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Assessment of applications of PTD in i-SANEX and EUROGANEX processes

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Summary

The present Deliverable collects the studies carried out, so far, within GENIORS on the Assessment of applications of PTD in i-SANEX and EUROGANEX processes. The results obtained are collected and divided according to the different partner.

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CONTENT

ABSTRACT

The present Deliverable collects the studies carried out, so far, within GENIORS on the Assessment of applications of PTD in i-SANEX and EUROGANEX processes. The results obtained are collected and divided according to the different partner.

INTRODUCTION

PTD-based stripping solvent, consisting of 0.08M PTD in 0.44 M HNO_3, has been widely investigated, especially by POLIMI, during the past European Joint Research projects dedicated to Minor Actinides partitioning and proved to be a promising candidate for the industrial implementation. In particular, the high MA selectivity has been demonstrated by batch extraction tests performed both at POLIMI and FZJ labs with a simulated aqueous feed (Ln, FPs, ^{241}Am and ^{152}Eu as tracers) and a feed comprising other TRU (^{239}Pu(IV), ^{237}Np(V-VI), ^{244}Cm(III)) at CEA facilities [1] [2]. Moreover, the complexation of Am(III), Pu(IV), Nd(III) and Eu(III) with PTD was studied by UV-Vis and ESI-MS techniques at POLIMI and at CEA. Further confirmation about PTD selectivity for MA was achieved by TRLFS experiments on Cm(III) and Eu(III) carried out at KIT [3]. The outstanding hydrolytic and radiolytic stability of PTD (*see* also Deliverable 2.2) was demonstrated by batch solvent extraction tests, HPLC-MS, FT-Raman and NMR analyses performed on irradiated and aged solutions [1] [4]. Finally, a single-stage centrifugal contactor test was performed at FZJ in 2015 with a synthetic HAR aqueous feed demonstrating the PTD applicability to such kind of industrial equipment [2].

SYNTHESIS OF PTD

(UNIPR: A. Casnati, A. Rastelli, F. Sansone, L. Baldini)

The UNIPR partner, was in charge to synthesize the pyridine-2,6-bis(triazolyl propanol) ligand, also named **PyTriDiol** or, shortly, **PTD**, used at POLIMI to carry out all the experimental activity reported in this Deliverable. The synthesis starts with the commercially available 2,6-dibromopyridine **1** which was coupled under Sonogashira conditions with trimethylsilyl acetylene to afford compound **2**. The latter compound was deprotected to 2,6-diethynyl pyridine **3** which was clicked with 3-azido propanol **4** under Huisgen cycloaddition conditions and using a microwave oven. This synthesis is currently carried out on a 2-3 gram scale and work should be done in the future to scale-up the preparation and especially purification of the intermediates and final compound.

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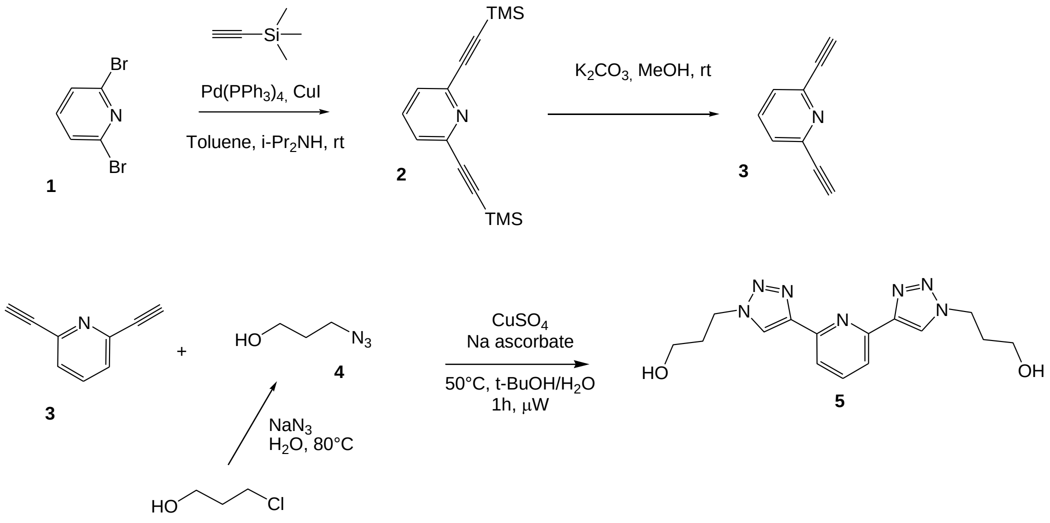

Scheme 1: Synthesis of PTD ligand.

PTD LOADING CAPABILITY

(POLIMI: E. Macerata, E. Mossini, M. Mariani, A. Ossola, M. Giola)

To date, PTD stripping performances have been assessed only at room temperature and with aqueous solutions with a TRU in trace amounts. However, the study of PTD behaviour in conditions closer to the process ones is a fundamental requirement for a possible future industrial implementation. Within GENIORS project, in order to assess the application of the PTD-based stripping solvent in the *i*-SANEX and EURO-GANEX processes, studies on the temperature dependence of the stripping performances have been performed at POLIMI, and, thanks to an abroad research period grant won within the GENIORS project, experiments on the PTD loading capability have been carried out within a collaboration between the Laboratories of Radiochemistry and Radiation Chemistry of POLIMI and Processes Department at CEA in Marcoule.

TEMPERATURE DEPENDENCE OF PTD STRIPPING PERFORMANCES

In a potential TRU/Ln separation process the temperature may exceed 30°C. Therefore, thermodynamic studies were carried out with PTD solutions, in order to obtain information about system performance in real process conditions. For this purpose, solvent extraction tests were performed at different controlled temperatures from 10 to 50°C. The results are reported in Figure 1 and Table A.1 in Annex A. A solution of 0.2 M TODGA in kerosene + 5 vol.% 1-octanol was loaded with trace amounts of trivalent ^{241}Am, ^{244}Cm, and ^{152}Eu from a 3 M nitric acid feed, afterwards scrubbed with 0.5 M nitric acid and finally employed in the stripping tests carried out at different temperatures. However, in the case of PTD, also the temperature effects on TODGA behaviour must be taken into account. For this reason, other stripping tests at different temperatures were performed by contacting loaded TODGA organic phases with 0.44 M HNO_3, namely the stripping solution without PTD ligand. The results of this second series of experiments are shown in Figure 2 and Table A.2 in Annex A.

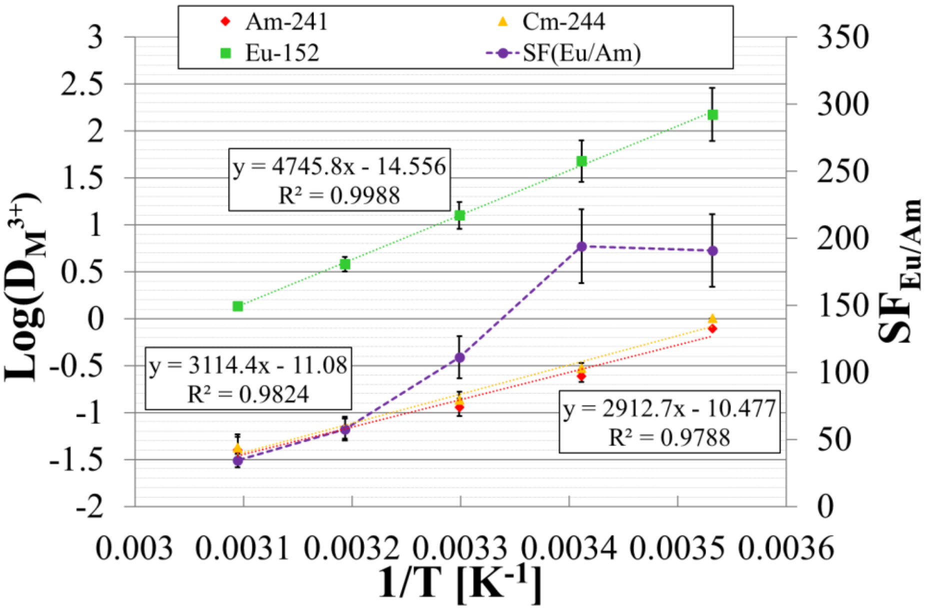

Figure 1 Logarithm of distribution ratios of ^{241}Am, ^{244}Cm and ^{152}Eu and $SF_{Eu/Am}$ as a function of 1/T for TODGA-PTD system. Organic phase: loaded and scrubbed 0.2 M TODGA in kerosene + 5 vol.% 1-octanol. Aqueous phase: 0.08 M PTD in 0.44 M HNO_3 solutions

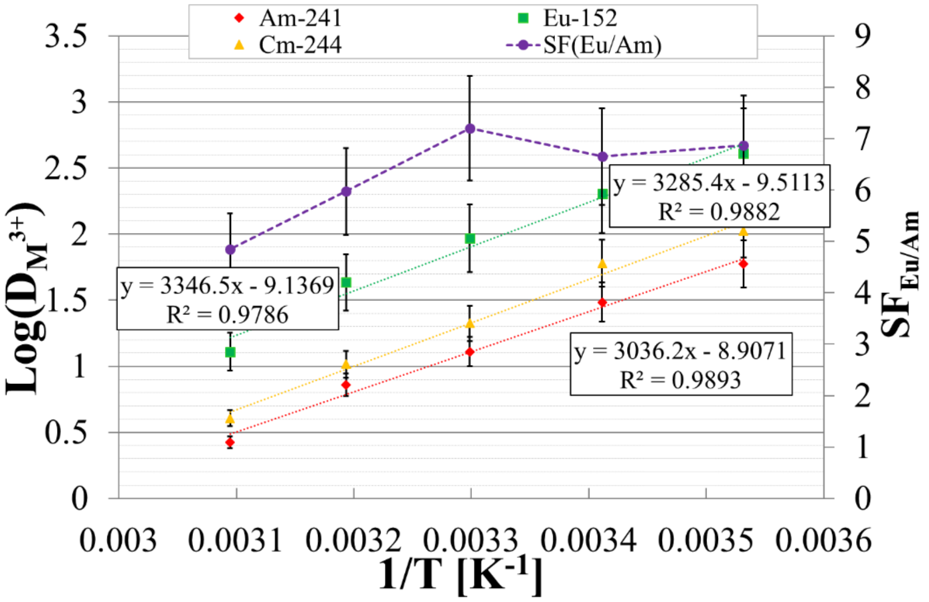

Figure 2 Logarithm of distribution ratios of ^{241}Am, ^{244}Cm and ^{152}Eu and $SF_{Eu/Am}$ as a function of 1/T for TODGA-HNO_3 system. Organic phase: loaded and scrubbed 0.2 M TODGA in kerosene + 5 vol.% 1-octanol. Aqueous phase: 0.44 M HNO_3 solutions

As observable from Figure 1 and Figure 2, since extraction decreases with increasing temperature, an exothermic nature of the extraction equilibria can be inferred. Moreover, since the slopes of *Log(D) vs. 1/T* plot in Figure 2 are comparable, it can be inferred that TODGA chelating efficiency towards ^{241}Am, ^{244}Cm and ^{152}Eu equally decreases with temperature. Instead, from the slopes of *Log(D) vs. 1/T* plot of Figure 1, a higher sensitivity to temperature for ^{152}Eu with respect to ^{241}Am and ^{244}Cm stripping can be deduced. In particular, PTD stripping efficiency towards ^{241}Am and ^{244}Cm increases of the same order of magnitude with increasing temperature, as in the above-mentioned case of TODGA alone (^{241}Am and ^{244}Cm slopes in the Figures are comparable), suggesting a negligible temperature effect on MA complexation by PTD. However, since ^{152}Eu release increases to a greater

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extent with the temperature in presence of PTD, the MA/Ln selectivity decreases from 190 at 10°C to 34 at 50°C. This aspect has to be more thoroughly investigated in view of process application, in particular to assess the behaviour of the most back-extracted Ln (*i.e.* La and Ce) at process temperatures (30-40°C).

Unfortunately, due to the complexity of the system under study, it was not possible to compute thermodynamic data for PTD, namely disregarding the TODGA contribution. Different kind of analytic techniques, such as TRLFS, UV-Vis or calorimetry, should be exploited.

^{241}Am LOADING EXPERIMENTS WITH PTD

In order to demonstrate the applicability of the novel PTD based extracting system to the *i*-SANEX process, its ^{241}Am loading capability has to be proved. To this aim, the 3 M nitric acid aqueous feed to be decontaminated was loaded with 0.001 M ^{241}Am (around 0.24 g/L), 0.02 M of Y and Ln (from lanthanum to gadolinium) and ^{152}Eu as a radiotracer. These concentrations correspond to activities of approximately 31 GBq/L and 0.14 GBq/L for ^{241}Am and ^{152}Eu, respectively. The so obtained aqueous feed was used to load the organic phase (0.2 M TODGA in kerosene + 5 vol.% 1-octanol) that was afterwards scrubbed with 0.5 M nitric acid and used to perform the stripping tests. Ligand performances were evaluated by executing stripping tests with fresh, aged (for around 1 month) and gamma irradiated (up to 200 kGy with 2.5 kGy/h dose rate) solutions of 0.08 M PTD in 0.44 M HNO_3, at the controlled temperature of 25°C. Stripping tests with only 0.44 M HNO_3 were performed as references. The acidity of all the phases involved in the extraction, scrubbing and stripping tests was checked by potentiometric titration with NaOH. As shown in Table 1, a slight decrease of H^+ concentration in the extraction step was highlighted, coherently with nitric acid extraction by the organic phase. This in turn led to an increase of H^+ concentration after the scrubbing step, due to nitric acid release by the organic phase. Afterwards, no remarkable variations were highlighted in the subsequent stripping steps.

Table 1 Comparison between initial and final (equilibrium) acidity of extraction, scrubbing and stripping aqueous phases; (*ii*) fresh, (*iii*) aged, (*iv*) irradiated at 100 kGy and (*v*) at 200 kGy. As reference: (*i*) fresh 0.44 M HNO_3.

	Initial	**Final (equilibrium)**
$[H^+]_{extraction}$, M	3.130 ± 0.282	3.061 ± 0.053
$[H^+]_{scrubbing}$, M	0.489 ± 0.007	0.679 ± 0.023
$[H^+]_{stripping}$, M	0.442 ± 0.005	0.523 ± 0.028 (*i*) 0.459 ± 0.024 (*ii*) 0.485 ± 0.031 (*iii*) 0.446 ± 0.040 (*iv*) 0.439 ± 0.027 (*v*)

The concentration of stable Ln was not measured after the tests due to the unavailability of an ICP-MS suitable for the manipulation of radioactive samples. In any case, the loading of the initial organic phase even with Ln allowed to better mimic the real waste composition. Remarkably, as appreciable from Figure 3 and Table B.1 in Annex B, PTD is still able to selectively separate macro-concentrations of americium from europium. In fact, by comparing the results of tests *i* and *ii* (Figure 3, Table B.1), the addition of just 0.08 M PTD is capable of substantially reducing D_{Am} from approximately 10.5 to about 0.1, while D_{Eu} remains far above 1. No variation from the stripping efficiency and MA selectivity obtained with spiked tests was highlighted [1]. As expectable from previous traced experiments, ^{241}Am and ^{152}Eu distribution ratios resulted to be almost unaltered towards hydrolysis and radiolysis with separation factors between ^{152}Eu and ^{241}Am around 200 in all the conditions tested [1].

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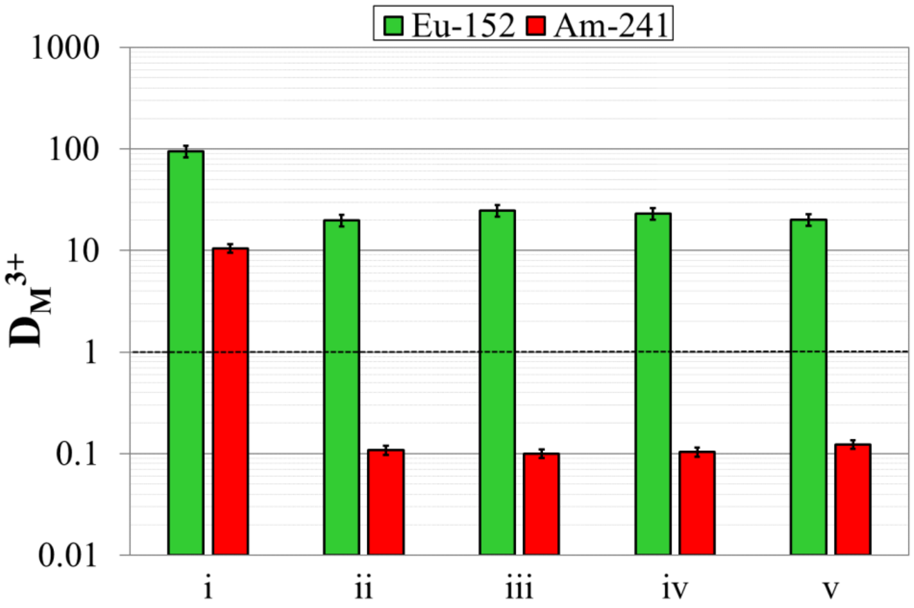

Figure 3 Distribution ratios of trivalent ^{241}Am and ^{152}Eu obtained by contacting loaded and scrubbed TODGA solutions with the following 0.08 M PTD in 0.44 M HNO_3 stripping solutions: (*ii*) fresh, (*iii*) aged, (*iv*) irradiated at 100 kGy and (*v*) at 200 kGy. As reference: (*i*) fresh 0.44 M HNO_3

The ^{241}Am decontamination factors of the loaded and scrubbed organic phase as a function of the stripping phase composition are reported in Table 2. They were calculated as the ratio between the activity of radionuclides in the organic phase before and after the stripping stage. As appreciable, in the case of nitric acid alone, no decontamination was accomplished since the metal ions remained complexed by TODGA in the organic phase. Conversely, the decontamination increases of 10 times just after the addition of 0.08 M PTD. Moreover, it remains almost constant even with aged and irradiated PTD solutions.

Table 2 ^{241}Am decontamination factors of the organic phase as a function of the stripping phase composition

	Decontamination factor
i	1.1 ± 0.1
ii	10.2 ± 1.0
iii	11.0 ± 1.1
iv	10.6 ± 1.1
v	9.1 ± 0.9

^{241}Am AND ^{239}Pu LOADING EXPERIMENTS WITH PTD

Concerning the application in the EURO-GANEX process, PTD loading capability towards americium and plutonium was investigated with an aqueous feed that is 3 M nitric acid solution containing 0.001 M ^{241}Am(III) (around 0.24 g/L), 0.015 M ^{239}Pu(IV) (around 3.8 g/L), 0.02 M of Y and Ln (from lanthanum to gadolinium) and ^{152}Eu(III) as radiotracer. These concentrations correspond to activities of approximately 33 GBq/L, 8.6 GBq/L and 0.21 GBq/L for ^{241}Am, ^{239}Pu and ^{152}Eu, respectively. The lipophilic ligand DMDOHEMA was added to TODGA in the extraction step since it is already known that it is able to increase TODGA loading capability for plutonium and prevent precipitate formation during the scrubbing step carried out at 0.5 M HNO_3 concentration of the aqueous phase [5]. Afterwards, stripping tests were performed only with fresh 0.08 M PTD solutions and also with the addition of 1 M AHA, already used in addition to the SO_3-Ph-BTP since it is known to be able to enhance ^{239}Pu(IV) extraction [6]. Stripping tests with only 0.44 M nitric acid and 1 M AHA in 0.44 M nitric acid were performed as references and the temperature was kept constant at 25°C for all the stripping tests. The acidity of all the phases involved in the extraction, scrubbing and stripping tests was checked with potentiometric titration with NaOH. The concentration of stable Ln was not measured after the tests due to the unavailability of an ICP-MS suitable for the manipulation of radioactive samples. In any case, the loading of the initial organic phase even with Ln allowed to better mimic the real waste composition.

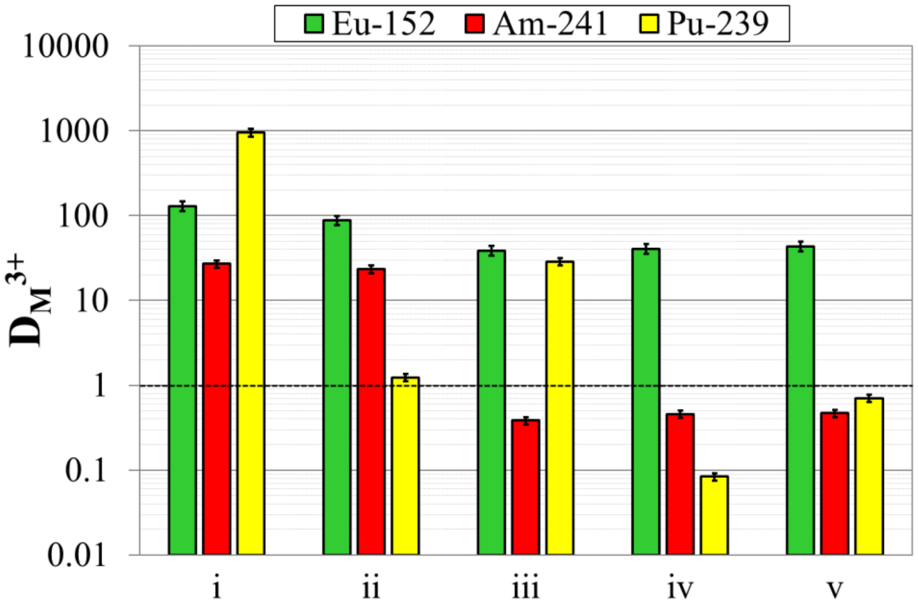

Figure 4 Distribution ratios of trivalent ^{241}Am and ^{152}Eu and tetravalent ^{239}Pu obtained by contacting loaded and scrubbed TODGA solutions with the following stripping solutions: (*i*) 0.44 M HNO_3, (*ii*) 1 M AHA in 0.44 M HNO_3, (*iii*) 0.08 M PTD in 0.44 M HNO_3, (*iv*) 0.08 M PTD + 1 M AHA in 0.44 M HNO_3 and (*v*) 0.08 M PTD + 0.08 M AHA in 0.44 M HNO_3

As observable from Figure 4 and Table C.1 in Annex C, analogously to SO_3-Ph-BTP ligand [6], the hydrophilic complexing agent alone (test *iii*) is not able to satisfactorily strip tetravalent ^{239}Pu, while the synergistic effect of 0.08 M PTD + 1 M AHA (test *iv*) allows the effective separation of macro-concentration of ^{241}Am(III) and ^{239}Pu(VI) from ^{152}Eu(III). Even the employment of an AHA concentration equal to that of PTD (test *v*) resulted to be effective in such separation. Interestingly, in the case of ligand equimolar concentrations, closer ^{241}Am(III) and ^{239}Pu(IV) distribution ratios were obtained. This would represent an advantage in the future optimization of the number of stripping stages.

Nevertheless, it should be noted that even if PTD is present at the same concentration as in the ^{241}Am loading tests, ^{241}Am and ^{152}Eu D-values reported in Figure 4 are considerably higher with respect to those showed in Figure 3, and the Eu(III)/Am(III) separation factors are reduced to approximately 100 (see Table C.2 in Annex C). The same conclusion can be drawn from the ^{241}Am(III) and ^{239}Pu(IV) decontamination factors of the loaded and scrubbed organic phases reported in Table 3.

Table 3 ^{241}Am and ^{239}Pu decontamination factors of the organic phase as function of the stripping phase composition

	Decontamination factor	
	^{241}Am(III)	**^{239}Pu(IV)**
i	1.0 ± 0.1	1.0 ± 0.1
ii	1.0 ± 0.1	1.8 ± 0.2
iii	3.6 ± 0.4	1.0 ± 0.1
iv	3.2 ± 0.3	12.9 ± 1.3
v	3.1 ± 0.3	2.4 ± 0.2

The Am(III) decontamination factor for stripping *iii* more than halved with respect to that reported in Table 2. Besides, as already observed from the extraction data, the comparison between ^{239}Pu(IV) decontamination factors of stripping *ii* and *iv* (1.8 vs. 12.9) confirms that the addition of 0.08 M PTD in stripping *iv* has a synergistic effect on ^{239}Pu(IV) extraction. Finally, the reduction of AHA concentration from 1 M to 0.08 M led to a considerably reduction of Pu(IV) decontamination factor.

The behaviour observed towards ^{241}Am(III) and ^{152}Eu(III) extraction can be explained considering that the presence of DMDOHEMA increases the nitric acid concentration of the stripping phases, thus changing the system equilibria. In particular, the presence of DMDOHEMA in the extraction step led to a higher extraction of nitric acid into the organic phase. This in turn causes the scrubbing with 0.5 M HNO_3 to be not enough to adjust the phase acidity for the subsequent stripping tests. Acidity data reported in Table 4 allowed to confirm these hypotheses. In fact, while the final H^+ concentration after the extraction step seems not so much influenced by DMDOHEMA, taking into account the greater error associated, almost double concentration was found after the scrubbing test. Accordingly, higher H^+ concentration was highlighted in the stripping tests, particularly in presence of 1 M AHA. These acidity data and the consequent ^{241}Am(III) and ^{152}Eu(III) extraction are still under study.

Table 4 Comparison between initial and final (equilibrium) acidity of extraction, scrubbing and stripping aqueous phases; (*i*) 0.44 M HNO_3, (*ii*) 1 M AHA in 0.44 M HNO_3, (*iii*) 0.08 M PTD in 0.44 M HNO_3, (*iv*) 0.08 M PTD + 1 M AHA in 0.44 M HNO_3.

	Initial	Final (equilibrium)
$[H^+]_{\text{extraction}}$, M	3.052 ± 0.146	3.074 ± 0.486
$[H^+]_{\text{scrubbing}}$, M	0.490 ± 0.007	0.902 ± 0.026
$[H^+]_{\text{stripping } i \text{ and } iii}$, M	0.442 ± 0.005	0.471 ± 0.101 (*i*) 0.509 ± 0.101 (*iii*)
$[H^+]_{\text{stripping } ii \text{ and } iv}$, M	0.847 ± 0.100	0.669 ± 0.101 (*ii*) 0.610 ± 0.101 (*iv*)

Consequently, in order to achieve the best organic phase decontamination in view of the industrial application, additional studies will be necessary for the optimization of scrubbing and stripping solvent formulation (*i.e.* acidity, PTD and AHA concentration).

Interestingly, after the stripping experiments, a change of the colour of the PTD + AHA solution (*iv* and *v*) was observed over time from dark brown to bright green. This colour change phenomenon was supposed to be originated by the progressive reduction of plutonium oxidation state from Pu(IV) to Pu(III). According to literature, AHA is known to be a good reductant for Pu(IV) and Pu(VI). In particular, Pu(IV) reduction is consistent with a mechanism in which Pu(IV) ions are complexed by AHA while some free hydroxamic acid undergoes hydrolysis. Afterwards, at a certain point, close to a 1:1 Pu(IV)/hydroxamic acid ratio, some Pu(IV) is released from the complex and its reduction with AHA takes place. [7] Coherently, it is reasonable to associate the different induction period, in which no Pu(III) is formed, to the lower Pu/AHA ratio. To support this hypothesis, the solution with lower AHA concentration (*v*) manifested a faster kinetics of colour change, while those containing only AHA (*ii*) and without AHA (*iii*) did not change colour, probably because of the too low concentration of Pu(IV) extracted by AHA and PTD alone, respectively. The low concentration of Pu extracted by PTD alone was further confirmed by UV-Vis spectrophotometric measurements. Furthermore, in order to verify the aforementioned hypothesis of colour change associated to Pu(IV) reduction, an UV-Vis kinetics experiment was performed with stripping solution *iv*. UV-Vis spectra were collected initially every 10 minutes, then every 30 minutes and finally every 2 hours, until no more changes were observed. As shown in Figure 5, the signals of Pu(IV) clearly decreased over time, while those of Pu(III) increased, thus confirming the supposed Pu(IV) reduction.

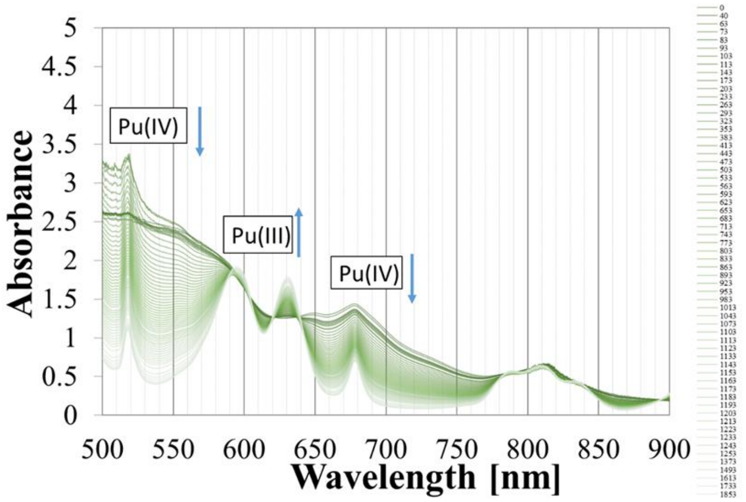

Figure 5 Pu(IV) → Pu(III) oxidation state evolution, UV-Vis spectra of the kinetics experiments.

Whether this phenomenon represents a problem in view of an industrial application, it still to be verified. In fact, in the above described tests, considering that they were performed in batch, the change of colour solutions was observed after the end of the liquid-liquid extraction tests. However, since on industrial scale these processes are carried out in multi-stage counter-current separation equipment, *i.e.* the organic phase decontamination is achieved over several stages, it should be verified if the change of Pu oxidation state during the process itself does not influence the overall system performance. Moreover, further and deepened investigation should be carried out to better clarify the role of AHA and PTD in Pu(IV) reduction phenomenon.

FLOW-SHEET CALCULATIONS WITH PTD

(KIT: A. Geist)

In preparation of a PTD *i*-SANEX process demonstration to be performed at JÜLICH, a flow-sheet for the An(III)-Ln(III) separation section was calculated. This section consists of two sub-sections, one for stripping Am(III) and Cm(III) from the loaded organic phase (0.2 mol/L TODGA + 5% 1-octanol in TPH) using an aqueous solution containing PTD, one for re-extracting co-stripped Ln(III), see Figure 6.

Calculations were performed using the *SX Process* code [8, 9, 10]. Distribution data from batch and single-stage centrifugal contactor experiments were used [11]. Since no single-stage results for the re-extraction of Ln(III) was available, stage efficiency for this sub-section was estimated based on results from the *i*-SANEX process run using SO_3-Ph-BTP [12]. Recoveries were calculated for Am(III), La(III) (which has distribution ratios closest to those of Am) and Eu(III). The proposed flow-sheet is shown in Figure 6.

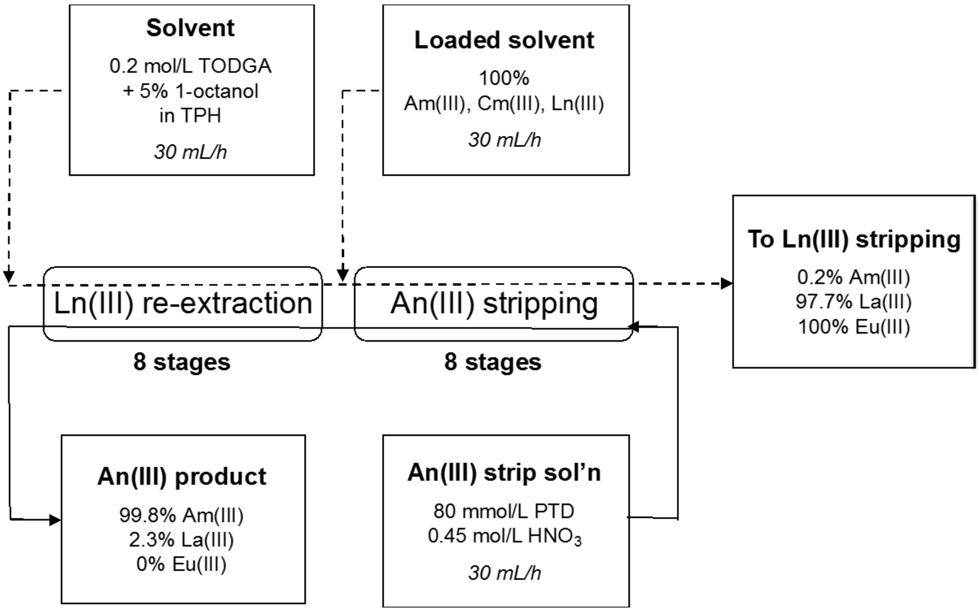

Figure 6. Calculated flow-sheet for the An(III)-Ln(III) separation section. Recoveries calculated using the *SX Process* code.

In total, 16 stages are used for the An(III)-Ln(III) separation section, which is the number of centrifugal contactors available at JÜLICH. The stages are evenly distributed between the two sub-sections. All flow-rates are 30 mL/h. This is lower than the 40 mL/h flow-rates applied for the SO_3-Ph-BTP *i*-SANEX process test [11].

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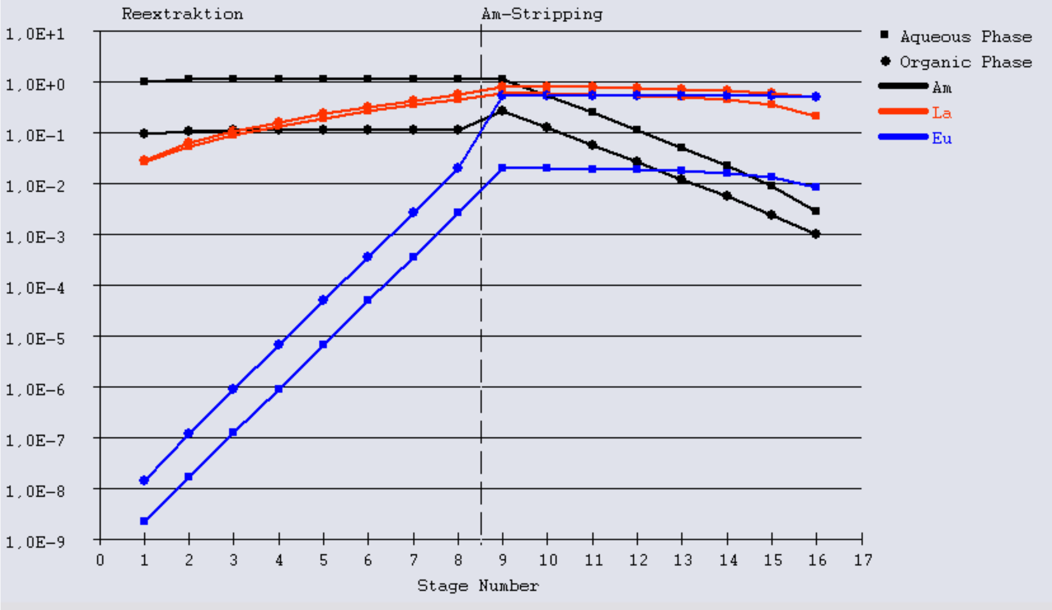

Figure 7. Stage profiles for the An(III)-Ln(III) separation section calculated using the *SX Process* code.

The calculations indicate that 99.8% of Am(III) should be recovered in the An(III) product solution, together with 2.3% of La(III) and practically zero Eu(III). It is worth noticing that Am(III) and Eu(III) recoveries are essentially insensitive to the respective stage efficiencies in the Ln(III) re-extraction section. La(III) recovery is only slightly affected: with a La(III) stage efficiency of 100% in the Ln(III) re-extraction section the La(III) loss to the An(III) product solution is calculated to 1.6%, down from 2.3%. The calculated stage profiles are shown in Figure 7.

CONCLUSION

The stripping behaviour of PTD, the current reference ligand for *i*-SANEX process, has been fully investigated by POLIMI acquiring information about the temperature dependence and the loading capacity. The studies performed have highlighted a decreasing trend of Eu(III)/Am(III) separation factor with temperature. This will require in further investigations, primarily regarding the behaviour of the lighter lanthanides(III) (La, Ce) at process temperature. Both ^{241}Am(III) and ^{239}Pu(IV) loading capabilities of PTD have been successfully demonstrated, leading to the first demonstration of PTD applicability to both *i*-SANEX and EURO-GANEX processes. The results were so promising that the system composed by PTD + AHA + TODGA and DMDOHEMA, prior due optimization, was selected as new EURO-GANEX reference system by the European scientific community of GENIORS project subject to future flowsheet tests. In fact, the replacement of the sulfonated SO_3-Ph-BTP ligand with the CHON compliant PTD ligand represents a huge breakthrough in the fulfilment of the process requirements.

In preparation of a PTD *i*-SANEX process demonstration to be performed at JÜLICH, a flow-sheet for the An(III)-Ln(III) separation section was calculated at KIT. Taking into account a 16-stage contactor and flow-rates are 30 mL/h, it was calculated that 99.8% of the Am(III) could be recovered together with 2.3% of La(III) while no Eu(III) is stripped.

All these data augurs well for the possible application of PTD in processes where the separation of An(III) from Ln(III) is required for the treatment of spent nuclear fuels.

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ANNEXES

ANNEX A: TEMPERATURE DEPENDENCE OF PTD STRIPPING PERFORMANCES

Table A.1 Distribution ratios of ^{241}Am, ^{244}Cm and ^{152}Eu and $SF_{Eu/Am}$ as a function of T for TODGA-PTD system.

Temperature, K	D_{Am}	D_{Cm}	D_{Eu}	$SF_{Eu/Am}$
283.15	0.79 ± 0.08	1.01 ± 0.101	150.21 ± 15.02	190.72 ± 26.97
293.15	0.25 ± 0.02	0.30 ± 0.030	47.55 ± 4.75	194.05 ± 27.44
303.15	0.11 ± 0.01	0.14 ± 0.014	12.64 ± 1.26	111.14 ± 15.72
313.15	0.07 ± 0.01	0.07 ± 0.007	3.80 ± 0.38	57.46 ± 8.13
323.15	0.04 ± 0.004	0.04 ± 0.004	1.36 ± 0.14	34.15 ± 4.83

Table A.2 Distribution ratios of ^{241}Am, ^{244}Cm and ^{152}Eu and $SF_{Eu/Am}$ as a function of T for TODGA-HNO_3 system.

Temperature, K	D_{Am}	D_{Cm}	D_{Eu}	$SF_{Eu/Am}$
283.15	59.49 ± 5.95	105.60 ± 10.56	408.63 ± 40.86	6.87 ± 0.97
293.15	30.47 ± 3.05	60.32 ± 6.03	202.69 ± 20.27	6.65 ± 0.94
303.15	12.91 ± 1.29	21.09 ± 2.11	92.96 ± 9.30	7.20 ± 1.01
313.15	7.22 ± 0.72	10.35 ± 1.03	43.12 ± 4.31	5.98 ± 0.85
323.15	2.65 ± 0.27	4.04 ± 0.40	12.88 ± 1.29	4.85 ± 0.68

ANNEX B: ^{241}Am LOADING EXPERIMENTS WITH PTD

Table B.1 Distribution ratios of trivalent ^{241}Am and ^{152}Eu obtained by contacting loaded and scrubbed TODGA solutions with the following 0.08 M PTD in 0.44 M HNO_3 stripping solutions: (*ii*) fresh, (*iii*) aged, (*iv*) irradiated at 100 kGy and (*v*) at 200 kGy. As reference: (*i*) fresh 0.44 M HNO_3

Aqueous stripping solution	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
Fresh 0.44 M HNO_3	10.663 ± 1.06	95.102 ± 9.51	8.92 ± 1.26
Fresh PTD solution	0.109 ± 0.01	19.854 ± 1.98	182.88 ± 25.86
Aged PTD solution	0.098 ± 0.009	25.701 ± 2.57	261.54 ± 36.98
PTD solution irradiated at 100 kGy	0.101 ± 0.01	24.201 ± 2.42	240.17 ± 33.96
PTD solution irradiated at 200 kGy	0.120 ± 0.01	18.601 ± 1.86	155.34 ± 21.97

ANNEX C: ^{241}Am AND ^{239}Pu LOADING EXPERIMENTS WITH PTD

Table C.1 Distribution ratios of trivalent ^{241}Am and ^{152}Eu and tetravalent ^{239}Pu obtained by contacting loaded and scrubbed TODGA solutions with the following stripping solutions: (*i*) 0.44 M HNO_3, (*ii*) 1 M AHA in 0.44 M HNO_3, (*iii*) 0.08 M PTD in 0.44 M HNO_3, (*iv*) 0.08 M PTD + 1 M AHA in 0.44 M HNO_3 and (*v*) 0.08 M PTD + 0.08 M AHA in 0.44 M HNO_3

Aqueous stripping solution	D_{Am}	D_{Pu}	D_{Eu}
Fresh 0.44 M HNO_3	29.705 ± 2.97	1127 ± 105	135.827 ± 13.58
1 M AHA solution	22.938 ± 2.01	1.31 ± 0.13	89.379 ± 8.94
0.08 M PTD solution	0.385 ± 0.04	28.61 ± 2.86	40.293 ± 4.03
0.08 M PTD + 1 M AHA solution	0.440 ± 0.04	0.08 ± 0.008	39.497 ± 3.95
0.08 M PTD + 0.08 M AHA solution	0.448 ± 0.04	0.598 ± 0.059	38.944 ± 3.89

Table C.2 Separation factors obtained by contacting loaded and scrubbed TODGA solutions with the following stripping solutions: (*i*) 0.44 M HNO_3, (*ii*) 1 M AHA in 0.44 M HNO_3, (*iii*) 0.08 M PTD in 0.44 M HNO_3, (*iv*) 0.08 M PTD + 1 M AHA in 0.44 M HNO_3 and (*v*) 0.08 M PTD + 0.08 M AHA in 0.44 M HNO_3

Aqueous stripping solution	$SF_{Eu/Am}$	$SF_{Eu/Pu}$	$SF_{Pu/Am}$
Fresh 0.44 M HNO_3	4.57 ± 0.65	0.12 ± 0.01	37.95 ± 4.95
1 M AHA solution	3.90 ± 0.55	68.09 ± 9.12	0.06 ± 0.005
0.08 M PTD solution	104.54 ± 14.32	1.41 ± 0.15	74.22 ± 10.01
0.08 M PTD + 1 M AHA solution	89.84 ± 11.69	495 ± 55	0.18 ± 0.01
0.08 M PTD + 0.08 M AHA solution	86.98 ± 10.97	65.13 ± 8.89	1.34 ± 0.13