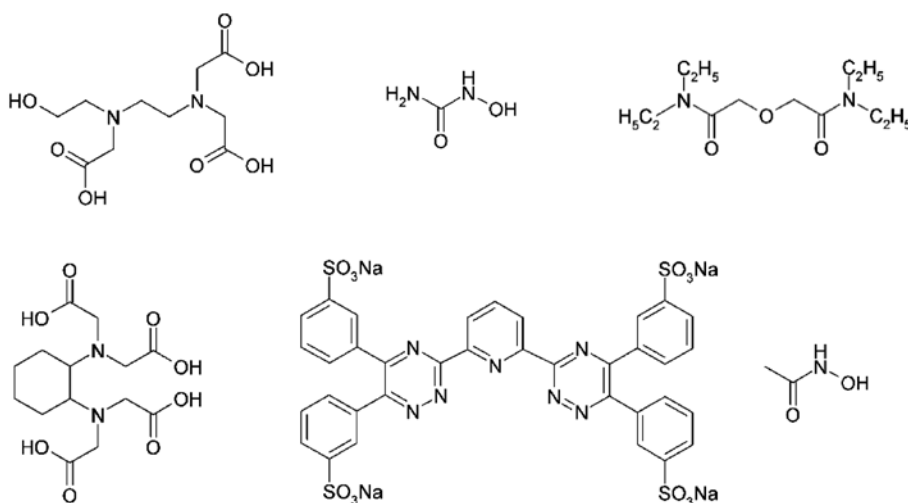


Figure 2: Water soluble complexing and reducing agents used in various GANEX flow-sheets: top, HEDTA, hydroxyurea, TEDGA; bottom, CDTA, SO₃-Ph-BTP, AHA.

(U,Pu)C or (U,Pu)N,C, irradiated between 1971 and 1976 in the Dounreay (UK) Fast Reactor (DFR) was used. These were some legacy fuels still held at the Joint Research Centre (JRC), Karlsruhe, Germany. The fuel pieces could not be assigned to a certain irradiation experiment. Therefore, the irradiation history and burn-up is unknown. The selected fuel pieces were approximately 8 mm long.

In total, 116.8 g (with cladding) of fast reactor fuel pieces was thermally treated to oxidise the carbides and nitrides to oxides, yielding predominantly U_3O_8 . For the oxidation process the fuel pieces were added to an alumina crucible, placed in a furnace in a hot cell and kept for 3 days under a slow air flow at a temperature of 600 °C [33]. The off-gas was treated by three alkaline gas traps attached to the set-up to capture iodine. Following this treatment, the fuel was completely powderised. The cladding pieces were visually inspected and appeared to be clean.

The powderised oxide material was subsequently dissolved in 600 mL of 6 mol/L HNO_3 by refluxing for 8 h. The solution was filtered twice (20 μm and 0.45 μm), producing

741.7 g solution and (after drying) 8.6 g precipitates and 17.9 g cladding material.

This solution was characterised by ICP-MS measurements for metals concentration (see Table 1) and titration for the acidity. The solution was then adjusted to a HNO_3 concentration of 5 mol/L by adding concentrated HNO_3 , producing approximately 620 mL of feed solution for the GANEX first cycle.

3 GANEX first cycle: U separation

3.1 Flow-sheet

The previous hot GANEX first cycle test [17] was carried out in mixer settlers at CEA's ATALANTE facility. The uranium and plutonium feed concentrations were 176 g/L and 2.5 g/L, respectively. Based on the experiences gained from this test, a new flow-sheet was designed using the CEA's PAREX code [34], see Figure 3.

A physicochemical model was developed and implemented in PAREX, based on experimental distribution ratios of HNO_3 , U [35], Pu and Tc [36], disregarding organic activity coefficients. The $UO_2(NO_3)_2 \cdot HNO_3 \cdot H_2O/DEHiBA-TPH$ system could be modelled taking into account three acid complexes and only one U complex, $(DEHiBA)_2(UO_2(NO_3)_2)$, in the organic phase. The extraction of Pu(IV) and Np(VI) was also represented by organic complexes involving two DEHiBA molecules, as in the case for U(VI). The extraction of Np(V) was modelled by considering the formation of the organic complex $(DEHiBA)(NpO_2(NO_3))$. The behaviour of Tc(VII), particularly in the presence of U(VI), governs the design of the scrubbing section. The extraction of pertechnetate acid

Table 1: ICP-MS analysis of collected fractions from the GANEX first cycle.

	Feed	Raffinate	Loaded solvent	U product	Stripped solvent
U	103,300	61	32,300	^a	20
Np	17	13	0.2	0.4	<LOD
Pu	22,700	18,100	8	34	<LOD
Am	330	246	<LOD	0.3	<LOD
Total Ln	860	726	<LOD	0.7	<LOD
Tc	41	18.3	2.8	3.5	1.6

^aU concentration in product solution was obviously erroneous. Concentrations in mg/L (<LOD = below limit of detection).

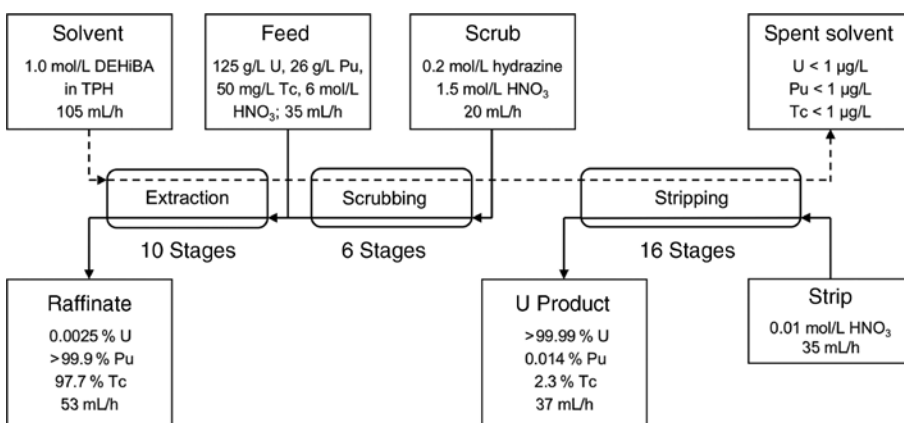


Figure 3: Adapted GANEX first cycle flow-sheet with calculated recoveries.

from a nitric acid solution can be accurately calculated taking into account the complexes $(\text{DEHiBA})(\text{HTcO}_4)$ and $(\text{DEHiBA})_2(\text{HTcO}_4)$. However, in the presence of uranyl nitrate, a mixed complex $(\text{DEHiBA})_2(\text{UO}_2(\text{NO}_3)(\text{TcO}_4))$ has to be considered as well.

Recently, the model was improved by the acquisition of new binary data for HTcO_4 [37], considering three complexes for HTcO_4 extraction by DEHiBA: $(\text{DEHiBA})_4(\text{HTcO}_4)$, $(\text{DEHiBA})_3(\text{HTcO}_4)(\text{HNO}_3)$ and $(\text{DEHiBA})_2(\text{HTcO}_4)(\text{HNO}_3)$. Furthermore, an additional complex $(\text{DEHiBA})_3(\text{UO}_2(\text{NO}_3)(\text{TcO}_4)(\text{HNO}_3))$ was taken into account to improve U and TcO_4^- extraction at elevated HNO_3 concentrations [38].

In comparison to the previous experiment, which reprocessed light water reactor (LWR) uranium oxide fuel in miniature mixer-settlers [17], modelling this flow-sheet had to account for the lower U feed concentration and the shorter hold up times of the 16-stage centrifugal contactor cascade used at the JRC. The higher concentration of Pu in this test has no impact on uranium extraction performance since Pu is only very slightly extracted. The total aqueous and organic flows were adapted in order to maintain sufficient residence time to ensure efficient uranium extraction and scrubbing. Furthermore, the organic/aqueous flow-rate ratio in the extraction section was decreased from 2.2 to 1.9 to account for the lower concentration of U in the feed (125 g/L vs. 176 g/L [17]). The flow rate ratio in the scrubbing section was kept unchanged. Since 16 stages (instead of 8 in the previous test) were proposed to strip uranium, it was possible to decrease the aqueous flow rate of the stripping section, yielding a more concentrated uranium product solution (125 g/L instead of 90 g/L).

The proposed first cycle flow-sheet is shown in Figure 3, together with calculated relative concentrations of actinides and technetium in the product and raffinate solutions.

3.2 Hot test

Due to the limited number of centrifugal contactors (16) available in the JRC hot cell facility, the GANEX first cycle test had to be run in two steps. The first step was extraction and scrubbing, yielding the raffinate containing the TRU that was to be used as the feed solution for the EURO-GANEX (second cycle) run. The loaded organic phase, containing U, was collected and back-extracted in the second step.

3.2.1 Part 1, preparation of the raffinate containing TRU

The flow-sheet which was run to prepare the TRU-containing raffinate is shown in Figure 4. Analysis of the feed solution revealed that it was diluted by a factor of 1.2 compared to what was assumed when calculating the flow-sheet. To compensate for the lower extractability of U due to the lower HNO_3 concentration (5 mol/L instead of 6 mol/L), flow-rates were adapted using the PAREX code. The organic to aqueous flow-rate ratio was raised from 1.9 to 2.2. The resulting lower U concentration in the organic phase is expected to reduce Tc co-extraction due to mixed U-Tc complexes, allowing an increase of the organic to aqueous phase flow-rate in the scrubbing section from 5.25 to 6.

The total running time to process the complete feed solution required that the experiment was run overnight. Due to experimental restrictions in the hot cell all flow-rates were down-scaled by a factor of 0.75. The final flow-sheet is shown in Figure 4.

The test was started up with a surrogate feed solution made up by 112.5 g/L U in 5 mol/L HNO_3 . During start-up, the organic product contained aqueous entrainment which was caused by a maloperation of contactor 16. This

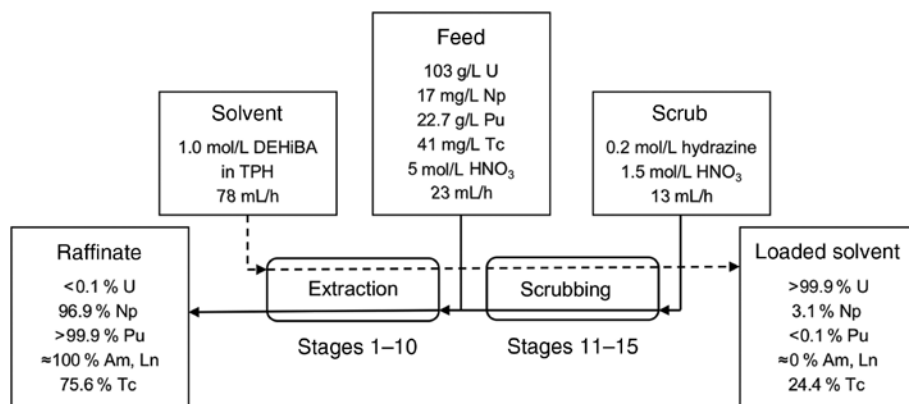


Figure 4: GANEX first cycle run, part 1, extraction and scrubbing: flow-sheet with measured flow rates and recoveries.

problem was solved by feeding the scrub solution to contactor 15 instead of contactor 16. Otherwise, the test ran for 16 h (with the genuine irradiated fuel feed) without further problems, yielding approximately 600 mL of raffinate solution, enough to be used as the feed for the second cycle test.

Excellent results were obtained (cf. Figures 4 and 5). U was almost completely routed to the loaded solvent, which contained approximately 3% of the Np inventory and only approximately 0.1% of the Pu inventory. Am and Ln were “quantitatively” routed to the raffinate, i. e. their concentrations in the loaded organic phase were below detection limits. Approximately one quarter of the Tc inventory was extracted, which is more than predicted by the initial calculations. This result is mainly explained by shorter residence times and a lower number of stages in the scrubbing section compared to the previous test performed in mixer-settlers. Tc(VII) reduction kinetics by hydrazine being relatively slow, the residence time might not have been sufficient to achieve a more complete stripping of Tc from the solvent. Nevertheless, a raffinate solution suitable as second cycle feed solution was produced, containing most of TRU and Ln, some Tc and almost no U.

3.2.2 Part 2, U back extraction

The collected loaded solvent was stored overnight and back-extracted on the following day. Sixteen stages were used to back extract U, the organic flow rate was 78 mL/h and the strip phase used was 0.01 mol/L HNO_3 at 73 mL/h. After back extraction, the organic effluent contained <0.04% of the U initially present in the loaded solvent, whereas Pu, Am and Ln were below the detection limit (LOD). Analysis of the U product revealed a fraction of

approximately 0.1% of the TRUs and 21% of Tc. Approximately 10% of the extracted Tc remained in the organic effluent after back-extraction. As demonstrated in the previous hot test [17], this can be minimised by using a more efficient scrubbing section (with eight instead of five stages). Alternatively, back extraction kinetics is accelerated by increasing the temperature of the scrubbing section to 35–40 °C.

3.2.3 GANEX first cycle, summary

Table 1 summarises the concentrations of the major elements obtained in the first cycle GANEX test. Essentially all uranium was selectively removed and all other actinides were routed to the raffinate. The main goal of this experiment was, therefore, demonstrated, i. e. removal of the major fraction of uranium before the GANEX second cycle. As expected, the high concentration of Pu, 22.7 g/L, did not influence the performance of the process. Approximately 600 mL of feed solution for the GANEX second cycle was produced, sufficient for a demonstration test, which was the main purpose of the GANEX first cycle flowsheet trial. An additional benefit, however, was the first successful demonstration of the GANEX first cycle in short residence time centrifugal contactors with a fast reactor fuel composition (high Pu content). Improvements in neptunium and technetium are needed but further optimisation of the scrubbing section is expected to address these minor issues.

4 EURO-GANEX (GANEX second cycle): TRU separation

The second GANEX cycle recovers TRU from the first cycle raffinate. The EURO-GANEX process [22] does this by co-extracting Np(VI), Pu(IV), Am(III), Cm(III) and Ln(III) into a solvent containing TODGA as the main extracting agent with DMDOHEMA added to allow for sufficiently high Pu(IV) loading [23, 26]. TRU are stripped from the solvent using a combination of two complexing agents, $\text{SO}_3\text{-Ph-BTP}$ [29] and AHA [30]. Finally, Ln(III) are stripped into 0.01 mol/L HNO_3 .

4.1 Flow-sheet

The flow-sheet used for the second cycle hot test is based on the flow-sheet tested in the “Pu-active” centrifugal contactor trials with a surrogate feed [31]. Following further modelling using the PAREX code, several modifications

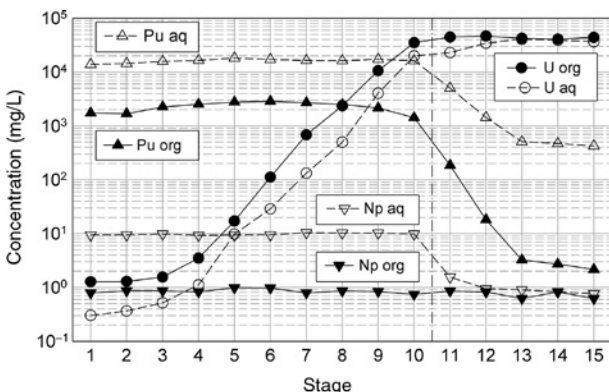


Figure 5: GANEX first cycle run, part 1, extraction (stages 1–10) and scrubbing (stages 11–15): U, Np and Pu concentration profiles. Vertical line, feed point.

were introduced to improve the control of key species (specifically Np, lanthanides) across the flow-sheet whilst adapting to the 16 stage set-up available for the hot test.

To help promote Np(V) oxidation to Np(VI) which is better extracted [23], the acidity of the feed solution was increased to 5.9 mol/L HNO₃. Rather than using eight stages for extraction and eight stages for scrubbing as was done in the Pu-active test, 12 stages were allocated for extraction and four stages for scrubbing. This change also aimed at optimising retention of Np(VI) in the organic phase resulting in improved Np extraction. The lower number of stages in the scrubbing section also reduced recycling and accumulation of Sr(II) between the extraction and scrubbing sections.

Finally, the TRU stripping section was modified to both simplify the set up in the hot cell and improve lanthanide decontamination. Calculations showed it would be possible to feed one stripping solution (containing 0.055 mol/L SO₃-Ph-BTP and 1 mol/L AHA) instead of the split stripping with two separate feeds into different stages (containing different concentrations of SO₃-Ph-BTP) as was used in the “Pu-active” test [31] whilst maintaining the efficient stripping of the actinides.

As 16 stages are not enough to cover the complete flow-sheet, the demonstration test was again divided into two parts to be run on consecutive days: 16 stages for extraction and scrubbing and 16 stages for back extraction. The respective flow-sheets are shown in Figure 6 (extract-scrub section) and Figure 12 (TRU back extraction/Ln re-extraction and Ln back extraction).

4.2 Hot test

The raffinate collected from the first cycle was conditioned before feeding to the extraction process. Conditioning involved dilution with HNO₃ by a factor of 1.8 to yield the target Pu feed concentration of 10 g/L (as used in the

surrogate test [31]) and to increase the HNO₃ concentration to 5.9 mol/L. 0.055 mol/L CDTA was added to suppress Zr and Pd extraction. The Np concentration was actually increased by adding Np-237 in order to ease the analysis.

4.2.1 Part 1, preparation of the loaded solvent

The flow-sheet for the first run, comprising extraction and scrubbing sections, is shown in Figure 6. The test was run for 6 h to attain steady state and a further 10 h to collect 300 mL of loaded solvent, sufficient for the subsequent TRU stripping run.

The major results were as follows (see also Figure 6 and Table 2): TRU and Ln were almost completely extracted to the organic phase; less than 0.1% of Np and approximately 0.01% each of Pu, Am and Ln were lost to the raffinate. The respective concentration profiles are shown in Figures 7 and 8. Other than TRU and Ln, the loaded organic phase also contained some Zr, Mo, Tc and Ru (as predicted from batch experiments [22]); other non-Ln fission products concentrations were in the sub-ppm range. The respective profiles are shown in Figures 9–11.

Pu, Am and Ln were very well extracted, as evident from the steep concentration profiles for stages 10–12 (see Figures 7 and 8). The flat profiles in stages 1–9 are most probably due to concentrations being below the limits of detection and/or contamination during sampling and analysis in the hot cell. The concentration profiles in the scrubbing section (stages 13–16) show that Pu, Am and Ln remained in the organic phase, as expected.

The Np concentration profile in the extraction section was less steep than the Pu and Am profiles. Since Np(VI) is readily extractable into the organic phase it is an indication of the presence of lesser extractable Np(V) even though the aqueous HNO₃ concentration in the extraction section was approximately 3.2 mol/L. Np also

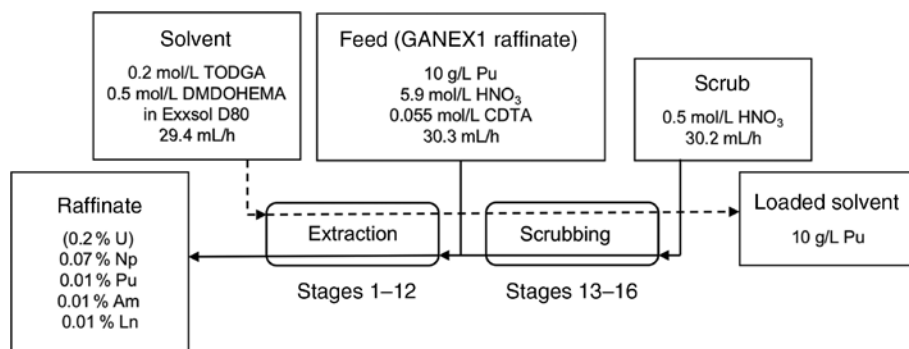


Figure 6: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction and scrubbing: flow-sheet with measured flow rates and recoveries.

Table 2: EURO-GANEX run, part 1, ICP-MS analysis of feed, raffinate and loaded solvent.

	Feed	Raffinate	Loaded solvent	% mass balance
Fe ^a	–	30 ^b	<LOD ^b	–
Sr ^a	13	3.9	<LOD	59
Zr	135	54	23	97
Mo	93	6.4	80	98
Tc	2.5 ^b (12)	0.02	2.4	95 ^b (19)
Ru	6 ^b (9.3)	2.1	2.2	105 ^b (68)
Rh	5.2	2.5	0.03	97
Pd	12	6 ^b (9.9)	0.2 ^b (1.0)	101 ^b (173)
Ag	3.5	2 ^b (0.4)	0.06	115 ^b (24)
Cd	2.6	1.1	0.5	106
Sn	1.1	0.4	0.6	127
Sb	0.24	0.07	0.2	130
Te	5.4	2.7	0.03	100
Cs	139	68	0.02	98
Ba	51	20	0.05	76
La	49	0.001	49	98
Ce	79	<LOD	83	102
Pr	44	<LOD	45	100
Nd	156	0.002	170	106
Sm	35	0.02	37	102
Eu	6.3	0.007	6.1	94
Gd	5.7	0.01	7.2	124
Tb	0.8	<LOD	0.8	99
Dy	1.2	<LOD	1.3	107
U	68	0.1	87	125
Np	97	0.03	88	88
Pu	10,200	0.04	10,200	98
Am	117	0.001	125	103
Cm	0.01	<LOD	0.02	230

^aFe and Sr did not attain steady state.

^bValues taken from analysis of contactor wells (feed, stage 12; raffinate, stage 1; loaded solvent, stage 16). Values from feed, raffinate and loaded solvent vessels given in parentheses. Concentrations in mg/L.

showed some accumulation in the scrubbing section where 0.5 mol/L HNO₃ is introduced as the scrub acid feed. It is well known that Np has a complex redox chemistry in HNO₃ [39] with the equilibrium between Np(V) and Np(VI) depending on nitric and nitrous acid concentrations (nitrous acid is a radiolysis product of HNO₃) [40]. Np(V) also disproportionates to Np(IV) and Np(VI) at high HNO₃ concentrations [39] and disproportionation is rapid in the organic phase [23]. The Np profile, therefore, reflects the changing Np oxidation state through the contactor bank as well as the differing extractabilities of the oxidation states (IV), (V) and (VI). Models of Np extraction have been developed for the analogous PUREX extract-scrub flowsheet that can be adapted to explain the behaviour of Np in the EURO-GANEX process [41–42]. However, in this test it was proven that

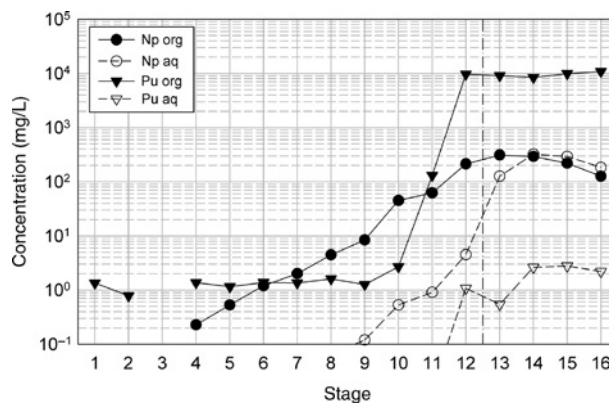


Figure 7: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction (stages 1–12) and scrubbing (stages 13–16): Np and Pu concentration profiles.

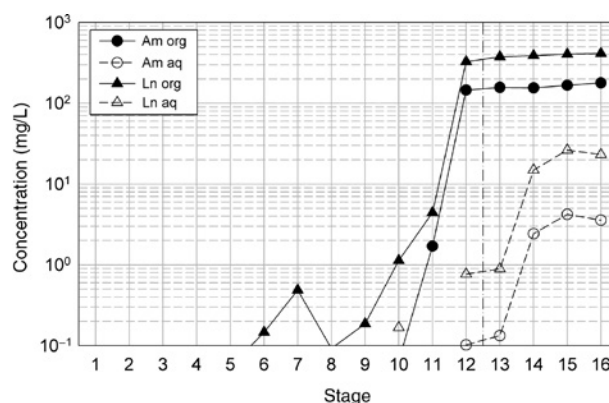


Figure 8: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction (stages 1–12) and scrubbing (stages 13–16): Am and total Ln (=La–Dy) concentration profiles.

Np reached a steady state value, where the feed input of Np to the scrub section balanced the organic output from stage 16, and that >99 % Np was routed with the organic phase in the extract-scrub section which is substantial improvement over the ‘cold’ test with a surrogate feed where ≈30 % was lost to the HA raffinate [31]. This can be attributed to the radiolytic generation of HNO₂ in the hot test that then catalysed the HNO₃ oxidation of Np(V) to Np(VI) and also the higher acidity of the feed that reduced the stability of Np(V).

Fe and Sr were extracted in the extraction section and both were very well back-extracted in the scrubbing section, leading to significant accumulation in the extraction section (Figure 9). This was to be expected from the respective distribution ratios, being >1 at the nitric acid concentration present in the extraction section and <1 in the scrubbing section [22]. The accumulation leads to increased concentrations and flatter extraction profiles across the extraction section. Fe and Sr were thereby

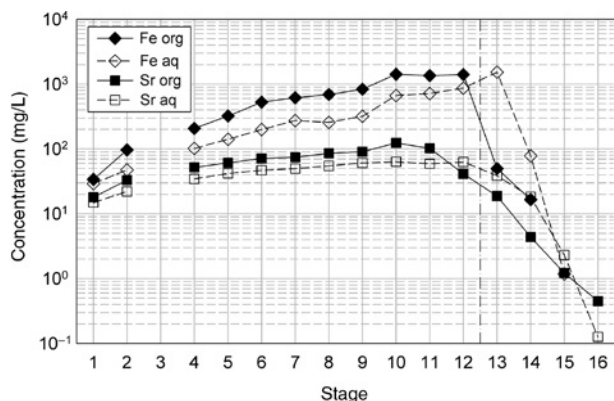


Figure 9: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction (stages 1–12) and scrubbing (stages 13–16): Fe and Sr concentration profiles.

routed into the raffinate with only minor losses to the Pu loaded organic phase. The profiles and mass balances indicate that steady state was not achieved for Fe and Sr.

Zr, Ru, Pd and Ag showed little extraction; the small fractions extracted were not scrubbed but stayed in the organic phase (Figure 10). The behaviour of Zr, Pd and Ag is explained by the effect of CDTA which was added to the feed solution and suppresses the extraction of these solutes [28]. CDTA was not added to the scrub solution: owing to the formation of stable organic species with very slow kinetics, back-extraction of Zr, Pd with CDTA is inefficient [28]. Hence, the fractions of Zr, Pd and Ag which were extracted in the extraction section were not back-extracted in the scrubbing section. Ruthenium is known to have a very complex behaviour with a range of species present in nitric acid and is difficult to decontaminate in the PUREX process [43]. Similar behaviour was observed in other processes using TODGA [44–45] or DMDOHEMA

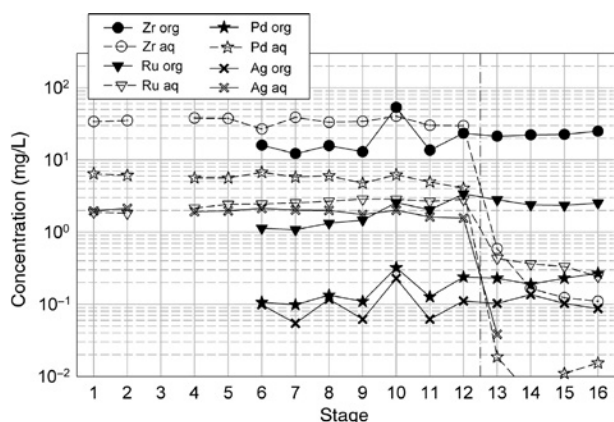


Figure 10: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction (stages 1–12) and scrubbing (stages 13–16): Zr, Ru, Pd and Ag concentration profiles.

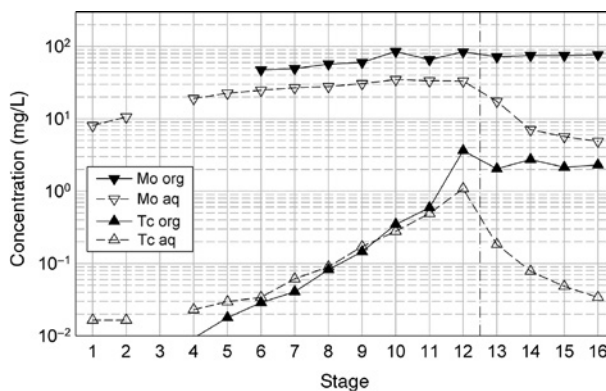


Figure 11: EURO-GANEX run, part 1 (preparation of loaded solvent), extraction (stages 1–12) and scrubbing (stages 13–16): Mo and Tc concentration profiles.

[46–47] and hence is suspected in the EURO-GANEX solvent system.

Mo and Tc concentration profiles are shown in Figure 11. Tc is most likely extracted as anionic pertechnetate and is thereby affected by nitrate competition (i.e. being less well extracted at higher nitric acid concentration). The profile indicates that Tc was well extracted in the extraction section and remained well extracted across the lower acidity scrub section. Molybdenum was also extracted in the extraction section and remained in the organic phase across the scrubbing section. Again, this behaviour is consistent with previously reported distribution ratios [22].

4.2.2 Part 2, TRU back extraction

The flow-sheet for the second day run is shown in Figure 12. TRU were stripped from the loaded solvent by contacting with a solution of $\text{SO}_3\text{-Ph-BTP}$ and AHA in 0.5 mol/L HNO_3 . Co-stripped Ln were re-extracted into fresh solvent. The solvent exiting the TRU stripping section, containing the Ln, was finally stripped by contacting with 0.01 mol/L HNO_3 . The test was run for 6 h to attain steady state.

Np, Pu (Figure 13) and Am (Figure 14) were well stripped from the loaded organic phase in the TRU stripping section (stages 7–12). Apparently, Pu was not further stripped in stages 10–12. This may be an effect of some background contamination. In any case, this represented only a very small part of initial organic Pu concentration. TRU concentration profiles in the Ln re-extraction section (stages 1–6) were flat, showing that they were not re-extracted and remained in aqueous phase as intended.

The total Ln concentration profile (Figure 14) shows that Ln were efficiently separated from TRU. The fraction

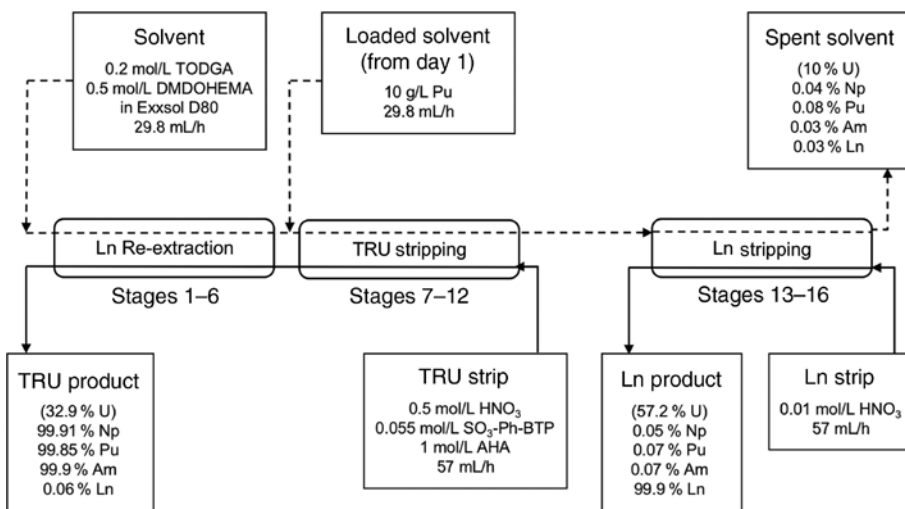


Figure 12: EURO-GANEX run part 2, TRU back extraction: flow-sheet with measured flow rates and recoveries (relative to concentrations in loaded solvent).

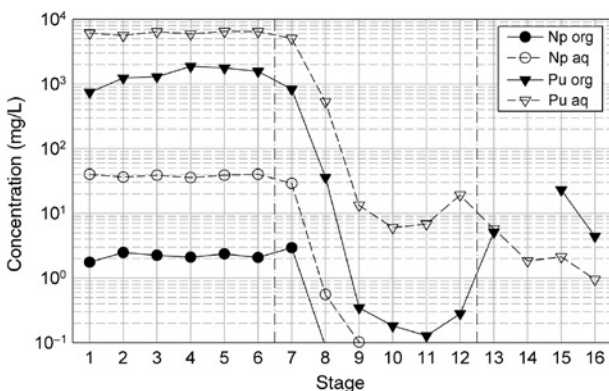


Figure 13: EURO-GANEX run, part 2 (stages 1–6, Ln re-extraction; stages 7–12, TRU stripping; stages 13–16, Ln stripping): Np and Pu concentration profiles.

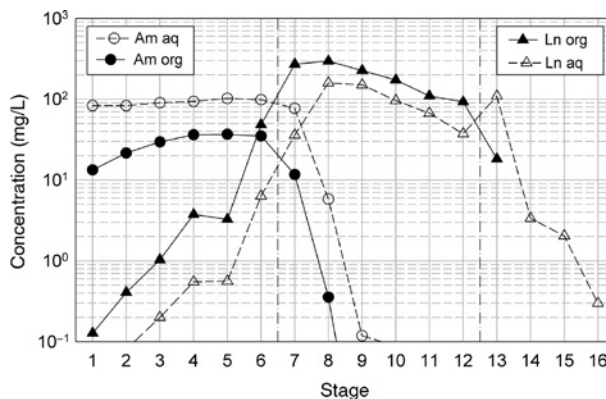


Figure 14: EURO-GANEX run, part 2 (stages 1–6, Ln re-extraction; stages 7–12, TRU stripping; stages 13–16, Ln stripping): Am and total Ln (=La–Dy) concentration profiles.

of Ln stripped from the organic phase together with the TRU in the TRU stripping section (stages 7–12) was re-extracted into fresh solvent in the Ln re-extraction section (stages 1–6). Thus, the losses of Ln to the TRU product solution were below 0.1%. Finally, Ln ions were efficiently stripped into 0.01 mol/L HNO₃ in the Ln stripping section (stages 13–16).

Further to Np, Pu, Am and Cm, the TRU product solution contained ≈ 15 mg/L U, ≈ 10 mg/L Zr, ≈ 30 mg/L Mo and ≈ 0.1 mg/L lanthanides. Analyses for other fission products were either below detection limit or inconsistent, which is understandable considering their rather low concentrations in the organic feed (see Table 2, column “loaded solvent”). The lanthanides product solution (which in an industrial situation would be vitrified together with the raffinate from the EURO-GANEX run part 1) contained

26 mg/L U, ≈ 4 mg/L Pu and ≈ 0.05 mg/L Am. Finally, the spent solvent (which in an industrial situation would be recycled to the extraction section) contained ≈ 4 mg/L U, ≈ 0.02 mg/L Np, ≈ 4 mg/L Pu, ≈ 0.02 mg/L Am, < 0.1 mg/L Ln, ≈ 5 mg/L Mo, < 1 mg/L Ru.

4.2.3 EURO-GANEX (GANEX second cycle) summary

A hot EURO-GANEX process has successfully been demonstrated. The solvent efficiently co-extracted 10 g/L Pu, together with Np, Am and lanthanides from the GANEX first cycle raffinate. Zr and Mo co-extraction was observed. Other fission products were well rejected. Using a solution containing SO₃-Ph-BTP and AHA, all TRU elements were efficiently stripped while lanthanides were retained in the

solvent. Co-extracted Zr and Mo were also stripped. Thus, in order to reduce Zr and Mo losses to the TRU product solution, their extraction must be suppressed or ways of scrubbing them from the loaded solvent must be devised.

5 Conclusions

A new separation process suitable for homogenous reprocessing of major (U, Pu) and minor (Np, Am, Cm) actinides in future closed fuel cycles has successfully been demonstrated with irradiated fast reactor fuel. This process involves two solvent extraction cycles, a first one to recover uranium and a second one to recover the TRU.

As expected from experience with an earlier test [17], U removal in the first cycle process proved to be highly efficient with less than 0.1% U routed to the aqueous raffinate containing the TRU actinide fraction. This was in good agreement with predictions from initial flow-sheet calculations. Pu, MA and Ln were not extracted and routed together with 97 % of the Np to the raffinate. Tc extraction was less well predicted. Compared to the earlier test, this hot test has extended experience with the GANEX first cycle by reprocessing fast reactor fuel with a much higher plutonium concentration and by running the test in short residence time centrifugal contactors.

TRU were recovered in the second cycle process with high efficiency (99.9%), together with only 0.06 % of the lanthanides inventory and the major fraction of Zr and Mo.

The sum of the TRU fractions lost to the first cycle solvent, the second cycle raffinate, second cycle lanthanide product and second cycle solvent are 3.3 % (Np), 0.26 % (Pu) and 0.11 % (Am), i. e. overall decontamination factors of $DF_{Np} = 30$, $DF_{Pu} = 380$ and $DF_{Am} = 910$. The TRU product decontamination factors for U and lanthanides are $DF_U = 3300$ and $DF_{Ln} = 1700$, respectively.

The EURO-GANEX process has thus been successfully demonstrated with high plutonium content irradiated fast reactor fuel (10 g/L Pu in the HA feed) and in centrifugal contactors for the first time. Improved results using a simplified flowsheet were obtained compared to the previously reported test using a surrogate feed [31].

6 Outlook

Despite the successful hot demonstration of the EURO-GANEX process, ongoing investigations aim at process optimisation. One direction of research is simplifying the solvent formulation. While DMDOHEMA is

required to ensure a sufficient plutonium loading capacity, its presence gives rise to the co-extraction of molybdenum. An improved solvent has been developed, comprising 0.5 mol/L *N,N,N',N'*-tetra-*n*-decyl-2,4-dimethyl-3-oxapentane diamide in *n*-dodecane [48]. This solvent has sufficient plutonium loading capacity (>30 g/L at 5 mol/L HNO₃) and significantly lower distribution ratios for some fission products and has the potential to replace the current EURO-GANEX solvent. Further investigations address the replacement of the sulfur containing stripping agent, SO₃-Ph-BTP, with a CHON [49] compound such as a hydrophilic 2,6-bis-triazolyl-pyridine [50–51].

7 Annex – Experimental

7.1 Chemicals

DEHiBA and DMDOHEMA were synthesised by Pharmasynthèse (France), TODGA was synthesised by Technocomm (UK). Diluents used were TPH (Novasep, France) and Exxsol D80 (ExxonMobil). SO₃-Ph-BTP was synthesised as described in references [29, 52]. All other chemicals used were from Merck (Germany) or Sigma-Aldrich (Germany).

7.2 Centrifugal contactor setup

The centrifugal contactor setup was installed in a hot cell. It consisted of 16 BXP 012 contactors (12 mm diameter) from Rousselet-Robatel (France). Piston pumps were used for feeding solutions. For further details see Ref. [53].

7.3 Analytics

At the end of a test, the system, i. e. pumps and centrifugal contactors, were simultaneously shut down. The liquids inside the contactor wells were emptied and centrifuged before the organic and the aqueous phases were separately collected and sampled. Organic samples were initially back-extracted using 0.1 mol/L HNO₃ with an organic to aqueous ratio of 100, i. e. 0.1 mL sample in 10 mL dilute HNO₃, yielding a dilution factor of 100. Further dilutions were done in 1 mol/L HNO₃. All aqueous samples were directly diluted into 1 mol/L HNO₃. The metal ion concentrations were determined by ICP-MS analysis (Thermo Fisher ELEMENT 2). Each sample was analysed with three dilution factors, i. e. 10³, 10⁴ and 10⁶. The limit of detection is in the range of 0.001 mg/L.

Acknowledgement: Financial support for this research was provided by the European Commission via the following projects: ACSEPT (contract N° FP7-CP-2007-211267), SACSESS (contract N° FP7-Fission-2012-323282) and GENIORS (Horizon 2020 grant agreement N° 755171).

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