Interinstitutional Study of the New EURO-GANEX Process Resistance by Gamma Irradiation Test Loops

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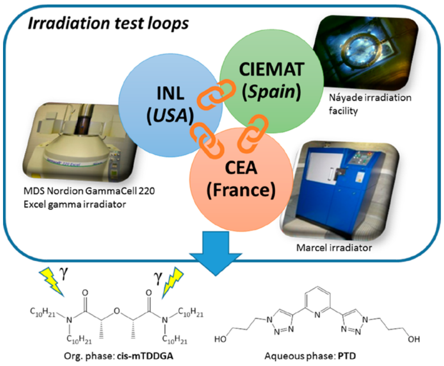
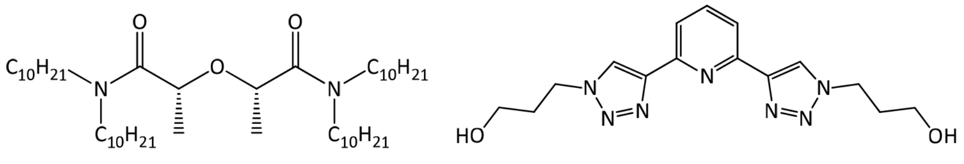


ABSTRACT: As part of the homogeneous actinide recycling strategy, the EURO-GANEX process is one of the most promising options to achieve the goal of minor actinides recovery. Improvements made to EURO-GANEX system have resulted in the emergence of the so-called New EURO-GANEX process, where the composition 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 2-fold: 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. The Náyade and 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 interinstitutional study shows that these three comparative tools provide similar trends in the radiolytic stability of a liquid–liquid extraction system. Favorable 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 transuranic 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 coextraction 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 coextraction 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 coextraction 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


cis-mTDDGA

PyTri-diol or PTD

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

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 byproducts. Therefore, the process needs to be further optimized to meet the criteria mentioned above 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 past 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_2TODGA revealed different distribution ratio values, even by 2 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_2TODGA.[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 the 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, the *cis*-mTDDGA solvent is useful to extract actinides and lanthanides from an acidic GANEX first cycle raffinate. After this coextraction step, the TRU elements are selectively stripped into the PTD aqueous solution, while *cis*-mTDDGA maintained rare earth elements in the organic phase.

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 the secondary waste and process costs.

In literature, several studies can be found which tackle the stability of diglycolamides toward 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_2TODGA), which showed less resistance to γ 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 toward γ radiation compared to TODGA. At least nine DCs with chemical structures typical 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 the 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, then 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

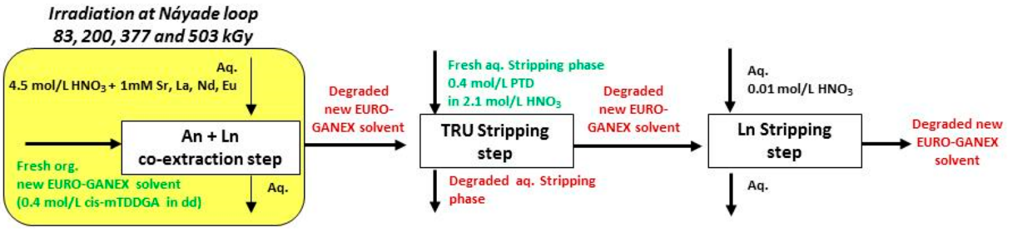


Figure 2. Scheme of the main steps of the new EURO-GANEX process simulated at the Náyade irradiation loop test.

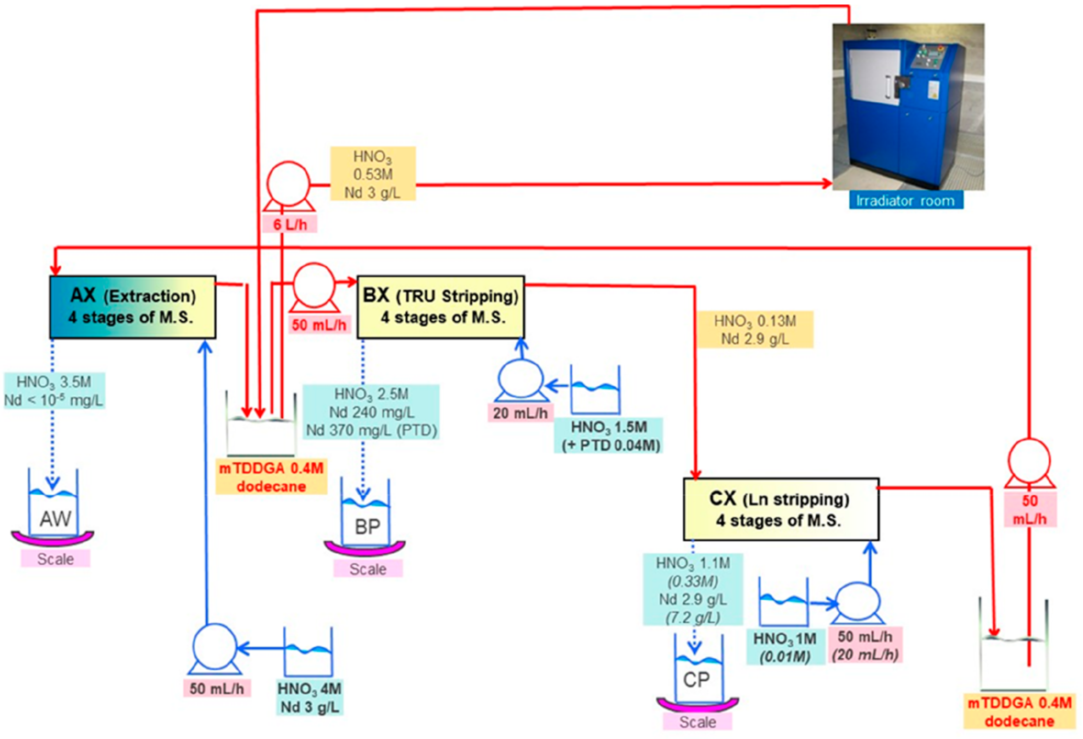


Figure 3. Flowsheet of the loop test following the CX hydrodynamic problem (italics indicate initial value). The CX outflow solvent samples for batch studies were taken after 56, 98, 147, 198, 249, 295, and 339 kGy (M.S. = mixer-settler).

preliminary batch experiments, in order to obtain extraction factors (distribution ratio × volumes or organic/aqueous flow rates) greater than 2 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 interinstitutional 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 center 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 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 65% nitric acid 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 deionized water (18 MΩcm). The radioactive tracer solutions of ^{241}Am and ^{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 and ^{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 the $Eu(NO_3)_3·6H_2O$ and $Ce(NO_3)_3·6H_2O$ powders.

2.2. Irradiation Test Loops. Three irradiation loops for this interinstitutional 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 coextraction, An stripping, and Ln stripping steps were evaluated. In the Náyade and INL loops, organic and aqueous phases were irradiated in contact; meanwhile, in the Marcel loop, only the organic phase was irradiated. The dose rates employed and the absorbed doses reached were comparable in all experiments (2.6 kGy/h and 503 kGy for CIEMAT, 0.78 kGy/h and 339 kGy for CEA and 2.2 kGy/h and 528 kGy for INL). The description of each irradiation test loop is summarized in the Appendix A of the Supporting Information.

2.3. Solvent Extraction Performance. *2.3.1. Náyade Loop.* The behavior of the New EURO-GANEX process after the three different steps mentioned before was assessed with spiked samples (^{241}Am and ^{152}Eu, 100 kBq/mL each). All extraction experiments were performed by mixing 500 μL of both, aqueous and organic phases, for 30 min at room temperature (22 ± 2 °C). Then, the phases were separated by centrifugation (5 min at 5000 rpm) and aliquots of each phase were taken for analysis (300 μL for gamma and 100 μL ICP-MS).

For high energy gamma spectroscopy measurements, a high purity-germanium detector with an intrinsic efficiency of 20% was used, using a Genie-2000 (Canberra) as analysis software. The gamma characteristic photopeaks at 59.5 and 121.8 keV were analyzed for ^{241}Am and ^{152}Eu, respectively.

The concentrations of the elements present in the initial aqueous solution (Sr, La, and Nd) as well as those coming from the stainless-steel corrosion products (Fe, Cr, Ni, and Mo) were determined by ICP-MS. The organic and aqueous phases were analyzed directly after a suitable dilution in HNO_3 (2−5%). All extraction results are reported as distribution ratio D ($D_M = C(M)_{org}/C(M)_{aq}$), where D_M between 0.01 and 100 exhibits a maximum error of ±5%. The limits 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 the LODs are 2.2×10^{-7}, 2.88×10^{-9}, 1.50×10^{-8}, 6.60×10^{-9}, 1.95×10^{-6}, 1.19×10^{-7}, 1.68×10^{-7}, and 3.85×10^{-8} mmol/L, respectively.

A schematic representation of the main steps of the irradiation loop setup, 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 Appendix A of the Supporting Information.

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 Appendix A of the Supporting Information.

These experiments were performed with 8 solvent samples: initial, 56, 98, 147, 198, 249, and 295 kGy, and 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 of performing, at first, an extraction with solvents and an aqueous phase containing trace amounts of ^{241}Am (127 kBq/mL) and ^{152}Eu (97 kBq/mL) with 4.7 mol/L HNO_3. Then a back-extraction of these cations was carried out with three aqueous solutions in parallel ($V_{aq} = V_{org}$, mixed for 30 min at 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 mol/L HNO_3. The same type of gamma spectrometer as used for CIEMAT was used to determine gamma activities in organic and aqueous phases.

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

Moreover, in order to observe the behavior of Nd in the mixer-settlers, each stage was emptied after the Marcel test was stopped. The aqueous phases in the settling chambers were sampled to measure the Nd concentration by ICP-OES for all 12 stages. There was no PTD in An stripping step (BX in Figure S3).

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

2.3.3. INL Loop. To determine the impacts of gamma radiolysis on the New EURO-GANEX solvent, extraction, scrub, and strip batch contact flowsheet tests were performed using the irradiated aqueous and organic phases. The Am, Ce, and Eu distribution ratios for these flow sheet tests were determined prior to and after the 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 mixture was scrubbed using 2.1 mol/L HNO_3. The actinide stripping solution consisted of 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 an ACE 3 C18-PFP column (50 mm × 2.1 mm) at 40 °C, 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

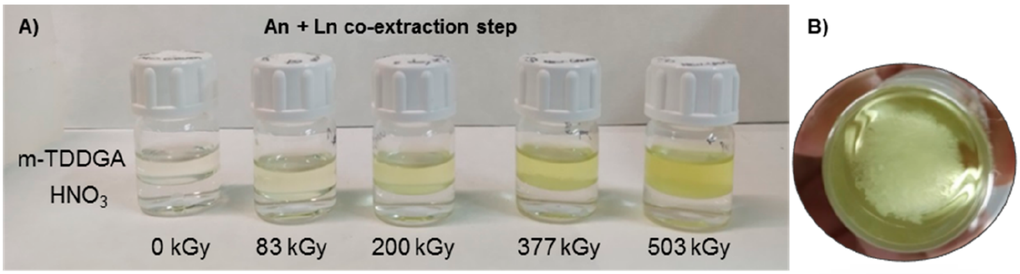


Figure 4. A) Samples of the first irradiation step. organic phase: 0.4 mol/L mTDDGA in dodecane, aqueous phase: 4.5 mol/L HNO_3, with an accumulated dose of 0, 83, 200, 377, and 503 kGy. B) Turbidity and small precipitate in the organic phase at 377 kGy.

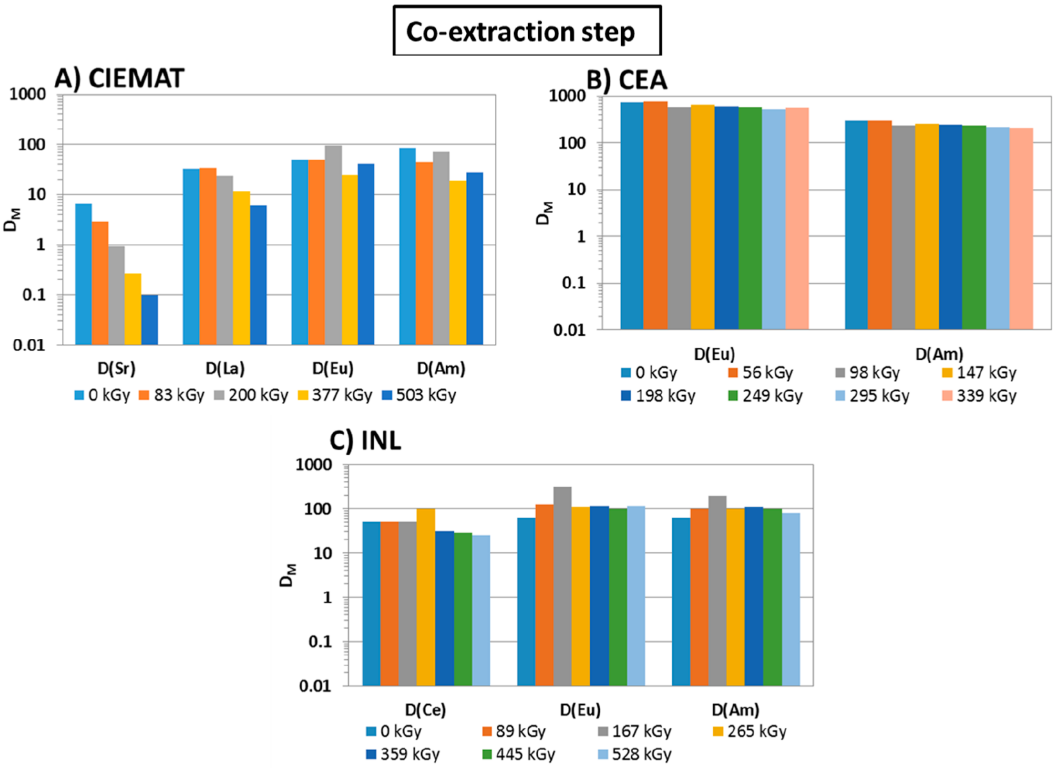


Figure 5. Distribution ratios of Sr(II), La(III), and Nd(III) and radioactive tracers ^{152}Eu, ^{139}Ce, and ^{241}Am as a function of the absorbed dose for the first step of irradiation in Náyade, INL and Marcel loop tests (An + Ln coextraction). A) CIEMAT experiment: Organic phase: irradiated 0.4 mol/L mTDDGA in dd. Aqueous 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 unsatisfactory measurement. B) CEA experiment: irradiated 0.4 mol/L mTDDGA in dd from the CX-Marcel loop test. Aqueous initial phase: 4.7 mol/L HNO_3 spiked with ^{241}Am and ^{152}Eu. C) INL experiment: Organic phase: irradiated 0.4 mol/L mTDDGA in dd. Aqueous 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.

show a maximum error of ±3%. The samples of the irradiated *cis*-mTDDGA was also analyzed in the CIEMAT facilities.

INL used HPLC to quantify the *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 photodiode 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 MΩ cm Nanopure water. The chromatographic separation was achieved with a C18 reverse-phase (RP-C18) column (Supelco, 25 cm × 4.6 mm, 5 μm) with a flow rate of 0.8 mL/min. The column temperature was maintained at 50 °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 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

Table 1. Composition of the Organic and Aqueous Phases during the An and Ln Stripping Experiments

step	solvent dose (Náyade loop) (kGy)	solvent dose (Marcel loop) (kGy)	solvent dose (INL loop) (kGy)	aqueous phase: An stripping 1.1	aqueous phase: An stripping B	aqueous phase: 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			

calibration standards, blanks, and check standards. All standard brackets reported within a few percent of the previous standard bracket, suggesting that 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 a Unitrode as electrode purchased from Metrohm. A dynamic equivalence point of titration was employed for the determination, where KOH or NaOH was added in variable volume steps. The electrode was calibrated by 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 irradiated samples were performed by using an Ubbelohde micro viscosimeter with a 0.40 mm diameter capillary. A digital stopwatch is used by a ViscoClock *plus* device using IR light barriers. After the time measured is corrected by the Hagenbach factor and then averaged on three measurements, the viscosity and associated uncertainty are calculated.

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

3. RESULTS AND DISCUSSION

3.1. An+Ln Coextraction Step. As described in the Supporting Information, 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 color from light to dark yellow, while the aqueous phase remained virtually unchanged (Figure 4A). For an absorbed dose of 200 kGy, a turbidity and small precipitate in the organic phase can be observed, as shown Figure 4B for the sample irradiated at 377 kGy. The same behavior was found in other studies carried out by Verlinden et al.,[46] wherethey 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.

In the case of the Marcel loop, also without any solvent treatment, the hydrodynamic behavior 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 coextraction 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 outlet of the step. Unlike the 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 the absorbed dose is shown in Figure 5 for the three loops. In the nonirradiated 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 microconcentrations of Eu, Nd, La, and 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 that 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 multistage 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

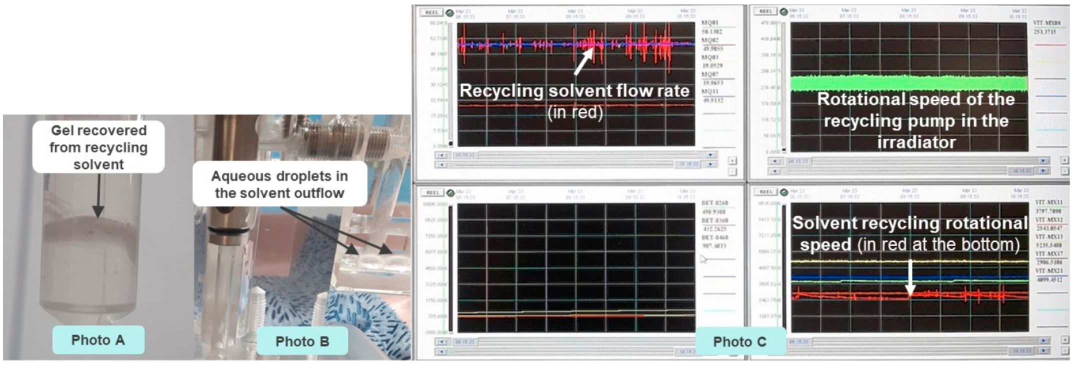


Figure 6. Photo A: gel recovered in the recycling solvent vial and in the flow meter. Photo B: droplets collected in the solvent outflow. Photo C: screenshots showing continued instability in the recycling solvent flow rate and pump speed during the Marcel loop test.

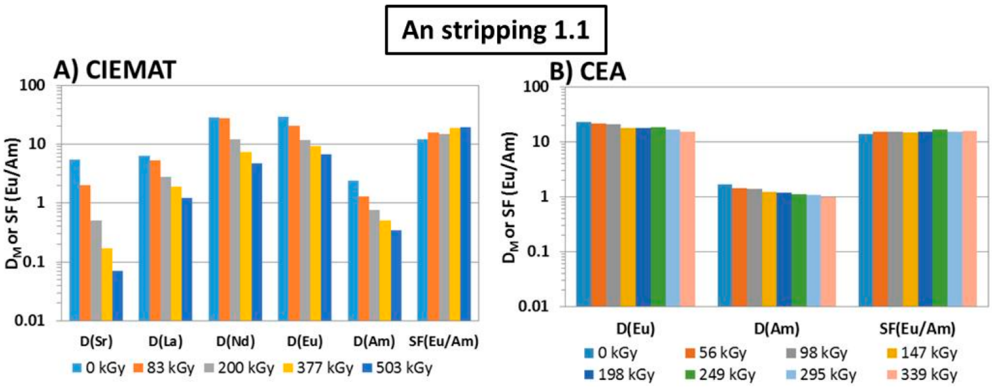


Figure 7. Distribution ratios and separation factors of different elements as a function of the absorbed dose for the An stripping 1.1 experiment at the CIEMAT and CEA. A) CIEMAT experiment: *D*(Sr), *D*(La), and *D*(Nd) obtained by ICP-MS and *D*(Eu) and *D*(Am) obtained by gamma spectrometry. B) CEA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

radiolysis gases are permanently purged in the CEA Marcel loop because the mixer-settlers are not hermetically sealed.

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 coextracts 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 coextraction 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).

A white precipitate was observed when the Náyade irradiated organic solvent was in contact with the An stripping 1.1 aqueous phase. This phenomenon did not occur in the INL loop, in their batch experiments, or in batch experiments from Marcel irradiated solvents. However, several hydrodynamic issues appeared during the Marcel loop test, especially in Ln stripping step 1.1 (CX in Figure S3). After 1 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 solvent recycling was completely blocked by this gel. After cleaning, the phenomenon was noticeable in monitoring 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.

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 coextraction step of Náyade facility. When this didecylamine was contacted with

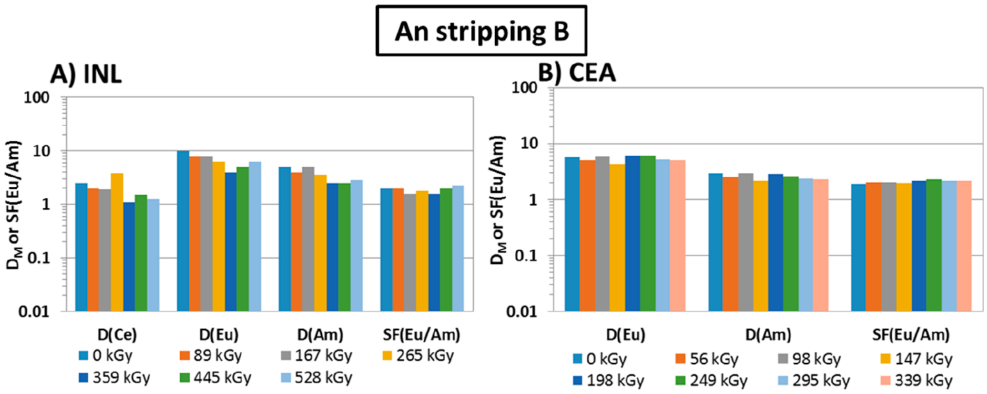


Figure 8. Distribution ratios and separation factors of different elements as a function of the absorbed dose for the An stripping B experiment at INL and CEA with 0.04 mol/L PTD instead of 0.4 mol/L PTD. A) INL experiment: *D*(Ce), *D*(Eu), and *D*(Am). B) CEA experiment: *D*(Eu) and *D*(Am) obtained by gamma spectrometry. Organic phase: fresh and irradiated 0.4 mol/L mTDDGA in dd up to 412 kGy. Aqueous phase: fresh 0.04 mol/L PTD 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 mol/L final HNO_3) for CEA, spiked with ^{241}Am and ^{152}Eu.

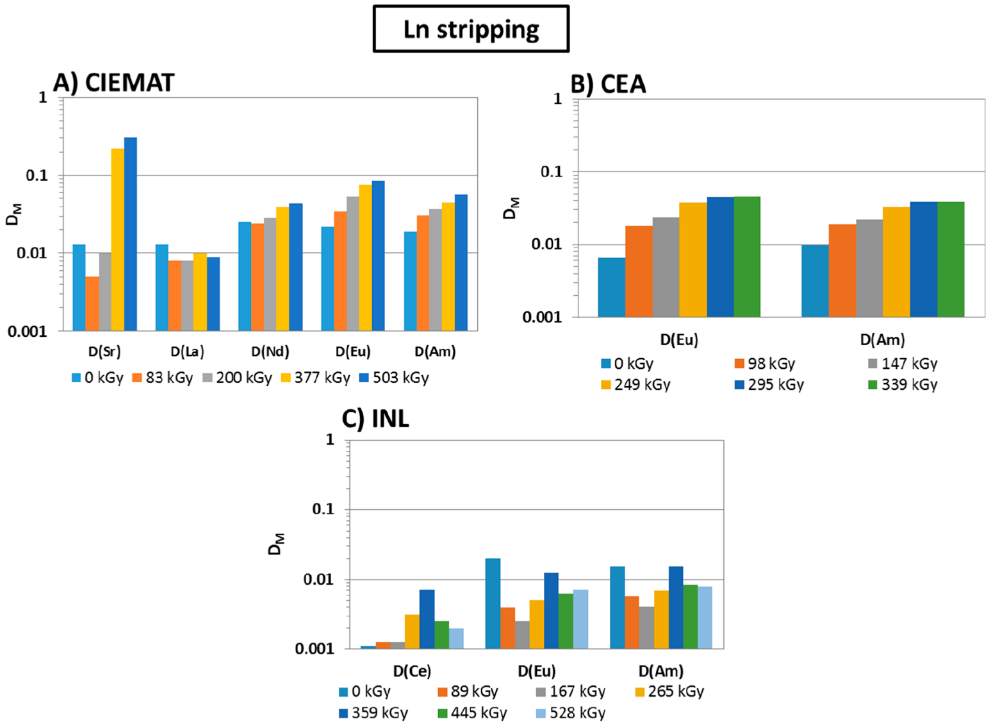


Figure 9. Distribution ratios of different elements as a function of the absorbed dose for the Ln stripping step corresponding to A) Náyade, B) Marcel, and C) INL tests loops. Organic phase: fresh and irradiated 0.4 mol/L mTDDGA in dd up to 503 kGy from An stripping experiment. Aqueous phase: 0.01 mol/L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

4−4.5 mol/L HNO_3 containing 5−20 mmol/L extractable cations, it became protonated and 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 downstream steps, whereas the precipitate occurred from an absorbed dose of 200 kGy in the Náyade An+Ln coextraction step because too much didecylamine must have accumulated above this dose, as the aqueous phase was not renewed. On the other hand, at low acidity, few of the didecylamine was protonated and the solubility of this molecule decreased in the aqueous phase, while no cation was complexed in the solvent anymore due to the aqueous Ln stripping conditions. In addition, the presence of a low proportion of decanoic acid could lead to hydrodynamic problems at low acidity, with a hydrophilic polar part containing OH^- and a long carbon chain remaining in the organic phase. Thus, extra-batch experiments have shown that hydrodynamic problems decreased with increasing acidity of the aqueous medium. This explains the change in the acidity and flow rate values of the CX step during the Marcel loop test (Figure S3). It was likely caused by a degradation compound of *cis*-mTDDGA, since during the first days of the test, no hydrodynamic problems were observed.

The variation of D_M as a function of absorbed dose is shown in Figure 7 under the conditions of the stripping 1.1 step for CIEMAT/CEA solvents (0.4 mol/L PTD). Figure 8 gives results in the case of the An stripping B step for INL/CEA solvents (0.04 mol/L PTD). With 0.4 mol/L PTD, an unexpected value of $D_{Am} > 1$ was measured with the initial organic phase by CIEMAT and CEA. According to the previous results carried out by Wilden et al., when both phases are fresh using these concentrations, this value should be lower than 1, allowing an efficient separation of these elements. The observed difference could be related to the purity of the solvent employed. By increasing the absorbed dose, a decrease in D_M is observed but the phenomenon is more pronounced for CIEMAT than for CEA. As shown in Figure 7, a better Eu/Am separation performance was obtained, reaching a $SF_{Eu/Am} = 19$ in the CIEMAT results, 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 the 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 was a consequence of the antagonism provided by some degradation compounds that are not present in an open system.

As already seen in the An+Ln coextraction step, Figure 7 shows that strontium extraction is more affected by radiolysis than the lanthanide behavior 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 and 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 of 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 9 shows the D_M obtained for the Ln stripping for all irradiation loops. As expected, all D values are lower than 0.1. However, it seems that some *cis*-mTDDGA degradation compounds extract Sr, Nd, Eu, or Am at low acidity since the D values increase as a function of absorbed dose. This phenomenon is less noticeable for La but very representative for the Sr element in the case of the CIEMAT experiments. As observed in the An extraction or An stripping step, the effect of radiolysis is less important for the solvents from the Marcel or INL loop test than that from the Náyade loop experiment. However, the increase in D_{Eu} is very high, about 4−7 times higher than the value obtained with a nonirradiated solvent. Fortunately, the distribution ratios remained low so that no risk of cation accumulation could occur. Nevertheless, the appropriate treatment of the solvent with basic aqueous solution could remove these unwanted degradation compounds.

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 interinstitutional 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, 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 ref 36, 0.0034 kGy^{-1} in ref 40, irradiating the organic phase with nitric acid aqueous phase in both studies), indicating the 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 extraction results between CEA and INL, in “An stripping B”, the results obtained by INL and CEA are more or less the same, but this is not the case in “Ln stripping”, where the INL solvent seems less affected by radiolysis. This means that there are more degradation products in the CEA solvent, which extracts more Am at a lower acidity. This is consistent with the lower degradation rate of *cis*-mTDDGA for the INL samples. As the dose rate of the CEA irradiator is lower than that of the INL, this additional degradation compared to the total dose comes from the longer residence time of the solvent in the CEA loop for the same total dose and, therefore, from a higher proportion of solvent degradation by hydrolysis. Taking into account these results, this degradation seems to have a limited impact on the extraction and separation performance of trace Am and Eu. Studies by Wilden et al. have shown that $D_{Am,Eu}$ vary linearly with the concentration of mTDDGA in the

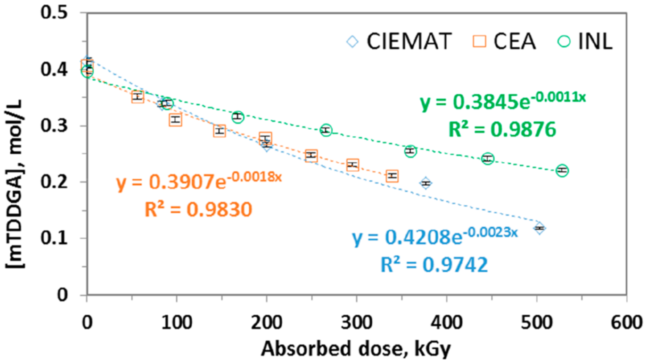


Figure 10. *cis*-mTDDGA concentration as a function of the absorbed dose in solvent samples from the CIEMAT, CEA, and INL loops.

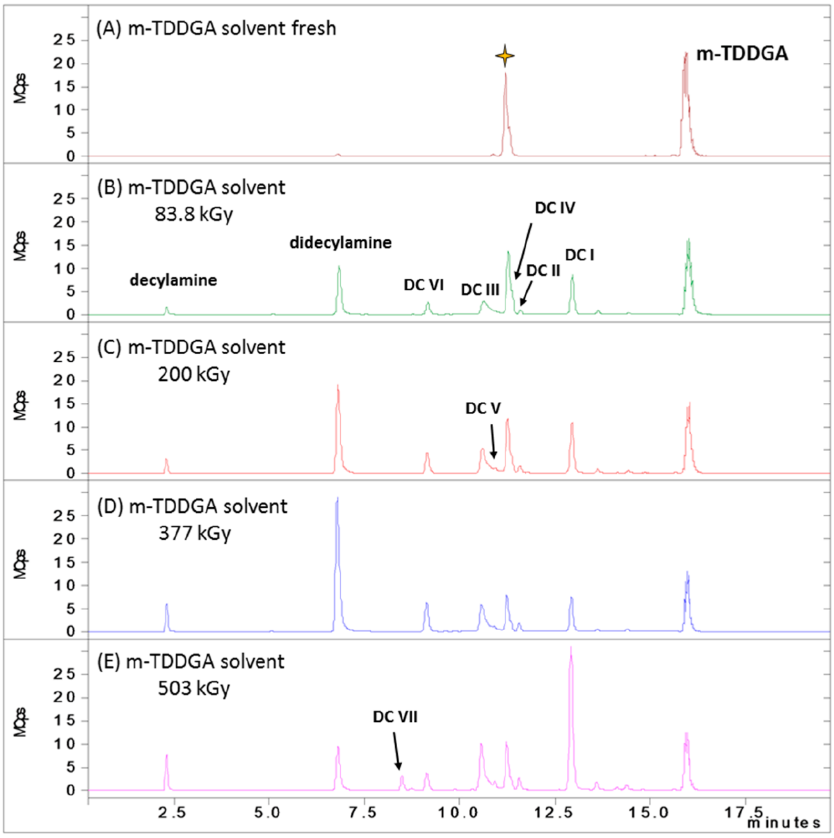


Figure 11. Qualitative HPLC-MS chromatograms of mTDDGA solvent obtained from the Náyade irradiation test loop: (A) fresh or reference sample, and irradiated in contact with 4.5 mol/L HNO_3 to (B) 84 kGy; (C) 200 kGy; (D) 377 kGy; and (E) 503 kGy. Since DC IV appears at the same time as impurity *m*/*z*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

solvent. In this work, with the decrease in *cis*-mTDDGA concentration by a factor of 2 at a dose of 339kGy, $D_{\mathrm{Am,Eu}}$ remain relatively stable in the extraction step (Figure 5) and in the stripping parts (Figure 7 and Figure 8). This means that the major degradation products compensate for the expected decrease in extractability due to the loss of *cis*-mTDDGA. On the contrary, the impact of degradation is more visible at low acidity (Ln stripping step, Figure 9) but could be managed in the process since distribution ratios remain relatively low. Overall, the degradation of *cis*-mTDDGA does not have a dramatic negative impact on the performance, which is very important for the process.

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 coextraction 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, rt = 16.1 min), a signal related to an impurity from the organic synthesis is detected (*m*/*z* = 340, rt = 11.3 min shown as a star in Figure 11A). When samples are irradiated in the coextraction 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 toward 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]

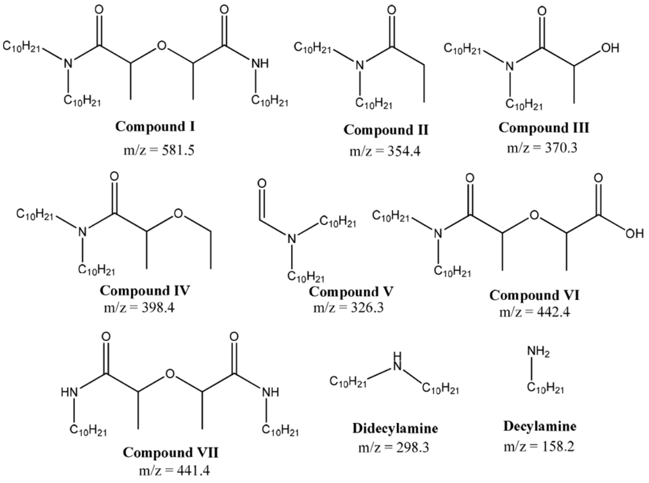


Figure 12. Chemical structures of the mTDDGA degradation compounds.

Table 2 gives the results of the densities and viscosities measured on the solvent samples at the beginning and 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

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

test and by 20% under 339 kGy for CEA experiment. The end of the 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 behavior of a liquid–liquid system in a nuclear reprocessing plant.

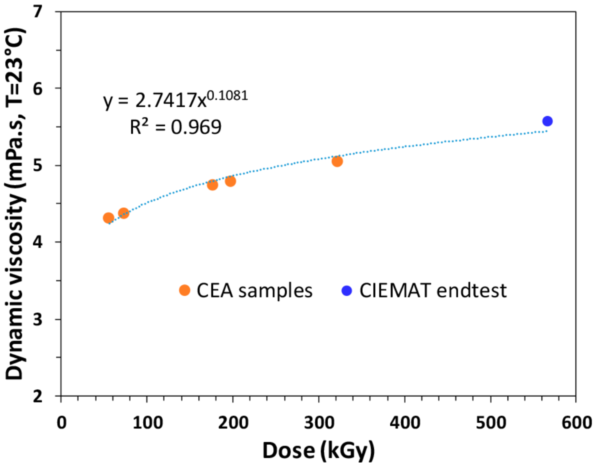


Figure 13. Dynamic viscosities measured at 23 °C on some irradiated samples from the CIEMAT or CEA loop test.

4. CONCLUSIONS

An interinstitutional study between CEA, INL, and CIEMAT has been performed under the most relevant and realistic experimental conditions to investigate the resistance of the *cis*-mTDDGA extraction system to gamma radiolytic degradation during a dynamic irradiation test simulating the main steps of the New EURO-GANEX process. In this work, the results of three experiments are presented for the studied steps of this process: An+Ln coextraction, TRU stripping, and Ln stripping, focusing on the stability of the organic solvent and extractant, and the findings contribute to demonstrate the performance of the new EURO-GANEX process, as a promising process to achieve the TRU recovery.

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

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

The major result of these experiments is the stability of the extraction performances and Ln/An selectivity measurements after undergoing an irradiation dose corresponding to a 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 behavior of the whole process taking into account the resistance of the aqueous phase for the An/Ln separation.

ASSOCIATED CONTENT

● Supporting Information

Appendix A. Irradiation test loops. Additional experimental details, including photographs of experimental setup of three irradiation test loops (CIEMAT, CEA and INL) employed and the scheme of the process studied; Appendix B. Analysis of corrosion products of reactor of Náyade test loop measured by ICP-MS; Appendix C. Details of the synthesis of *cis*-mTDDGA including ^{1}H NMR spectra for all compounds employed in the synthesis (PDF)

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Author Contributions

I.S.-G., X.H., and D.R.P.: investigation, methodology, formal analysis, writing - original draft, writing - review and editing. H.G., A.G., and A.W.: supervision, conceptualization, validation, writing - review and editing. S.J.-P.: synthesis of *cis*-mTDDGA compound and review and editing. M.C.G. and A.C.: synthesis of PTD reagent and review and editing. S.C., S.B., and J.S.: experimental work at CEA and review and editing, T.S.G. and K.R.A.: experimental work at INL and review and editing. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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

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APPENDIX A. Irradiation test loops

2.2.1 CIEMAT Irradiation test loop

The CIEMAT Náyade irradiation facility consists of a pool of a 1.2 m^2 by 4.5 m deep containing water as the biological shield [1]. At the bottom of the pool, there are 60 sources of ^{60}Co with a total activity of $3.22 \cdot 10^{14}$ Bq. The cylindrical irradiation container receives a homogeneous irradiation flux. Solvents to be irradiated are mixed outside of the pool then pumped by peristaltic pumps through a 316 stainless steel coil to the irradiation container. The volume of each phase was 130 mL. The flow rate was adjusted to maintain the volume ratio (in the range of 0.31 L/h). More details about the Náyade facility are given in [2].

Thanks to Fricke dosimetry measurement [3], the effective dose rate was measured at 32 kGy/h in static conditions, whereas it was 2.62 kGy/h according to phase residence time, in dynamic operating conditions.

Náyade irradiation loop has been configured to simulate the two main steps of new EURO-GANEX process, i.e. An + Ln co-extraction and TRU stripping steps. 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 **Table S1**.

To simulate the effect of irradiation in the An + Ln co-extraction step, where all fission products and TRU are present, an effective irradiation dose up to 503 kGy was applied to 0.4 mol/L *cis*-mTDDGA in dd in contact with surrogate GANEX first cycle raffinate (4.5 mol/L HNO_3 with 1 mmol/L of Sr, La, Nd, Eu).

Along this irradiation step, the extraction assessment was performed in batch experiments by sampling both phases and spiking with ^{241}Am and ^{152}Eu as actinide and lanthanide analogues, respectively. As the irradiation reactor (coil) is composed of 316 stainless steel, main corrosion metals (Fe, Ni, Cr and Mo) were also considered. To investigate the stripping of TRU second step, the irradiated solvents from the tube extractions described above were contacted with an aqueous phase containing 0.4 mol/L PTD in 2.1 mol/L HNO_3. This is the optimal composition of the aqueous phase. Finally, in order to simulate Ln stripping step, batch experiments were carried out with an aqueous phase containing 0.01 mol/L HNO_3 and the irradiated solvent samples.

Table S1. Composition of the organic and aqueous phases in the different steps of the irradiation test loop and the following extraction experiments.

Experiments		**Solvent formulation**	
		Organic phase	Aqueous phase
An+Ln co-extraction Step	a) Before Irradiation	Fresh new EURO-GANEX solvent	Fresh 4.5 mol/L HNO_3 + 1 mM Sr^{2+}, La^{3+}, Nd^{3+} and Eu^{3+}
	Dynamic Irradiation (83, 200, 377 and 503 kGy)		

	b) Extraction after irradiation	Irradiated new EURO-GANEX solvent (84, 200, 377 and 503 kGy)	Irradiated (84, 200, 377 and 503 kGy) 4.5 mol/L HNO_3 + 1 mM Sr^{2+}, La^{3+}, Nd^{3+} and Eu^{3+}
TRU stripping Step	An stripping 1.1	Irradiated new EURO-GANEX solvent from the previous step (503 kGy)	Fresh 0.4 mol/L PTD in 2.1 mol/L HNO_3
Ln stripping Step	Ln stripping 1.1	Irradiated new EURO-GANEX solvent	0.01 mol/L HNO_3

2.2.2 CEA Irradiation test loop

The CEA irradiator called Marcel (Advanced Radiolysis Module in Liquid-Liquid Extraction Cycles) is composed of four ^{137}Cs sources with a total activity of 173 TBq (**Figure S1**). This device is connected via a stainless steel pipe to a process platform. Thus, it is possible to irradiate continuously, an organic phase and/or an aqueous phase circulating in the platform: these facilities replicate a mini reprocessing plant using, for example, mixer-settlers or centrifugal contactors [4]. Figure S2 shows an overview of the PROUST platform with its monitoring tool. The Marcel irradiator is located in an adjacent room and is connected to PROUST by 23 m of PTFE tubing with an internal diameter of 2 mm.

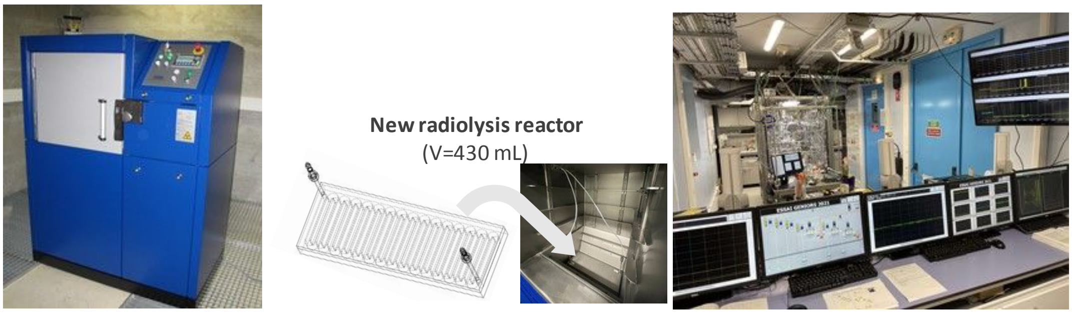

Figure S1. Marcel irradiator with its radiolysis reactor inside (connected by PTFE pipes to the platform) and view of the platform with its supervision.

In spent fuel reprocessing, the solvent in the first extraction step is undergoing high radiolysis effects because all radioisotopes are present. Therefore, to simulate reality, the solvent in the loop is injected into the radiolysis reactor just after the extraction step. However, unlike a real reprocessing plant, the aqueous phase is not continuously irradiated with the organic phase. The CIEMAT and INL loops offer this possibility, since irradiation is done for both phases. However, the impact of radiolysis on the hydrodynamic behaviour could be followed directly in Marcel thanks to the coupling between the continuous irradiation and the liquid-liquid extraction platform. For this test, a new radiolysis reactor was designed to minimise its volume and maximise the irradiation dose to the solvent (central picture in **Figure S1**).

As with the Náyade irradiation loop, the dose rate in this new reactor was estimated to be 0.78 kGy/h using the Fricke method [3]. With 430 mL in this device and a solvent flow rate of 50 mL/h as proposed in the flowsheet, the solvent undergoes approximately 6.7 kGy/cycle. As this test started with 1 L of solvent, a process cycle lasts 20 hours and thus every week the organic phase was exposed to a dose of 56 kGy. In the case of a plutonium-extracting solvent, in-plant processing of MOX fuel involves an irradiation dose of 28-29 kGy per week (MOX fuel cooled for 5 years with a ratio (Pu+Am)/(U+Pu+Am) of 8.2% and a burnup of 43.5 GWj/t). The Marcel loop therefore accelerates degradation by radiolysis compared to a nuclear fuel processing plant. A similar calculation was also performed on a reagent injected in the aqueous phase of the An stripping step, such as PTD. With the same assumptions, PTD is expected to undergo about only 8 kGy per cycle and is not expected to be recycled at this time.

The Marcel loop test was carried out during 6 weeks, continuously, in order to follow the impact of radiolysis on the hydrodynamics and the performance behaviour in a GANEX-type process. The flowsheet reproduced the three main steps, taking into account the volume constraint of the solvent:

1. An+Ln co-extraction (AX) in nitric acid medium (> 4 mol/L) (4 stages)
2. TRU stripping step (BX) thanks to PTD reagent solubilized in moderated nitric acid medium (≈ 2.1 mol/L) (4 stages)

3. Ln stripping step (CX) in weak nitric acid medium (0.01 mol/L < $[H^+] < 1$ mol/L) (4 stages)

As the operating conditions for the solvent treatment were not clearly defined, this step was not implemented, which could lead to some drawbacks such as the accumulation of some degradation compounds that could be removed during the solvent treatment. As CIEMAT and INL did not carry out any solvent treatment, this allowed us to compare directly the results between the three loops.

The liquid-liquid extraction stages consisted of poly(methyl methacrylate) (PMMA) mixer-settlers where the two phases flowed in countercurrent, as shown in Figure S2. All the aqueous solutions were injected into the mixer-settlers using rotary piston pumps, while the solvent was circulated using gear pumps. The two phases were mixed using perforated stainless steel blades rotating at 1700 rpm. Flow rates were regulated by a Coriolis mass flow meter. All this equipment is controlled and monitored by a dedicated control system. Optical probes were placed at the outlet of each battery to measure the Nd concentration by on-line spectrophotometry.

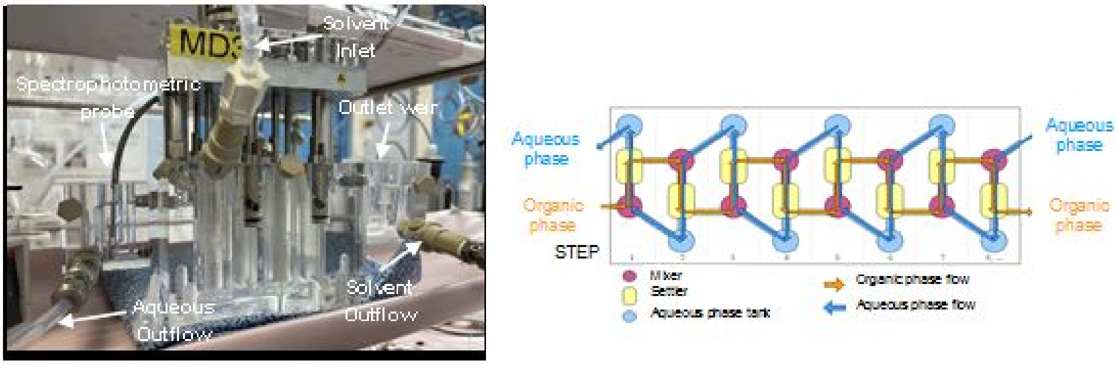

Figure S2. Picture and schematic drawing illustrating the principles of PMMA mixer-settlers.

After every dose about 25 kGy, solvent samples were taken from the Ln stripping step (CX). As with the Náyade loop, the extraction assessment was carried out in batch experiments by taking the irradiated solvent and contacting it with four fresh aqueous phases:

1. An-Ln co-Extraction Step (irradiated solvent with 4.5 mol/L HNO_3 spiked with ^{241}Am and ^{152}Eu).

   After this first extraction, theses solvents were contacted, in parallel, along with these three above aqueous solutions.

2. TRU Stripping Step (solvent from 1. with 0.4 mol/L PTD, initial HNO_3 at 2.1 mol/L *i.e.* final HNO_3 at 2.4 mol/L)

3. TRU Stripping Step B (solvent from 1. with 0.04 mol/L PTD, initial HNO_3 at 1.5 mol/L *i.e.* final HNO_3 at 1.7 mol/L)
4. Ln Stripping Step (solvent from 1. with initial HNO_3 at 0.01 mol/L *i.e.* final HNO_3 at 0.5 mol/L)

The doses chosen for these batch studies were 56 kGy, 98 kGy, 147 kGy, 198 kGy, 249 kGy, 295 kGy and finally 339 kGy.

In contrast to CIEMAT, each solvent was stripped with 0.01 mol/L HNO_3 (V/V) to avoid any residual neodymium and acidity before the extraction batch experiments. Thus, the bad effect of trace amount of an extractive degradation compound is better noticeable.

2.2.3 INL Irradiation test loop

The irradiation source was an MDS Nordion GammaCell 220 Excel self-contained ^{60}Co gamma irradiator (see Figure S3). The gamma dose rate was approximately 2.2 kGy/h at the center of the irradiation chamber at the time irradiations were performed. The original INL test loop has been described previously [5, 6]. A new test loop apparatus has been constructed. The main improvement is the elimination of loop components located outside the gamma irradiator sample chamber. A stainless convoluted provides compressed air to the air base. An air-driven magnetic stirrer sits atop the airbase and drives a magnetic stir bar.

Figure S3. MDS Nordion GammaCell 220 Excel gamma irradiator (left). Re-designed test loop irradiation vessel installed in sample chamber (right).

Determination of the gamma dose rate for the original test loop required two dosimetry techniques. The center-line dose rate in the irradiation chamber was measured using the Fricke dosimeter [3, 7]. In the new test loop design (see Figure S5), the entire volume of the experiment is held in the irradiation vessel. This arrangement simplifies dosimetry by eliminating the "fraction of irradiated volume" correction required for the previous test loop where only 40% of the total volume was present in the irradiation chamber at any time.

According to the Fricke dosimeter, the slope of the linear regression to the absorbance versus time data is used to calculate the gamma dose rate. This slope corresponds to an absorbed gamma dose of 3.91 kGy/h.

As with the Náyade loop, the extraction assessment was carried out in batch experiments by taking the irradiated solvent and by contacting successively with aqueous phases corresponding to the simplified New EURO-GANEX flowsheet with successive four fresh aqueous phases:

1. An-Ln co-Extraction Step (irradiated solvent with initial millimolar of Eu, Ce nitrates at 4.5 mol/L HNO_3 spiked with ^{241}Am, ^{152}Eu and ^{139}Ce)
2. Acidity Scrubbing (solvent from 1. with initial HNO_3 at 2.1 mol/L *i.e.* final HNO_3 at 2.4 mol/L)
3. TRU Stripping Step B (solvent from 2. with 0.04 mol/L PTD, initial HNO_3 at 2.1 mol/L *i.e.* final HNO_3 at 2.2 mol/L)
4. Ln Stripping Step (solvent from 3. with initial HNO_3 at 0.01 mol/L *i.e.* final HNO_3 at 0.22 mol/L)

The lower PTD concentration was used to conserve reagent (0.04 mol/L instead of 0.4 mol/L). The doses chosen for these batch studies were 89 kGy, 167 kGy, 265 kGy, 359 kGy, 445 kGy and finally 528 kGy.

APPENDIX B. Analysis of corrosion products of reactor of Náyade test loop

The potential corrosion products of the 316 stainless steel Náyade reactor coil were also measured by ICP-MS and the results are shown in Figure S6. Mo was not detected in the aqueous and organic phases. **Figure S4** shows the increase in Fe, Ni and Cr concentrations as a function of absorbed dose during An+Ln co-extraction step. These metals are mainly found in the aqueous phase with a concentration of ~1.31 mmol/L, ~0.33 mmol/L and ~0.18 mmol/L, respectively. Only a low concentration of Fe (~0.01 mmol/L) was found in the organic phase. This result highlights that *cis*-mTDDGA co-extracts these elements much less than the previous EURO-GANEX solvent even at high acidity, as reported [2, 8, 9], and is in agreement with studies found in literature [10, 11].

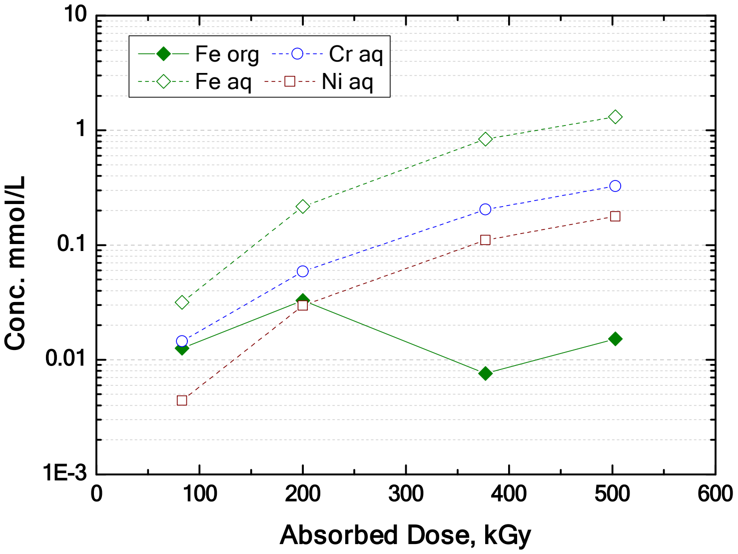

Figure S4. Evolution of the concentration of stainless steel corrosion products Fe, Cr and Mo during An+Ln co-extraction step of Náyade irradiation loop.

APPENDIX C. Synthesis of *cis*-mTDDGA

Synthesis of **N,N-didecyl-2-hydroxypropanamide** [13]: Didecylamine (1.49 mol, 444 g) was dissolved in 300 mL of o-xylene in a round bottom flask equipped with Dean-Stark apparatus and condenser. The mixture was heated (up to 50 ˚C) to facilitate the dissolution of amine. Then, lactic acid (1.49 mol, 158.1 g, 85% purity) was added in portions (the salt formation is slightly exothermic process!). Afterwards, the reaction mixture was heated at 150 ˚C for 12 hours. An aliquot was taken and analyzed using ^{1}H NMR spectroscopy, which showed that 1/3 of the salt remains. The reaction mixture was then heated at 210 ˚C for another 12 hours. The conversion of salt into product was confirmed using ^{1}H NMR spectroscopy. The solvent was then removed via simple distillation and the residue was heated at 70 ˚C under high vacuum to remove trace amounts of solvent. The product was obtained as a light orange oil (540 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 4.39 (q, $J = 6.7$ Hz, 1H), 3.82 (d, $J = 7.7$ Hz, 1H, OH), 3.62-3.52 (m, 1H), 3.27-3.02 (m, 3H), 1.62-1.48 (m, 4H), 1.33-1.20 (m, 28H), 1.31 (d, J = 6.5 Hz, 3H), 0.92-0.84 (m, 6H).

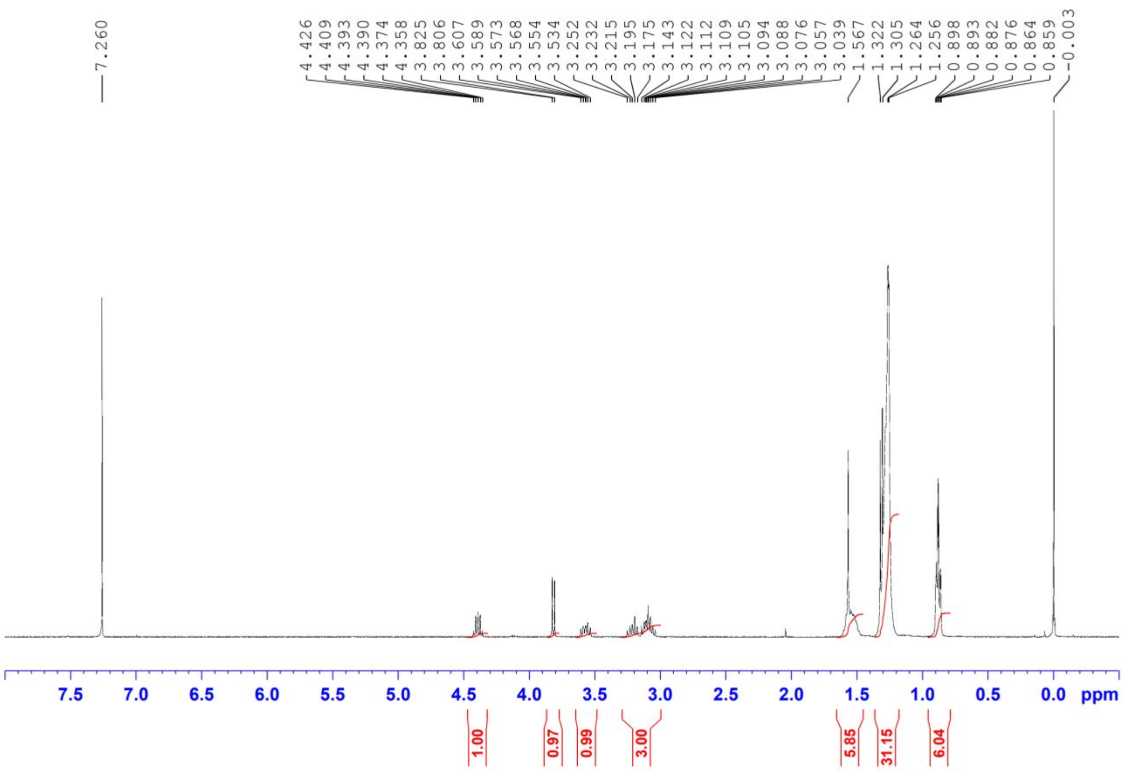

Figure S7. 1H NMR spectrum of N,N-didecyl-2-hydroxypropanamide in $CDCl_3$.

Synthesis of **2-bromo-N,N-didecylpropanamide**: The didecylamine (2.3 mol, 688 g) solution in anhydrous CH_2Cl_2 (0.68 M) was cooled in ice/water bath. To this solution triethylamine (2.3 mol, 322 mL) and 2-bromopropionyl bromide (2.3 mol, 236 mL) were added and the reaction mixture was mixed from 2 hours. Afterwards, the reaction mixture was diluted with hexanes and filtered through a short Celite® plug, rinsed with Et_2O. The solvent was evaporated under reduced pressure on a rotary evaporator. The residue was dissolved in Et_2O and filtered through a short silica gel-Celite® plug. After removal of solvent, the product (770 g, 77% yield) was used in the next step without any further purification. ^{1}H NMR (400 MHz, CDCl$_3$): 4.52 (q, *J* = 6.6 Hz, 1H), 3.60-3.50 (m, 1H), 3.50-3.39 (m, 1H), 3.17-3.01 (m, 2H), 1.81 (d, *J* = 6.6 Hz, 3H), 1.73-1.62 (m, 1H), 1.57-1.43 (m, 3H), 1.36-1.19 (m, 28H), 0.92-0.83 (m, 6H).

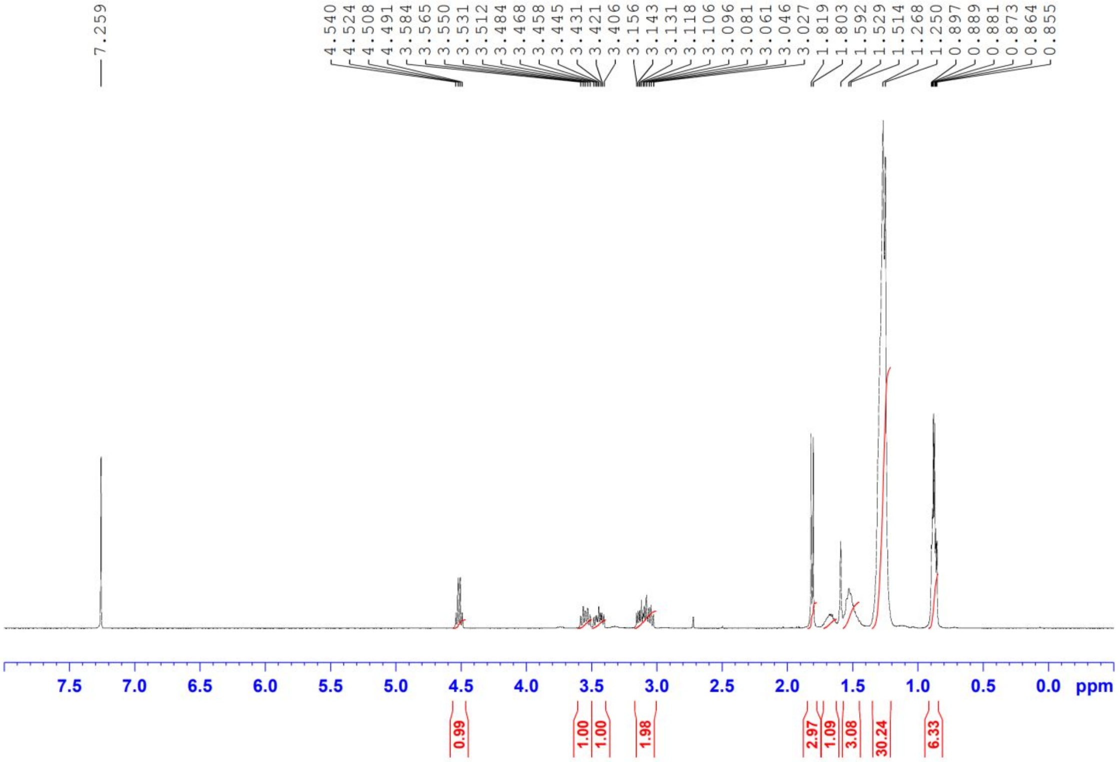

Figure S8. ^{1}H NMR spectrum of 2-bromo-N,N-didecylpropanamide in CDCl$_3$.

Experimental procedure for the synthesis of **(S)-N,N-didecyl-2-(((R)-1-(didecylamino)-1-oxopropan-2-yl)oxy)propenamide (*cis*-mTDDGA)**: In a 2 L round bottom flask equipped with a magnetic stir bar, N,N-didecyl-2-hydroxypropanamide (0.358 mol, 132.3 g) was dissolved in anhydrous THF (0.25 M, 1.2 L total volume) under inert atmosphere. To this solution NaH was added in portions (60% dispersion in mineral oil, 0.358 mol, 14.3 g). The reaction mixture was stirred at 25 ˚C for 12 hours. Then, 2-bromo-N,N-didecylpropanamide (0.358 mol, 154.6 g) dissolved in anhydrous THF was added via cannula. The reaction mixture was then refluxed for 12 hours. The reaction mixture was filtered through a Celite® plug and rinsed with Et_2O. The solvent was evaporated under reduced pressure on a rotary evaporator. The mixture was then purified using an Automated CombiFlash Rf chromatography system on the RediSep Gold Normal Phase 330 g Silica Column (20-40 micron) with gradient 0-50% EtOAc in Hexanes as an eluent system. The S,S-dr elutes first followed by R,S-dr. Note: the RediSep Normal Phase 330 g Silica Column (40-60 micron) did not yield the separation of S,S- and R,S-diastereomers. The *cis*-mTDDGA product was isolated as an orange oil; 147 g, 57% yield. The reaction/purification was repeated multiple times to yield ~600 g of *cis*-mTDDGA with ~95% purity (based on ^{1}H NMR spectroscopic analysis). 0.4 M *cis*-mTDDGA in *n*-dodecane was prepared: *1.005 L of 0.4 M cis-mTDDGA was sent to CEA, 0.505 L to INL, and 0.255 L to CIEMAT.* The spectroscopic data for *cis*-mTDDGA agree with the reported data [14].

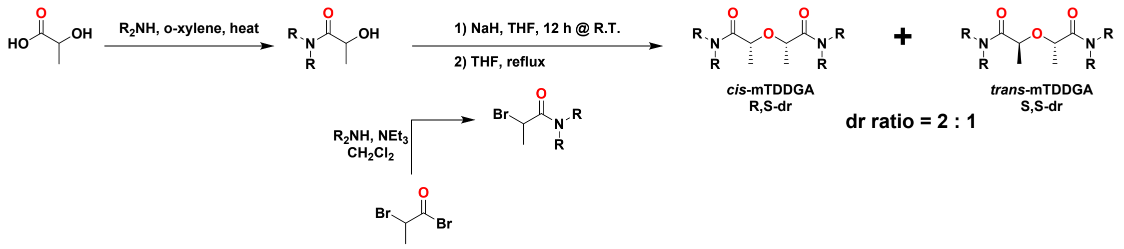

Figure S9. Synthesis scheme for *cis*-mTDDGA. R = *n*-decyl.

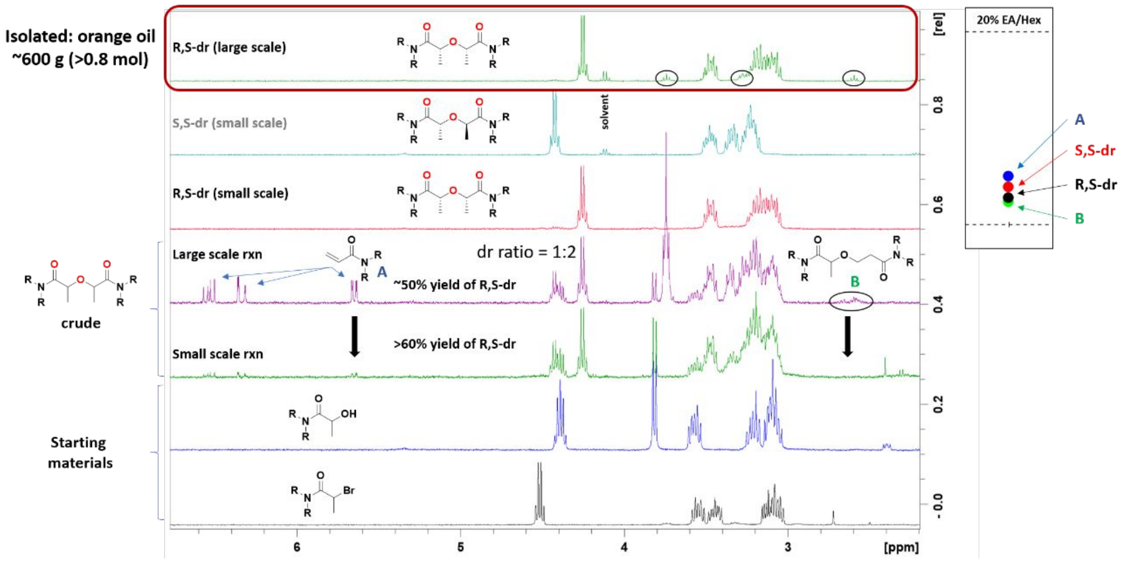

Figure S10. Overlay of ^{1}H NMR spectra of starting materials, reaction mixtures, products, and by-products. R = *n*-decyl. Thin layer chromatography (TLC) plate illustrating the separation of products and by-products.

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