# Inter-institutional study of the New EURO-GANEX process resistance by gamma irradiation test loops

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## ABSTRACT

As part of the homogeneous actinides recycling strategy, the EURO-GANEX process is one of the most promising options to achieve the goal of minor actinides recovery. Improvements made to EURO-GANEX system have resulted in the emergence of the so-called New EURO-GANEX process, where the composition of the solvent has been modified by replacing TODGA and DMDOHEMA with *cis*-mTDDGA in the organic phase and $SO_3$-Ph-BTP with PyTri-Diol in the aqueous phase in order to resolve important issues. The objective of this work is twofold: evaluate the gamma radiolytic resistance of the new EURO-GANEX process by dynamic irradiation conditions simulating the three main steps of the process, and validate the design of CIEMAT Náyade, CEA Marcel and INL irradiation loop devices since each of them mimics different aspects of the real process. Náyade and the INL loops could irradiate the organic and aqueous phases together, whereas in the CEA loop, the irradiated solvent is recycled continuously inside a platform with several stages of mixer-settlers containing aqueous flows simulating the three main steps of the process. The extraction performances and changes in the composition of the solvent have been analyzed during the irradiation experiment by different techniques: gamma spectrometry and ICP-MS/OES for cations or radioactive tracer extraction, and HPLC-MS to identify and quantify the degradation compounds. Despite some differences between the three-

irradiation facilities, this inter-institutional study shows that these three comparative tools provide similar trends in the radiolytic stability of a liquid-liquid extraction system. Favourable extraction results for the different steps are obtained according to the static irradiation studies found in literature. However, the degradation of *cis*-mTDDGA is appreciable leading to degradation compounds, some of which form precipitates and produce important changes in viscosity, important aspects that must be addressed prior to the successful industrial application of the new EURO-GANEX process.

## 1. INTRODUCTION

Future advanced nuclear fuel cycles are currently under development around the world with the purpose of increasing nuclear fuel cycle sustainability and reducing the long-term radiotoxicity and heat load of nuclear waste by means of separation and transmutation of the transuranium elements (TRU), specifically the minor actinides (MA: Np, Am, Cm), that together with Pu, have the highest contribution to the long-term radiotoxicity of spent nuclear fuel [1-3]. With this aim, new separation processes based on solvent extraction for the recovery of TRU are being developed globally, which could follow the heterogeneous or homogeneous strategy for the actinides recycling [3-8].

Within the homogeneous strategy, which addresses the recycling of U and the transuranic elements (TRU= Np, Pu, Am, Cm) contained within a single fuel type and distributed homogeneously throughout the reactor core, GANEX (*Group ActiNide EXtraction*) is the most promising process to recover all of them [9]. In the GANEX concept, bulk uranium is removed in a first cycle, followed by the co-extraction of all actinides in a second cycle. Three options exist for this second cycle, the CEA-GANEX, EURO-GANEX and CHALMEX processes [4, 8]. The EURO-GANEX is one of the most promising options to achieve the desired goals [10] and is based on the co-extraction of all actinides using a mixture of *N,N,N′,N′*-tetraoctyl-diglycolamide (TODGA) [11, 12] and *N,N′*-dimethyl-*N,N′*-dioctyl-2-hexylethoxy-malonamide (DMDOHEMA) [13] extractants. TODGA exhibits high affinity for actinides and lanthanides, but the addition of DMDOHEMA is essential to avoid precipitation caused by the high Pu concentration in the organic phase [10, 14]. After the co-extraction of An and Ln into the organic phase, a separation between both can be obtained by selective stripping of the actinides as a group, using a mixture of 2,6-bis-(5,6-di(sulfophenyl)-

1,2,4-triazin-3-yl)-pyridine ($SO_3$-Ph-BTP) [15] and acetohydroxamic acid (AHA) [16]. The EURO-GANEX process was tested in an irradiation loop [17] and successfully demonstrated with high Pu content using genuine nuclear fuel solution in centrifugal contactors for the first time [18], obtaining excellent results. However, EURO-GANEX also has some drawbacks: one of them is that the combination of two extractants in the organic phase (TODGA and DMDOHEMA) complicates solvent management; another one is that the sulfonated BTP reagent employed in the aqueous phase does not accomplish the "CHON principle" [19], leading to troublesome sulfur-containing by-products. Therefore, the process needs to be further optimized to meet the above-mentioned criteria and to simplify the process as much as possible.

The complexity of the solvent composition may be reduced by using a single extractant in a kerosene diluent and using complexants which adhere to the CHON principle, to reduce secondary waste and downstream target fabrications issues. In order to achieve the former option, an organic solvent containing only one extractant capable of extracting high Pu concentrations is required. Taking into account that diglycolamides were found to be suitable for the extraction of Ln and An from used nuclear fuel solutions, different structural modifications of the TODGA molecule were studied over the last decade [20-24]. For the organic phase, the new modified dimethyl-*N,N,N',N'*-tetradecyl-diglycolamide (mTDDGA) was proposed to simplify the current version of the EURO-GANEX solvent extraction system [23]. In previous years, a study with $Me_2$TODGA revealed different distribution ratio values, even by two orders of magnitude, for trivalent actinides and lanthanides depending on the diastereomer used, producing better results with the extractant with the two methyl groups oriented in the same direction (R,S or meso form, *cis*-diastereomer), related to differences in the outer-sphere complexation of nitrate ions and steric interaction with the backbone methyl

groups of $Me_2$TODGA [21]. Following these results, in the case of mTDDGA, the *cis*-diastereoisomer (Figure 1, left) was selected for further studies [25].

In order to replace $SO_3$-Ph-BTP, a novel molecule which meets the CHON principle, 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl)]pyridine (PyTri-Diol, or PTD) is proposed (Figure 1, right). This agent was found to have high actinide selectivity and radiochemical stability [26-31] and could be suitable for the application as a stripping agent not only in GANEX process but also in *i*-SANEX (*Innovative Selective Actinide Extraction*) process involved in the heterogeneous strategy of actinides recycling [28, 31, 32].

These improvements made to EURO-GANEX system have resulted in the emergence of the so-called New EURO-GANEX process, with *cis*-mTDDGA/dodecane (dd) in the organic phase and PTD in the selective TRU back-extraction aqueous solution (Figure 1). As in the EURO-GANEX process, *cis*-mTDDGA solvent is useful to extract actinides and lanthanides from an acidic GANEX first cycle raffinate. After this co-extraction step, the TRU elements are selectively stripped into the PTD aqueous solution while *cis*-mTDDGA maintained rare earth elements in the organic phase.

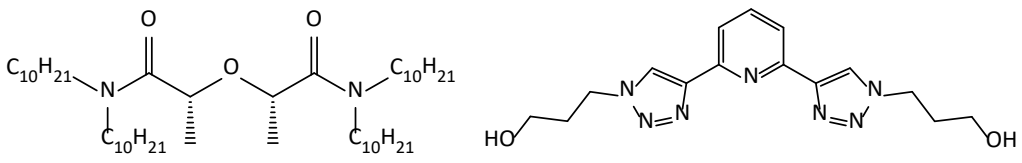



Figure 1. Chemical structures of cis-mTDDGA and PTD, currently under study to be used in a new EURO-GANEX process.

In order to validate new nuclear separation processes, solvents must be resistant to radiolysis and hydrolysis in addition to exhibiting good extraction efficiency. Due to the

highly radioactive solutions and the high nitric acidity, degradation compounds (DCs) are formed and can lead to a decrease in extraction performance, selectivity or a change in the physicochemical properties of the solvent. This can increase secondary waste and process costs.

In literature, several studies can be found which tackle the stability of diglycolamides towards radiolysis [17, 24, 33-45]. These studies were focused not only on TODGA [33, 34, 36, 40, 44, 45], but also on the methylated derivatives of TODGA (MeTODGA and $Me_2$TODGA), which showed less resistance to gamma radiation than TODGA [24, 38, 42]. A study performed by Wilden et al. concluded that the degradation rates decrease with increasing molecular weight of DGA [42]. Therefore, based on this finding, cis-mTDDGA should be more stable than TODGA. However, only few studies about the *cis*-mTDDGA radiolytic resistance have been performed [25, 46, 47], irradiating solutions of 0.05 mol/L *cis*-mTDDGA alone and in contact with 2.5 mol/L $HNO_3$ in static conditions. Based on these initial studies, *cis*-mTDDGA exhibits increased radiolytic stability towards gamma radiation compared to TODGA. At least nine degradation compounds (DCs) with typical chemical structures for DGA degradation, were detected.

Regarding the stability of PTD, only a few studies [29-31] have appeared in the literature. These studies show that PTD exhibits excellent radiochemical stability when PTD is irradiated alone or in the presence of TODGA extractant under static conditions up to 200 kGy. This highlights its potential applicability to *i*-SANEX and GANEX processes. Given that the aqueous phase with aqueous PTD is not supposed to be recycled in the extraction process, studying the stability of this agent is not the objective of this work. If recycling of this molecule is expected in the future, a more detailed study on the stability of its performance will have to be carried out.

However, according to the best of our knowledge, there are no studies on the radiolytic stability of the combined system composed of *cis*-mTDDGA and PTD under the conditions of the New EURO-GANEX process using dynamic irradiation. Therefore, the objective of this work is to perform a study in order to investigate the resistance of the new EURO-GANEX extraction system under dynamic irradiation experiment simulating the main steps of the New EURO-GANEX process as well as the cis-mTDDGA stability. The steps in this process consist of an An-Ln extraction at high acidity (4-5 mol/L), followed by the selective stripping of the An with the PTD aqueous reagent at moderate nitric acidity (2-2.5 mol/L) and the stripping of the Ln at low acidity (< 0.1 mol/L). The operating conditions were set on the basis of the results of preliminary batch experiments, in order to obtain extraction factors (distribution ratio x volumes or organic/aqueous flow rates) greater than two for the metals to be extracted, whereas this parameter must be less than 0.5 for correct stripping of cations. Moreover, this work is involved as part of an inter-institutional collaboration between CEA (*Commissariat à l'énergie atomique et aux énergies alternatives*) in France, INL (*Idaho National Laboratory*) in the United States, and CIEMAT (*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas*) in Spain. For this collaboration, each research centre employed its irradiation loop device to evaluate the resistance of the New EURO-GANEX process to gamma radiolytic degradation using similar conditions and same solutions.

## 2. METHODOLOGY

### 2.1. Materials

*Cis*-mTDDGA solution was prepared and provided by Oak Ridge National Laboratory (synthesis route included in the Appendix C of the supporting information) and PTD

was synthesized and supplied by the University of Parma, using the published synthesis routes [26]. The products complied with published analytical results and were used without further purification. These solutions were the same for CEA, CIEMAT and INL experiments in order to perform a comparative study.

CIEMAT, CEA and INL used nitric acid 65% with the grade AnalaR NORMAPUR for analysis purchased from VWR Chemical or Sigma Aldrich. The $HNO_3$ solutions were prepared by diluting concentrated nitric acid with de-ionized water (18 MΩcm). The radioactive tracer solutions of $^{241}$Amand $^{152}$Eu, were obtained as $MCl_3$, in 1 mol/L HCl, from Isotope Products Laboratories, California (US), for CIEMAT, and from LEA (the Radioactivity Standards Laboratory - *Laboratoire d'Etalons d'Activité* in French), subsidiary of the Orano Group (France) for CEA. The INL batch distribution were carried out with $^{241}$Am, $^{243}$Am isotopes from INL laboratory stocks and with $^{154}$Eu and $^{139}$Ce radioisotopes obtained from Eckert and Ziegler. The neodymium solution for the CEA test was prepared with $Nd(NO_3)_3 \cdot 6H_2O$ (99.9%). CIEMAT surrogate GANEX first cycle raffinate was a mixture of SrO, $La(NO_3)_3$, $Nd_2O_3$, and $Eu(NO_3)_3 \cdot 6H_2O$ powder solubilized in nitric acid. SrO (99.5% purity) was supplied by Thermo Scientific, $La(NO_3)_3$ (99.99% purity) and $Nd_2O_3$ (99.9% purity), were obtained by Sigma-Aldrich and $Eu(NO_3)_3 \cdot 6H_2O$ (99.9% purity) was supplied by Thermo Scientific Chemicals. The aqueous extraction solution of INL was prepared from $Eu(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ powders.

## 2.2. Irradiation test loops

Three irradiation loops for this inter-institutional study of the new EURO-GANEX processes radiolytic stability were employed corresponding to CIEMAT (Náyade loop), CEA (Marcel loop) and INL irradiation test loops. With the three loops, the co-

199 extraction, An stripping and Ln stripping steps were evaluated. In Náyade loop and INL
200 loop, organic and aqueous phases were irradiated in contact meanwhile in Marcel loop
201 only the organic phase was irradiated. The dose rates employed and the absorbed doses
202 reached were comparable in all experiments (2.6 kGy/h - 503 kGy for CIEMAT, 0.78
203 kGy/h - 339 kGy for CEA and 2.2 kGy/h - 528 kGy for INL). The description of each
204 irradiation test loop is summarized in the Appendix A of the supporting information.

205 2.3. Solvent extraction performance

206 2.3.1 Náyade loop

207 The behaviour of the New EURO-GANEX process after the three different steps
208 mentioned before was assessed with spiked samples ($^{241}$Am and $^{152}$Eu, 100 kBq/mL
209 each). All extraction experiments were performed by mixing 500 µL of both, aqueous
210 and organic phases, for 30 min at room temperature (22 ± 2 ºC). Then, the phases were
211 separated by centrifugation (5 min at 5000 rpm) and aliquots of each phase were taken
212 for analysis (300 µL for gamma and 100 µL ICP-MS).

213 For high energy gamma spectroscopy measurements, a High Purity-Germanium
214 detector with an intrinsic efficiency of 20% was used, using Genie-2000 (Canberra) as
215 analysis software. The gamma characteristic photopeaks at 59.5 keV and 121.8 keV
216 were analysed for $^{241}$Am and $^{152}$Eu, respectively.

217 The concentration of the elements present in the initial aqueous solution (Sr, La and Nd)
218 as well as those coming from the stainless-steel corrosion products (Fe, Cr, Ni and Mo)
219 were determined by ICP-MS. The organic and aqueous phases were analyzed directly
220 after a suitable dilution in $HNO_3$ (2-5%). All extraction results are reported as
221 distribution ratio $D$ ($D_M = C(M)_{org}/C(M)_{aq}$), where $D_M$ between 0.01 and 100 exhibit a

maximum error of ±5%. The limit of detection (LOD) for $^{241}$Am and $^{152}$Eu is 2 and 6 Bq/L, respectively, and for Sr, La, Nd, Eu, Fe, Cr, Ni, and Mo is $2.2 \cdot 10^{-7}$ mmol/L, $2.88 \cdot 10^{-9}$ mmol/L, $1.50 \cdot 10^{-8}$ mmol/L, $6.60 \cdot 10^{-9}$ mmol/L, $1.95 \cdot 10^{-6}$ mmol/L, $1.19 \cdot 10^{-7}$ mmol/L, $1.68 \cdot 10^{-7}$ mmol/L and $3.85 \cdot 10^{-8}$ mmol/L, respectively.

A schematic representation of the main steps of the irradiation loop set-up, the composition of the phases during the different irradiation steps and the corresponding extraction experiments is shown in Figure 2. More details are summarized in the Appendix A of the supporting information.

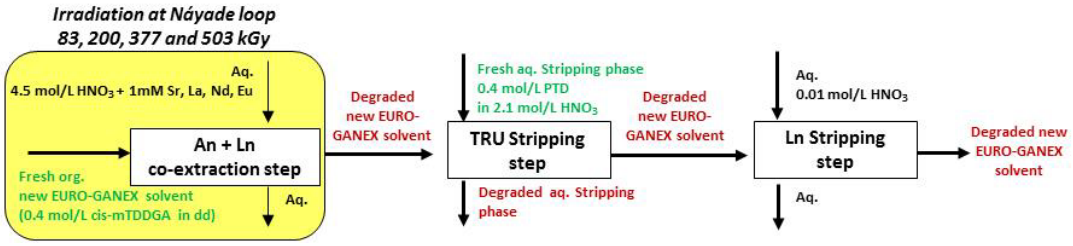



Figure 2. Scheme of the main steps of new EURO-GANEX process simulated at Náyade irradiation loop test.

### 2.3.2 Marcel loop

Solvent samples were collected in the CX outflow (see Figure 3), every 25 kGy of irradiation dose in order to characterize them and to carry out $^{241}$Am/$^{152}$Eu batch experiments. More details are summarized in the Appendix A of the supporting information.

These experiments were performed with 8 solvent samples: initial, 56 kGy, 98 kGy, 147 kGy, 198 kGy, 249 kGy, 295 kGy, Final (339 kGy). All solvents were contacted with 0.01 mol/L $HNO_3$ ($V_{aq}$=$V_{org}$, mixed for 30 min at 25°C) then centrifuged to strip acidity and residual neodymium. The protocol consisted in performing, at first, an extraction

242 with solvents and an aqueous phase containing trace amounts of $^{241}$Am (127 kBq/mL)
243 and $^{152}$Eu (97 kBq/mL) with 4.7 mol/L $HNO_3$. Then a back-extraction of these cations
244 was carried out with three aqueous solutions in parallel ($V_{aq}$=$V_{org}$, mixed for 30 min at
245 25°C): 0.4 mol/L PTD – 2.1 mol/L $HNO_3$, 0.04 mol/L PTD – 1.5 mol/L $HNO_3$ and 0.01
246 mol/L $HNO_3$. The same type of gamma spectrometer as CIEMAT was used to
247 determine gamma activities in organic and aqueous phases.

248 The batch Am/Eu protocols of CIEMAT/CEA were similar except that there were only
249 trace amounts of $^{241}$Am and $^{152}$Eu for CEA instead of 1 mM Sr, La, Nd, Eu for
250 CIEMAT. Furthermore, the initial aqueous nitric acid for the extraction step was, 4.7
251 mol/L for CEA instead of 4.5 mol/L for CIEMAT. These two observations mean that
252 the CIEMAT solvents contained fewer free extractant molecules, and that the final
253 aqueous nitric acid concentrations for the CEA batch extractions were higher: about 4.2
254 mol/L instead of about 4 mol/L.

255 Moreover, in order to observe the behaviour of Nd in the mixer-settlers, each stage was
256 emptied after the Marcel test was stopped. The aqueous phases in the settling chambers
257 were sampled to measure the Nd concentration by ICP-OES for all twelve stages. There
258 was no PTD in An stripping step (BX in Figure S3).

259 All extraction results are reported as distribution ratio D ($D_M = C(M)_{org}/C(M)_{aq}$), where
260 $D_M$ between 0.007 and 800 exhibit a maximum error of ±10%. The limit of detection
261 (LOD) for $^{241}$Am and $^{152}$Eu is 1.6 kBq/L and 0.5 kBq/L, respectively, and $7.10^{-6}$ mol/L
262 for Nd.

263

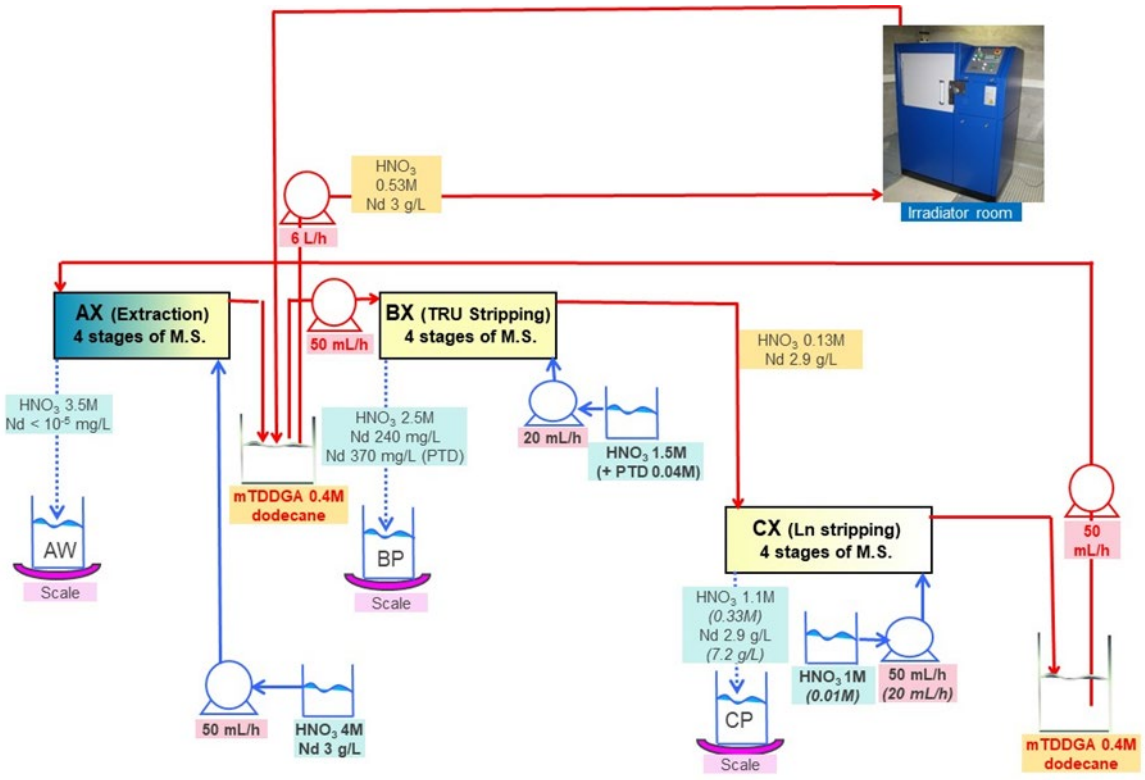



Figure 3. Flowsheet of the loop test following CX hydrodynamic problem (italics indicate initial value). The CX outflow solvent samples for batch studies were taken after 56 kGy, 98 kGy, 147 kGy, 198 kGy, 249 kGy, 295 kGy and finally 339 kGy (M.S. = mixer-settler).

### 2.3.3 INL loop

To determine the impacts of gamma radiolysis on the New EURO-GANEX solvent, extraction, scrub, strip batch contact flowsheet tests were performed using the irradiated aqueous and organic phases. The Am, Ce, and Eu distribution ratios for these flowsheet tests were determined prior to and after irradiation of the solvent in the INL test loop. The concentration of radiotracers ($^{241}$Am, $^{154}$Eu, $^{139}$Ce) present in the organic and aqueous phases was analyzed by gamma spectrometry. All flowsheet contacts were carried out using organic to aqueous phase volume ratios (O/A) corresponding to the simplified New EURO-GANEX flowsheet. The extraction batch contacts were performed using 4.5 mol/L $HNO_3$ containing millimolar concentrations of europium and

cerium nitrate salts. The loaded organic was scrubbed using 2.1 mol/L $HNO_3$. The actinide stripping solution was 0.04 mol/L PTD in 2.1 M $HNO_3$. The lanthanides were stripped using 0.01 mol/L $HNO_3$. The PTD aqueous stripping reagent was not irradiated in these experiments.

### 2.4. Solvent composition analysis

CIEMAT determined the chemical composition of the irradiated organic samples by an HPLC-MS Bruker EVOQ™(Triple Quadrupole detector) with a ACE 3 C18-PFP column (50 mm x 2.1 mm) at 40 ºC, using a gradient of mobile phase [(A: 0.1% HCOOH in $H_2O$), (B: 0.1% HCOOH in $CH_3CN$)]. The atmospheric pressure chemical ionization (APCI) ionization mode was used for the *cis*-mTDDGA quantification; meanwhile electrospray ionization (ESI) mode was used for the PTD quantification and the identification of the *cis*-mTDDGA DCs. The quantification of *cis*-mTDDGA DCs was not carried out due to the absence of the DCs isolated as standards. Samples for HPLC-MS studies were analyzed without pre-evaporation and diluted 1:30,000 in HPLC grade MeOH. Calibration curves were performed for *cis*-mTDDGA and PTD from 10 to 1000 ppb, and the correlation coefficients in all cases were in the range of 0.996-0.999. All measurements were performed in duplicate in order to have uncertainty analysis where results show a maximum error of ±3%. The samples of the irradiated *cis*-mTDDGA was also analysed in the CIEMAT facilities.

INL used HPLC to quantify *cis*-mTDDGA concentration in the irradiated solvent samples. The device was a Dionex (Sunnyvale, CA, USA) ICS-5000 ion chromatograph equipped with an autosampler, a quaternary gradient pump with degasser, a photo-diode array detector, and Chromeleon 7 software. The mobile phase was a 80:20 ratio of 4% (v/v) 1-octanol in 2-propanol with 0.1 % (v/v) formic acid in 18 MΩcm Nanopure

water. The chromatographic separation was achieved with a C18 reverse-phase (RP-C18) column (Supelco, 25 cm x 4.6 mm, 5 µm) with a flow rate of 0.8 mL /min. The column temperature was maintained at 50º C. The absorbance of the column effluent was monitored at 220 nm. All solvents used for sample dilution and mobile phases were HPLC or HPLC Plus grade (Sigma Aldrich, St. Louis, MO, USA). Samples were initially diluted by a factor of 100 in hexane. The samples were then further diluted by a factor of 80 in 4% (v/v) 1-octanol in 2-propanol eluent to an analytical concentration of 50 µmol/L cis-mTDDGA (assuming a starting concentration of 0.4 mol/L *cis*-mTDDGA) prior to analysis. Calibration standards were prepared in the same fashion, spanning the equivalent of 20 µmol/L to 100 µmol/L *cis*-mTDDGA. A check standard was prepared from a separate source of neat *cis*-mTDDGA by mass and dissolved in hexane to a concentration of 5.0 mmol/L *cis*-mTDDGA. The check standard was then further diluted by a factor of 100 in 4% (v/v) 1-octanol in 2-propanol eluent to an analytical concentration of 50 µmol/L *cis*-mTDDGA. Each diluted sample was injected in triplicate from the same vial and bracketed by calibration standards, blanks, and check standards. All standard brackets reported within a few percent of the previous standard bracket, suggesting the generated calibration curve was valid for the entire run.

The proton concentration in the aqueous phases was determined potentiometrically by acid-base titration with KOH (CIEMAT) or NaOH (CEA, INL) using an automatic titrator (Metrohm 798 MPT titrino) with an Unitrode as electrode purchased from Metrohm. A dynamic equivalence point of titration was employed for the determination, where the KOH or NaOH was added in variable volume steps. The electrode was calibrated employing buffer solutions of pH 4.00 and 7.00 supplied by Metrohm.

In CIEMAT, the density of different samples was determined by the average data of three analyses using the gravimetric method. Viscosity measurements of fresh and

328 irradiated samples were performed by using an Ubbelohde micro viscosimeter with a
329 0.40 mm diameter capillary. A digital stopwatch is used by ViscoClock *plus* device
330 using IR light barriers. After the time measured is corrected by the Hagenbach factor
331 and then averaged on three measurements, the viscosity and associated uncertainty are
332 calculated.

333 In CEA, densities and viscosities were measured three times at 23°C using an Anton
334 Paar SVM 3000 / G2 Stabinger viscometer.

335

## 3. RESULTS AND DISCUSSION

### 3.1 An+Ln co-extraction step

As described in the supporting information section, in the Náyade loop, 0.4 mol/L *cis*-mTDDGA in dodecane (dd) was irradiated up to 503 kGy in contact with 4.5 mol/L $HNO_3$ containing 1 mmol/L of SrO, $La(NO_3)_3$, $Nd_2O_3$, and $Eu(NO_3)_3 \cdot 6H_2O$, without any treatment of the solvent that should be present in a full-scale reprocessing plant. During irradiation, the organic phase changed colour from light to dark yellow, while the aqueous phase remained virtually unchanged (Figure 4A). For an absorbed doses of 200 kGy, a turbidity and small precipitate in the organic phase can be observed, as it is shown Figure 4B for the sample irradiated at 377 kGy. The same behaviour was found in other studies carried out by Verlinden et al [46], where they found a precipitate at high absorbed doses (~454 kGy), related to a *cis*-mTDDGA DC. For the extraction experiments, a homogenized organic sample was used.

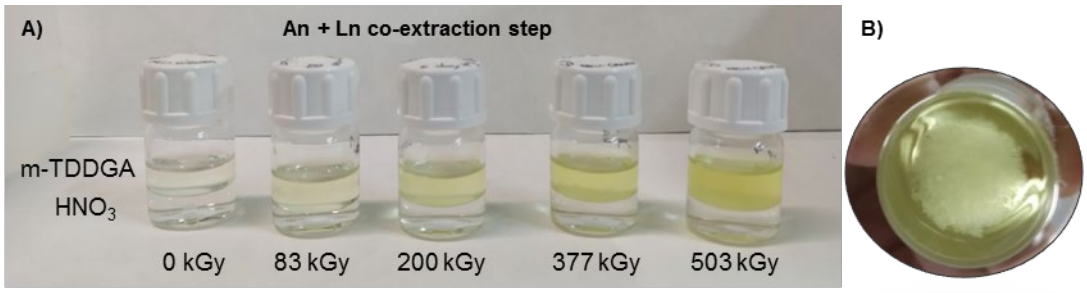



Figure 4. A) Samples of the first irradiation step. Org. phase: 0.4 mol/L mTDDGA in dodecane, Aq. Phase: 4.5 mol/L $HNO_3$, with an accumulated dose of 0 kGy, 83 kGy, 200 kGy, 377 kGy and 503 kGy. B) Turbidity and small precipitate in the organic phase at 377 kGy.

In the case of Marcel loop, also without any solvent treatment, the hydrodynamic behaviour of the two-phase system did not change significantly after several irradiation

cycles. Some carryover of aqueous droplets in the output solvent of the An+Ln co-extraction step was observed throughout the Marcel GANEX loop test (photo B in the Figure 6). This phenomenon increased moderately during the test, requiring daily draining of the aqueous phase into the solvent outlets of the step. Unlike Náyade loop, no gel or precipitate was observed in this part of the process until the end of the test (~339 kGy). This difference may be due to the renewal of the aqueous phase at each stage, partially solubilizing certain degradation products, and the continuous transfer of the organic phase to the less acidic TRU stripping step.

The variation of $D_M$ as a function of absorbed dose is shown in Figure 5 for the three loops. In the non-irradiated samples *cis*-mTDDGA extracts Ln and An, but also coextracts Sr. This is in agreement with previous studies found in the literature [23]. Except for Sr, all metals are well extracted into the organic phase even at high absorbed dose ($D_M > 10$), although there is a slight decrease in the D values. Therefore, under the irradiation loop conditions, the system can still extract Am, Cm and rare earth elements also after 500 kGy absorbed dose. The effect of radiolysis on the extraction of Sr is higher, leading to a decrease in $D_{Sr}$ to 0.1, which means that this fission product is no longer extracted, hence a positive effect of radiolysis. All these results are coherent and in agreement with the studies performed by Verlinden et al [46].

The $D_{Eu,Am}$ obtained by CIEMAT and INL are approximately the same while those of the CEA Marcel solvents are higher. This difference could be explained by the presence of only Am, Eu in CEA system instead of micro-concentrations of Eu, Nd, La, Sr in the CIEMAT experiments or millimolar concentrations of europium nitrate and cerium salts in the case of INL. Consequently, the CIEMAT solvents contained less free extractants than the CEA solvents. Moreover, the initial aqueous concentration of nitric acid in the CEA experiments is also slightly higher than in the CIEMAT or INL studies, which

could also be the reason for a higher distribution ratio for the CEA. Another difference is the less noticeable impact of radiolysis on $D_{Eu,Am}$ in the CEA Marcel or the INL loop than in the CIEMAT Náyade loop. This could be explained by the positive effect of a continuous multi-stage contact with various acidic media simulating a reprocessing flowsheet, carried out in mixer-settlers banks during the CEA Marcel loop test. Thus, some degradation compounds could be stripped into the aqueous phase and do not remain in the irradiated solvent. However, the INL and CIEMAT loops are quite similar in design; the difference in performance stability could perhaps be explained by a less efficient purging of the radiolysis gases during the extraction step for CIEMAT, leading to their accumulation and a deleterious effect on performance. These radiolysis gases are permanently purged in the CEA Marcel loop because the mixer-settlers are not hermetically sealed.

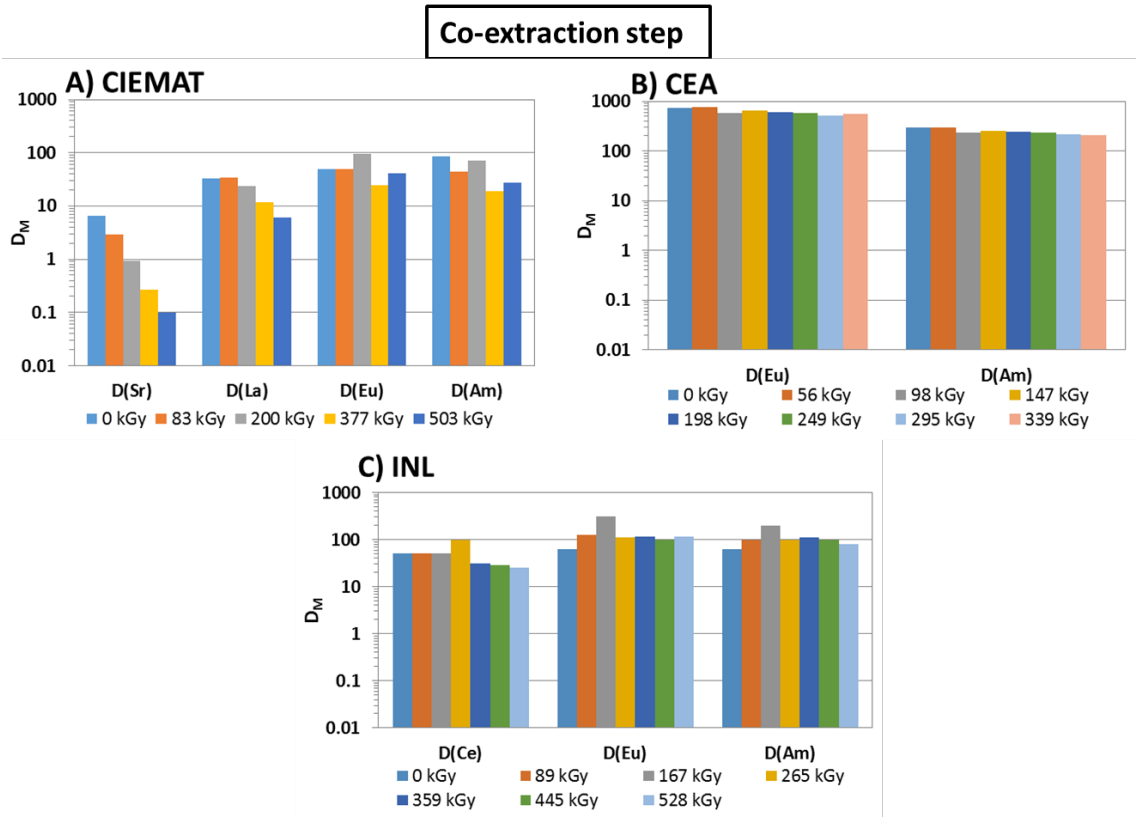


Figure 5. Distribution ratios of Sr(II), La(III) and Nd(III) and radioactive tracers $^{152}$Eu, $^{139}$Ce and $^{241}$Am as a function of the absorbed dose for the first step of irradiation in Náyade, INL and Marcel loop tests (An + Ln co-extraction). A) CIEMAT experiment: Org. phase: Irradiated 0.4 mol/L mTDDGA in dd. Aq. initial phase: Irradiated 4.5 mol/L $HNO_3$ with 1 mmol/L of Sr, La, Nd and Eu and spiked with $^{241}$Am and $^{152}$Eu. Nd and Eu data obtained by ICP-MS were not included due to its not-satisfactory measurement. B) CEA experiment: Irradiated 0.4 mol/L mTDDGA in dd from CX-Marcel loop test. Aq. Initial Phase: 4.7 mol/L $HNO_3$ spiked with $^{241}$Am and $^{152}$Eu. C) INL experiment: Org. phase: Irradiated 0.4 mol/L mTDDGA in dd. Aq. Initial phase: Irradiated 4.5 mol/L $HNO_3$ with 1 mmol/L of Ce and Eu and spiked with $^{241}$Am, $^{152}$Eu and $^{139}$Ce.

The potential corrosion products of the 316 stainless steel Náyade reactor coil were measured by ICP-MS and the results are shown in Figure S6 in appendix B of the supporting information. From these results it can be concluded that *cis*-mTDDGA co-extracts these elements much less than the previous EURO-GANEX solvent even at high acidity, as reported [17, 18, 48] in agreement with studies found in literature [23, 46].

### 3.2 TRU and Ln Stripping steps

For CIEMAT and CEA, the irradiated organic samples from An+Ln co-extraction were contacted with fresh 0.4 mol/L PTD in 2.1 mol/L $HNO_3$ (TRU stripping 1.1) or 0.04 mol/L PTD in 1.5 mol/L (TRU stripping B) and then replaced with 0.01 mol/L $HNO_3$ (Ln Stripping 1.1), to simulate the sequence of TRU and Ln stripping steps respectively. In the case of INL, an additional scrubbing step in 2.1 mol/L $HNO_3$ was inserted before the Ln stripping step with fresh 0.04 mol/L PTD in 2.1 mol/L $HNO_3$. The purpose of

this experiment was to evaluate the effects of radiolysis on the An and Ln stripping performances due to the degradation of the solvent and the formation of *cis*-mTDDGA degradation compounds. Table 1 shows the composition of both phases during this experiment (An Stripping 1.1 / An Stripping B + Ln Stripping 1.1).

Table 1. Composition of the organic and aqueous phases during the An Stripping and Ln Stripping experiments.

| Step | Solvent dose (Náyade loop) (kGy) | Solvent dose (Marcel loop) (kGy) | Solvent dose (INL loop) (kGy) | Aq. ph.: An Stripping 1.1 | Aq. ph.: An Stripping B | Aq. ph.: Ln Stripping 1.1 |
|---|---|---|---|---|---|---|
| **An Stripping 1.1 + Ln Stripping 1.1** | 0 | 0 | 0 | Fresh 0.4 mol/L PTD in 2.1 mol/L $HNO_3$ | Fresh 0.04 mol/L PTD in 1.5-2.1 mol/L $HNO_3$ | Fresh 0.01 mol/L $HNO_3$ |
| | - | 56 | - | | | |
| | 84 | 98 | 89 | | | |
| | - | 147 | 167 | | | |
| | 200 | 198 | - | | | |
| | - | 249 | 265 | | | |
| | - | 295 | - | | | |
| | 377 | 339 | 359 | | | |
| | - | - | 445 | | | |
| | 503 | - | 528 | | | |

A white precipitate was observed when the Náyade irradiated organic solvents was contacted with the An Stripping 1.1 aqueous phase. This phenomenon did not occur in the INL loop, nor in their batch experiments nor in batch experiments from Marcel irradiated solvents. However, several hydrodynamic issues appeared during the Marcel loop test, especially in the Ln Stripping step 1.1 (CX in the figure S3 of ESI). After one week (56 kGy), the platform was automatically shut down following the appearance of a white gel in the last Ln stripping stage. The flow meter upstream of the solvent recycling was completely blocked by this gel. After cleaning, the phenomenon was noticeable in the monitoring of the recycling solvent flow rate and pump speed. Figure 6

shows a photo of this gel and some examples of monitoring screenshots during the Marcel loop test.

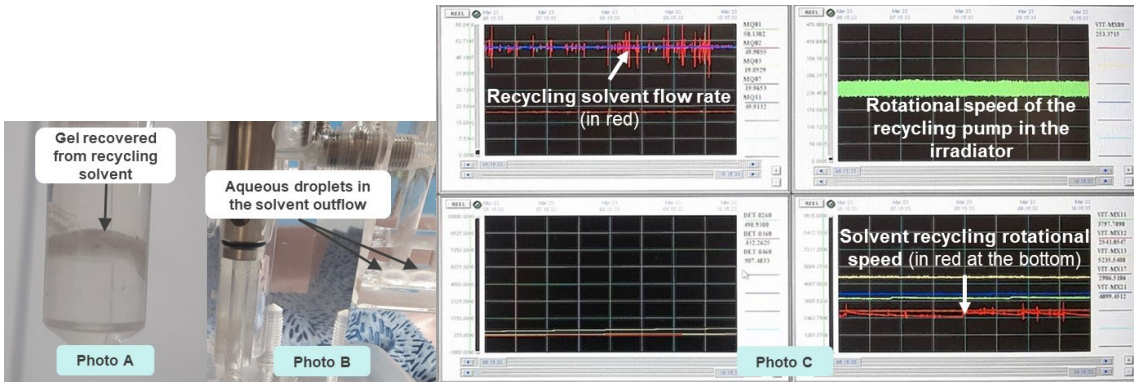



Figure 6. Photo A: gel recovered in the recycling solvent vial and in the flow meter. Photo B: droplets collected in the solvent outflow. Photo C: screenshots showing continued instability in the recycling solvent flow rate and pump speed during the Marcel loop test.

The gel/precipitate obtained in the CIEMAT batch experiment was filtered but not completely dried, thus containing traces of the organic solution. After a light wash with n–dodecane, this gel/solid was dissolved in a small amount of methanol to be analyzed by HPLC-MS. The analysis showed mainly the presence of didecylamine, which is in agreement with the studies performed by Verlinden et al. [46]. GC-MS analysis showed, besides didecylamine, the presence of didecylglycine and decanoic acid as expected in literature [49]. This identification of the amine could explain why this gel was not observed in the first An-Ln extraction step of the Marcel loop test (AX in Figure S3) at high acidity and only from an absorbed dose of 200 kGy in the An+Ln co-extraction step of Náyade facility. When this didecylamine was contacted with 4-4.5 mol/L $HNO_3$ containing 5-20 mmol/L of extractable cations, it became protonated, thus partially soluble in the aqueous phase or formed a solvent-soluble complex. In Marcel loop test, some of the didecylamine was stripped in the high nitric acid aqueous stages or in the

453 downstream steps, whereas the precipitate occurred from an absorbed dose of 200 kGy
454 in the Náyade An+Ln co-extraction step because too much didecylamine must have
455 accumulated above this dose, as the aqueous phase was not renewed. On the other hand,
456 at low acidity, few of the didecylamine was protonated and the solubility of this
457 molecule decreased in the aqueous phase while no cation was complexed in the solvent
458 anymore due to the aqueous Ln stripping conditions. In addition, the presence of a low
459 proportion of decanoic acid could lead to hydrodynamic problems at low acidity with a
460 hydrophilic polar part containing $OH^-$ and a long carbon chain remaining in the organic
461 phase. Thus, extra-batch experiments have shown that hydrodynamic problems
462 decreased with increasing acidity of the aqueous medium. This explains the change in
463 the acidity and flow rate values of the CX step during the Marcel loop test (Figure S3).
464 It was likely caused by a degradation compound of *cis*-mTDDGA, since during the first
465 days of the test, no hydrodynamic problems were observed.

466 The variation of $D_M$ as a function of absorbed dose is shown in Figure 7 under the
467 conditions of the An Stripping 1.1 step for CIEMAT/CEA solvents (0.4 mol/L PTD).
468 Figure 8 gives results in the case of the An Stripping B step for INL/CEA solvents (0.04
469 mol/L PTD). With 0.4 mol/L PTD, an unexpected value of $D_{Am} > 1$ was measured with
470 the initial organic phase by CIEMAT and CEA. According to the previous results
471 carried out by Wilden et al., when both phases are fresh using these concentrations, this
472 value should be lower than 1, allowing an efficient separation of these elements. The
473 observed difference could be related to the purity of the solvent employed. By
474 increasing the absorbed dose, a decrease in $D_M$ is observed but the phenomenon is more
475 pronounced for CIEMAT than for CEA. As shown in Figure 7, a better Eu/Am
476 separation performance was obtained, reaching a $SF_{Eu/Am} = 19$ in the CIEMAT results
477 while the separation factors increase moderately in the CEA experiments, even at the

same dose, 198-200 kGy for instance. In the case of An stripping B (Figure 8), as with extraction step, the effect of radiolysis is comparable between the Marcel and INL solvents. The distribution ratios from INL are slightly higher than those of CEA, which is a consequence of a higher final acidity. The Am/Eu separation factors are stable as a function of radiolysis dose and lower than for An Stripping 1.1 due to the smaller PTD concentration. This lesser radiolysis impact observed for the CEA or INL compared to CIEMAT results could be explained by the continuous removal of some radiolysis gases. This means that most of the decrease in $D_M$, observed in the Náyade loop experiment, was not a consequence of *cis*-mTDDGA degradation but certainly of the antagonism provided by some degradation compounds that are not present in an open system.

As already seen in the An+Ln co-extraction step, Figure 7 shows that strontium extraction is more affected by radiolysis than the lanthanides behaviour which are expected to remain predominantly in the solvent, even under these radiolytic conditions. $D_{Sr}$ decreased dramatically meaning that a degraded cis-mTDDGA solvent would strip Sr along with the An. However, as we have seen previously, Sr is much less extracted from the high nitric than Am, Cm, so it is easy to design a flowsheet with efficient scrubbing of Sr after extraction part, without loss of An, even with a degraded solvent.

These first results are promising since extraction and separation performances are not too much altered by radiolysis. Furthermore, it seems that a simple nitric acid solution could remove some problematic degradation compounds from the irradiated cis-mTDDGA solvent. Further studies on solvent treatment could improve this efficiency and suppress the occurrence of hydrodynamic disturbances by continuously withdrawing degradation compounds. However, due to the high number of carbon atoms, very efficient operating conditions might be difficult to find.

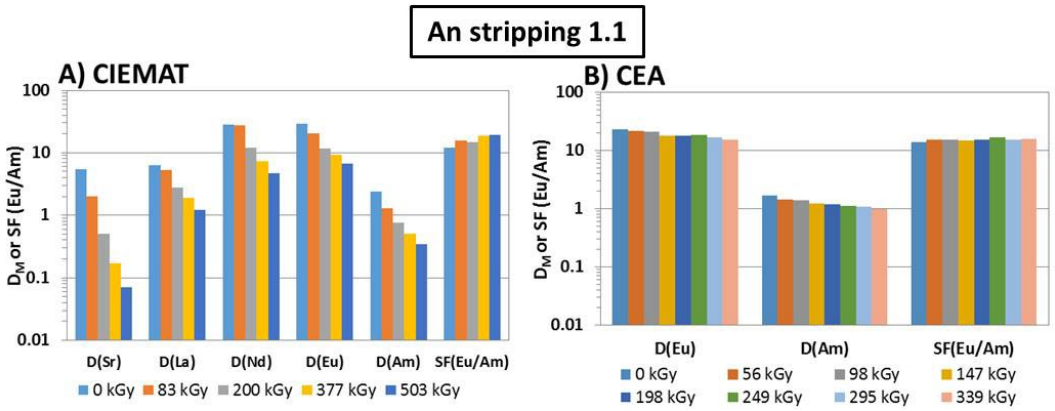



Figure 7. Distribution ratios and separation factors of different elements as a function of the absorbed dose for the An stripping 1.1 experiment at CIEMAT and CEA. A) CIEMAT experiment: D(Sr), D(La) and D(Nd) obtained by ICP-MS and D(Eu) and D(Am) obtained by gamma spectrometry. B) CEA experiment: D(Eu) and D(Am) obtained by gamma spectrometry. Org. Phase in the two experiments: Fresh and Irradiated 0.4 mol/L mTDDGA in dd up to 503 kGy. Aq. Phase: Fresh 0.4 mol/L PTD in 2.1 mol/L $HNO_3$ and spiked with $^{241}Am$ and $^{152}Eu$.

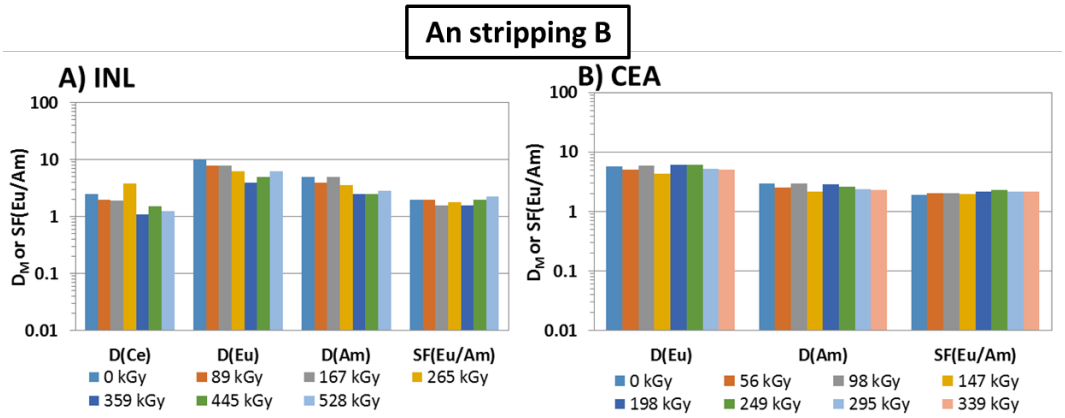
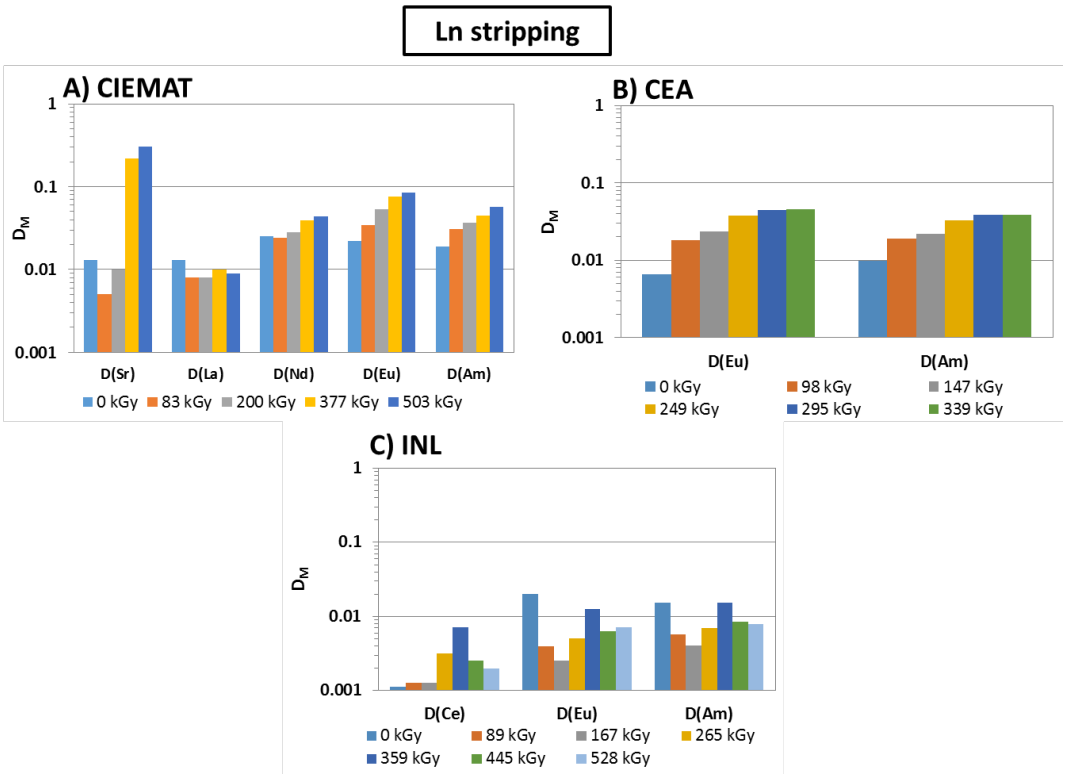



Figure 8. Distribution ratios and separation factors of different elements as a function of the absorbed dose for the An stripping B experiment at INL and CEA with 0.04 mol/L PTD instead of 0.4 mol/L PTD. A) INL experiment: D(Ce), D(Eu) and D(Am). B) CEA experiment: D(Eu) and D(Am) obtained by gamma spectrometry. Org. Phase: Fresh and Irradiated 0.4 mol/L mTDDGA in dd up to 412 kGy. Aq. Phase: Fresh 0.04 mol/L PTD

517 in A) 2.1 mol/L $HNO_3$ (2.2 mol/L final $HNO_3$) for INL, or B) in 1.5 mol/L $HNO_3$ (1.7
518 mol/L final $HNO_3$) for CEA, spiked with $^{241}Am$ and $^{152}Eu$.

519 Figure 9 shows the $D_M$ obtained for the Ln stripping for all irradiation loops. As
520 expected, all D values are lower than 0.1. However, it seems that some cis-mTDDGA
521 degradation compounds extract Sr, Nd, Eu or Am at low acidity since the D values
522 increase as a function of absorbed dose. This phenomenon is less noticeable for La but
523 very representative for Sr element in the case of the CIEMAT experiments. As observed
524 in the An extraction or An stripping step, the effect of radiolysis is less important for the
525 solvents from the Marcel or INL loop test than for those from the Náyade loop
526 experiment. However, the increase in $D_{Eu}$ is very high, about 4 to 7 times higher than
527 the value obtained with a non-irradiated solvent. Fortunately, the distribution ratios
528 remained low, so that no risk of cation accumulation could occur. Nevertheless,
529 appropriate treatment of the solvent with basic aqueous solution could remove these
530 unwanted degradation compounds.




531

Figure 9. Distribution ratios of different elements as a function of the absorbed dose for the Ln stripping step corresponding to A) Náyade, B) Marcel and C) INL tests loops. Org. Phase: Fresh and Irradiated 0.4 mol/L mTDDGA in dd up to 503 kGy from An stripping experiment. Aq. Phase: 0.01 mol/L $HNO_3$.

### 3.3 Study of the composition of phases

In order to get an overall picture of what happened and a more complete understanding of the system, the composition of the organic solutions used in this inter-institutional experiment was studied by HPLC-MS.

Figure 10 shows the concentration of cis-mTDDGA remaining in the irradiated solvent samples from the CIEMAT Náyade, CEA Marcel and INL loop tests. As Verlinden et al. reported [47], the degradation of cis-mTDDGA follows a kinetic law of pseudo first order with respect to the monoamide concentration. By plotting the concentrations C as a function of absorbed dose (in kGy), it is possible to determine a constant k' according to the following equation: $C = C_0\ e^{-k'dos}$. This kinetic degradation constant k' allows to compare the overall stability of extractants, independently of their concentration in solution. From the results obtained in Figure 10, k' is 0.0023 $kGy^{-1}$ for CIEMAT, 0.0018 $kGy^{-1}$ for CEA samples and 0.0011 $kGy^{-1}$ for INL. The CIEMAT and CEA values are in agreement with the one obtained by Verlinden et al., (0.0028 $kGy^{-1}$ when 0.05 mol/L cis-mTDDGA is irradiated in contact with 2.5 mol/L $HNO_3$) [47]. This is lower than the TODGA dose constant (0.0038 $kGy^{-1}$ in [36], 0.0034 $kGy^{-1}$ in [40], irradiating the organic phase with nitric acid aqueous phase in both studies), indicating higher stability of cis-mTDDGA against radiolysis. However, the observed degradation rate of cis-mTDDGA for INL samples is lower, producing a smaller amount of DCs, which is in agreement with the different extraction results shown above. Regarding the

556 extraction results between CEA and INL, in "An stripping B", the results obtained by
557 INL and CEA are more or less the same, but this is not the case in "Ln Stripping" where
558 the INL solvent seems less affected by radiolysis. This means that there are more
559 degradation products in the CEA solvent, which extracts more Am at a lower acidity.
560 This is consistent with the lower degradation rate of cis-mTDDGA for INL samples. As
561 the dose rate of the CEA irradiator is lower than that of the INL, this additional
562 degradation compared to the total dose comes from the longer residence time of the
563 solvent in the CEA loop for the same total dose and therefore from a higher proportion
564 of solvent degradation by hydrolysis. Taking into account these results, this degradation
565 seems to have a limited impact on the extraction and separation performance of trace
566 Am and Eu. Studies by Wilden *et al* have shown that $D_{Am,Eu}$ vary linearly with the
567 concentration of mTDDGA in the solvent. In this work, with the decrease in cis-
568 mTDDGA concentration by a factor of 2 at a dose of 339kGy, $D_{Am,Eu}$ remain relatively
569 stable in the extraction step (Figure 5) and in the stripping parts (Figure 7 and Figure 8).
570 This means that the major degradation products compensate for the expected decrease in
571 extractability due to the loss of cis-mTDDGA. On the contrary, the impact of
572 degradation is more visible at low acidity (Ln stripping step, Figure 9) but could be
573 managed in the process since distribution ratios remain relatively low. Overall, the
574 degradation of cis-mTDDGA does not have a dramatic negative impact on performance,
575 which is very important for the process.

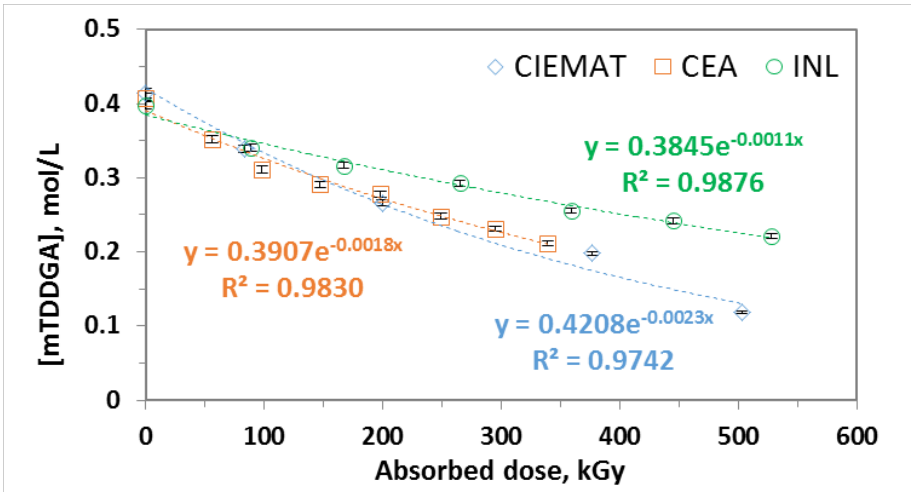
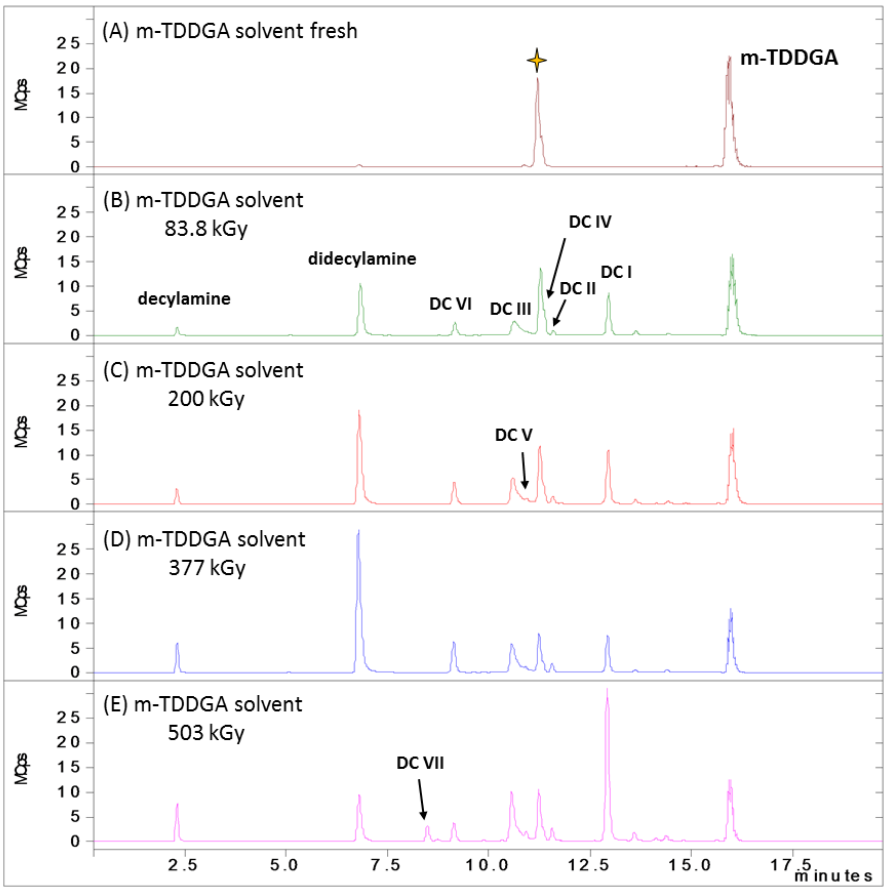



Figure 10. cis-mTDDGA concentration as a function of the absorbed dose in solvent samples from the CIEMAT, CEA and INL loops.

The degradation compounds of cis-mTDDGA were identified qualitatively for the CIEMAT and CEA samples. Figure 11 shows the HPLC-MS analysis of the reference and irradiated samples corresponding to CIEMAT samples after the An+Ln co-extraction and the An stripping of the Náyade irradiation loop. The results of the CEA samples are not included here as they are similar to those of CIEMAT. For the fresh solvent (Figure 11A), in addition to the peak related to cis-mTDDGA (m/z = 721.5, r.t = 16.1 min), a signal related to an impurity from the organic synthesis is detected (m/z = 340, r.t= 11.3 min shown as star in Figure 11A). When samples are irradiated in the co-extraction step (Figure 11B-D), nine degradation compounds (I, II, III, IV, V, VI, VII, decylamine and didecylamine) can be identified with their probable structures shown in Figure 12. The intensity of the peak at m/z = 340, corresponding to the impurity, decreases, showing the instability of this molecule towards radiolysis. No study has been carried out on this impurity, but it could explain why the distribution coefficients of trace americium are higher with this cis-mTDDGA solvent than with Wilden's data. This hypothesis should be confirmed by further experiments. All cis-mTDDGA DCs observed are in agreement with the studies performed by Verlinden et al. [46, 47].




595

596 Figure 11. Qualitative HPLC-MS chromatograms of mTDDGA solvent obtained from
597 the Náyade irradiation test loop: (A) fresh or reference sample, and irradiated in contact
598 with 4.5 mol/L $HNO_3$ to (B) 84 kGy; (C) 200 kGy; (D) 377 kGy and (E) 503 kGy.
599 (Note: Since DC IV appears at the same time as impurity m/z 340 (indicated as star in
600 the chromatogram), the signal is overlapped and therefore it is shown in that way.)

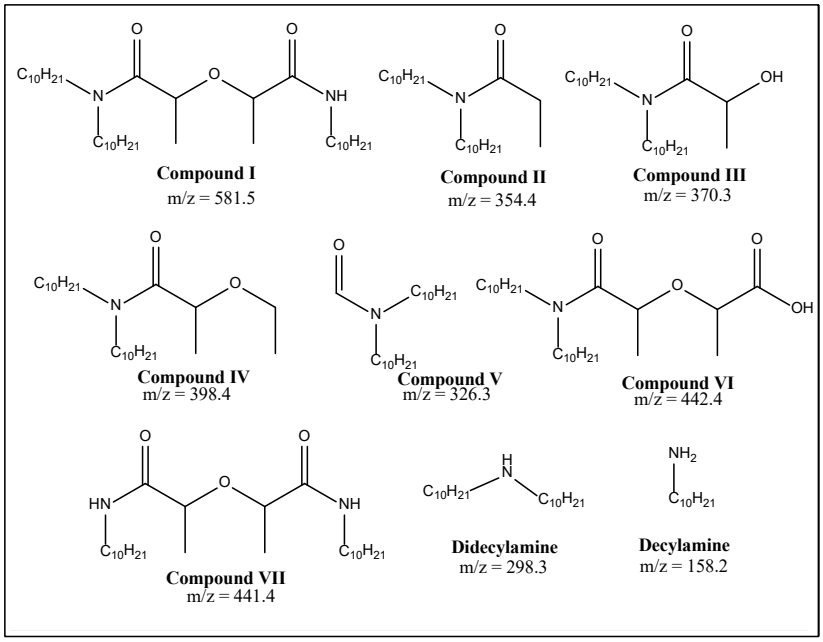



Figure 12. Chemical structures of mTDDGA degradation compounds.

Table 2 gives the results of the densities and viscosities measured on the solvent samples at the beginning and the end of the Náyade and Marcel loop tests. While the density was virtually unaffected during the irradiation test, the viscosity increased by 30% under 566 kGy at the end of CIEMAT loop test and by 20% under 339 kGy for CEA experiment. The end of CIEMAT loop test (566 kGy) corresponds to 503 kGy in contact with 4.5 mol/L $HNO_3$ with 1 mmol/L of Sr, La, Nd and Eu + 63 kGy with 0.04 mol/L PTD in 2.1 mol/L $HNO_3$ (data from this last step is not shown in this work). The viscosity changes are significant but, as the long loop test at Marcel shows, manageable in mixer-settlers. In addition, the implementation of a solvent treatment step could limit the increase in viscosity, certainly due to the formation of degradation compounds.

As shown in Figure 13, the viscosity value obtained for CIEMAT at 566 kGy follows the same trend as those measured in the CEA Marcel loop test. Together with the previous results of the batch experiments and the hydrodynamic phenomena observed, this confirms that both loops lead to a similar effect on the irradiated solvent. This

means that the irradiation of the organic phase with an aqueous solution (Náyade loop) or the continuous operation in mixer-settlers of an irradiated solvent (Marcel loop) leads to the same effect and is a good step to validate the behaviour of a liquid-liquid system in a nuclear reprocessing plant.

Table 2. Density and dynamic viscosity results for different samples for the new EURO-GANEX test loop irradiation experiment.

| | Samples | Density ($g/cm^3$ at T=23°C) | Dynamic viscosity (mPa·s at T=23°C) |
|---|---|---|---|
| Náyade loop | mTDDGA 0 kGy | 0.796 ± 0.001 | 4.286 ± 0.05 |
| | mTDDGA 566 kGy | 0.801 ± 0.003 | 5.578 ± 0.05 |
| Marcel loop | mTDDGA 0 kGy | 0.796 ± 0.001 | 4.204 ± 0.07 |
| | mTDDGA 339 kGy | 0.804 ± 0.003 | 5.048 ± 0.05 |

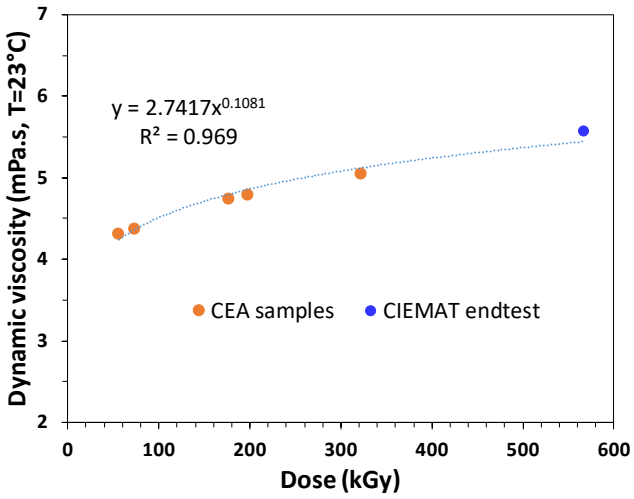



Figure 13. Dynamic viscosities measured at 23°C on some irradiated samples from CIEMAT or CEA loop test.

## 4. CONCLUSIONS

An inter-institutional study between CEA, INL and CIEMAT has been performed under the most relevant and realistic experimental conditions to investigate the resistance of

630 the cis-mTDDGA extraction system to gamma radiolytic degradation during a dynamic
631 irradiation test simulating the main steps of the New EURO-GANEX process. In this
632 work, results of three experiments are presented for the studied steps of this process:
633 An+Ln co-extraction, TRU stripping and Ln stripping, focusing on the stability of the
634 organic solvent and extractant and the findings contribute to demonstrate the
635 performance of the new EURO-GANEX process, as a promising process to achieve the
636 TRU recovery.

637 Although there are some differences between the three irradiation facilities, this inter-
638 institutional study shows that these three comparative tools provide similar trends in the
639 radiolysis stability of a liquid-liquid extraction system. These tools are very useful in
640 understanding the phenomena or issues that could occur in a genuine nuclear facility,
641 where an organic solvent is continuously recycled and undergoes degradation due to
642 hydrolysis and radiolysis.

643 Despite a good stability performance of the extraction data for the continuously
644 irradiated solvents, there are several considerations that need to be taken into account:
645 namely, how effectively a solvent treatment could remove the problematic organic
646 degradation compounds. For example, some of these compounds produced insoluble
647 species and third phases. In addition, some of them increase the extraction of
648 lanthanides at low acidity, which could decrease their final extraction before solvent
649 recycling. These problems need to be controlled in a future reprocessing plant, mainly
650 by specific treatment of the solvent.

651 The major result of these experiments is the stability of the extraction performances and
652 Ln/An selectivity measurement after undergoing an irradiation dose corresponding to a
653 residence time of 19 weeks in a reprocessing plant for MOX fuel. Further studies are

needed to improve its stability and to achieve an optimal reprocessing process at an industrial level, with adequate solvent treatment as well as to evaluate the behaviour of the whole process taking into account the resistance of the aqueous phase for the An/Ln separation.

## AUTHOR CONTRIBUTIONS

Ivan Sánchez-García, Xavier Heres and Dean R. Peterman: Investigation, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. Hitos Galán, Andreas Geist and Andreas Wilden: Supervision, Conceptualization, Validation, Writing - review & editing. Santa Jansone-Popova: Synthesis of cis-mTDDGA compound and review & editing. Maria Chiara Gullo and Alessandro Casnati: Synthesis of PTD reagent and review & editing. Sylvain Costenoble, Sylvain Broussard, Johan Sinot: experimental work at CEA and review & editing**,** Travis S. Grimes and Kash R. Anderson: experimental work at INL and review & editing**.** All authors have given approval to the final version of the manuscript.

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683 SUPPORTING INFORMATION

684 The following information are provided:

685 • Appendix A. Irradiation test loops. Additional experimental details, including
686 photographs of experimental setup of three irradiation test loops (CIEMAT,
687 CEA and INL) employed and the scheme of the process studied.

688 • Appendix B. Analysis of corrosion products of reactor of Náyade test loop
689 measured by ICP-MS.

690 • Appendix C. Details of the synthesis of cis-mTDDGA including 1H NMR
691 spectra for all compounds employed in the synthesis.

692

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***Graphical Abstract***