

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Modeling and flowsheet design of an Am separation process using TODGA and H₄TPAEN

V. Vanel^{*a}, C. Marie^a, P. Kaufholz^b, M. Montuir^a, N. Boubals^a, A. Wilden^b, G. Modolo^b,
A. Geist^c, C. Sorel^a

^a CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, Bagnols-sur-Cèze, F-30207, France

^b Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Nuclear Waste Management and Reactor Safety, D-52428, Germany

^c Karlsruher Institut für Technologie (KIT), Institut für Nukleare Entsorgung (INE), Karlsruhe, Germany

Abstract

Recycling americium from spent fuels is an important consideration for the future nuclear fuel cycle, as americium is the main contributor to the long-term radiotoxicity and heat power of the final waste, after separation of uranium and plutonium using the PUREX process. The separation of americium alone from a PUREX raffinate can be achieved by co-extracting lanthanide (Ln(III)) and actinide (An(III)) cations into an organic phase containing the diglycolamide extractant TODGA, and then stripping Am(III) with selectivity towards Cm(III) and lanthanides. The water soluble ligand H₄TPAEN was tested to selectively strip Am from a loaded organic phase.

Based on experimental data obtained by Jülich, NNL and CEA laboratories since 2013, a phenomenological model has been developed to simulate the behavior of americium, curium and lanthanides during their extraction by TODGA and their complexation by H₄TPAEN (complex stoichiometry, extraction and complexation constants, kinetics). The model was gradually implemented in the PAREX code and helped to narrow down the best operating conditions. Thus, the following modifications of initial operating conditions were proposed:

- An increase in the concentration of TPAEN as much as the solubility limit allows.
- An improvement of the lanthanide scrubbing from the americium flow by adding nitrates to the aqueous phase.

A qualification of the model was begun by comparing on the one hand constants determined with the model to those measured experimentally, and on the other hand, simulation results and experimental data on new independent batch experiments.

^{*} Corresponding author. Tel.: +33-4-66-39-78-66.
E-mail address: vincent.vanel@cea.fr

A first sensitivity analysis identified which parameter has the most dominant effect on the process. A flowsheet was proposed for a spiked test in centrifugal contactors performed with a simulated PUREX raffinate with trace amounts of Am and Cm. If the feasibility of the process is confirmed, the results of this test will be used to consolidate the model and to design a flowsheet for a test on a genuine PUREX raffinate. This work is the result of collaborations in the framework of the SACSESS European Project.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: TPAEN; Am separation; extraction and complexation modelling; PAREX code

1. Objectives of the EuroEXAm process for the Am stripping step

The EuroEXAm process aims at recovering Am alone from a PUREX raffinate. This process was developed within the SACSESS project in a 3-year collaboration between the CEA, Jülich and NNL. The TODGA extractant at 0.2 M + 5%vol. *n*-octanol in TPH is used to co-extract trivalent lanthanides and actinides from highly concentrated nitric acid solutions^[1]. Americium (III) is stripped selectively from Cm(III) and Ln(III) into an aqueous phase containing H₄TPAEN at around pH 1. The Am extraction step had already been developed and demonstrated by the Jülich team within the i-SANEX process. The loaded solvent is used as feed solution for the Am stripping step.

This article summarizes the work undertaken to design the flowsheet of the Am stripping step in preparation for demonstration tests at Jülich and ITU:

- Acquisition of batch experimental data for the model,
- Development of the model, flowsheet design and sensitivity analysis.

Nomenclature

TODGA	<i>N,N,N',N'</i> -tetraoctyldiglycoamide
H ₄ TPAEN	<i>N,N,N',N'</i> -tetrakis[(6-carboxypyridin-2-yl)methyl]-ethylenediamine

During the Am extraction step, significant amounts of curium and lanthanides are extracted with americium (more than 99%)^[1]. The challenge of the Am stripping step is to combine the following performances:

- An Am recovery rate as high as possible, typically over 99%.
- A decontamination factor between Am(III) and Cm(III) typically over 500, in order to limit the radiation protection necessary when producing AmO₂ pellets.
- A mass percentage of lanthanides in americium below 5%, as Ln are neutron-absorbing elements negatively impacting reactor operations. With the TODGA-TPAEN chemical system, the light lanthanides, especially lanthanum, are the least separated elements. A DF(Am/La) greater than 200 was suggested.

Therefore, a study in theoretical stages (without any kinetics effect) was performed to have a first estimation of the number of stages necessary to jointly achieve a high Am recovery rate and a sufficient purification from curium and lanthanides. The number of theoretical stages was evaluated depending on:

- The Am recovery rate.
- The separation factor between americium and contaminants (SF(La/Am) ~ 2-2.5, SF(Cm/Am) ~ 5).

To recover more than 99% of americium with a DF(Am/La) around 200, a minimum of between 20 and 30 stages is needed. However for demonstration tests, only 16 stages of centrifugal extractors are available both in Jülich and ITU. It was considered that tests should demonstrate the capacity of the process to decontaminate the Am flow. If this objective was reached, it would be possible to extrapolate the process to recover more americium with a greater number of stages. Thus, for demonstration tests, an Am recovery rate of 60-70% was targeted.

2. Batch experimental data acquisition

Since the beginning of the SACSESS project in 2013, batch experimental data have been acquired in order to better understand the effects of the following parameters on distribution ratios and separation factors: H_4TPAEN and lanthanide concentrations, H^+ and nitrate concentrations, kinetics and effects of temperature. The main experimental results are summarized below.

2.1. Separation between americium and contaminants (curium and lanthanides)

H_4TPAEN makes separation between Am and Cm, as well as Am and light lanthanides, possible. For both concentrations of lanthanides (6.9 mM and 17.7 mM), the most difficult separation to perform is between americium and light lanthanides especially lanthanum. Heavy lanthanides and yttrium will remain in the organic phase. The separation factors are from the lowest to the highest (see figure 1):

$$\text{La} < \text{Ce} \sim \text{Pr} < \text{Cm} \sim \text{Nd} \ll \text{Sm} < \text{Gd} \sim \text{Eu} \ll \text{Y}$$

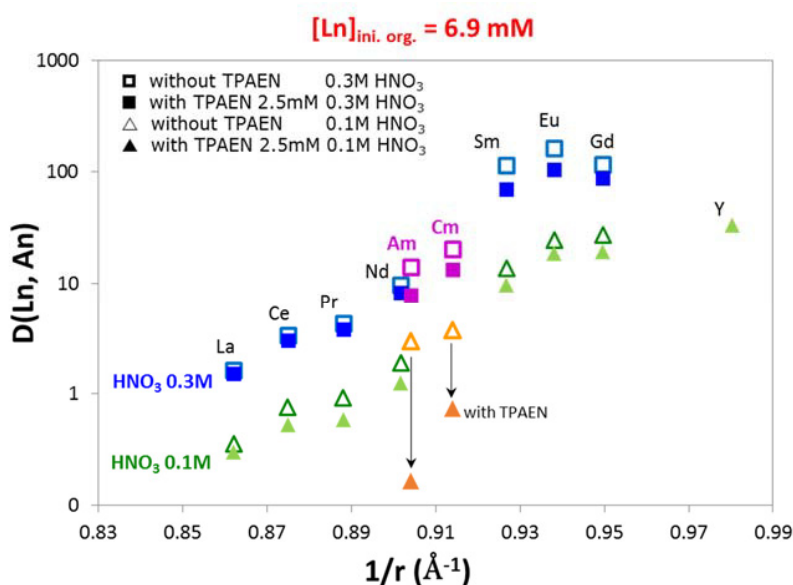


Fig. 1: Distribution ratios of cations depending on pH and the H_4TPAEN and lanthanide concentrations

When acidity increases, the complexing power of H_4TPAEN is significantly reduced and it is no longer possible to separate Am from curium and light lanthanides. The operating domain for the acidity of the aqueous phase appears to be very limited, around pH 1.

2.2. Improving the separation factor between americium and contaminants

Two series of experiments were carried out to observe the effect of the concentration of H_4TPAEN and lanthanides on distribution ratios. Neither parameter has a significant effect on the behavior of lanthanides. Nevertheless, the distribution ratios of actinides decrease when the concentration of H_4TPAEN increases or when the amount of lanthanides in the loaded solvent is lower. Consequently, there are two different ways to improve separation factors between Am and lanthanides (see figure 2):

- Increase the concentration of H_4TPAEN to the solubility limit (5 mM). With the help of the modelling, a concentration of H_4TPAEN of 4 mM was chosen as an optimum (initial concentration of 2.5 mM H_4TPAEN).

- Limit the concentration of lanthanides in the loaded solvent. It is helpful to dilute the loaded solvent with the fresh solvent from the Ln scrubbing step. It would also be useful to limit the extraction of lanthanides at the previous extraction step. Nevertheless, there is a risk of losing americium in the extraction raffinate.

In addition, the separation factor between americium and curium remains nearly constant whatever the concentration of H_4 TPAEN and lanthanides (except, of course, if there is no H_4 TPAEN).

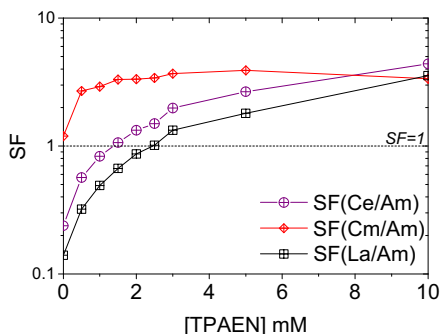


Fig. 2: Separation factors between Am and Cm, Ce, La depending on the TPAEN and lanthanide concentrations

2.3. Effect of nitrate concentration

During the first flowsheet design, it appeared difficult to efficiently scrub lanthanides from the Am production flow. Thus, nitrates were added to promote cation extraction by TODGA, in order to increase the distribution ratios of actinides and lanthanides. As lanthanides are poorly complexed by H_4 TPAEN, the addition of nitrates enhanced the separation factor between americium and lanthanides.

Different salts were tested (sodium nitrate, ammonium nitrate, lithium nitrate and hydroxylamine nitrate). $NaNO_3$ was found to be the best compromise between separation performances and chemical properties, and was chosen for the flowsheet design.

2.4. Kinetics

At 25°C, a kinetic effect was observed for actinides for around 200 seconds, but not for lanthanides (see figure 3). Cation complexation by H_4 TPAEN was assumed to be a rate-limiting reaction and therefore a stronger impact would be measured on actinides.

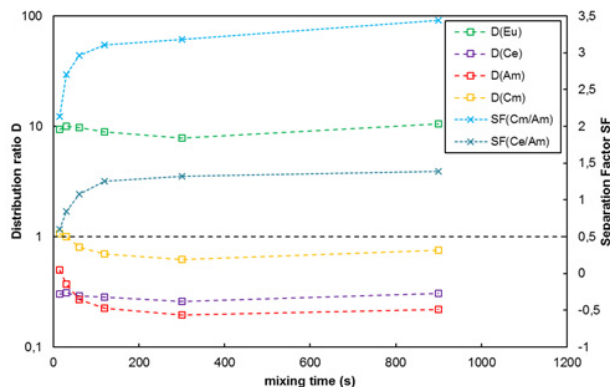


Fig. 3: Kinetics effect on Am, Cm, Ce, Eu extraction at 25°C

3. Development of thermodynamic model for TODGA extraction and H₄TPAEN complexation

3.1. TODGA extraction (0.2 M)

Nitric acid constants were taken from a previous CEA project (see table 1).

Table 1. Nitric acid extraction constants for TODGA.

Extraction complex	Optimized constants	Literature
(HNO ₃) ₂ octanol ₂	0.020	0.019 ^[2]
(HNO ₃)TODGA	0.535	0.5 ^[2]
(HNO ₃)TODGA ₂	0.016	-
(HNO ₃)TODGA ₃	0.00015	-

Various extraction complexes were assumed: M(NO₃)₃TODGA₂ or M(NO₃)₃TODGA₃ or a mix of M(NO₃)₃TODGA₂ and M(NO₃)₃TODGA₃. The best agreement between experimental and simulated data was obtained with a 3-TODGA-extraction complex. Co-extraction of cations and nitric acid by TODGA could be ignored at pH 1. With these hypotheses, constants were optimized and related uncertainties were evaluated (± 0.2 except Y ± 0.5) (see table 2).

Table 2. Actinide and lanthanide extraction constants for TODGA.

Extraction complex	Optimized constants	Literature
Am(NO ₃) ₃ TODGA ₃	4.75 \pm 0.2	6.95 ^[2,3]
Cm(NO ₃) ₃ TODGA ₃	4.81 \pm 0.2	-
La(NO ₃) ₃ TODGA ₃	3.85 \pm 0.2	-
Ce(NO ₃) ₃ TODGA ₃	4.19 \pm 0.2	-
Pr(NO ₃) ₃ TODGA ₃	4.27 \pm 0.2	-
Nd(NO ₃) ₃ TODGA ₃	4.61 \pm 0.2	-
Sm(NO ₃) ₃ TODGA ₃	5.34 \pm 0.2	-
Eu(NO ₃) ₃ TODGA ₃	5.62 \pm 0.2	7.80 ^[2,3]
Gd(NO ₃) ₃ TODGA ₃	5.53 \pm 0.2	-
Y(NO ₃) ₃ TODGA ₃	5.73 \pm 0.5	-

The relative gap between americium and europium is of the same order of magnitude for the two studies (respectively 0.87 and 0.85). Differences between the 2 optimizations are difficult to explain, because the acidity range is wider (up to 2 M for ref.^[2,3]) and the chemical system is not exactly the same (SO₃-Ph-BTP instead of H₄TPAEN). As constants with H₄TPAEN were consistent with the literature, those given above were retained.

3.2. H₄TPAEN complexation

The main assumptions taken into account were:

- The following acidity constants were used for H₄TPAEN^[4,5]: pK_{a1} 2.8, pK_{a2} 3.2, pK_{a3} 3.9, pK_{a4} 5.1, pK_{a5} 7.8.
- H₄TPAEN was considered as the complexing form of TPAEN for cations.
- A 1:1 complex was assumed between cations and TPAEN: (M³⁺, H₄TPAEN) M=(Am, Cm, Ln)

Some phenomena were not considered for this study: the chemical activity of the aqueous phase, the H₄TPAEN extraction in the organic phase and the effect of irradiation on H₄TPAEN.

Simulated and experimental constants were in good agreement for Cm, Ce, Pr, Nd and Eu (see table 3). As constants for TODGA alone and with H₄TPAEN were determined separately, optimized constants for TODGA alone seem to be in the right order of magnitude. Two values of constants will need to be refined:

- Am. As the experimental complexation constant may be too high and optimized constants too low, the true value is probably in between. Nevertheless, given optimization uncertainties, the Am constant should be in the right order of magnitude.
- La. The behavior observed for this element varied from one experiment to another, as sometimes it seemed more complexed than Ce, sometimes not. A complexing effect which rises with the atomic number was assumed.

The constants for Sm, Gd and Y may be inaccurate (explaining why the uncertainties for these elements are higher) but they are not essential for simulating the process as they largely remain in the organic phase.

Table 3. Complexing constants of cations for TPAEN.

TPAEN complex	Optimized constants	Literature
Am(H ₄ TPAEN)	5.43 ± 0.5	6.1 ± 0.2 ^[6]
Cm(H ₄ TPAEN)	4.56 ± 0.5	4.3 ± 0.2 ^[7]
La(H ₄ TPAEN)	2.01 ± 0.5	2.79 ± 0.05 ^[8]
Ce(H ₄ TPAEN)	2.31 ± 0.5	2.57 ± 0.04 ^[8]
Pr(H ₄ TPAEN)	2.92 ± 0.5	3.19 ± 0.02 ^[8]
Nd(H ₄ TPAEN)	3.45 ± 0.5	4.2 ± 0.1 ^[6] , 3.26 ± 0.02 ^[8]
Sm(H ₄ TPAEN)	2.00 ± 0.8	2.97 ± 0.01 ^[8]
Eu(H ₄ TPAEN)	2.46 ± 0.5	2.5 ^[6] , 2.4 ± 0.2 ^[7] , 2.75 ± 0.02 ^[8]
Gd(H ₄ TPAEN)	1.09 ± 0.8	-
Y(H ₄ TPAEN)	2.22 ± 0.8	-

Each experimental data set was simulated with the PAREX code in order to qualify the model. For each element, the distribution ratios were evaluated, and also the main separation factors. Two key issues were encountered related to:

- The understanding of La behavior given the different experimental data sets.
- Data simulation is extremely sensitive to pH (lower than 0.1 pH unit) and nitrate concentrations. Sometimes inactive and active pH are measured with 2 different pH probes and a difference of around 0.2 pH units occurs. It may explain why simulation results are relatively dispersed.

Simulations implemented in the PAREX code and experimental data are in sufficiently good agreement to be used to design a flowsheet. However, the flowsheet will require adjustments and an accurate monitoring because of its high sensitivity to proton and nitrate concentrations.

4. Flowsheet design

4.1. Feed solution composition

The composition of the solvent loaded from the extraction step is shown in table 4. The amount of lanthanides was around 14 mM.

Table 4. Composition of the loaded solvent.

Element	Cation concentration in the organic phase		Element	Cation concentration in the organic phase	
H ⁺	0.02	M	Nd	860.3	mg/L
Am	44	μg/L	Sm	143.9	mg/L
Cm	3.3	μg/L	Eu	29.3	mg/L
La	213.7	mg/L	Gd	41.2	mg/L
Ce	482.0	mg/L	Y	79.3	mg/L
Pr	189.3	mg/L			

4.2. Principles considered when designing the flowsheet

The flowsheet was designed with the PAREX code (see figure 4) by taking into account the following principles:

- To have efficient complexation of Am by H₄TPAEN, pH should be around 1,
- As lanthanides are in macro concentrations and Am is in trace amounts, it is necessary to add nitrates to the stripping aqueous phase in order to maintain lanthanides in the organic phase,
- The flowsheet was simulated at 25°C. Compared to the spiked test conditions at Jülich, the simulation may be pessimistic,
- The DF(Am/Ln) over 200 (especially for La) and an Am recovery rate as high as possible needed to be reached in 16 stages,
- The flowsheet sensitivity to operational conditions (flow rates, concentrations of cations in the feed solution, concentrations of reagents) had to be as low as possible.
- To reach the steady state as quickly as possible, the amount of Am accumulated in contactors had to be as low as possible,
- A limited number of flow rates should be tested, in order to correct the flowsheet more easily (this is why the aqueous solution in the Ln scrubbing step was removed in this first version).

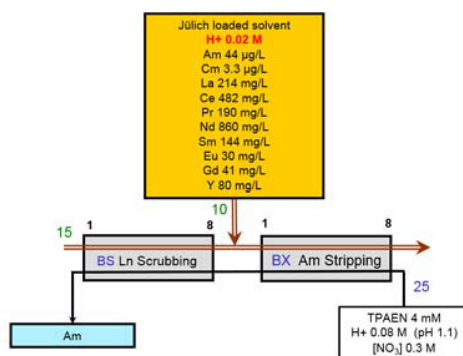


Fig. 4: Proposed flowsheet for spiked test at Jülich

5. Conclusions

Experiments were carried out to study and identify the main phenomena that occurred when varying cations, TODGA, H₄TPAEN, acidity and temperature. Based on these data, a model was developed to simulate the behavior of actinides and lanthanides under TODGA extraction and H₄TPAEN complexation (complex stoichiometry, extraction / complexation constants). The model was qualified at 25°C, essentially without nitrates. Complexation constants determined for H₄TPAEN were consistent with experimental constants measured by CEA/DEN/DRCP/SMCS/LILA.

This enabled a flowsheet to be designed for a spiked test in Jülich that took into account kinetics effect. This chemical system appears to be highly sensitive to the concentrations of protons and nitrates in the aqueous phase.

Modeling and process design were conducted simultaneously. As simulation showed, chemical conditions may be adapted to obtain an appropriate flowsheet. The chemical conditions were changed (concentration of H₄TPAEN, addition of nitrates, effect of temperature). While the chemical system chosen manages to recover sufficiently pure americium, some ways to further improve the model can be suggested, to extend its scope of qualification:

- A new constant determination with the latest experiments with nitrates and a new qualification of the model.
- The effect of temperature on TODGA extraction and H₄TPAEN complexation needs to be studied separately to simulate the behavior of cations at different temperatures more accurately.

Acknowledgements

Financial support for this research was provided by the European Commission (FP7 SACSESS Eur 753 323 282).

References

1. Wilden A., Modolo G., Kaufholz P., Saowski F., Lange S., Sypula M., Magnusson M., Müllich U., Geist A., Bosbach D. Laboratory-scale counter-current centrifugal contactor demonstration of an innovative-SANEX process using a water soluble BTP, *Solvent Extraction and Ion Exchange*, 2015, 33 (2), 91-108.
2. Magnusson, D.; Geist, A.; Malmbeck, R.; Modolo, G.; Wilden, A. Flow-sheet design for an innovative SANEX process using TODGA and SO₃-Ph-BTP. *Procedia Chem.* 2012, 7, 245-250.
3. Geist, A.; Müllich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T. Actinide(III)/Lanthanide(III) Separation Via Selective Aqueous Complexation of Actinides(III) Using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-yl)-Pyridine in Nitric Acid. *Solvent Extr. Ion Exch.* 2012, 30 (5), 433-444.
4. Mazzanti M., Method for obtaining highly luminescent lanthanide complexes, WO 2007/031640 (22.03.2007 Gazette 2007/12).
5. Chatterton, N.; Bretonniere, Y.; Pecaut, J.; Mazzanti, M. An efficient design for the rigid assembly of four bidentate chromophores in water-stable highly luminescent lanthanide complexes. *Angew. Chem., Int. Ed.* 2005, 44 (46), 7595-7598.
6. Manie G. Etude de la complexation des lanthanides(III) et de l'américium(III) par le TPAEN, 08/2014 (CEA/DEN/MAR/DRCP/SMCS/LILA)
7. Geist A., Müllich U., Panak P., Wagner C., personal communication
8. Chaneac L., Etude du procédé i-SANEX d'un point de vue thermodynamique, 09/2015 (CEA/DEN/MAR/DRCP/SMCS/LILA)