FLOWSHEETS FOR THE VALIDATION OF THE REFERENCE AMSEL SYSTEM

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Abstract. Recycling americium (Am) from spent nuclear fuels is an important option considered for the future nuclear fuel cycle as americium is the main contributor to the long-term radiotoxicity and heat power of the ultimate waste. The AmSEL flowsheet aims at recovering and purifying americium from a PUREX raffinate. This separation can be achieved by co-extracting lanthanide(III) (Ln) and actinide(III) cations (Am(III) and Cm(III)) into an organic phase containing the TODGA extractant (*N,N,N',N'*-tetraoctyl diglycolamide), and then stripping Am(III) selectively towards curium and lanthanides. The water-soluble ligand SO_3-Ph-BTBP (6,6'-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine) is used to selectively strip Am from the loaded organic phase. The objective of this work is to design a flowsheet for the Am stripping and Cm re-extraction steps to recover americium selectively from Cm and Ln, with TODGA as extractant and SO_3-Ph-BTBP as complexing reagent. The test was implemented in August 2023 at FZ Jülich with trace amounts of americium and curium.

1. Introduction

1.1 Presentation of the i-SANEX flowsheet

The AmSEL flowsheet aims at recovering americium alone from a PUREX raffinate. This separation can be achieved by co-extracting lanthanide(III) (Ln) and actinide(III) cations (Am(III) and Cm(III)) into an organic phase containing the TODGA extractant (*N,N,N',N'*-tetraoctyl diglycolamide in figure 1) [1], and then stripping Am(III) with selectivity towards curium and lanthanides. The water-soluble ligand SO_3-Ph-BTBP (6,6'-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine in figure 1) [2] is used to selectively strip Am from the loaded organic phase [3].
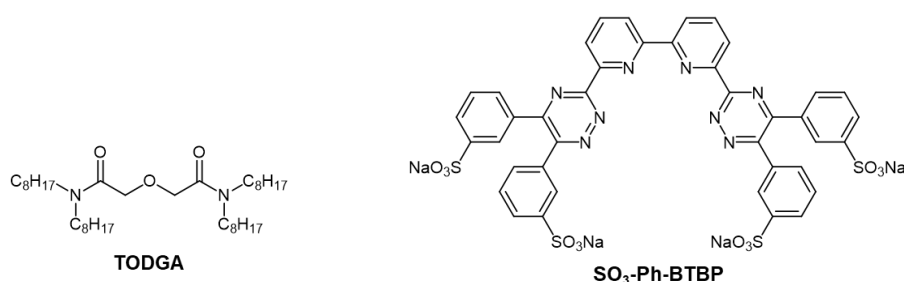

Fig. 1. Chemical structures of TODGA and SO_3-Ph-BTBP.

1.2 Scope of this work

The objective of this work is to design a flowsheet for the Am stripping and Cm re-extraction steps to recover americium selectively from Cm and Ln, with TODGA as extractant and SO_3-Ph-BTBP as complexing reagent. The extraction and scrubbing steps were already tested in the framework of the European SACSESS project [1]. This flowsheet was run at FZ Jülich facility in August 2023 [4]. The AmSEL flowsheet is given in figure 2 [1].
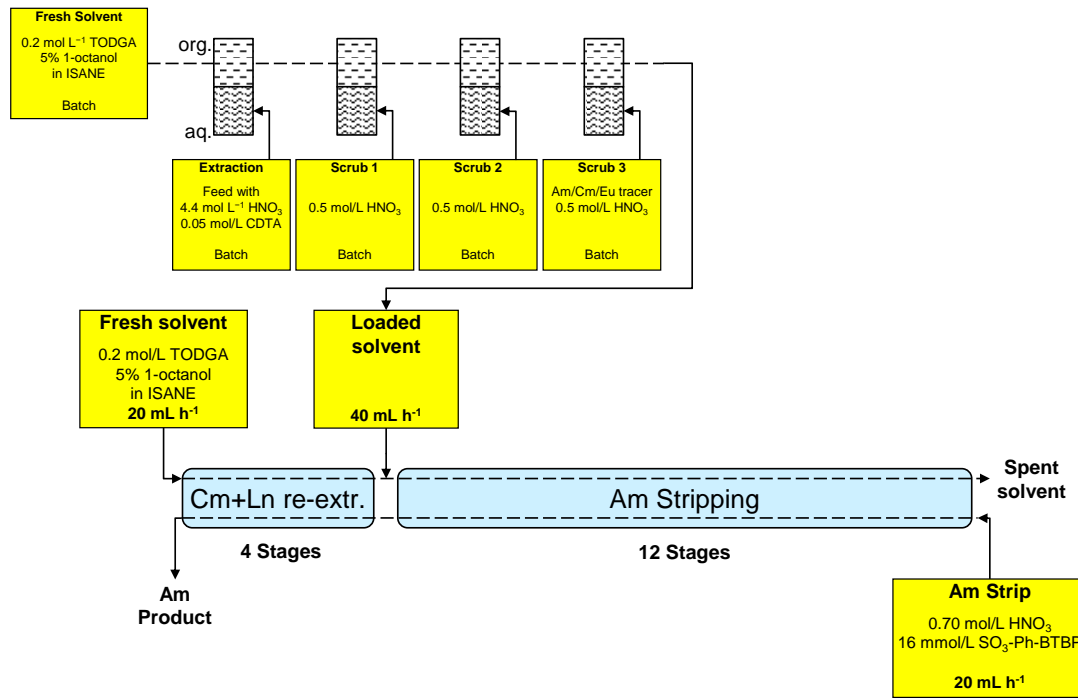
Fig. 2. The AmSEL flowsheet.

2. Modelling of the AmSEL chemical system

2.1 Modelling of the TODGA extracting capacity

Based on experimental data obtained by the FZ Jülich and the CEA teams since 2013 within the former EU-SACSESS project, a phenomenological model was developed to simulate the extraction of americium, curium and lanthanides by TODGA [5]. This model is modified to add the complexation of americium and curium by SO₃-Ph-BTBP.

2.2 Modelling of SO₃-Ph-BTBP complexing behaviour

The complexation of Cm and Eu by SO₃-Ph-BTBP is described in literature [2-3, 6-7] and can be modelled by two reactions:

- The speciation of SO₃-Ph-BTBP in five species L, L^-, L^{2-}, L^{3-}, L^{4-}
- A 1:2 complex for Eu and Cm with L^{4-}.

2.2.1 The SO₃-Ph-BTBP speciation

A single acidity constant for SO₃-Ph-BTBP is available [2]. As the different acidity constants are not known, a global acidity constant between L and a deprotonated form of L (see equation 1 where L is SO₃-Ph-BTBP) is used. This deprotonated form of SO₃-Ph-BTBP complexes Am or Cm with a stoichiometry of two SO₃-Ph-BTBP per actinide. This complexation reaction is modelled by a kinetic reaction (see equation 2), where M is either Am or Cm. The ratio between the direct and reverse reactions is given by the equilibrium constant $K_{eq,M}$. The complexation of lanthanides by SO₃-Ph-BTBP was disregarded, as the measured distribution ratios are higher than 5, with lanthanum being the least separated element.

$$[L] = K_L[L^-][H^+] \tag{1}$$

$$\frac{d[ML_2]}{dt} = k_M[M][L^-]^2 - \frac{k_M}{K_{eq,M}}[ML_2] \tag{2}$$

This model is implemented in the PAREX+ code (see presentation of the code and flowsheet design in reference [8]). Parameters are set to simulate single-stage centrifugal contactor tests implemented at FZ Jülich, as these contactors will be used for the FZ Jülich and NNL tests. The concentration of SO₃-Ph-BTBP is 10 mM and the acidity of the aqueous phase is in the range of 0.67 − 0.78 M. The distribution ratios were measured depending on time. Only the data near the steady-state is considered. Table 1 indicates the minimal and maximal values measured for each distribution ratio. Five series of experimental data were carried out corresponding to various O/A configurations (O is the organic flow rate in mL/h and A is the aqueous flow rate in mL/h). The constants determined are summarized up in table 2 and distribution ratios simulated with these constants are shown in table 1.

Table 1. Experimental and simulated data at steady-state acquired with one single-stage centrifugal contactor (experimental data are in italics).

	$\frac{O}{A}$	D(Am) γ	D(Am) α	D(Cm) α
BX1 (0.78 M HNO₃)	$\frac{80}{40}$	*2.04 − 2.24*	*1.88 − 2.43*	*4.57 − 6.43*
		2.17	2.17	5.42
	$\frac{40}{20}$	*1.54 − 1.71*	*1.51 − 1.82*	*3.81 − 4.77*
		1.64	1.64	3.99
BX2 (0.70 M HNO₃)	$\frac{40}{20}$	*1.23 − 1.42*	*1.02 − 1.3*	*2.68 − 3.54*
		1.2	1.2	2.92
	$\frac{20}{10}$	*1.22 − 1.32*	*1.05 − 1.23*	*2.5 − 3.09*
		1	1	2.37
BS (0.67 M HNO₃)	$\frac{20}{20}$	*0.61 − 0.67*	*0.61 − 0.71*	*0.94 − 1.14*
		0.72	0.72	1.14

Table 2. Constants determined for SO₃-Ph-BTBP complexation.

	Determined constants	Literature
K_L (equation 1)	8.5 L.mol⁻¹	–
k_{Am} (equation 2)	3.8.10⁹ L.mol⁻¹.s⁻¹	–
$\log(K_{eq,Am})$ (equation 2)	7.5	7.5 +/-0.2 (Wagner)
k_{Cm} (equation 2)	1.5.10⁹ L.mol⁻¹.s⁻¹	–
$\log(K_{eq,Cm})$ (equation 2)	7.2	7.3 +/-0.3 (Wagner)

According to the results shown in table 1, the model simulates experimental data correctly. Some limitations of the model are already identified:

- One limitation of the model is the speciation of SO₃-Ph-BTBP and the effect of the H⁺ concentration on the complexation reactions. The acidity for the available data was around 0.67 M − 0.78 M.

- The speciation of SO₃-Ph-BTBP is simplified and may not work for different concentrations of the ligand. All data were acquired at 10 mM SO₃-Ph-BTBP.

3. Flowsheet design for the FZ Jülich test

3.1 Feed solution composition

The feed solution composition for the FZ Jülich test is given in table 3. This solution is introduced at the extraction step (see figure 2 [1]).

Table 3. Feed solution composition for the FZ Jülich test.

Element M	[M]	Element M	[M]
Am	10^{-4} mM	Sm	0.95 mM
Cm	10^{-4} mM	Eu	0.22 mM
La	1.7 mM	Gd	0.15 mM
Ce	3.9 mM	Y	0.97 mM
Pr	1.5 mM	HNO_3	4.46 M

3.2 Flowsheet design

Depending on the separation factors measured (approximatively 2 – 2.5), it appears that at least 20 to 30 theoretical stages are necessary to achieve simultaneously an americium recovery rate over 70% and a decontamination factor between americium and curium of 300 (see figure 3). This number of stages and sensitivity are consistent with similar Am/Cm separation processes. The flowsheet is designed to reach the following performances with Am(III) and Cm(III) in trace amounts in the feed solution. With 16 stages and a separation factor of 2, a decontamination factor DF of 300 (see equation 3) can hardly be achieved and a low Am recovery rate is expected (50% or less). The performances towards the lanthanides have not been evaluated.

$$DF = \frac{\left(\frac{[Impurity]}{[Product]}\right)_{initial}}{\left(\frac{[Impurity]}{[Product]}\right)_{final}} \tag{3}$$

Different configurations of flowsheet were simulated to find the most appropriate flowsheet for the FZ Jülich test whilst remaining as close as possible to the experimental data conditions used to optimize the constant of the model (BS is Cm re-extraction step and BX Am stripping step).

- A first type of flowsheet with 4 stages for BS and 12 stages for BX.

- A second type of flowsheet with 4 stages for BS and 12 stages for BX and an introduction of an acid flow at BS. This flow aims at increasing the distribution factor of Cm.

- A third type of flowsheet with 12 stages for BS and 4 stages for BX.

The first type of flowsheet leads to a limited accumulation of Am and exploitable profiles (for Am a slope in BX and nearly a plateau in BS and the contrary for Cm) but with poor performances. For instance, with a 4BS-12BX configuration, the decontamination factor between Am and Cm is around 5. In this configuration, it is difficult to have a decontamination factor above 20. This might need dozens of stages to reach a DF around 300.

The second type of flowsheet leads to an accumulation of Am. For instance, with an introduction of 10 mL/h of a 2-molar nitric acid solution in a 4BS-12BX configuration, a decontamination factor around 330 can be reached but the peak of Am is one hundred times the Am aqueous outlet. The Am recovery rate is around 15%. The nitric acid concentration is around 1.1 M at BS (slightly higher than the experimental data at 0.78 M).

The third type of flowsheet improves the achievable decontamination factor to around 670 but the Am recovery rate is poor (around 19%). The difficulty of this flowsheet is that both Am and Cm profiles are with a slope in BS and a plateau in BX. Consequently, adding stages to the Am stripping step BX does not improve significantly the Am recovery rate (because it is a plateau).

At the end, to have exploitable Am and Cm profiles and a limited time to reach the steady state (as low accumulation as possible), the first flowsheet was proposed with a 12-stage "Am stripping" BX step and a 4-stage "Cm+Ln re-extraction" BS step for the test at FZ Jülich. However, this flowsheet leads to a rather poor decontamination factor between Am and Cm.
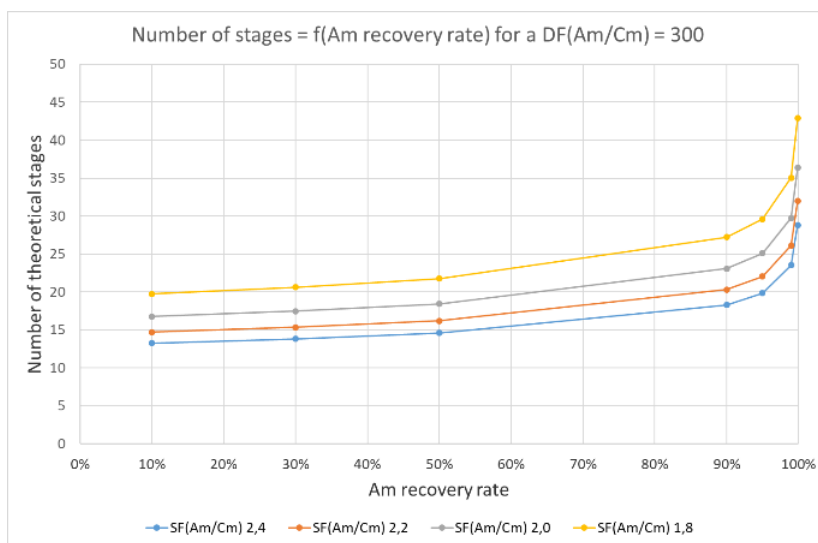

Figure 3. Evaluation of the number of necessary theoretical stages depending on the separation factor between Am and Cm.
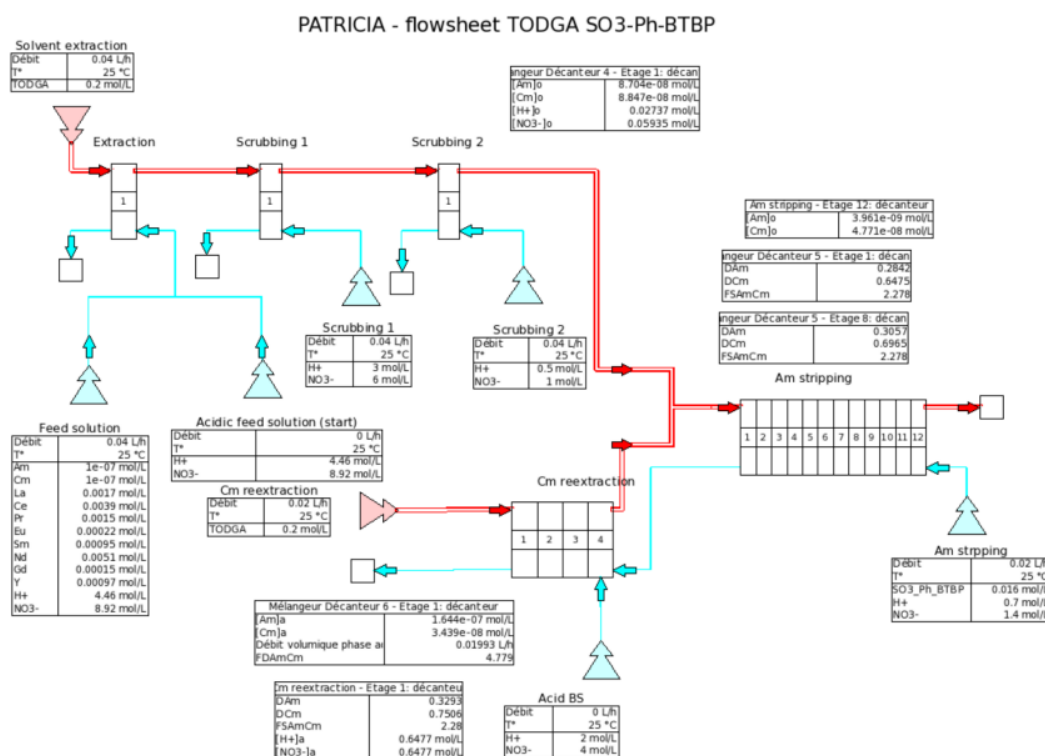

Figure 4. The designed AmSEL flowsheet for the Am stripping and Cm scrubbing steps.

According to the simulation, the concentration of SO$_3$-Ph-BTBP has a strong influence on the distribution ratios, D, and a moderate impact on the separation factor, SF. To have extraction factors suitable for the flowsheet design (O/A ratio around 2), the concentration of SO$_3$-Ph-BTBP was fixed at 16 mM.

The flowsheet proposed for the test is shown in figure 4 (the nitrate concentrations should be divided by two to obtain the real concentration used in the simulation). The Am recovery rate expected is

around 80% when the decontamination factor between Am and Cm is around 5. The Am profile of concentrations shows an accumulation of Am in the flowsheet, responsible for a 100-hour time to reach the steady state according to simulation.

The flowsheet is highly sensitive. Large variations of the performances are observed for low changes of the parameters. Table 4 shows the effect of a 0.1 M HNO_3 change in the acidity on performances of the Am stripping aqueous flow.

Table 4. Flowsheet sensitivity to the acid concentration in the aqueous phase.

Acidity of the stripping solution (M HNO_3)	Am recovery rate	Decontamination factor between Am and Cm
0.4	99.9%	16
0.5	68%	880
0.6	13%	1970

4. First exploitation of the results of the experimental test

Two modifications are needed to simulate the experimental results:

First, the HNO_3 aqueous profile was not consistent with the experimental data, especially in the Cm re-extraction step. The nitric acid concentration in the loaded solvent was fixed initially at 0.03 M (from the simulation of the extraction step). It was not possible to simulate the Am / Cm profiles with this acidity profile. The acidity profile has to be corrected by fixing the nitric acid concentration at 1 M, both in the loaded solvent and in the fresh solvent. This is not satisfactory but without an experimental profile in the organic phase, it is the most viable solution. With this adjustment, the acidity profile is closer to the experimental one.

Secondly, the acidity constant of SO_3-Ph-BTBP is decreased from 8.5 to 6.5, all extraction and complexing constants remaining as given in table 2 and [5]. The simplified model considered for the speciation, making it difficult to extrapolate, may explain this change. The concentration for batch experiments was 10 mM SO_3-Ph-BTBP, instead of 16 mM for the FZ Jülich test.

With these two modifications, the experimental profiles of the test are simulated correctly (see figure 5). However, the accumulation is not located exactly at the same stage experimentally and by simulation. In the Am production flow, the Am recovery rate (Am in production flow / Am in the loaded solvent) is simulated at 39% compared to 45% obtained experimentally and the decontamination factor between Am and Cm is simulated at 9.3 compared to 8.7 obtained experimentally. The Am concentration in the Am production flow reaches the steady-state in around 8 hours, becoming consistent with what is observed during the test (around 9 hours). The rise to the steady-state is different and should be investigated.
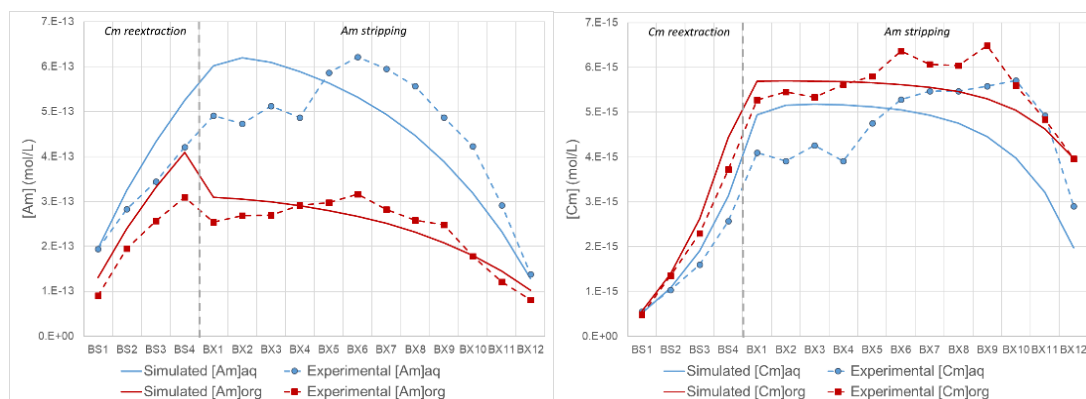

Figure 5. Simulation of the Am profiles of the FZ Jülich test.

5. Conclusion

Based on an extraction model by TODGA previously developed in the framework of the SACSESS project, a model was implemented in the PAREX+ code to simulate the complexation of americium and curium by SO_3-Ph-BTBP. The model evaluates correctly the five series of tests in single-stage centrifugal contactor. The determined complexation constants at equilibrium are consistent with those reported in literature. The main limitation of the model is the small range of acidity (0.67 M – 0.78 M) of the experimental data and the simplified SO_3-Ph-BTBP speciation (data at 10 mM SO_3-Ph-BTBP).

With this model, different configurations of flowsheets were studied. A flowsheet was proposed and implemented by the FZ Jülich team in August 2023. Depending on the separation factor between Am and Cm, Am recovery rate and decontamination factor between Am and Cm could hardly be achieved simultaneously and the flowsheet was highly sensitive to experimental parameters.

At the end of the test, it was possible to recover 45% of americium in the Am production flow, with a decontamination factor between Am and Cm around 9. The first exploitation of the FZ Jülich test results shows that it is necessary to adapt the SO_3-Ph-BTBP speciation constant (flowsheet at 16 mM SO_3-Ph-BTBP) and the acidity profile. With these adaptations, it is possible to correctly simulate the Am and Cm profiles. Nevertheless, some points need to be further investigated: the profile of acid concentration and the extraction of SO_3-Ph-BTBP by TODGA.

These results were used to design the flowsheet implemented at NNL in February 2024.

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