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Reference N°	Creation Date	
SCK CEN/51081205	2024-02-20	
Alternative Reference N°	Revision	Version
N/A	1.0	3
ISC	Revision Status	
Public	Approved	

## Deliverable\_1.1.2.\_2022-10-07\_-\_ASOF\_WP1.docx

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### Review information since previous revision\*

Name	Outcome	Date
Karen Van Hecke	Reviewed	2024-02-20
Thomas Cardinaels	Reviewed	2024-02-20

### Approval information for current revision\*

Name	Outcome	Date
Thomas Cardinaels	Approved	2024-02-20

### Change log\*

Revision	Version	Status	Date	Description of change
1.0	3	Approved	2024-02-20	

*\*This automatically generated cover page shows references and document information as were available in the Alexandria document management system on 2024-02-20. Please refer to Alexandria for current and complete metadata, or to the document contents and/or author for additional information.*

**ISC motivation**


ISC was automatically assigned.



# Validation of concept continuous counter-current separation of Platinum Group Metals and Am(III) from a simulated high active raffinate solution

## Centrifugal contactor development and solvent extraction studies

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Met de steun van  **economie**

Contract name: ASOF (Advanced Separation for Optimal management of spent Fuel)  
Contract number: CO-90-18-4699-00  
Publication date: 2024-02-20



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Stichting van Openbaar Nut - Fondation d'Utilité Publique - Foundation of Public Utility

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## Glossary of abbreviations

ACC: annular centrifugal contactor

[A336][NO<sub>3</sub>] or Aliquat-336 nitrate: a mixture of various quaternary ammonium nitrates with three C<sub>8</sub>-C<sub>10</sub> chains and one methyl group – a room temperature ionic liquid

CyMe<sub>4</sub>BTPPhen: 2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline

GENIV reactors: fourth generation advanced nuclear reactor concepts

HAR: Highly Active Raffinate

HLW: High Level Waste

LWR: Light Water Reactor

MYRRHA: Multi-purpose hYbrid Research Reactor for High-tech Applications

MOX: Mixed OXide fuel

PMMA: poly(methyl) methacrylate (plexiglass)

PUREX: Plutonium-Uranium Redox Extraction

P&T: Partitioning and Transmutation

SNF: Spent Nuclear Fuel

TBP: tri-*n*-butylphosphate

TEDGA: *N,N,N',N'*-tetraethyldiglycolamide

UOX: Uranium OXide fuel

## Abstract

The separation of Am(III) from the chemically similar Cm(III) and fission product lanthanides (Ln(III)) is a key challenge in any credible closed nuclear fuel cycle scenario. Co-management of the strong neutron emitter Cm with Am and other actinides would pose significant technical challenges, both with respect to the target fabrication and the reactor management. Most available selective Am(III) extraction systems suffer from slow kinetics, which is a limiting factor towards process upscaling. Besides the challenge of Am(III)-only partitioning, the management of the interfering fission products (Pd, Ru, Mo and Zr) had to be integrated into the flow sheet design.

Counter-current multi-stage solvent extraction is a powerful method to separate metal ions with highly similar chemical properties. Various types of equipment are commonly used in the industry for continuous counter-current solvent extraction; pulsed columns, mixer settlers, agitated columns, centrifugal contactors etc. Of these, annular centrifugal contactors offer certain advantages for solvent extraction in nuclear environment: short contact times, efficient mixing and separation in one unit and very limited solvent hold-up volumes which limit radiolysis issues. Small centrifugal contactors can be used to test bench-top separation concepts at minimal cost and time enabling a process development which would be prohibitively expensive to perform at larger scale. The short contact times related to the standard centrifugal contactor design can act as serious process restraints. To open up a wider operational window (in terms of residence times and associated kinetics) the original mixing zone design and rotor length were modified in this study.

The present report gives an insight to the chemical process development and equipment development that were conducted in parallel between 2020 and 2022. The report is not meant to be comprehensive, the detailed scientific results will be published in peer-reviewed journals.

*Note: the results and conclusions that are discussed in this work are solely the opinion of the authors. The General Direction Energy is not liable for any use of the information of this work.*

## Samenvatting

De scheiding van Am(III) van Cm(III) en de lanthanide splijtingsproducten is een belangrijke uitdaging om de nucleaire brandstofcyclus te kunnen sluiten. Co-management van de sterke neutronenemitter Cm met Am en andere actiniden zou aanzienlijke technische uitdagingen met zich meebrengen, zowel wat de targetfabricage betreft als wat het besturen van de reactor betreft. De ontwikkelde selectieve Am(III)-extractiesystemen hebben last van een trage kinetiek, wat een beperkende factor is voor het opschalen van het proces. Afscheiding van de interfererende splijtingsproducten (Pd, Ru, Mo en Zr) diende te worden geïntegreerd in de flow sheet.

Continue tegenstroom solvent extractie is een van de krachtigste methoden om metaalionen met vergelijkbare chemische eigenschappen van elkaar te scheiden. In de industrie worden verschillende soorten apparatuur gebruikt voor deze continue tegenstroom solventextractie: gepulseerde kolommen, mixersettlers, roerkolommen, centrifugale contactoren enz. Annulaire centrifugaal contactoren beschikken over enkele eigenschappen die ze bijzonder interessant maken voor toepassing voor de afscheiding van americium: efficiënte menging en fasescheiding, zeer korte contacttijden, waardoor met lagere solvent volumes kan worden gewerkt en de radiolyse veel minder impact heeft. Mini-centrifugaal contactoren zijn interessant om scheidingsconcepten te testen tegen een aanvaardbare kostprijs. Ze maken procesontwikkeling op laboschaal mogelijk. Bij de commercieel verkrijgbare mini-centrifugaal extractoren is de contacttijd zodanig kort dat deze apparatuur voor processen met een tragere kinetiek niet geschikt is. Het oorspronkelijke ontwerp (mengzone en rotorlengte) werd tijdens deze studie aangepast om de contacttijden te vergroten.

Dit rapport geeft inzicht in de chemische procesontwikkeling en de ontwikkeling van apparatuur die parallel werden uitgevoerd tussen 2020 en 2022. Het rapport is niet bedoeld om allesomvattend te zijn, de gedetailleerde wetenschappelijke resultaten zullen worden gepubliceerd in peer-reviewed tijdschriften.

*Nota: de resultaten en conclusies die in dit werk worden uiteengezet vormen uitsluitend de mening van de auteurs. De Algemene Directie Energie is niet aansprakelijk voor het eventuele gebruik van de informatie uit dit werk.*

## Keywords

Minor actinide partitioning  
Valuable fission product recovery  
Process development and process upscaling  
Centrifugal contactors  
Solvent extraction equipment development  
Speciation studies

## Introduction

Minor actinide content of spent nuclear fuel dominates the long term heat load and radiotoxicity of the highly active waste after its final disposal. Currently all countries with running civilian nuclear program face the challenge of the management of spent nuclear fuel. The most secure solution seems to be the deposition of the highly radioactive waste in deep underground repositories located in a suitable geological host rock formation. To prevent posing a risk of releasing radionuclides into the biosphere requires a combination of engineered and geological barriers to be placed around the waste form.

Some countries (Sweden, Finland) have chosen for the option of direct spent fuel disposal without any prior chemical treatment or any major conditioning step apart from the re-packaging of the intact fuel elements in thick copper cylinders (open nuclear fuel cycle or once through cycle, OTC). Other countries investigate or actively follow the option of recovering the major actinides (uranium and plutonium) for re-utilization and convert the remaining fission products and minor actinides (MA: americium, curium and neptunium) in a chemically stable borosilicate glass waste form (France, Japan, Russia). This option is often called twice-through cycle (TTC). This option allows the saving on the front-end of the nuclear fuel cycle (by a reduction of 17 % of the mining activities and a concomitant reduction of environmental footprint). The produced spent MOX fuel on the other hand is much more problematic to handle in comparison to spent UO<sub>x</sub> fuel, given the significantly higher minor actinide content in spent MOX fuel (approximately one order of magnitude higher MA).

The selective removal of americium (besides the recovery of uranium and plutonium for further irradiation) would reduce the heat generation rate of the waste packages allowing a more compact placement in an underground repository without the breach of the design temperature limit.<sup>[1]</sup> Irrespective of the waste form selected (re-packaged spent fuel elements or vitrified highly active waste etc.) a deep underground repository has significant physical limitations that needs to be respected during the placement and filling up of a repository. Water insulating layered silicates such as clay or bentonite are considered as most suitable for either as a back-filling material of galleries and/or as host rock in which the tunnels themselves should be drilled. These types of materials lose their advantageous insulating properties if heated above 90 °C due to loss of crystalline water in their structure. Such a structural change must be avoided in a repository by design, as such an event would be equal to the loss of one of the most important geological barriers between the biosphere and the radionuclides present in the highly active waste. In a filled repository, where there is no conductive removal of the decay heat (e.g. by air flow) produced from the radionuclides the only way to guarantee that the temperature is not exceeded at any moment in time (over a geological time scale) is the increase of distance between the individual waste packages. The increase of tunnel length at the depth of ~ 500 m underground obviously has a tremendous impact on the construction cost of the repository. The vitrified highly active waste obtained as a result of spent fuel treatment processes can be disposed in a more compact arrangement in comparison with the direct disposal of untreated spent nuclear fuel elements. As a result, the total volume of the most problematic, highly active waste fraction is lower in the twice-through nuclear fuel cycle than in the open nuclear fuel cycle.

Studies on the advancement of the twice-through nuclear fuel cycle therefore aim at improving the efficiency of recovery of the economically valuable major actinides and at the recovery of minor actinides to reduce the heat density of the final waste form. The separated major and minor actinides are foreseen to be irradiated in reactors characterized by a fast neutron spectrum. Such reactors were studied among others in France, USA, Japan, Russia and China. Currently only Russia (Beloyarsk 3 and 4) and China (China Experimental Fast Reactor) have operational fast reactors, some of which are at the scale of commercial, electricity producing light water moderated reactors (LWRs). In Europe and in the US only two fast-reactor projects are still ongoing, the MYRRHA<sup>[2]</sup> of SCK CEN and the Versatile Test Reactor (VTR), both of which are only in R&D phase. In fast reactors the coolant is liquid metal, therefore the neutrons are not moderated (slowed down by collision with light elements' nuclei). The higher energy neutrons are more efficient in the neutron-induced splitting (or transmutation) of all actinide nuclei than moderated (or thermalized) neutrons. With a thermalized neutron spectrum (prevalent in LWR) nuclear fission is only limited to the odd isotopes of U and Pu (<sup>235</sup>U and <sup>239/241</sup>Pu respectively), while all the other actinide nuclei absorb neutron in parasitic reactions, leading to the build-up of minor actinide inventory in the fuel.

Irrespective of the choice for the continuation or discontinuation of nuclear programs and on the introduction of fast reactors in the nuclear power plant park, one or other spent nuclear fuel management options needs to be selected within a reasonable period of time as the temporary storage methods are not suitable for long term safe storage of spent nuclear fuel.

Minor actinide partitioning research has been conducted since decades with the aim to elaborate a robust chemical separation strategy, which can be implemented seamlessly to the existing PUREX process applied already on an industrial scale for the recovery of U and Pu from spent fuel. The long experience collected by research groups all around the world have yielded a set of selection criteria to be met by any candidate process and candidate chemical components before they can be considered as a realistic option for the MA partitioning. Among these criteria are: possibility of eliminating spent solvent via incineration (CHON –principle), fast extraction kinetics, reversibility of extraction, compatibility with high acidic



and highly radioactive environment, resistance against oxidation, high selectivity for the complexation of An(III) ions over Ln(III) and other fission product ions, negligible or manageable interference with the extraction of other elements than the desired one(s), possibility to recycle and re-use the solvent etc.

Studies have mainly focused on the use of solvents composed of one or more lipophilic extractants and an aliphatic diluent (such as kerosene, *n*-dodecane, 1-octanol etc.). Such diluents are typically cheap, commercially available in large quantities and due to their low viscosity the phase separation and the kinetics of extraction are rapid. Their disadvantage is the often high vapor pressure, low electric conductivity and low flash point which requires stringent fire safety measures to prevent static charge build-up and spark formation. The low polarity of the aliphatic diluent often results in a low solubility of the extracted metal-ligand complexes, which are polarized species. Often the low complex solubility manifests in precipitation or the splitting of a highly loaded organic phase to a lighter (diluent-rich) and a heavier (metal-ligand complex rich) liquid phase. This phenomenon (also called third-phase formation) leads to maloperation of a continuous solvent extraction equipment (centrifugal contactors, mixer settlers or pulsed columns etc.), because these are designed for the mixing and separation of two immiscible phases only, but not of three.

A relatively new class of diluents, room-temperature ionic liquids, have recently been investigated as alternative diluents to be used in nuclear fuel treatment processes. The ionic liquids are chemical substances that are entirely composed of cations and anions (and most often a few percent of water) and which are liquid at room temperature. While aliphatic and ionic liquids might look and behave similar on a macroscopic scale, the cohesive forces and chemical properties on a microscopic scale are fundamentally different. Ionic forces acting between anions and cations expand over longer ranges than the cohesive forces effective in aliphatic diluents. The result is an almost negligible vapor pressure of ionic liquids, combined with good electric conductivity and high polarity. The higher polarity of the ionic liquids often prevents the splitting of the metal-ion loaded organic phase, which is of great practical importance. Our choice for an incinerable room temperature ionic liquid, Aliquat-336 nitrate ([A336][NO<sub>3</sub>]), for the purpose of minor actinide separation was based on these considerations.

Radiation resistance studies indicated a considerably higher stability of the reference extractant, TODGA in a solvent containing [A336][NO<sub>3</sub>] diluent instead of *n*-dodecane.<sup>[3]</sup> Group separation of An(III) + Ln(III) from a simulated, tracer-spiked highly active raffinate feed solution was demonstrated to be feasible with [A336][NO<sub>3</sub>] diluent and TODGA as extractant.<sup>[4]</sup> Some fission products, abundantly present in the HAR, such as Ru, Pd and Mo proved to interfere with the An(III)+Ln(III) co-extraction. These unwanted transition metals are actually extracted by the ionic liquid component of the solvent. Selective masking strategy is feasible for retaining Pd and Zr quantitatively in the aqueous phase (by the application of CDTA complexant). For Ru and Mo, a similar efficient masking agent is to date not identified. This problem led us to investigate another strategy for the co-management of Am(III)-only extraction and the Platinum Group Metals (PGMs: Ru, Pd and Rh) in one process and with the use of the same chemicals.

The present deliverable document provides a broad, but not comprehensive overview of the performed work after the Deliverable D 1.1.1 "Proof of concept: Actinide Separation" was submitted in 2020 September.

The chemistry behind the studied extraction processes can be grouped into two domains:

- i) extraction of Pd+Ru (+ Mo) ahead of the Am(III)/Cm(III)+Ln(III) ions
- ii) selective extraction of Am(III) from Cm(III) and Ln(III)

For the first domain, a CHON-compliant quaternary ammonium ionic liquid, [A336][NO<sub>3</sub>] was chosen based on the previously acquired experience during a previous PhD study of the author. According to batch acid dependency studies, the removal of Pd+Ru and under limited circumstances Mo and Rh can be performed with this cheap ionic liquid. The recovery of the extracted metal ions was foreseen to be performed with electrodeposition (Pd) and/or voloxidation (Ru). A European project funding request was submitted to the European Commission (project title: "ITISMORE") in 2021 to investigate this domain in detail. However the Commission rejected the grant of the funding for these critical metals in early 2022. In the present project, the investigation was limited to the feasibility of removing these metal ions ahead of the intended Am(III)-selective extraction step, but further studies on their recovery was out of the scope (lack of time and work force).

The second domain – actually being the main purpose of the study concerned the selective extraction of Am(III) from the chemically highly similar Cm(III) and Lanthanides (Ln(III)). The chemical similarity (identical charge and very close ionic radii, and an extremely complex matrix) renders this separation one of the most challenging one in the field of inorganic chemistry. To perform the separation, a combination of a lipophilic extractant (CyMe<sub>4</sub>BTPPhen) and a hydrophilic complexant (TEDGA) were foreseen, also on the basis of prior studies during the PhD of the author. The chemical structures of the compounds used are shown in Figure 1. The two compounds show an opposite selectivity towards the Am(III)/Cm(III) and Am(III)/Ln(III) couples and the joint use of them under the right experimental conditions can exploit a higher separation factor than the

use of a single compound. As the achievable separation factor in one step is rather low for the Am(III)/Cm(III) couple; a quantitative separation mandates the use of continuous, counter-current processes. This study was focusing on the upscaling of the concept from batch extractions towards the implementation on a continuous counter-current process using a laboratory-scale centrifugal contactor bench: BXP-012 type from Rousselet Robatel (Annonay, France).

## Solvent extraction process development

Solvent extraction process development that aims at going beyond fundamental concept studies requires the generation of a set of data obtained from batch liquid-liquid extraction experiments conducted at conditions relevant for the foreseen process. These data, in combination with the single stage efficiency values need to be fed into a simulation code that serves as a predictive model, prior to a multi stage counter current test can be run and validated. Several codes have been developed, most of which are proprietary and not accessible even on a commercial basis due to nuclear non-proliferation concerns. We had access to the SX Process, a code written by Dr. Daniel Magnusson at KIT.

The requirement of performing an *a priori* simulation of the metal ion concentration profiles is dictated by the complexity of the predictive models and the constant change of extraction conditions (metal ion concentration in each phase, distribution ratios, nitric acid concentration in each phase, etc.). Without a simulation, the number of tests and related analyses would be prohibitively large (in terms of time and cost). By performing a limited number of targeted experiments such as constructing distribution isotherms and single stage kinetic studies, the simulation code can be used with rather high certainty on the expected outcome of a multi-stage test.

In this part of the WP1 of ASOF the overall aim was the concept development of a solvent extraction process where Am(III) is selectively removed from a simulated highly active raffinate (HAR) solution which represents a solvent that is obtained after processing irradiated (or spent) nuclear fuel (SNF) with a hypothetical treatment process. The selected reference composition and history of such SNF was chosen to reflect a typical spent nuclear fuel element discharged from a Light Water Reactor (LWR) using UO<sub>2</sub> fuel with an average enrichment of 4.2 % with respect to <sup>235</sup>U/<sup>238</sup>U. In this hypothetical scenario the fuel would be kept in the reactor to reach a burn-up of 50 GWd<sub>tHM</sub> and cooled for a period of 10 years after discharging from the reactor. After the 10 years cooling period, it is assumed that the SNF element would undergo a mechanical disassembly, chopping, dissolution in nitric acid at a ratio of 1 ton SNF/5000 L after which U, Pu and Np would be removed by a PUREX process or any similar, advanced fuel treatment process. This is a current practice at industrial reprocessing facilities such as the La Hague plant of Orano (former Areva). The remaining liquor would contain ~ 4 M HNO<sub>3</sub> and all fission as well as activation products, including trivalent minor actinides (Am, Cm).

This latter, particularly complex liquor is often called PUREX Highly Active Raffinate (HAR) and is seen as the aqueous feed solution to be treated in any downstream minor actinide partitioning scenario. In fact the HAR solutions are always a mix of various treated (chopped, dissolved and further processed) spent nuclear fuel elements (which themselves are never completely identical). Therefore in a real reprocessing facility, the composition of the HAR is always a mixture of fuels with slightly different burn up and consequently fission and activation product composition. In addition, the SNF is a heterogeneous material, with noble metal inclusions that are only partially dissolved during the dissolution step due to their chemical inertness. In the present study, the rather conservative assumption was that all fission products are completely dissolved.

The present study took into account this selected fuel enrichment, history and subsequent treatment scenario as a basis, in order to keep ion concentrations comparable throughout the duration of the process development. Validated Monte Carlo simulation codes (such as Origen or SCALE) allow a reliable prediction of the amount of fission products that would be generated with a certain selected fuel scenario. The calculations used for the preparation of simulated HAR feed solutions were performed by Dr. Kevin Govers using SCALE code prior to the commencement of the ASOF project. The concentrations of the metal ions derived from a hypothetical fuel history and fuel treatment scenario are described in *Table 1*.

*Table 1. Chemical composition of the simulated highly active raffinate used as a basis to determine the required metal ion concentrations.*

Element	Concentration (mg L <sup>-1</sup> )	Element	Concentration (mg L <sup>-1</sup> )	Element	Concentration (mg L <sup>-1</sup> )	Element	Concentration (mg L <sup>-1</sup> )
Ag	23.34	Cu	20	Np	145.34	Sn	15.142
Al	2	Dy	0.3742	Pd	447.2	Sr	223.8
Am	182.92	Eu	40.72	Pm	3.256	Tc	236.8
Aa	546	Fe	1900	Pr	335	Te	143
Br	6.18	Gd	44.4	Pu	2190	U	187120

Cd	28.96	La	366.2	Rb	104.72	Y	133.58
Ce	705.2	Mn	0	Rh	133.62	Zn	24
Cm	14.06	Mo	1015.8	Ru	690.8	Zr	1090.2
Co	0	Na	1600	Sb	2.642		
Cr	93	Nd	1219.4	Se	15.91		
Cs	718.8	Ni	44	Sm	245		

The Am(III) and Cm(III) concentrations relevant for the chosen HAR scenario (*Table 1*) could not be used in those experiments that were executed in a fume hood, due to radiological limitations. A separate set of solvent loading experiment was therefore designed in accordance with the ALARA principle to be executed in a lead-glass shielded glove-box. The solvent loading experiment was carried out on the solvent formulation that proved to be the most promising in terms of kinetics. Extraction and scrubbing kinetics are the main the bottleneck of this extraction process.

Besides the radioprotection constraints, achieving the required concentrations were also not possible using the diluted tracer  $^{241}\text{Am(III)}$  solutions that are typically used for the batch liquid-liquid extraction experiments. Therefore a more concentrated  $^{241}\text{Am(III)}$  source was necessary to achieve a realistic HAR composition. A legacy solution with a known  $^{238/239/240/241}\text{Pu}$  impurity was selected as the source of high concentration liquid source for the solvent loading experiments. This Pu impurity had to be removed from the Am(III) solution because the  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  alpha decay energies overlap in the alpha spectra making the quantification of  $^{241}\text{Am}$  in the presence of even trace amount  $^{238}\text{Pu}$  unreliable. For this reason a set of manipulations were set forth in a dedicated Risk Assessment and dose rate estimation before requesting permission from the IDPBW unit to address any identified risk. The estimate of the absorbed dose on hand was conservative and it has been confirmed by the readings of the ring dosimeter after performing the experiment.

Solvent loading experiments serve as an important test where aqueous solutions of increasing metal ion concentration are contacted with an organic solvent, and the concentration of extracted metal ion is plotted against the remaining concentration of metal ion in the aqueous phase. The obtained curve is called distribution isotherm, the slope of which is the distribution ratio ( $D$ ) of a certain metal ion. The  $D$  values are not constant, but vary as a function of many parameters (e.g. temperature, extractant concentration, metal ion concentration, acid or salt concentration, presence of synergists/antagonists, interference caused by unwanted elements), therefore a very accurate knowledge of the change of  $D$  values as function of the most important process parameters is needed for making a predictive model on the concentration profile in the design of a multi-stage counter-current process.

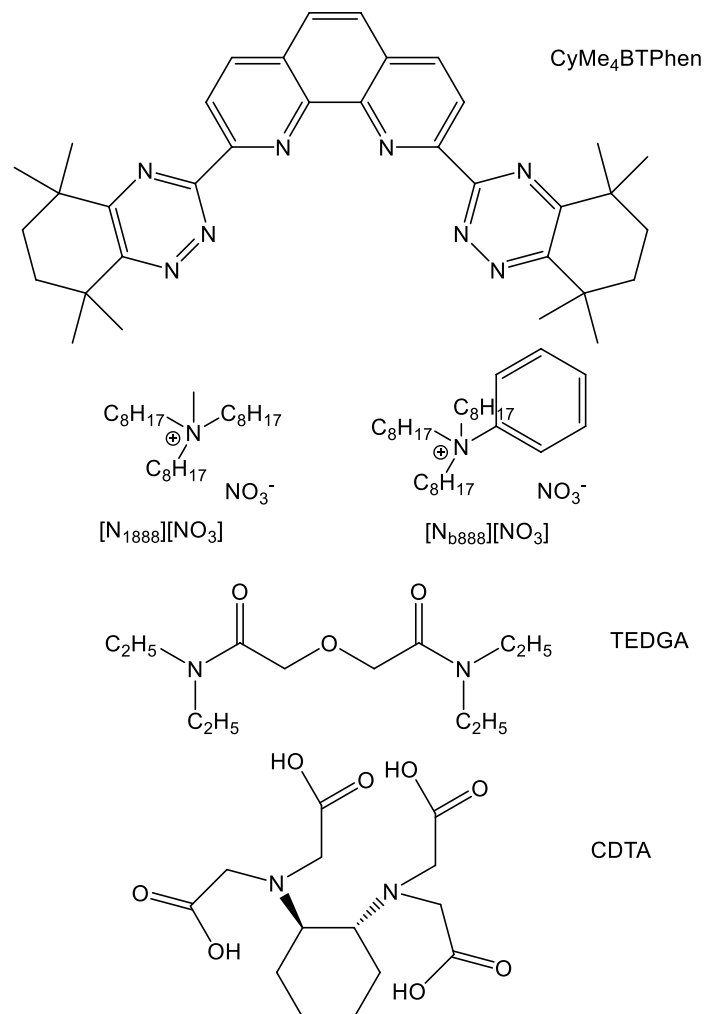
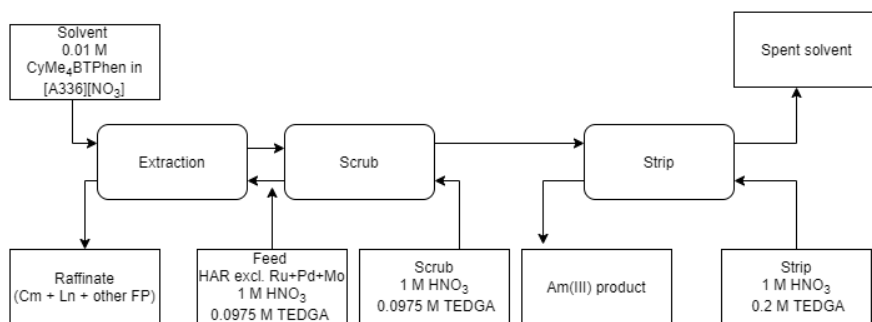
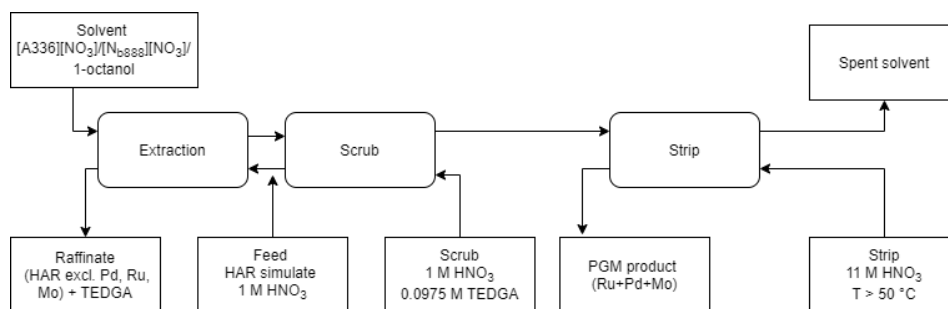


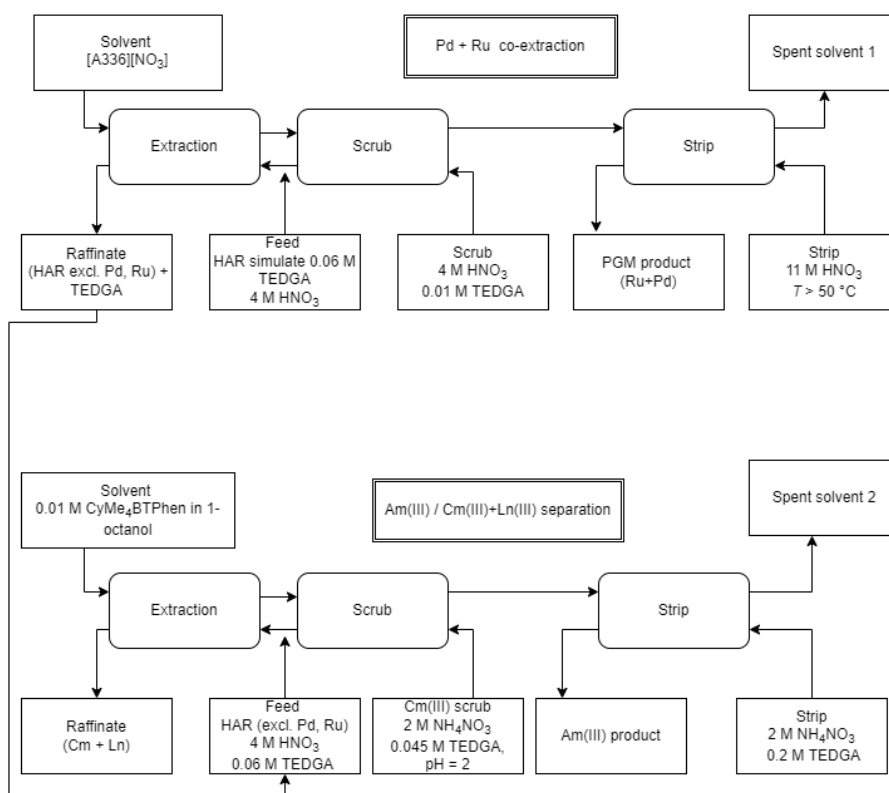
Figure 1. Chemical structures of the extractants and complexants used for the PGM and Am(III) partitioning

In addition to the distribution isotherms, in a continuous counter-current process, the extraction, scrubbing/stripping kinetics of metal ion phase transfer was necessary to be evaluated using single stage centrifugal contactor tests. These tests were run using various versions of mixing zones and rotor lengths. Slow extraction kinetics were already anticipated from batch extraction studies in the case of Ru extraction by [A336][NO<sub>3</sub>] as well as for both extraction and scrubbing of Am(III) using CyMe<sub>4</sub>BTPhen in an organic diluent.

The flow sheets were initially determined taking into consideration of the acid dependency of the distribution ratios of Pd, Ru and Mo obtained in batch studies. Kinetic studies already suggested rapid and quantitative extraction of Pd(II), while slow extraction of Ru(III) and Mo. After performing the first successful single stage kinetic studies, the Mo extraction had to be abandoned (due to the too slow kinetics) and the acidity was increased to 4 M HNO<sub>3</sub> in the tests. This higher concentration of nitric acid has the advantage that the aqueous feed doesn't require the acidity adjustment of the HAR solution prior to the foreseen Pd+Ru and subsequent Am(III) separation. The initial and the adjusted flow sheets are described in Scheme 1 and Scheme 2, respectively. Note the change of the diluent from Aliquat-336 nitrate to 1-octanol, this had to do with the observed too slow kinetics which could not be resolved.



Scheme 1. Initial flow sheet aiming at the joint separation of Pd+Ru+Mo from a 1 M HNO<sub>3</sub> feed acidity



Scheme 2. Revised flow-sheet for the sequential separation of Ru+Pd from a 4 M HNO<sub>3</sub> HAR and subsequent Am(III) separation

## Centrifugal contactor (extraction equipment) development

The adverse hydrodynamic behavior with the original design of the Robotel BXP-012 centrifugal contactors hindered the collection of consistent data due to regular maloperations from the beginning. The maloperations manifested in fluctuating residence times, emulsion formation and blockage of the inner channels or flooding of several stages when multiple

contactors were connected in a series. An internal design and subsequent fabrication with several iteration were needed to find a more optimal prototype that could be used without the abovementioned hydrodynamic issues.

These maloperations were all overcome by changing the annular (Couette-) gap between the rotor outer wall and the mixing zone inner wall. Tests conducted with the re-designed mixing zone showed that the previously encountered problems (unstable residence time due to liquid level fluctuations, flooding of adjacent stages, emulsion formation) all could be solved with this one single modification. 16 copies of various Couette-gap mixing zones were fabricated from transparent plexi (PMMA) glass. At the time of the writing of the present deliverable these pieces are being assembled into rotors. The new rotors and the mixing zones are designed in such a way that the most important modules (heavy and light phase weir, rotor length as well as mixing zone length) can be changed. Such a modularity or flexibility was not possible with the original, commercial version of the rotors. Besides a reliable hydrodynamic behavior, the plexi mixing zones allow a visual observation of the liquid levels in the mixing zone during the operation. This way, the rotation speed can be used to adjust the liquid level inside the mixing zone. In addition to the rotor modifications, an external temperature control was also implemented using a recirculating chiller/heater and several in-house developed copper blocks that transfer the heat to the housing metal blocks in which the rotors are placed. The temperature control was highly necessary for the work with viscous ionic liquid solvents.

### Purification of a high activity $^{241}\text{Am(III)}$ solution in a shielded glove box

Purification of the  $^{241}\text{Am(III)}$  nitrate solution in an unknown concentration of  $\text{HNO}_3$  was performed after an initial sampling and hot-ICP-MS (Table 2) as well as alpha and gamma spectrometry. The solution was sampled inside a lead-glass shielded glove box and transferred into a more secure recipient thick borosilicate glass bottle with a screw cap. 0.1 mL aliquots were taken from the various liquid fractions (both before the purification and during the various purification steps). The recipient glass vials were welded out in the presence of the radiation protection officer, then transferred to a dedicated glove box where all liquid samples were pipetted into clean, new recipients and released from the glove box using the airlock system.

Table 2. Hot ICP-MS concentrations measured on 1:10 diluted samples prior and after the purification process.

	$^{237}\text{Np}$	$^{238}\text{U} + ^{238}\text{Pu}$	$^{239}\text{Pu}$	$^{240}\text{Pu}$	$^{241}\text{Am} + ^{241}\text{Pu}$	$^{242}\text{Pu}$	$^{243}\text{Pu} + ^{243}\text{Am}$
Concentration before purification in 1:10 diluted sample (ng/g)	$7600 \pm 800$	$290 \pm 40$	$13700 \pm 2700$	$5600 \pm 1100$	$133000 \pm 27000$	$1180 \pm 120$	$< 39$
Concentration after purification in 1:10 diluted sample (ng/g)	$1170 \pm 130$	$< 2.2$	$39 \pm 15$	$17 \pm 7$	$101000 \pm 10000$	$7.4 \pm 3.1$	$0.45 \pm 0.20$

After the first analysis, extra, tracer metal grade nitric acid was added to the  $^{241}\text{Am}$  stock solution to guarantee that the free acid concentration exceeds  $4 \text{ mol L}^{-1}$  (this step resulted in a slight dilution of the original concentration). Afterwards the solution was contacted with three aliquots of 30 vol.% TBP in *n*-dodecane to remove Pu and Np impurities from the solution. The organic and aqueous phases were mixed using a small magnetic stirrer and a stirring bar at room temperature. Phase separation was done by pipetting after the phases settled and separated. The extracted Pu was stripped with  $0.37 \text{ mol L}^{-1}$  acetohydroxamic acid in  $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ . The collected aqueous strip phase was acidified again to have a  $5 \text{ mol L}^{-1} \text{ HNO}_3$  concentration, followed by passing the entire liquid volume through a column containing TEVA resin. The Pu this way is retained in the column, while the Am(III) remained in solution. In a second step, the Am(III) was loaded on a DGA resin-filled column, from which it was eluted using  $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ . The set-up used for the column purification is shown on (Figure 2).



Figure 2. Image taken from the set-up used for securing the chromatographic column during the various steps of Am(III)/Pu(IV) separation

The still extracted  $^{241}\text{Am(III)}$  was removed from the organic phase by contacting it with  $1 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$  in MilliQ water (according to batch test, the Am(III) stripping is instantaneous and quantitative in one contact  $D_{\text{Am}} \approx 0.0049$ ). The separated aqueous phase was re-acidified to a final  $5 \text{ mol L}^{-1} \text{ HNO}_3$  acidity, after which it was successively poured through a TEVA column, to remove Pu content and the eluate Am(III) fraction was loaded onto a DGA column, from which it was eluted using  $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ . The Am(III) inventory from the organic phase decontamination could be recovered and remained available for later use in tracer studies in a pure form and known matrix ( $0.01 \text{ M HNO}_3$ ).

The Am(III) fraction recovered after the purification using solvent extraction (30 vol.% TBP in *n*-dodecane), was not purified further on a column, to avoid losing a large part of the activity due to a possible blockage of the column which can occur due to improper column loading, gas bubble formation or radiolytic degradation to the resin. According to the second hot  $-\text{ICP-MS}$  analysis, the purification by TBP allowed a significant reduction of the Pu content (by a factor of  $> 350$  with respect to  $^{239}\text{Pu}$ ) with only minor losses or dilution of the aqueous solution.

### Inactive solvent loading experiments using Eu(III) nitrate in 4 M $\text{HNO}_3$

In a separate (inactive) solvent loading study, the solubility of CyMe<sub>4</sub>BTPPhen was tested in 3 different diluents: 1-octanol, 1-decanol and [A336][NO<sub>3</sub>] (Table 3). The maximum loading of the three solvents with highest ligand concentration were also tested both in the presence and the absence of TEDGA. In the case of samples with added TEDGA, the [TEDGA] concentration was determined to have a stoichiometrically matching concentration with the Eu(III).

Table 3. Solubility limits of uncomplexed CyMe<sub>4</sub>BTPPhen and Eu(III) –CyMe<sub>4</sub>BTPPhen complexes in various diluents

	1-octanol	1-decanol	[A336][NO <sub>3</sub> ]
[CyMe <sub>4</sub> BTPPhen] <sub>max.</sub> (mol L <sup>-1</sup> )	0.536	0.409	0.022
[Eu(CyMe <sub>4</sub> BTPPhen) <sub>2</sub> ] <sup>3+</sup> <sub>org.</sub> (mol L <sup>-1</sup> )	0.0067	0.0035	0.0055
Limit where no precipitate is observed for the highest [CyMe <sub>4</sub> BTPPhen] concentration	0.01103 M [Eu(III)] <sup>3+</sup> <sub>org.</sub> (with initial 0.0804 M TEDGA <sub>aq.</sub> )		

The distribution ratio for the 1-octanol diluent was determined with gamma spectrometry after adding  $^{152}\text{Eu(III)}$  tracer to the sample. These tests were carried out with the primary purpose to maximize metal loading for preparing XAFS samples.

## Solvent loading experiment using macro concentrations of $^{241}\text{Am(III)}$ nitrate

Equal volumes of the purified  $^{241}\text{Am(III)}$  stock solution and of the  $^{244}\text{Cm(III)}$  stock solution were added to Ln(III) stock solution to have a final composition as shown in

Table 4. The solvent loading experiment was performed according to the phase volume ratio variation method. According to this method, the ligand and metal ion concentrations are kept the same in each samples and only the phase ratio of the organic and aqueous phases are varied. In the case of each sample (with different Org/Aq. volume ratios), the aqueous phase was composed of 50 vol.% of the feed and 50 vol.% of the scrubbing solution (the latter being composed of 2 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> 0.045 mol L<sup>-1</sup> TEDGA at pH 2).

Table 4. List of trivalent metal ion concentrations aimed at in the aqueous feed used for the solvent loading experiment with macro concentrations of  $^{241}\text{Am(III)}$  and  $^{244}\text{Cm(III)}$  in 4 M HNO<sub>3</sub> and 0.06 M TEDGA.

Cation	Concentration (goal) / g L <sup>-1</sup>	Concentration (actual) / g L <sup>-1</sup>
Am(III)	0.182	0.177 ± 0.006
Cm(III)	0.014	0.013 ± 0.004
La(III)	0.366	0.364 ± 0.036
Ce(III)	0.705	0.640 ± 0.060
Pr(III)	0.335	0.326 ± 0.033
Nd(III)	1.219	1.160 ± 0.120
Sm(III)	0.245	0.253 ± 0.026
Eu(III)	0.040	0.047 ± 0.005
Gd(III)	0.044	0.092 ± 0.009

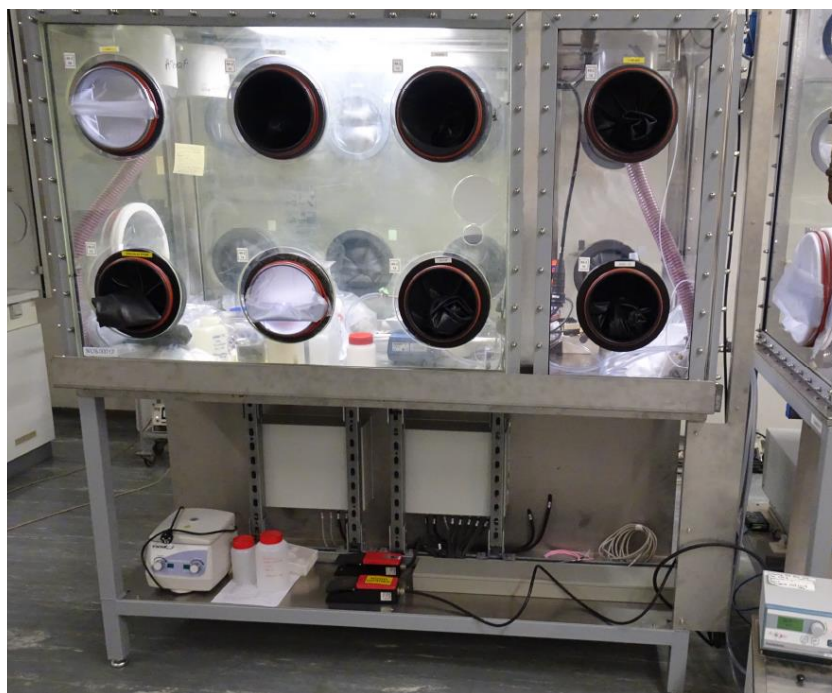


Figure 3. Image of the experimental work station (glove box with a connected recirculating heater/chiller) used for the solvent loading experiment.



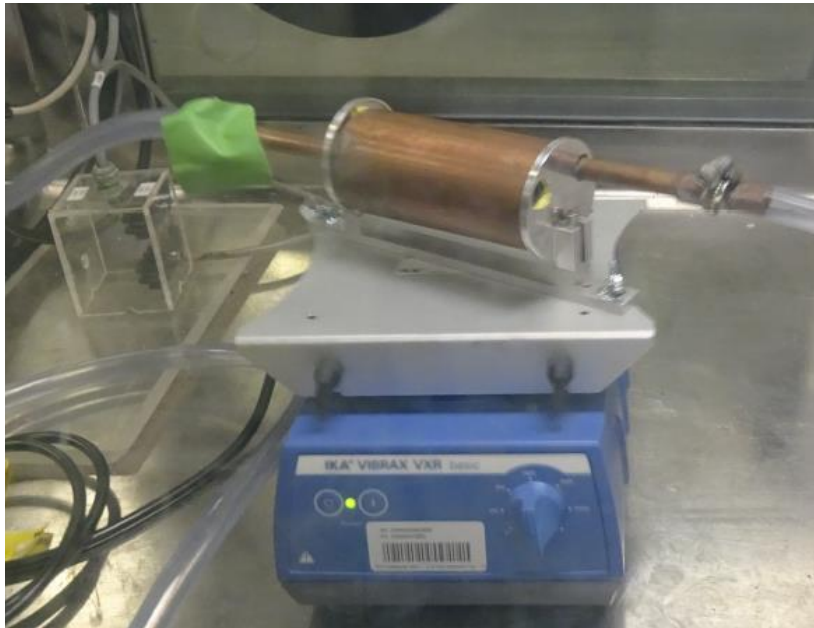


Figure 4. Picture taken from the thermostated orbital shaker used for the solvent loading experiment inside the shielded glove box.

The phases were separated by pipetting and transferred to clean recipient vials using a transfer glove box equipped with an interlock. From the undiluted samples a 1:100 dilution was prepared, homogenized and the activity of each sample were determined using a HPGe detector at 12 cm measurement distance. The efficiency calibration of the detector was previously performed using the same sample geometry and a multi-gamma calibration source traceable to international standards. The determined activity concentrations (organic and aqueous phases) were converted to mass concentrations and plotted in Figure 5.

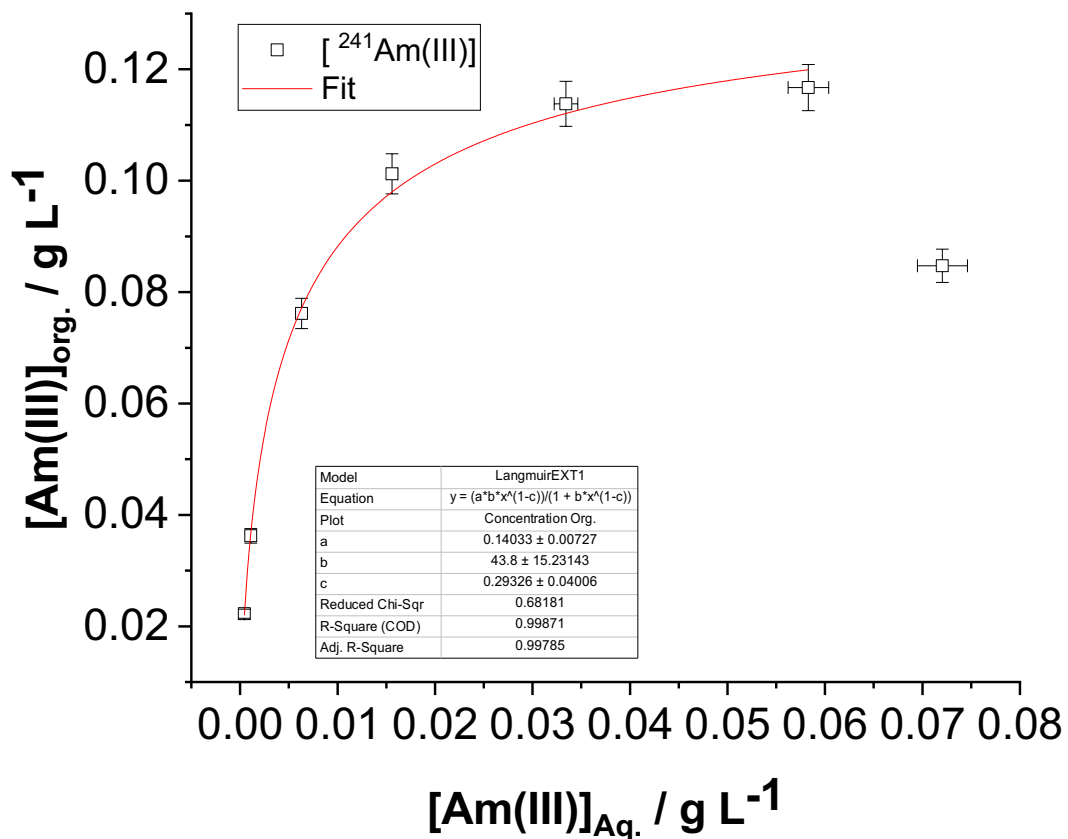


Figure 5. Distribution isotherm of  $^{241}\text{Am(III)}$  extraction from a feed solution containing  $4 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $0.06 \text{ mol L}^{-1} \text{ TEDGA}$ ,  $0.182 \text{ g L}^{-1} \text{ }^{241}\text{Am(III)}$ ,  $0.014 \text{ g L}^{-1} \text{ }^{244}\text{Cm(III)}$  and stable  $\text{Ln(III)}$  ions with the expected concentration of the reference HAR solution using  $0.01 \text{ mol L}^{-1} \text{ CyMe}_4\text{BTPPhen}$  in 1-octanol as organic phase and a scrub solution composed of  $0.01 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $2 \text{ mol L}^{-1}$

<sup>1</sup> NH<sub>4</sub>NO<sub>3</sub> and 0.045 mol L<sup>-1</sup> TEDGA. Results obtained via gamma measurements of the separate phases after a 1:100 dilution. Extraction at 40 °C, 500 rpm shaking for 1 h.

The extracted [Am(CyMe<sub>4</sub>BTPPhen)<sub>2</sub>]<sup>3+</sup><sub>org.</sub> complexes reached the solubility limit beyond 0.12 g/L in 1-octanol indicating that with the current solvent formulation and the foreseen phase ratios, the PUREX HAR taken as a basis of the study could be processed without any need for a previous dilution (NB: the scrubbing step inherently dilutes the aqueous feed concentration by a factor of 2).

Results of the solvent loading experiments will be published within the paper planned on single stage Am(III) / Cm(III)+Ln(III) separation.

## Single stage kinetic studies with BXP-012 centrifugal contactor using modified mixing zones

The results of these studies will be published in separate peer reviewed publications for the PGM extraction and one for the Am(III) / Cm(III)+Ln(III) separations.

## Multi-stage kinetic studies with BXP-012 centrifugal contactor

A multi (4) stage extraction and 8-stage scrubbing test was conducted using 1-decanol diluent and widened mixing zones for the Am(III) partitioning step. The results showed that the scrubbing kinetics mandate the switch to 1-octanol diluent due to the sluggish scrubbing kinetics. Results of this study will be included in the publications mentioned above.

## Speciation studies for Eu(III) complexation in the CyMe<sub>4</sub>BTPPhen / TEDGA system in various organic diluents

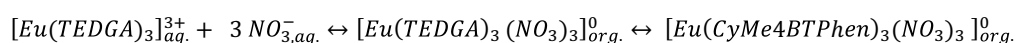
The speciation of stable Eu(III) in various complexes was studied using the XAFS method at the MARS beamline of the SOLEIL synchrotron (Paris, France) in liquid phases with Eu(III) as absorbing atom and either TEDGA or CyMe<sub>4</sub>BTPPhen as added complexants.

The aim of the experiment was to gain understanding in the underlying molecular reason for the i) *increased extraction kinetics* and ii) *decrease in selectivity* of CyMe<sub>4</sub>BTPPhen for Am(III) over Eu(III) observed at 40 °C when changing the diluent from a pure ionic liquid [A336][NO<sub>3</sub>] to an aliphatic alcohol. These two observations are assumed to be both related to a change in the speciation of metal ions in the organic phase (i.e. change in the solubility of one of the complexes or a change in the composition of the complexes): either the hydrophilic homoleptic [Eu(TEDGA)<sub>3</sub>]<sup>3+</sup>-complexes are partially soluble in aliphatic alcohols or lipophilic heteroleptic [Eu(TEDGA)<sub>x</sub>(CyMe<sub>4</sub>BTPPhen)]<sup>3+</sup> complexes are formed besides [Eu(CyMe<sub>4</sub>BTPPhen)<sub>2</sub>]<sup>3+</sup>.

### 1. Identification of the nature of the Eu(III) complex present in the aqueous phase and in the 1-octanol phase in the absence of CyMe<sub>4</sub>BTPPhen and the presence of TEDGA.

The recorded XAFS spectra confirmed in accordance with the hypothesis that [Eu(TEDGA)<sub>3</sub>]<sup>3+</sup> complexes get partially extracted into aliphatic alcohols such as 1-octanol or 1-decanol. The solubility is higher in the shorter chain length alcohols. Probably due to the higher polarity of the diluent, the charged complexes are more stable in the shorter chain length alcohols and less stable in longer chain length alcohols. This observation strongly suggests, that TEDGA acts as hydrophilic complexant and due to the solubility in the organic phase, also act as a phase transfer catalyst for Eu(III) according to Equation 1.

Equation 1 Extraction mechanism describing the partitioning of Eu(III) and its complexes between the aqueous and organic phases.



### 2. Identification of complex compositions from the peak positions:

A second finding is that the extracted Eu(III) ions are present in two different types of complexes i) a homoleptic [Eu(TEDGA)<sub>3</sub>]<sup>3+</sup> and a homoleptic [Eu(CyMe<sub>4</sub>BTPPhen)<sub>2</sub>]<sup>3+</sup> and not in a complex that contains different types of ligands. The evidence for this conclusion is that while the TEDGA complexes have a characteristic intensive peak at 2 Å distance, the

CyMe<sub>4</sub>BTPhen have two characteristic peaks one at a similar 2 Å distance and in addition one at 3 Å distance. In the case there would be a complex where both TEDGA and CyMe<sub>4</sub>BTPhen would be present at the same time, the peak position representing the second coordination sphere would also be noticeably changed compared to the pure case of the pure Eu(III)-CyMe<sub>4</sub>BTPhen complexes. As this is not the case (the position of the second peak remained the same even if TEDGA complexes are present), it can be concluded that the peak shift representing the first coordination sphere of Eu(III) is due to the presence of two homoleptic complexes.

The spectra, where both TEDGA and CyMe<sub>4</sub>BTPhen complexes of Eu(III) co-exist, show a slight shift of the first peak's position towards lower distances. This is due to the fact that EXAFS method all species are visible and the observed reflection pattern is an average of all reflections present if the investigated central atom type.

*Results of the speciation study will be published in a high impact factor peer reviewed journal.*

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