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Development of a selective americium separation process using TPAEN as a water-soluble stripping agent

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Abstract – Recycling americium from spent fuels is an important option considered for the future nuclear cycle. The PUREX solvent extraction process can be used to separate U and Pu from a dissolution solution of spent fuel in nitric acid. Then in a second step americium should be separated from fission products and especially lanthanides but also from curium. For this purpose, a new liquid-liquid extraction process is under development using TODGA as an extractant in the organic phase and TPAEN as a selective Am stripping agent in the aqueous phase. With this promising system it is possible to co-extract Am, Cm and lanthanides at high acidity and then selectively strip americium from the loaded organic phase at pH around 1 with TPAEN. Batch data were acquired to evaluate best conditions to develop a liquid-liquid extraction flowsheet and the effect of several parameters on Am/Cm was evaluated like concentration of ligand, cations, temperature, etc.

I. INTRODUCTION

In the future nuclear fuel cycle, one promising strategy considered by few countries for the management of high activity and long-lived final waste is a closed cycle supporting partitioning and transmutation of actinides. In the framework of the 2006 French Waste Management Act, several strategies were defined to totally or partially recycle minor actinides (An) from spent nuclear fuels in Generation IV systems.^[1] After recycling U, Pu and Np, the remaining long term radiotoxicity is mainly due to minor actinides, essentially americium and curium.^[2] It will take 10,000 years for wastes to reach the natural uranium radiotoxicity level instead of few centuries if americium and curium are removed. More recently, a focus was put on recycling Am alone, leaving Cm with vitrified fission products. Indeed, after 100 years, americium is the main contributor to heat emissions in final spent fuel wastes. Removing Am would allow to significantly reduce the surface necessary for a geological repository of vitrified waste. Moreover, Cm reprocessing would be difficult to implement due to its very significant neutron emissions which would require very thick shielding at any step of the fuel cycle. In this context, a liquid-liquid extraction process should be developed to recover Am alone from a PUREX raffinate (a nitric acid solution of spent fuel dissolution liquor already cleared from U, Np and Pu).

The EXAm process is under development at the CEA to perform this specific separation.^[3-4] A mixture of a malonamide (DMDOHEMA) and a dialkylphosphoric acid (HDEHP) in TPH is used as solvent to extract Am and light lanthanides (Ln) while Cm stays into the aqueous phase with heavier Ln and other fission products (FP). The complexing agent TEDGA (a diglycolamide) is introduced in the acidic aqueous phase to improve the Cm/Am selectivity. The separation factor between Cm and Am is 2.6 and additional steps are necessary to strip molybdenum and then separate Am from light lanthanides which are not separated in the first Cm/Am separation step.

In order to simplify and improve the process, a new complexing agent was selected and studied in the framework of the SACSESS European Project (TPAEN, Figure 1). This ligand can be used as a selective stripping agent to back-extract Am from a loaded organic phase selectively from Cm but also from lanthanides.^[5-7] The extractant TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) could be used in the solvent to co-extract Am, Cm and lanthanides at high acidity from a PUREX raffinate before stripping selectively Am. With this promising extractant/ligand combination (TODGA/TPAEN), Am can be selectively stripped while Cm and Ln remain extracted in the organic phase with a separation factor (SF) between Cm and Am around 3.5 - 4 at pH 1.

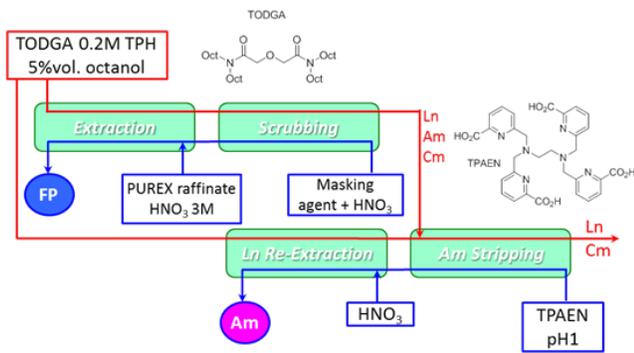


Fig. 1. Simplified flowsheet of the TODGA-TPAEN process and structures of TPAEN and TODGA.

Additional batch data were necessary to evaluate best conditions to develop a liquid-liquid separation flowsheet.

I. PRELIMINARY DATA ON LN SERIES

The TPAEN ligand can be solubilized until 5-20 mM in water (the exact solubility is significantly dependant on the batch of TPAEN and the way it was synthesized/purified).

In the following experiments, the solvent consists of TODGA 0.2M in TPH with 5%_{vol.} *n*-octanol. Octanol is added as a phase modifier to prevent from third phase formation. This organic phase is loaded with lanthanides and actinide cations at 1M HNO₃. Then Am is stripped using a solution of TPAEN at pH close to 1.

Distribution ratios of Ln and An cations at the stripping step with HNO₃ 0.1M (no ligand) or a TPAEN solution at 10 mM and pH 1 are reported in Figure 2 with lanthanide concentrations in the initial loaded organic phase in Table 1.

TABLE I

Concentrations of cations loaded in the initial organic phase

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Y	total
[] mmol/L	3.8	0.35	0.29	1.5	8.3	2.1	1.7	1.6	20

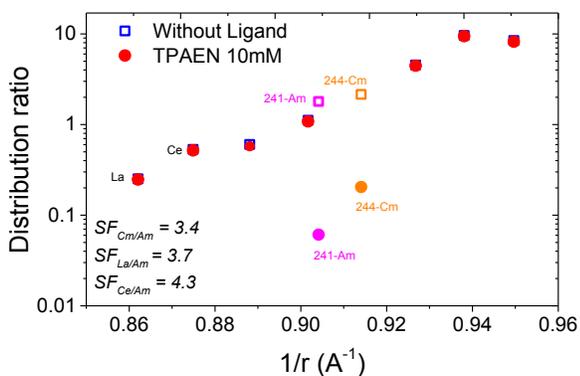


Fig. 2. Am stripping experiments with a solution of TPAEN 10 mM at pH_{initial} = 1 (25°C, 30 min. shaking, pH_{eq.} = 0.8). Organic phase: TODGA 0.2M with *n*-octanol 5%_{vol.} in TPH

preliminarily loaded with lanthanides (20 mM), ²⁴¹Am, ²⁴⁴Cm and ¹⁵²Eu (radiotracers) at 1M HNO₃.

The trend along the lanthanides series confirms higher extraction of heavy Ln by the TODGA extractant. The introduction of TPAEN has no significant impact on Ln distribution ratios at this acidity (pH_{eq.} = 0.8). Nevertheless, the distribution ratio of Am drops from 2.1 to 0.2. The system shows selectivity between Cm and Am with a SF_{Cm/Am} close to 3.4. Nevertheless, the separation of Am from light lanthanides is also a limiting factor. Indeed, a SF_{La/Am} of 3.7 is obtained in those conditions.

II. EFFECT OF LIGAND CONCENTRATION

The influence of TPAEN concentration on Cm/Am selectivity was studied with concentrations of TPAEN varying from 1 to 10 mM. Lanthanides were analysed by ICP-AES and the same experiment was reproduced in glove-box to obtain ²⁴¹Am and ²⁴⁴Cm data. The organic phases were also loaded with ¹⁵²Eu radiotracer. Distribution ratios and separation factors are reported in Figure 3.

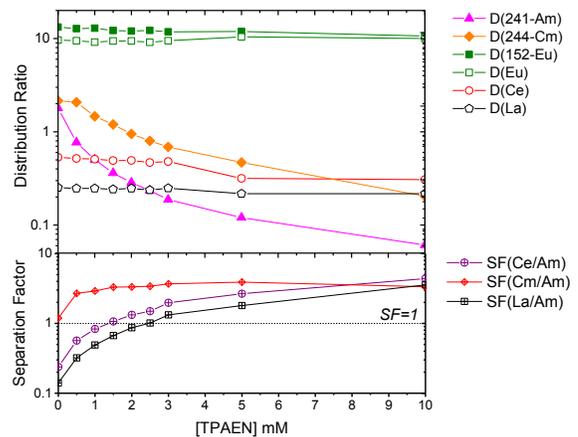


Fig. 3. Am stripping experiments with solutions of TPAEN (1 to 10 mM) at pH_{initial} = 1 (25°C, 30 min. shaking, pH_{eq.} = 0.8). Organic phase: TODGA 0.2M with *n*-octanol 5%_{vol.} in TPH preliminarily loaded with lanthanides (22 mM), ²⁴¹Am, ²⁴⁴Cm and ¹⁵²Eu (radiotracers) at 1M HNO₃.

The results show that at lower concentration of TPAEN and high organic Ln concentration (22 mM), the light lanthanides (La and Ce) are not correctly separated from americium in these conditions. As observed in Figure 3, the concentration of TPAEN has no effect on Ln distribution ratios but a straight effect on Am and Cm extraction. Indeed, the Ce/Am separation factor can be improved at higher ligand concentration (at 10 mM the Ce/Am separation factor is around 4.3). The Cm/Am separation factor increases when the concentration of TPAEN gets higher and tends to reach a plateau at around 3 mM of TPAEN with a maximum separation factor of 3.9

in these conditions. Since TPAEN solutions are not very stable at pH 1 depending on the TPAEN batch, it is preferred to maintained the concentration of TPAEN at around 2.5 mM to avoid precipitation of the stripping solution. This experiment was performed at very high loading of cations in the organic phase (22 mM) and it was then important to study the influence of lanthanides cations on the separation.

III. EFFECT OF CATIONS LOADING

During the back-extraction with TPAEN, several stages of separation will be necessary to reach a high decontamination factor of Am versus light lanthanides and curium. Depending on the flowsheet and the type of UOx fuel reprocessed, the total concentration of lanthanides arriving in the Am stripping battery should be around 10-20 mM. In the following experiment we studied the effect of Ln concentration on Am separation factors (versus Ln and Cm). The results (D ans SF) are reported in Figure 4. While distribution ratios of Ln are not significantly influenced by the total concentration of cations, Am and Cm are less stripped in the aqueous phase, potentially due to a saturation effect of the TPAEN ligand by Ln.

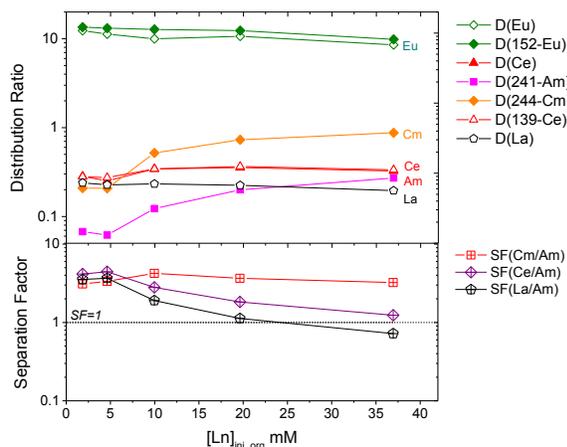


Fig. 4. Am stripping experiments with a solution of 2.5 mM TPAEN at $\text{pH}_{\text{initial}} = 1$ (25°C , 30 min. shaking, $\text{pH}_{\text{eq.}} = 0.8$). Organic phase: TODGA 0.2M with n-octanol 5%vol. in TPH preliminarily loaded with lanthanides (from 1 to 37 mM), ^{241}Am , ^{244}Cm , ^{139}Ce and ^{152}Eu (radiotracers) at 1M HNO_3 .

It was already observed before that the separation between La and Am is possible if the concentration of TPAEN is higher than 3 mM (with 22 mM of Ln). Nevertheless, this new experiment shows that La/Am selectivity is also strongly correlated to the total concentration of lanthanides in the organic phase. Indeed, the $\text{SF}_{\text{La/Am}}$ is higher than 3 when $[\text{Ln}]_{\text{ini, org.}} < 10\text{mM}$ at 2.5 mM TPAEN. Hence it should be possible to separate efficiently Am from light lanthanides with 2.5 mM of TPAEN if the concentration of Ln in the organic phase

coming from the “Extraction-Scrubbing” section is lower than 10 mM.

IV. AMERICIUM MACRO-CONCENTRATIONS EXPERIMENT

In order to evaluate the loading capacity of the complexing molecule TPAEN and determine $\text{SF}_{\text{Cm/Am}}$ and $\text{SF}_{\text{Ln/Am}}$ with nominal concentrations of Am (representative of a PUREX raffinate), macroconcentrations of ^{241}Am were loaded in the TODGA/octanol solvent and then stripped with solutions of TPAEN 2.5 mM at pH 1 and 1.75. The TODGA solvent was loaded with lanthanides and variable concentrations of ^{241}Am : $2 \cdot 10^{-2}$ to 1.5 mM. As observed in Figure 5, an increase of the acidity (from pH 1.1 to 0.7 at equilibrium) reduces the efficiency of Am back extraction. The distribution ratio of Am only slightly increases when the initial concentration of ^{241}Am in the organic phase gets higher. Even at pH 0.7 and with 1.5 mM in the initial organic phase, Am is correctly stripped by TPAEN without any precipitation in the aqueous phase, even few days after the experiment. With a distribution ratio of 0.15 (at pH 1.1 and 1.5 mM of Am), it means that 1.3 mM of ^{241}Am is complexed by 2.5 mM of TPAEN, which is very promising for further process development with this molecule.

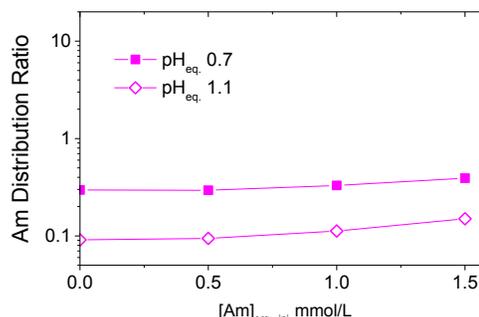


Fig. 5. Am stripping experiments with a solution of 2.5 mM TPAEN at $\text{pH}_{\text{initial}} = 1$ or 1.75 (25°C , 30 min. shaking, $\text{pH}_{\text{eq.}} = 0.7$ and 1.1). Organic phase: TODGA 0.2M with n-octanol 5%vol. in TPH preliminarily loaded with ^{241}Am (from 2 μM to 1.5 mM) and lanthanides (24mM) at 1M HNO_3 .

Additional data on Cm and lanthanides distribution ratios are in progress in these conditions (with macroconcentrations of Am) in order to determine the feasibility of this process starting from a genuine PUREX raffinate (Hot Tests).

V. BATCH KINETICS

In order to evaluate time necessary to reach equilibrium during Am stripping, an aqueous phase containing 2.5 mM of TPAEN at pH 1 was contacted to a loaded TODGA/octanol solvent in a thermostated cell with

mechanical stirring. To determine the distribution ratios as a function of time, aliquots of the mixing emulsion were sampled and both phases were analyzed by ICP-AES. The same experiment was run in glove box with traces amounts of ^{241}Am , ^{244}Cm , ^{152}Eu and ^{139}Ce . Figure 6 shows the variation of the distribution ratios of La, Ce, Am and Cm over time.

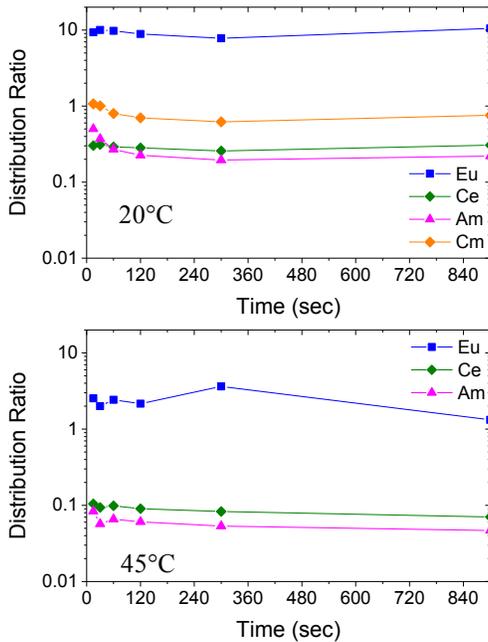


Fig. 6: Distribution ratios of selected lanthanides, Am and Cm versus the mixing time at 20 (top) and 45°C (bottom). Am stripping with a solution of 1.9 mM TPAEN at $\text{pH}_{\text{initial}} = 1.2$ ($\text{pH}_{\text{eq.}} = 1.0$). Organic phase: TODGA 0.2M with n-octanol 5%vol. in TPH preliminarily loaded with lanthanides (15 mM), ^{241}Am , ^{244}Cm , ^{139}Ce and ^{152}Eu (radiotracers) at 0.5M HNO_3

From Figure 6 it can be seen that all lanthanides quickly reach distribution ratios close to their equilibrium values, even after 15 seconds of stirring. Am and Cm are slower compared to the lanthanides. Around 2 minutes are necessary to reach equilibrium. But it is possible to reach equilibrium faster for Am and Cm by increasing the temperature. As seen in Figure 6, at 45°C, equilibrium is reached within 30 seconds for Am.

VI. EFFECT OF TEMPERATURE

To provide additional thermodynamic data for the process modelling, extraction experiments were carried out at different temperatures (from 8°C to 44°C). The stripping was carried out using a 2.5 mM TPAEN solution in diluted HNO_3 at pH 1 with only traces amounts of Am, Cm, Ce and Eu. Figure 7 shows the Van t'Hoff plot ($\ln(D)=f(1/T)$) of Am, Cm, Ce and Eu.

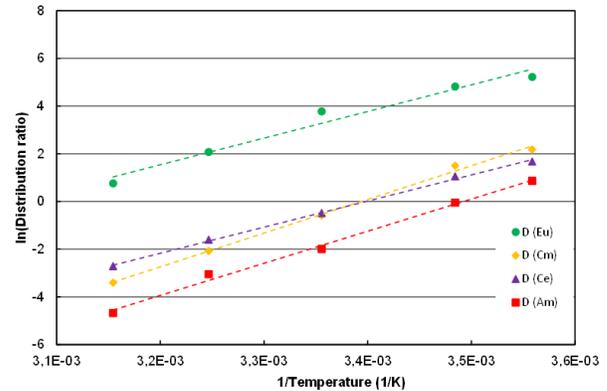


Fig. 7: Van t'Hoff plot of Am, Cm, Eu and Ce; Conditions: Org: 0.2 mol/L TODGA in TPH 5 vol.-% n-octanol loaded by traces amounts of ^{241}Am , ^{244}Cm , ^{152}Eu and ^{139}Ce . Aq: 2.5 mM TPAEN in aqueous HNO_3 at $\text{pH}_{\text{eq.}} 0.7$; different temperatures between 8 and 44 °C; mixing time = 30 min.

The stripping of Am, Cm, Ce and Eu by TPAEN ligand from TODGA-octanol/TPH is exothermic. A very strong impact of the temperature on the distribution ratios is clearly visible for all elements tested. Moreover, this experiment shows that the Ce/Am separation factor depends on the temperature and increases from 2 (8°C) to 7 (44°C) while the Cm/Am separation is not significantly affected (Table II). This increase of Ce/Am selectivity with the temperature is very interesting and heating could be used in the process to enhance light Ln/Am separation during the stripping step.

TABLE II

Distribution ratios of Am and separation factors as a function of temperature during Am stripping with 2.5 mM TPAEN

T (°C)	D(Am)	SF _{Cm/Am}	SF _{Ce/Am}
8	2.5	3.5	2.2
14	0.95	4.7	3.0
25	0.14	4.0	4.7
44	0.009	3.6	7.1

IV. CONCLUSIONS

TPAEN ligand can be used in a solvent extraction process in order to separate Am alone from a PUREX raffinate (and leave Cm and lanthanides with fission products). In such a process, the solvent could be made of TODGA 0.2M in TPH with 5%vol. octanol. The influence of several parameters ([Ln], [TPAEN], pH, temperature) was studied by performing batch extraction tests at the laboratory scale. TPAEN could be used in the aqueous phase at 2.5mM and pH 1 to strip Am from a loaded organic phase with selectivity towards Cm ($\text{SF}_{\text{Cm/Am}} = 3.5-4$). While the separation between Cm and Am seems to be maintained in various conditions, the separation between light lanthanides (and especially La and Ce) is lost if the

concentration of lanthanides in the system gets too high. The La/Am separation factor is highly sensitive to ligand and cation concentrations but also to temperature. As a consequence, the flowsheet will have to be precisely adjusted to allow the recovery of an americium raffinate with high decontamination versus Cm AND light Ln cations.

Those experimental data should allow to develop a chemical model which will be implemented in the PAREX simulation code to propose a flowsheet for the TODGA-TPAEN process.

Besides these extraction data, spectroscopic and thermodynamic studies are in progress to provide detailed knowledge about the chemical species formed in the aqueous phase with TPAEN (UV-visible, TRLIFS, ESI-MS, microcalorimetry and EXAFS).

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NOMENCLATURE

D: Distribution Ratio
DMDOHEMA : *N,N'*-dimethyl-*N,N'*-dioctylhexyloxyethyl malonamide
EXAm: Extraction of Americium process
FP : Fission Products
HDEHP : Di-2-ethylhexylphosphoric acid
Ln: Lanthanides
SF: Separation Factor
TEDGA : *N,N,N',N'*-tetraethyldiglycolamide
TODGA: *N,N,N',N'*-teraoctyldiglycolamide
TPAEN: *N,N,N',N'*-tetrakis[(6-carboxypyridin-2-yl)methyl]-ethylenediamine
TPH: Hydrogenated TetraPropylene

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