

Beyond U/Pu separation: Separation of americium from the highly active PUREX raffinate

P. Zsabka^a, A. Wilden^b, K. Van Hecke^a, G. Modolo^b, M. Verwerft^a, T. Cardinaels^{a,c,*}

^a Institute for Nuclear Materials Science, Belgian Nuclear Research Center (SCK CEN), Mol 2400, Belgium

^b Institute of Energy and Climate Research – Nuclear Waste Management (IEK-6), Forschungszentrum Jülich GmbH, Jülich 52428, Germany

^c Department of Chemistry, KU Leuven, Leuven 3001, Belgium

ARTICLE INFO

Keywords:

Actinides
Fuel cycle
Americium
Partitioning
Reprocessing
Purex

ABSTRACT

This review provides a comprehensive overview of published hydrometallurgical chemical processes capable of separating americium from curium and the lanthanides. A search for highly selective and robust americium separation methods is motivated by the fact that americium isotopes contribute significantly to the long-term heat load and residual radiotoxicity of high level waste originating from the PUREX process, nowadays still the key reprocessing technology to recycle uranium and plutonium from spent nuclear fuel. The separation (partitioning) and subsequent nuclear transmutation (or burning) of americium would allow a substantial improvement in the construction of an underground final repository and provide safety benefits – highly relevant for the exploitation of such a facility over extended periods of time. Besides the discussion of basic properties of the various separation methods, an evaluation of their compatibility with upstream and downstream processes as well as the treatment of secondary waste streams is also provided.

List of abbreviations

ADAAM(EH) alkyl diamide amine
AHA acetohydroxamic acid
ALSEP Actinide-Lanthanide Separation Process
BK-1 2,2,3,3-tetrafluoropropan-1-ol carbonate
BIMET (2*S*,2'*S*)-4,4'-(ethane-1,2-diylbis(sulfanediy))bis(2-aminobutanoic acid)
BTrzPhen 2,9-bis-triazolyl-1,10-phenanthroline
CEA commissariat à l'énergie atomique et aux énergies alternatives
(ClPh)₂PSSH bis(chlorophenyl)dithiophosphinic acid
CMPO octyl-phenyl-*N,N*-diisobutyl carbamoyl methyl phosphine oxide
BTP(s) abbreviation referring to 2,6-di [5-(alkyl or aryl)-1,2,4-triazol-5-yl]pyridine and 2,6-di [5,6-di(alkyl or aryl)-1,2,4-triazin-3-yl]pyridine type of molecules
CyMe₄BTPPhen 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline
DBBP dibutylbutylphosphate

DAAP diamylamylphosphonate
DHOA *N,N*-dihexyloctanamide
DEHBA *N,N*-di-(2-ethylhexyl)butyramide
DEHiBA *N,N*-di-(2-ethylhexyl)isobutyramide
DIAMEX DIAMide EXtraction
DMDOHEMA DiMethyl-DiOctyl-HexylEthoxy MalonAmide
DOODA(C2) *N,N,N',N'*-tetraethyl-3,6-dioxaoctanamide
DOODA(C8) *N,N,N',N'*-tetraoctyl-3,6-dioxaoctanamide
DTPA diethylenetriamine pentaacetate
EBR-II Experimental Breeder Reactor II
EH-BTrzPhen 2,9-bis(1-(2-ethylhexyl)1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline
EtOH-BPTD 3,3'-([2,2'-bipyridine] – 6,6'-diylbis(1*H*-1,2,3-triazol-4,1-diyl))bis(ethan-1-ol)
FS-13 phenyl trifluoromethyl sulfone
FZJ Forschungszentrum Jülich GmbH
GEN IV reactors fourth generation advanced nuclear reactor concepts
H₂BP18C6 *N,N'*-bis [(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6
HAR Highly Active Raffinate

Abbreviations: EOI, End of Irradiation.

* Corresponding author: Institute for Nuclear Materials Science, Belgian Nuclear Research Center (SCK CEN), Mol 2400, Belgium.

E-mail address: thomas.cardinaels@sckcen.be (T. Cardinaels).

<https://doi.org/10.1016/j.jnucmat.2023.154445>

Received 19 December 2022; Received in revised form 16 March 2023; Accepted 11 April 2023

Available online 12 April 2023

0022-3115/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

HDEHP	bis(2-ethylhexyl)-phosphoric acid
HD(DIBM)P	bis(2,6-dimethyl-4-heptyl) phosphoric acid
HEH [EHP]	(2-ethylhexyl)phosphonic acid mono(2-ethylhexyl) ester
HLW	High Level Waste
H ₄ TPAEN	<i>N,N,N',N'</i> -tetrakis [(6-carboxypyridin-2-yl)methyl] ethylenediamine
Isopar-M	isoparaffin fluid (crude oil distillate product of ExxonMobil)
INL	Idaho national laboratory
JAEA	Japanese atomic energy agency
KIT	Karlsruhe institute of technology
LWR	light water reactor
LHPA	lacunary polyanionic ligand
MYRRHA	Multipurpose hYbrid Research Reactor for High-tech Applications
MOX	Mixed OXide fuel
NTA	nitroiloacetic acid
NTAamide(C8) (HONTA)	<i>N,N,N',N',N'',N''</i> -hexaoctyl-nitritoltriacetamide
PAREX code	a chemical process simulation computer code developed by CEA for solvent extraction process simulation in steady or transient states
PrOH-BPTD	3,3'-([2,2'-bipyridine] -6,6'-diylbis(1 <i>H</i> -1,2,3-triazol-4,1-diyl))bis(propan-1-ol)
PUREX	plutonium uranium reduction extraction
P&T	partitioning and transmutation
SCE	standard calomel electrode
SNF	spent nuclear fuel
SO ₃ Ph-BTBP	3,3',3'',3'''-([2,2'-bipyridine] -6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate
TBP	tri- <i>n</i> -butylphosphate
TEDGA	<i>N,N,N',N'</i> -tetraethylglycolamide
TEHDGA	<i>N,N,N',N'</i> -tetraethylhexyl diglycolamide
TEHP	tris(2-ethylhexyl)phosphate
t _{HM}	tonnes of heavy metal
TODGA	<i>N,N,N',N'</i> -tetraoctyldiglycolamide
TOPO:	trioctylphosphine oxide
TPH	hydrogenated tetrapropylene (branched chain industrial aliphatic diluent)
TRUEX	trans-uranic element extraction/recovery process based on a modified PUREX solvent (CMPO+TBP in alkane diluent)
TTA	2-theonyl trifluoroacetone
UOX	Uranium OXide fuel
UMOF	unconventional metal organic framework
UREX	uranium extraction process (a modified version of PUREX where Pu extraction is prevented by the addition of acetohydroxamic acid reductant to the feed)
VTR	versatile test reactor

1. Introduction

The long-term management of spent nuclear fuel (SNF) after reactor operation needs to ensure the confinement of the radionuclide inventory from the biosphere and ensure that the long term heat emission of the ultimate waste form will not impair engineered and geological barriers beyond design. It is useful to distinguish the short term (< 100 years after end of irradiation) issues from the long term issues (> 100 years after end of irradiation). Short term issues relate mostly to engineering concerns (the on-site cooling, intermediate storage, transports, reprocessing, etc.) and long term issues relate to biosphere issues (stability of geological barriers, radionuclide migration and release to the biosphere, etc.). A particular concern with geological disposal is the thermal impact that spent nuclear fuel or vitrified waste may have on its stability. The residual heat load of the spent nuclear fuel is an important design parameter for a deep geological repository. When taking end of irradiation + 100 years (EOI + 100 y) as reference period for the start of geological disposal, plutonium and americium isotopes dominate the

residual heat for both UOX and MOX fuels, and this situation remains unchanged for the next centuries. In the case of Belgium for example, it is estimated that in total 4825 t_{HM} irradiated UOX and 66 t_{HM} irradiated MOX fuel will have to be treated or disposed of [1]. The estimated total minor actinide inventory in the fuel assemblies would amount 7.5 tons of Am, 200 kg Cm and 3.5 tons of Np [1]. The worldwide SNF inventory in storage according to the most recent estimation by IAEA amounts 263,000 t_{HM} besides 127,000 t_{HM} reprocessed [2].

Geological disposal is widely considered to be the best solution for long term management of higher activity radioactive wastes, including spent nuclear fuel if the open fuel cycle is to be followed. This waste management option requires the creation of deep underground galleries in a suitable, geologically stable host formations to isolate the radiotoxic elements from the biosphere. The heat emission of Pu and Am imposes a minimal distance between highly active waste packages, to prevent that the surroundings are overheated and lose their insulating properties.

The removal of minor actinides from the highly active waste stream would have a beneficial impact on the heat load reduction and so the footprint of the underground repository as shown by various impact studies [3–9]. In a scenario where U and Pu multi-recycling is implemented for further use as nuclear fuel in advanced fast reactors and Am is removed from the final waste, the underground disposal footprint could be reduced by a factor of 7 compared to an open nuclear fuel cycle scenario with a direct disposal of spent nuclear fuel [10–12]. The repository footprint area reduction is almost exclusively the result of the removal of ^{241+242m+243}Am nuclides. The contribution of Cm and Np to the heat load at EOI + 100 y is considerably less. As the critical Cm isotope present in LWR SNF is ²⁴⁴Cm (t_{1/2} = 18.1 y), it is an option to allow the Cm-containing waste fraction to decay into ²⁴⁰Pu, before the ultimate disposal as vitrified waste. A 40 year decay storage (2 half-lives) already allows the decay of 80% of the initial ²⁴⁴Cm content in addition to the reduction of the heat load from short-lived fission products (e.g. ¹³⁷Cs, ⁹⁰Sr) [13]. Fast spectrum nuclear reactors have been studied since many decades and were implemented in many countries to ensure a more sustainable management of uranium resources. More recently, fast neutron reactor concepts have also been worked out with the objective of minor actinide transmutation, principally Am. Some concepts aim at heterogeneous transmutation in which high Am-loaded “targets” are inserted in the core (e.g. the MYRRHA concept), or aim at homogeneous transmutation. In the latter scenario, Am is deliberately added in low concentrations to the reactor driver fuel (e.g. the ASTRID concept).

Actinide recycling strategies can thus be divided into two strategies: homogeneous or heterogeneous. In the case of homogenous recycling, the fuel cycle foresees the group separation of all actinides in the spent nuclear fuel treatment processes and the co-management of the separated actinides in the subsequent irradiation cycle. In such a fuel cycle scenario the fast reactor core would be loaded with a mixed actinide fuel and the inner part and outer blanket locations would be filled with essentially the same type of fuel assemblies resulting in a rather homogenous nuclide composition across the core diameter. On the contrary, in the case of heterogeneous recycling, the major actinides are separated ahead of minor actinides and their material flow is kept separate also in the subsequent fuel fabrication and reactor loading patterns; the reactor core is foreseen to show a large radial heterogeneity (MOX driver fuel surrounded by a minor actinide-rich blanket). The scheme of the most important heterogeneous recycling processes for minor actinides and their connectivity to the PUREX process is shown in Fig. 1 according to Geist et al. [14].

As all versions of the homogenous reprocessing methods foresee the co-management of all major and minor actinides no attempt was made towards an Am/Cm separation. In the heterogeneous minor actinide partitioning domain, the option of Am/Cm separation is left open. Separation of curium from americium is a key problem to solve in any credible closed fuel cycle scenario. Co-management of curium with americium in the back-end of a closed nuclear fuel cycle would impose

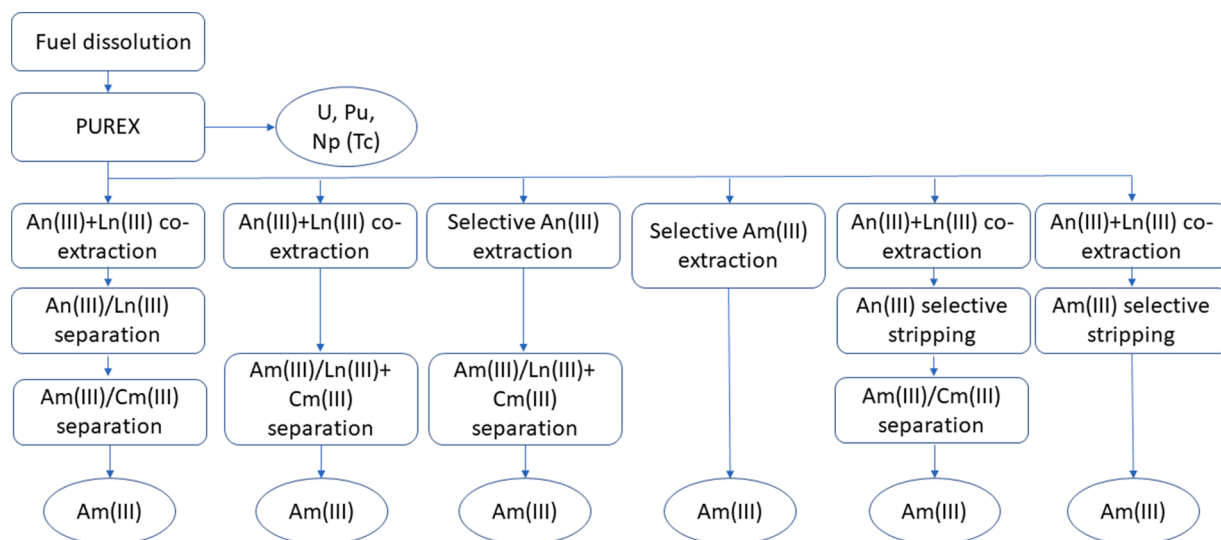


Fig. 1. Scheme of heterogeneous minor actinides partitioning strategies adapted from [14].

significant drawbacks for all stages of minor actinide transmutation target preparation, irradiation and reprocessing in comparison to the management of americium only due to the high neutron and heat emission of curium isotopes and their in-reactor behavior [15]. Therefore, the removal of the Cm inventory originating from LWR (UOX and MOX) spent fuel as well as Cm bred during Am-bearing target irradiation in fast reactors is a valid pathway. The highly similar chemical properties of trivalent Am(III) and Cm(III) ions limits the possibilities of elaborating Am(III)-selective extraction processes. This review is focused on the discussion of several processes which can cope successfully with this challenging task.

Many excellent review papers have been written on the minor actinide partitioning schemes [14,16–21], or on the research quest for ever more selective extractants [22–24]. Recently, two reviews were issued that specifically focused on Am separation: one that focusses on the recent development and coordination chemistry studies of triazinylpyridine *N*-donor ligands (BTPs, BTBPs, BTPHens) in the context of An(III) and Ln(III) partitioning [25] and one on the solvent extraction systems for selective Am(III)-extraction by solvent extraction methods [26]. The present review focuses on the relevant chemistry behind processes dedicated to “Am-only” separation (wherever available) and provides insight in strengths and weaknesses of the described different processes. Particular attention is paid to redox-reaction based methods, redox-free liquid-liquid and solid-liquid extraction methods. For an overview of all described chemical compounds, the reader is referred to Table 5.

No attempts were made to attribute technological readiness levels (TRL) to the different processes, and the interested reader is referred to other review papers [21,27]. Due to the similar redox potential of transuranium elements, dry routes, or pyrochemical methods are mainly suited for the group separation of actinides from irradiated metallic fuel, and fall outside the scope of the present review [28,29].

2. Liquid-liquid extraction methods for the separation of Am(III) from Cm(III) and Ln(III) without changing the oxidation states

Liquid liquid-extraction methods are based on the preferential partitioning of certain components between two immiscible liquid phases that are brought into contact. The organic phase is typically a mixture of a diluent (aliphatic/aromatic hydrocarbons or ionic liquids) and one or more extractants and synergists. As good phase separation of organic and aqueous phases is necessary to avoid emulsion formation during mixing, phase modifiers can be added to the organic phase to increase its

polarity, to prevent precipitate or third phase formation. The aqueous phase is most often adjusted in its acidity or pH and often contains masking or hold-back agents to prevent unwanted, interfering ions from being extracted to the organic phase along with the preferred species.

In batch mode, liquid-liquid extraction consists of combining two phases in a vessel, mixing the phases and separating them by gravitational force. On an industrial scale the counter-current, multi stage mixing and separation is the typical mode of operation, because counter-current arrangement allows the achievement of high decontamination factors. The liquids flow in an opposite direction, forcing the aqueous phase to flow from one stage to another where it is being mixed with and separated from an organic phase which has an increasing free ligand concentration along the direction of the flow of the aqueous phase. In this way the driving force of the extraction is maximized along a process section. Usually three types of process sections are distinguished: extraction, scrubbing and back extraction or stripping. The extraction section is the part of the chemical process, where the target metal ion is extracted from the aqueous phase to the organic phase via complexation by extractants dissolved in the organic phase. The goal in this stage is that unwanted elements mainly remain in the aqueous phase, but a fraction of the interfering ions might be co-extracted to the organic phase. The unwanted ions and a part of the co-extracted acid is washed back to the aqueous stream in the scrubbing section. The new aqueous stream in the scrubbing is merged with the aqueous feed stream in all the stages of the scrubbing. At the last stage of the scrubbing the organic phase is only loaded with the target metal ion, while all unwanted ions remain in the aqueous raffinate. The organic phase enters in the last, back-extraction section where it is being contacted with a separate aqueous stream, with a composition suitable to back-extract the target metal ions into an aqueous phase product, free from other metallic contaminants.

For the mixing and separation, several different types of equipment were developed, such as pulsed columns, mixer settlers, annular centrifugal contactors to name a few. The various types of equipment perform the same two functions in principle: mixing and separation of the two phases. All three designs have found use in hydrometallurgical processes for spent fuel treatment. Pulsed columns are robust equipment, capable of large material flow throughput, with no moving mechanical parts and also very reliable in the presence of undissolved fine particles. Mixer settlers are preferred for solvent extraction systems where the extraction kinetics is slow and/or the phase separation takes long time. As the settling compartments need to ensure long residence times, the footprint of one stage can be rather large. Centrifugal

contactors were designed to allow a rapid mixing and rapid separation in a single unit. Their advantage is the short residence time, efficient mixing and the very efficient separation due to the use of centrifugal force for the phase separation. The short contact time minimizes the exposure of organic solvents to radiation. The downside of centrifugal contactors is that they are mechanically complex, requiring regular maintenance and servicing (e.g. replacement of rotor axes, ball bearings etc.) which is a challenging task in a hot cell workshop.

Extraction agents of interest for industrial-size applications would need to meet certain requirements for being considered towards implementation [30]. In general, these compounds should be easy to synthesize with reproducible quality (also on large scale), show good solubility in diluents compatible with the foreseen application, should be selective and show suitably high distribution ratios and metal-loading capacity and should be resistant against acid-induced hydrolysis, thermal degradation and third-phase or crud formation. The extraction is of use only, if the extracted metal ions can be back-extracted to an aqueous phase, therefore reversibility is equally important. In the context of minor actinide partitioning, besides these general requirements, additional conditions need to be met by solvents, especially resistance towards radiolysis and fast kinetics.

The methods discussed in this section exploit the observed slight selectivity of lipophilic extractant and combine it with a lipophilic synergist or with a hydrophilic complexant that shows a reverse affinity towards the same combination of ions. As most extractant/complexant combinations only show a rather low separation factor for the Am(III)/Cm(III) couple (typically between 2 and 3), a counter-current, multi-stage process is necessary to reach any useful decontamination level of the feed solution from the Am(III) inventory.

The binding affinity follows the order of the lanthanide and actinide contraction in the case of hard donor molecules such as diglycolamides. With the increase of charge density along the series, the complex stability increases. Both the inter-group (higher selectivity for lanthanides versus actinides) and intra-group (along the series with the increase of atomic number) selectivity can be well explained with the Pearson's Hard-Soft Acid-Base theory [31].

Typically soft-donor (nitrogen or sulfur), heterocyclic extractants show interesting An(III)/Ln(III) (thus inter-group) separation factors, as evidenced by the ligand development work for minor actinide partitioning purposes that was started more than thirty years ago [22,23,32–36]. The adjacent non-bonding electron pairs of *N*-atoms cause a decrease in basicity of the free ligands and at the same time increase their affinity for complexing of softer over harder cations. The overlap of the non-coordinating lone electron pair with the coordinating lone electron pair is assumed to cause an increase in the covalent character of the bonding between the metal and the ligand, and this effect is more expressed with the spatially diffuse 5*f* orbitals (available in An(III) ions) than with the 4*f* orbitals of Ln(III) [22,37]. As a result, these type of complexants are able to selectively complex An(III) ions in An(III)+Ln(III) mixtures even at acidities relevant for spent fuel treatment processes ($\geq 1 \text{ mol L}^{-1} \text{ HNO}_3$). Understanding for An(III)/Ln(III) selectivity among heterocyclic *N*-donor molecules came through the recognition of the role of the α -effect that is present in heterocycles with two adjacent *N*-donor atoms, such as it is the case with BTPs [33], CyMe₄BTBP or CyMe₄BTPhen molecules containing 1,2,4-triazinyl moieties [38]. The term α -effect in this context refers to the increased reactivity of the lone electron pair of the *N*-donor atom responsible for the An(III) coordination. The presence of an adjacent, non-coordinating lone electron pair (i. e. in the α position of the ring) increases the electron density on the nucleophilic center (i. e. the electron donating *N*-atom).

For the intra-group selectivity within the An(III) series of ions the trend is less clear and so far no predictive model could be established between chemical structures of soft donor complexants' relative binding affinity with respect to Am(III) or Cm(III). Within one complexant, multiple donor atoms might be present, which can show differences in their complexing affinity. The overall binding preference of the binding

pocket of the molecule is a sum of all various donor-acceptor interactions. One example of the complexity of this issue was shown recently in a quantum chemical study conducted on Am(III), Cm(III) and Eu(III) complexes of two BTrzPhen types of molecules. The study showed that the Am(III) and Cm(III) complexes have almost identical geometrical structures [39]. In the same type of complex, the Am(III)-N_{Phenanthroline} bond is slightly shorter than the Cm(III)-N_{Phenanthroline} bonds, and the Am(III)-N_{Triazolyl} bond is longer than the Cm(III)-N_{Triazolyl} bond. A Quantum Theory of Atoms-in-Molecules (QTAIM) analysis of the same complexes also indicated that in these tetradentate BTrzPhen molecules, soft donor N-atoms in different positions show different preference for binding with respect to the Am(III) or Cm(III). Bond strength orders were the following: Am(III)-N_{Phenanthroline} > Cm(III)-N_{Phenanthroline} and Am(III)-N_{Triazolyl} < Cm(III)-N_{Triazolyl} in accordance with the bond lengths. Strangely enough, within the same molecule, the nitrogen atom in the six-membered pyridine type of ring has a higher affinity towards the Am(III) cations. On the contrary, the binding nitrogen atom in the 1,2,4-triazolyl, five-membered ring prefer the binding to Cm(III).

In the light of these theoretical findings, it might be that the overall preference of a soft-donor complexant - with various donor atoms - for either cation of the Am(III)/Cm(III) couple will depend on relative strength of donor-acceptor interactions present in a complex. The results discussed in this section range from basic liquid-liquid extraction studies to in-depth structural speciation studies. Table 1 provides an overview of the typical Am(III)/Cm(III) separation factors achieved with a given method. Within the European research framework, the search for new extraction molecules and diluents was focused on compounds composed of only four elements: carbon, hydrogen, oxygen and nitrogen (CHON) so that all secondary organic process waste can be treated via incineration without solid residues [38].

2.1. LUCA process

The Lanthaniden Und Curium Americium Trennung (LUCA)-process was one of the first redox-free Am-selective processes demonstrated with a centrifugal contactor battery of 24 stages [40]. The chemistry of this process is based on the synergistic combination of a dithiophosphinic acid ((ClPh)₂PSSH and tri(2-ethylhexyl)phosphate (TEHP). The basic process was developed in FZ-Jülich in collaboration with FZ-Karlsruhe INE (now KIT-INE) during the European NEWPART and PARTNEW projects [35].

The process is based on the selective extraction of Am(III) applied on a PUREX/DIAMEX product (thus a product containing Am(III), Cm(III)

Table 1
Overview of redox-free Am(III)/Cm(III) liquid-liquid separation processes.

Origin/ Process	Lipophilic extractant	Hydrophilic complexant	Typical $SF_{Am/Cm}$	Reference
FZ-Jülich / LUCA	(ClPh) ₂ PSSH + TEHP	–	8	[40,41]
CEA / EXAm	DMDOHEMA+HDEHP	TEDGA	2.5	[42,43, 44–47]
CEA / DIAMEX II	DMDOHEMA	–	1.6	[48]
CEA / EURO- EXAm	TODGA	H ₄ TPAEN	3.5–4.0	[49–51]
FZ-Jülich KIT / AmSel	CyMe ₄ BTPhen TODGA	TEDGA SO ₃ Ph-BTBP	2–3 2.5	[52] [53]
	TODGA	Pr-OH-BPTD	2–2.3	[54]
INL	HDEHP	H ₂ BC18C6	6.5	[55,56]
INL	TEHDGA and HEH [EHP]	H ₂ BC18C6	6.5	[56]
JAEA	NTAamide	TEDGA	6.5	[57]
JAEA	ADAAM(EH)	TEDGA	5.7	[58–60]

and Ln(III) resulting from applying a DIAMEX process on a PUREX raffinate) in dilute nitric acid with 0.5 mol L⁻¹ NaNO₃ and a solvent composed of *bis*-(chlorophenyl)-*di*-thiophosphinic acid ((ClPh)₂PSSH) and *tri*-ethylhexylphosphate (TEHP, added as synergist) in *t*-butylbenzene (TBB) and isooctane (80/20 vol.% mixture). The loaded solvent is subsequently scrubbed to remove co-extracted Cm(III) and Ln(III) with 0.5 mol L⁻¹ NaNO₃ in dilute nitric acid solution and the Am(III) is stripped with 0.7 mol L⁻¹ HNO₃. The mechanism of M(III) extraction was described as a cation exchange between the thiol protons and M(III) upon extraction according to Eq. (1).



Slope analysis was used to determine the stoichiometric numbers in the extracted complexes [61]. At 25 °C, pH = 1, the extracted complex of trivalent metal ions contains three (ClPh)₂PSS⁻ (represented by A in Eq. (1)) and various numbers of TEHP (represented by S in Eq. (1)), depending on the element. For Am, Cm the stoichiometric number (*n*) of TEHP equals 1, for light lanthanides (La-Sm) *n* = 2; while for heavy lanthanides (Sm – Lu) *n* = 3. The entropy difference of the complex formation was identified as the underlying reason for the high Am(III)/Ln(III) and Am(III)/Cm(III) separation factors. The use of the van't Hoff equation based on distribution ratios determined at various extraction temperatures is a generally applied method for comparing the thermodynamic data of complex formation with various metal ions. The small variation of ΔG° Gibbs free energy along the Ln(III) series and the An(III) suggested that the geometrical arrangement of the complexants around the metal ion center should be highly similar for trivalent *f*-elements. However, speciation studies performed with EXAFS on the Cm(III) and Eu(III)-loaded solvents showed the contrary. The inner coordination sphere of the complexed Cm(III) ions contain bidentate (ClPh)₂PSS⁻ anions while Eu(III) metal ions prefer to coordinate to O-atoms of the synergist [35].

To date this system is still the most performant liquid-liquid extraction system for the separation of Am(III) from Cm(III) and the Ln(III) with separation factors $SF_{Am/Cm} > 7$ and $SF_{Am/Eu} > 500$. Even the best performing CHON-compliant N-donor extractants or extractant/complexant combinations cannot achieve comparable Am(III)/Cm(III) separation factors. In a tracer-spiked centrifugal contactor study (7 stages of extraction, 9 stages of scrubbing and 8 stages of back-extraction), Modolo *et al.* found that 99.8% of Am(III) can be recovered in the Am(III)-product with very high decontamination factors: $DF_{Am/Cm} = 214$, $DF_{Am/Cf} \approx 1700$, $DF_{Am/Eu} \approx 7700$ [41]. Less than 0.08% of Am(III) was retained in the solvent after stripping and Cm(III), Cf(III) and Eu(III) inventory were completely obtained in the raffinate (> 99.5%, > 99.9% and > 99.9%, respectively). The feed and scrubbing solution contained a nitrate salt load to suppress emulsification observed during batch tests with feed solutions containing less than 0.2 mol L⁻¹ HNO₃. However, validation of the process on a real HAR solution is lacking.

Hydrolysis studies have shown that upon contacting an organic solution of (ClPh)₂PSSH in toluene with an aqueous phase containing 3 mol L⁻¹ HNO₃, the extractant completely degrades after 20 days, but the addition of either urea, hydrazine or amidosulphuric acid as anti-nitrous reagents was found to effectively mitigate the hydrolysis. During radiolysis, (ClPh)₂PSSH is converted to oxidized products such as (ClPh)₂POOH and (ClPh)₂PSOH [62].

2.2. EXAm process

The EXAm process developed at CEA in France is a redox-free process that aims at selective Am-extraction starting from a PUREX raffinate [47]. The EXAm process is based on the combination of the lipophilic malonamide *N,N'*-dimethyl-*N,N'*-dioctyl-hexyloxyethyl-malonamide (DMDOHEMA) and di-2-ethylhexylphosphoric acid (HDEHP) and the hydrophilic *N,N,N',N'*-tetraethyldiglycolamide (TEDGA). This is a

combination of two lipophilic and a hydrophilic ligands with opposite solubility and opposite selectivity with respect to Am(III) and Cm(III)+Ln(III) [63]. The process is based on the observed slightly higher affinity of DMDOHEMA for Am(III) over Cm(III) ($SF_{Am/Cm} = 1.6$). The use of DMDOHEMA alone (so-called “DIAMEX II process”) for the separation from Am(III) from Cm(III) was successfully tested on a spiked surrogate feed using a large number stages (64) [48]. As the process conditions heavily affect the performance with such low separation factors, further improvements were necessary. Initial studies involved the investigation of the effect of adding a hydrophilic complexant to further enhance the Am(III)/Cm(III) separation factor, however, neither diethylenetriamine pentaacetate (DTPA) nor crown-ethers resulted in any noticeable improvement of the separation factor [35]. The addition of TEDGA increased the Am(III)/Cm(III) separation factor to typically 2.5 when extracting directly from a PUREX raffinate. The chemically similar Cm(III) + heavy Ln(III) are completely retained in the aqueous phase, while Am(III) + light Ln(III), Mo and Ru are extracted by DMDOHEMA and HDEHP mixture in TPH diluent. The interfering Mo and Ru can be stripped from loaded organic phase using a buffered citrate solution at pH 3. Am(III) can be stripped using DTPA with a malonate buffer at pH 2.6. HDEHP as an acidic extractant is needed to keep the co-extracted light Ln(III) in the organic phase during the Am(III) stripping and it also helps to prevent third phase formation. In the last step of the process the remaining light Ln³⁺, Fe³⁺ and Ru need to be removed from the solvent using a mixture of TEDGA and oxalic acid.

TEDGA, however, was found to be also slightly distributing between the organic phase and the aqueous phase, affecting the selectivity of the separation system between light Ln(III) and Am(III), due to the formation of Ln(TEDGA)₃³⁺ and Ln(TEDGA)₂³⁺ complexes with light lanthanides (La and Pr) [44]. On the contrary, the heavier lanthanides form mainly 1:3 complexes with TEDGA and these are completely retained in the aqueous phase. The lanthanides in the middle of the 4f-series form complexes with all the three known stoichiometric ratios (1:1-1:3). The extracted Ln(TEDGA)_n³⁺ - complexes are coordinated by the lipophilic DMDOHEMA and DEHP⁻ in the form of Ln(TEDGA)_n(DMDOHEMA)_x(DEHP)_y(NO₃)_{3-y} (where *n* = 1, 2; *x* = 1; *y* = 1, 2). The Am(III)/Cm(III) separation by the combination of the three molecules can be explained by the progressive change of complex stoichiometry between Am(III) and Cm(III) along the An(III) contraction series: by analogy with the Ln(III), the relative abundance of An(TEDGA)_n³⁺ complexes vary in the direction of 1:1 < 1:2 < 1:3. This difference in the aqueous phase speciation determines the relative amount of Am(III) or Cm(III) distributing to the organic phase to form quaternary complexes of An(TEDGA)_n(DMDOHEMA)_x(DEHP)_y(NO₃)_{3-y} composition. The larger relative amount of 1:3 An(TEDGA)₃³⁺ complex (in the case of Cm(III)) thus means lower relative amount of extractable metal ion (An(TEDGA)₁³⁺ and An(TEDGA)₂³⁺) and thus lower distribution ratio.

Various short chain length hydrophilic DGAs were synthesized and their extraction properties were compared with TEDGA by Chapron *et al.* [42]. Methyl, ethyl, and propyl groups were linked centro-symmetrically to the diglycolamide core of the molecules to obtain *N,N,N',N'*-tetramethyl diglycolamide, *N,N'*-diethyl-*N,N'*-dimethyldiglycolamide; *N,N'*-diethyl-*N,N'*-dipropyldiglycolamide and *N,N,N',N'*-tetrapropyl diglycolamide. The hydrophilicity decreased with the increase of total number of carbon atoms in the aliphatic chains. The *N,N,N',N'*-tetrabutyl diglycolamide analogue proved to be not soluble in the aqueous phase. According to this screening study, TEDGA provided the highest $SF_{Am/Cm}$ of the five hydrophilic DGA molecules.

Flow-sheet modeling with the PAREX code [64] was carried out based on the batch extraction data and speciation studies. Several continuous processes were run in ATALANTE facility of CEA between 2011 and 2015 (inactive surrogate feed – tracer-spiked PUREX HAR surrogate – genuine PUREX HAR – genuine, concentrated PUREX HAR) [45,46]. The last demonstration (using 68 stages of mixer-settlers) allowed the recovery of 2.4 g Am (95.5%) with only 0.6% Cm ($DF_{Am/Cm} \approx 50$). Besides, the product contained fission and corrosion

product contaminants, such as Ln (1.7%), Fe (0.3%), Mo (0.05%), Pd (0.7%) and Ru (1.1%).

2.3. Am(III)-extraction with a size-selective extractant

The combination of the lipophilic extractant HDEHP in *o*-xylene and the hydrophilic, size-selective complexant *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6 ($H_2bp18c6$) was studied in US by Jensen et al. [55,65]. The goal was to expand the already existing ALSEP process and perform the Am(III)/Cm(III)+Ln(III) separation in such a way, that is chemically compatible with the existing upstream chemistry. The ALSEP process is based on a first An(III)+Ln(III) co-extraction step by a solvent containing TEHDGA and HDEHP in an aliphatic diluent [66–68]. The An(III) are stripped by a polyaminocarboxylic complexant at pH 3. Similarly to the French EXAm process, the Ln(III) are retained in the organic phase by the acidic HDEHP extractant under the An(III) stripping conditions. Replacement of the polyaminocarboxylic acid with a size-selective hydrophilic complexant aims at stripping selectively Am(III) from the loaded organic phase, therefore both Cm(III) and the Ln(III) remain in the organic phase.

The $bp18c6^{2-}$ anionic crown ether ion has four soft-donor *N*-atoms and 4 ether O-atoms. It shows a selectivity for Am(III) over Cm(III) based on their ionic radii probably due to the fact that this complexant entirely fills the first coordination sphere of the Am(III) ions. On the opposite, HDEHP has a slightly higher affinity towards Cm(III) over Am(III) and the heavier Ln(III). With this combination of ligands, light lanthanides (La–Nd) are kept in the aqueous phase with the Am(III) fraction, while Cm(III) and the heavy lanthanides (Sm–Gd) are extracted by HDEHP. The method showed interesting equilibrium separation factors: $SF_{Cm/Am} = 6.5$ and $SF_{Nd/Am} = 10$ with rapid kinetics in laboratory batch extraction experiments (equilibrium reached within 5 min), when extracting from a feed solution of 1 mol L⁻¹ NaNO₃ buffered with lactate at pH 3. Slope analysis method showed that the An(III)-($bp18c6$)⁺ complexes exhibit a 1:1 stoichiometry and according to DFT calculations, the An(III) ions are mainly coordinating via the nitrogen donor atoms of pyridine moieties. The lipophilic extractant's concentration, however, in this system cannot be raised high enough to be of practical use for the treatment of feed solutions with a composition similar to that of PUREX HAR. Notably, HDEHP is too strongly complexing M(III)-ions, in comparison to the hydrophilic complexant, and lowering the [HDEHP] concentration would result in the formation of precipitates $M(DeHP)_3(HDEHP)_3$ when the solvent is loaded more than 70% of its theoretical loading capacity. Reaching the solubility limit also means that the solvent cannot extract the entire Ln(III) content present in the feed solution. To overcome this limitation, Jensen et al. investigated the use of a modified ALSEP solvent containing a mixture of *N,N,N',N'*-tetraethylhexyl diglycolamide (TEHDGA) and (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl)ester (HEH [EHP]) in *n*-dodecane [65].

In this modified system, the weaker complexing ability of HEH [EHP] resulted in the gross rejection of lighter lanthanides (La–Ce) in the aqueous feed of 2 mol L⁻¹ HNO₃, while the heavier Ln(III) and the An(III) were completely extracted. The lower extraction of lighter Ln(III) in this case is a clear advantage, since they are interfering with the selective Am(III)-stripping with $bp18c6^{2-}$ ligand. From the loaded organic phase, the Am(III) could be selectively stripped into an aqueous solution containing $bp18c6^{2-}$ buffered to pH 3 with sodium lactate.

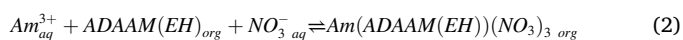
2.4. ADAAM(EH)/TEDGA process

Several fully CHON compatible redox-free extraction concepts have been elaborated at JAEA in Japan based on the use of a hydrophilic diglycolamide (TEDGA) and either *N,N,N',N',N'',N''*-hexaoctyl-nitrilotriacetamide (NTAA) [57] or the tridentate alkyl diamide amine (ADAAM(EH)) type of extractant [58–60]. This class of novel compounds was designed to include both soft *N*-donor and hard carbonyl oxygen donors in the amide groups. The design of this molecule thus

combines the already well-known advantageous properties of diglycolamides (excellent kinetics, solubility, solvation, reversibility) with a *N*-donor moiety.

The use of a solvent containing NTAAmide(C8) [69] shows only modest $SF_{Am/Cm} \approx 1.7$ –1.8, however, the addition of the hydrophilic TEDGA showed a combined effect [59], with an overall observed $SF_{Am/Cm} \approx 6.0$ –6.5. The distribution ratios D_{An} decreased with the increase of feed HNO₃ molarity, due to the protonation of (soft) donor atoms in the NTAAmide molecule. Interestingly, while the slope analysis in low acidity feed solutions (0.2 mol L⁻¹ HNO₃) showed a clear difference between An(III)-NTAAmide and Ln(III)-NTAAmide complex stoichiometries (1:2 and 1:1 respectively), at higher nitric acid concentrations, the slope analysis showed a clear change in the An(III)-NTAAmide complex stoichiometry (slope values decreased from 2.2 to 1.3–1.5 for An(III)), with a diminishing difference between An(III) and Ln(III) complexation.

In comparison to NTAAmide, which shows its highest selectivity at low feed acidities [57], ADAAM(EH) molecule is less basic than NTAAmides and can be used at higher acidities [58]. Even though the $SF_{Am/Eu}$ values are an order of magnitude lower than that achievable with tetradentate *N*-donor molecules of the BTBP and BTBPhen type (thus in the order of 25 instead of > 200), an organic solvent comprised of 0.2 mol L⁻¹ ADAAM(EH) in *n*-dodecane is capable of separating Am(III) from Cm(III) from acidic feed solutions ([HNO₃] \approx 1–1.5 mol L⁻¹) with separation factors in the region of 5.5 even without using a hydrophilic complexant. Equilibrium of extraction was achieved with very fast kinetics (< 1 min contact time). In the case of a prior gross An(III)/Ln(III) separation, the molecule is promising to obtain an Am-only product, supposing that the upstream purification steps ensure that interfering light lanthanides are removed from the aqueous product. The M:ADAAM(EH) complex is reported to be 1:1 with 3 nitrate ions being involved in a solvation-type complex formation (Eq. (2)).



Due to the addition of the hydrophilic TEDGA (which is known to show higher affinity towards Cm(III) and the heavier Ln(III)), the $SF_{Am/Cm}$ further increased to values ranging from 5.7 to 41 [59]. The increase was more remarkable though at low distribution ratios ($D_{An(III)} < 1$), where both metal ions are completely retained in the aqueous phase. The concept has been also implemented in a continuous lab-scale mixer-settler process equipment using a tracer-spiked Ln(III)+An(III) feed at an acidity of 1.5 mol L⁻¹ HNO₃ and an organic phase comprised of 0.25 mol L⁻¹ ADAAM(EH) in *n*-dodecane. Under these conditions the solvent has a loading capacity of 40 mmol L⁻¹ Nd(III), which is sufficient for the treatment of An(III) streams derived from high burn-up spent nuclear fuel treatment processes. As the D_{An} vs. [HNO₃] function shows a maximum around 1.5 mol L⁻¹ acidity the extraction was performed at this acidity with 8 stages of extraction, 8 stages of scrubbing with 1.5 mol L⁻¹ HNO₃ and 16 stages of stripping with 0.05 mol L⁻¹ HNO₃. These conditions allowed a nearly quantitative (99.8%) recovery of Am(III) with a 9.6% Cm(III) contamination of the Am(III) product.

2.5. CyMe₄BTPhen / TEDGA process

Lange et al. demonstrated the feasibility of selective Am(III) extraction from simulated PUREX raffinate feed solution using the hydrophilic complexing agent TEDGA and the lipophilic 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-1,10-phenanthroline (CyMe₄BTPhen) in 1-octanol [52]. CyMe₄BTPhen has a slightly higher affinity for Am(III) over Cm(III), while TEDGA has a higher affinity for Cm(III) over Am(III) and especially for Ln(III) over An(III) [70]. The combined effects of these two compounds yielded an overall $SF_{Am/Cm}$ up to 4.9, when extracting directly from a simulated PUREX HAR feed without the need to implement a prior group-separation of An(III)+Ln(III). Several fission and corrosion products such as Pd, Cu, Ni, Mo and Cd showed an

interference with the selective Am(III) extraction process. In that study, 0.01 mol L⁻¹ (2S,2'S)-4,4'-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid) (Bimet) was used for the masking of Ag and Pd, which effectively retained Ag and Pd in the aqueous phase. Apart from Bimet (which can also be replaced by CDTA for Pd masking) this is one of the few methods listed in this review which complies with the so-called CHON principle.

Upscaling towards a continuous process has not been performed yet. One of the shortcomings of the tetradentate, selective, but at the same time bulky compounds (e.g. CyMe₄BTPhen, CyMe₄BTBP), is that only a handful of good diluents have been found for them. These type of compounds are non-soluble in apolar aliphatic diluents such as *n*-dodecane or kerosene. Polar diluents such as 1-octanol or 1-octanol/toluene mixtures and cyclohexanone can keep sufficiently high concentration of the ligands and metal-ligand complexes in solution, but many of these diluents would be excluded for safety reasons in a larger-scale minor actinide treatment process. Other, non-conventional diluents, such as phenyl trifluoromethyl sulfone (FS-13) [71], 2,2,3,3-tetrafluoropropan-1-ol carbonate (BK-1) [72] or Aliquat-336 nitrate ([A336] [NO₃]) [73,74] ionic liquid were also studied by other groups with the conclusion that an elimination of 1-octanol from the solvent can improve the radiation stability of the rather expensive CyMe₄BTPhen without impairing its selectivity, but usually at the expense of the kinetics which is often drastically slower. With the high viscosity [A336] [NO₃] the contact times need to exceed several hours to reach equilibrium, while the residence time in a mixer settler is in the range of a few minutes or a just a few seconds in the case of a centrifugal contactor. A peculiarity of the CyMe₄BTPhen extractant, unprecedented among all the other compounds discussed in this review, is that it shows a significant difference of extraction kinetics between Am(III) and Cm(III). Higher than equilibrium $SF_{Am/Cm}$ values were observed at short contact times, under non-equilibrium conditions in different diluents ($SF_{Am/Cm} = 7.9$ in cyclohexanone [75,76] or $SF_{Am/Cm} =$ up to 18 in [A336] [NO₃] [74,77]).

2.6. Am(III) stripping using selective hydrophilic ligands

The strategy of a selective Am(III)-stripping from a loaded organic phase was followed in a series of studies as discussed below. The common feature in these concepts is that the An(III) and Ln(III) are co-extracted with TODGA in an aliphatic diluent after which Am(III) is selectively stripped into the aqueous phase by a hydrophilic tetradentate soft-donor complexant. The hydrophilicity is provided usually by crafting sulphonic acid groups on the phenanthroline or bipyridine triazole structures.

2.7. EURO-EXAm process

To overcome the problem posed by the distribution of TEDGA complexes into the TPH-based EXAm solvent, a new Euro-EXAm process was elaborated within the framework of the European SACCESS project [19,78]. The selectivity towards Am(III)/Cm(III)+Ln(III) is reversed in comparison with the EXAm process in the case of the combination of lipophilic *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) and hydrophilic pyridine-2,6-dicarboxylic acid (dipicolinic acid or PDCA), its derivatives and *N,N,N',N'*-tetrakis [(6-carboxypyridin-2-yl)methyl]ethylenediamine (H₄TPAEN) [49–51]. H₄TPAEN in combination with TODGA offered highly similar Am(III)/Cm(III) separation factors (3.5 – 4.0), but with lower separation factors towards the light lanthanides than the CEA EXAm system.

In the case of the Euro-EXAm process, Ln(III) and An(III) are co-extracted first from a PUREX raffinate into the organic phase (0.1 mol L⁻¹ TODGA in TPH). Am(III) is then selectively back-extracted ($D_{Am} < 1$) from Cm(III) and Ln(III) (D_{Cm} and $D_{Eu} > 1$) with H₄TPAEN in dilute HNO₃. While TODGA alone shows only a modest selectivity for Cm(III) ($SF_{Cm/Am} = 1.2$), the addition of H₄TPAEN increases the selectivity

almost three-fold: ($SF_{Cm/Am} = 3.4$ at pH = 1). The remaining metal ions can be stripped using dilute nitric acid.

The separation factor can be slightly improved for the Cm(III)/Am(III) couple by increasing the salt concentration of the scrubbing solution. When the concentration of NaNO₃ is increased from 1 to 3 mol L⁻¹, the $SF_{Cm/Am}$ increases from 3.13 to 3.76 – 4.02. The increase of salt concentration on the other hand results in an order of magnitude increase in $SF_{Eu/Am}$: from 12 to 331 – 323. These values are higher than what is achievable with the CEA EXAm solvent formulation. The main limitation of this process is related to the fact that H₄TPAEN has a very low solubility in acidic solutions (5 mmol L⁻¹) in comparison to TEDGA and the solubility is further reduced by the addition of 3 mol L⁻¹ NaNO₃ to 1 mmol L⁻¹. Further studies have shown that at pH = 1, 2.5 mmol L⁻¹ H₄TPAEN can be applied. However, the solubility was found to vary from one batch to the other mainly due to differences in the crystallization procedure following the ligand synthesis. Whether the solubility limitations would really pose a practical limitation on the application in a process is not clear, since macro-concentrations of ²⁴¹Am (1.6 μmol L⁻¹ – 2 mmol L⁻¹) could be stripped selectively with only 2.5-fold molar excess of the complexant in the presence of Ln(III) nitrates loaded to a TODGA-containing solvent.

An extensive synthetic work was carried out and combined with solvent extraction studies with the aim to modify the H₄TPAEN structure to improve its aqueous solubility without impairing the selectivity [51]. The modification of spacer moieties between the pyridine rings typically helped to increase compound solubility at the expense of loss of affinity. Among the investigated H₄TPAEN analogues, 6,6',6''',6''''-(ethane-1,2-diylbis(azanetriyl))tetrakis(-methylene)-tetrakis(4-methoxypicolinic acid) showed an improved solubility (up to 5 mmol L⁻¹) at pH 1.5 with $SF_{Cm/Am} = 3.2$, thus comparable to H₄TPAEN.

The Cm(III)/Am(III) and Ln(III)/Am(III) separation factors depend on the concentration of the hydrophilic complexant, Ln(III) concentration, and temperature [79]. The increase of the H₄TPAEN concentration in the scrubbing solution has no effect on the distribution ratios of Ln(III) ions, while the distribution ratios of both Am(III) and Cm(III) decrease, hence the Ln(III)/An(III) separation factors can be adjusted easily. The light lanthanides (La, Ce), however, are the least separated from Am(III), with separation factors around or below 5. Several options are available to mitigate the light lanthanides' carry-over to the Am-product: diluting the loaded TODGA-solvent (to reduce the concentration of Ln(III)) or adding NaNO₃ to the scrubbing solution. Flow sheet modeling with the PAREX code indicated that the system is extremely sensitive to pH and nitrate ion concentration of the scrubbing section [50].

Borrini et al. studied the selective Am(III) back-extraction with PDCA, PDCA derivatives and H₄TPAEN from a solvent (0.1 mol L⁻¹ TODGA in TPH) loaded with An(III)+Ln(III) [80]. The hydrophilic complexants were dissolved in dilute nitric acid solutions containing NaNO₃. The crafting of electron-withdrawing or electron-donor groups on the PDCA did not have a significant impact on the Eu(III)/Am(III) selectivity. The basicity of the ligand had an influence on the observed distribution ratios because of the competition between H⁺ and M(III) ions.

The structures of An(III) or Ln(III)-TPAEN complexes were studied (single-crystal XRD, EXAFS, TRIFS and microcalorimetric methods on Ce(III)/Eu(III)-TPAEN, Am(III)-TPAEN, Cm(III)-TPAEN and on Ln(III)-TPAEN complexes, respectively) [49,81]. These studies confirmed that the decadentate *N,N,N',N'*-tetrakis [(6-carboxypyridin-2-yl)methyl]ethylenediamine (H₄TPAEN) forms 1:1 complex with An(III) and Ln(III) ions. At pH = 1 the complexant is deprotonated and the central metal ions are coordinated by ten donor (four carboxyl O, four pyridine N and two ternary amine N) atoms of the same anion (TPAEN⁴⁻) with the exclusion of water molecules from the first coordination sphere of the metal ions. The difference between the Gibbs free energy of complexation of Am(III) and Cm(III) by TPAEN ($\Delta(\Delta G^\circ_{Am/Cm}) = -RT \ln(SF_{Am/Cm}) = -1.1$ kJ mol⁻¹) was in the region of that of TODGA ($\Delta(\Delta G^\circ_{Cm/Am}) = -1$ kJ mol⁻¹) [82], while the combined application of TODGA+TPAEN

resulted in an overall $SF_{Am/Cm} = 3.5 - 4.0$ with $\Delta(\Delta G_{Cm/Am}) = -3$ kJ mol⁻¹. Wagner et al. chose a different combination of ligands with opposite solubility and opposite selectivity towards americium and curium for the Americium Selective extraction from a PUREX raffinate (AmSel process) [53]. In that study, trivalent actinides and lanthanides were co-extracted using 0.2 mol L⁻¹ *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) in an *n*-dodecane/1-octanol mixture (95/5 vol.%) and Am(III) was selectively stripped using sodium 3,3',3'',3'''-([2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzene sulfonate (SO₃-Ph-BTBP) in nitric acid. Tracer-level extractions showed a $SF_{Cm/Am} \approx 2.5$ and $SF_{Eu/Am} > 1000$ in nitric acid media. Interestingly, the heavier lanthanides (Tb-Lu) would also be routed with the Am(III) product, but as their fission yield ins very low, they don't play much of a role in used nuclear fuel management. TRLFS studies confirmed that this tetravalent complexant forms mainly 1:2 An(III) complexes ($[M(SO_3\text{-Ph-BTBP})_2]^{3+}$) in the aqueous phase. The strategy represented by the AmSel process became the reference method Am(III)-partitioning under European research programs, meaning that later developments focus on finding a CHON analogue to replace the SO₃-Ph-BTBP.

Kaufholz et al. studied the feasibility of a selective Am(III) stripping with 3,3',3'',3'''- [3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzene sulfonic acid (TS-BTPhen), from a loaded solvent composed of TODGA or Me-TODGA in kerosene with 5 vol.% 1-octanol [82,83]. This novel sulfonated ligand allowed to obtain Cm(III)/Am(III) separation factors of 3.3 – 3.5 at relatively high nitric acid concentrations with fast kinetics, but the organic synthesis of the ligand was less reproducible than the lipophilic version of the BTPhen molecule [82,84,85]. As an alternative for the hydrophilic complexant TS-BTPhen, TODGA in combination with tridentate 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine (PyTri-Diol or PTD) [86,87]. allowed a separation factor of Cm/Am of only 1.4, not significantly higher than the selectivity shown by TODGA alone ($SF_{Cm/Am} = 1.2$).

The same concept (selective Am(III) stripping from a loaded TODGA containing solvent) was studied with a novel, CHON-compliant hydrophilic BTrzPhen molecule by Edwards et al [88]. Their short communication revealed that the TODGA/BTrzPhen extractant/complexant combination can allow a $SF_{Cm/Am} = 2.5$ in the stripping step. A systematic follow-up study for the optimization of process conditions (acidity, complexant concentrations, temperature etc.) would be useful for this version of the AmSel concept.

In a recent publication Weßling et al. has shown that a hydrophilic N-donor complexant: 3,3'-([2,2'-bipyridine]-6,6'-diyl-bis(1*H*-1,2,3-triazol-4,1-diyl))bis(propan-1-ol) (PrOH-BPTD) in dilute nitric acid (0.33 – 0.39 mol L⁻¹) can be effectively used for selective stripping of Am(III) from a loaded solvent composed of 0.2 mol L⁻¹ TODGA in TPH/1-octanol [54]. The hydrophilic complexant shows sufficiently fast kinetics (equilibrium is achieved within 5 min) and the selectivity is comparable to the lipophilic soft-donor ligands ($SF_{Cm/Am} = 2.0 - 2.3$). Interestingly the chain length of the alcohol moiety determines the metal-ligand complex stability to a large extent, EtOH-BPTD being a substantially weaker complexant than PrOH-BPTD.

A lipophilic triazole-functionalized phenanthroline ligand (2,9-bis(1-(2-ethylhexyl)-1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline (EH-BTzPh en)) has been synthesized and tested earlier in our group [89]. This compound showed a similar selectivity towards Am(III) over Cm(III) and the Ln(III) as the PrOH-BPTD, but at extremely slow kinetics: equilibrium was achieved typically with contact times longer than a day. In the case of aliphatic alcohol diluents such as 1-octanol extraction of An(III) was only possible with the addition of 2-bromohexanoic acid synergist. In the case of the lipophilic EH-BTzPhen and the hydrophilic PrOH-BPTD molecules, the binding pocket is essentially the same: both molecules are tetradentate *N*-donors with an identical phenanthroline/bipyridine central moiety and two, symmetrical triazole moieties. Notwithstanding the similarity in electronic structure and geometry in the case of the hydrophilic Am(III)-selective ligand, the kinetics is significantly faster than in the case of the lipophilic version.

This observation suggests that the diluent plays an important role in the kinetics, not necessarily only due to slower diffusion caused by higher viscosity, but perhaps also via the differences in the solvation around the ligand, which might make the complex formation hindered in one case compared to others. As the faster kinetics is essential for process upscaling in counter-current flow equipment with short residence times, the route via selective Am(III)-stripping with a CHON-compatible hydrophilic complexant is the way forward towards process development.

3. Liquid-liquid extraction methods for the separation of selectively oxidized americium

The selective oxidation methods, redox potentials, thermodynamic properties and their use in separation studies based on higher oxidation states of Am were collected in a review by Runde and Mincher [90]. The methods based on the oxidation of Am(III) to a higher oxidation state (Am(IV), Am(V), Am(VI)), combined with a selective extraction of the oxidized Am try to achieve a large separation factor between the Am/Cm and Am/Ln+FP group of elements in one step. The selective Am(III) oxidation aims at causing a marked change in the charge density and coordination geometry of Am-ions to enable a more straightforward separation from Ln(III) and Cm(III). The oxidation of Am(III) to higher oxidation states is an interesting approach, as most lanthanides (with the exception of Ce) and Cm remain in their trivalent state, hence in aqueous solutions. There is a large number of complexants available that show selectivity towards higher oxidation states of An and very low affinity towards Ln(III) and An(III). Table 2 provides an overview of the methods combining oxidation of Am with solvent extraction.

The main challenge with this approach is that higher oxidation states of Am are themselves strong oxidants and enter redox reactions with fast kinetics both with nitric acid and the radiolysis products. For this reason, higher Am-oxidation states are only relatively stable in alkaline solutions or in complexes that exclude potential reductants (even water or dissolved oxygen) from the first coordination sphere. In the presence of even low concentrations of nitric acid, un-complexed Am(IV/VI) undergo reduction both due to the self-radiolysis or redox-reactions with water. The fate of Am(V) in aqueous solutions depends on the acidity. In dilute acids, it undergoes auto-reduction, while at higher acidities it disproportionates to the hexa- and trivalent states. The reductive radiolysis products of H₂O/HNO₃ mixture (H₂O₂ and HNO₂) generated during the absorption of the energy of the emitted alpha particles interact chemically with the emitting ion itself. The same phenomenon was observed in HCl or HClO₄ solutions [90]. To put it simply, the instability of the nuclei of isotopes of Am result in chemical changes of the environment that result in the instability of all oxidation states different from Am(III). The challenge is thus to somehow maintain the desired oxidation state within the required timeframe to perform an extraction process from trivalent actinides or lanthanides. Since oxidized americium is a powerful oxidant itself too, any extractant of choice should be sufficiently stable against oxidation by the chelated

Table 2

Summary of methods where redox chemistry can be combined with solvent extraction for the separation of americium from curium.

Origin	Oxidant	Complexant	Americium oxidation state	Reference
France	Electrochemically generated Ag(II)	LHPA, TBP	Am(IV/V/VI)	[91–94]
Japan	NaBiO ₃	TTA / HDEHP	Am(V)	[95,96]
US	Na ₄ XeO ₆ + Ag(II)	–	Am(VI)	[97]
US	NaBiO ₃	TBP, CMPO, DAAP, DBBP, DEHBA, DEHiBA, DHOA,	Am(V/VI)	[98–103]
Russia	NaBiO ₃ , Na ₄ XeO ₆	TBP, TOPO	Am(VI)	[104]
US	KNa ₄ Cu(HIO ₆) ₂	DAAP	Am(VI)	[105]

metal ion.

The chemical composition of the feed solution (especially its acidity) determines downstream process selection. The oxidation of Am(III) directly to Am(VI) in an acidic environment was so far only found to be feasible with a very limited number of oxidizing agents such as Ag(II), (below 0.5 mol L⁻¹ HNO₃); SO₄²⁻ -being the decomposition product of the peroxodisulphate-ion: S₂O₈²⁻ (peroxodisulphate) and NaBiO₃. All these methods have the disadvantage of introducing another chemical reagent to the highly active waste stream. In this respect the use of a gaseous oxidant, such as ozone would be beneficial, however, it only works in alkaline solutions at temperatures above 90 °C [106].

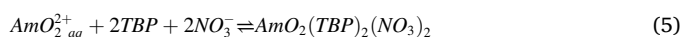
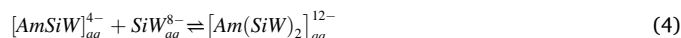
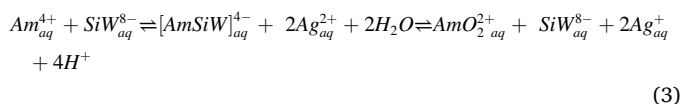
One of the earliest separation methods of high-valence americium from trivalent lanthanides and curium was based on the oxidation of Am(III) to Am(V) by hypochlorite in a concentrated carbonate solution at 95 °C [107]. Upon oxidation, the pentavalent americium ions precipitate as hydroxide or carbonate, while the trivalent metals remain mainly in solution. The disadvantage of the method is that highly corrosive OCl⁻ ions are required, besides an alkaline environment, both being incompatible with the upstream PUREX process. The upscaling of precipitation methods also poses considerable engineering challenges.

3.1. Electrochemical oxidation method

One of the initial concepts investigated by French researchers for the selective extraction of Am was based on the two-step oxidation [91, 92]. In the first step of the “Selective Extraction and Separation of Americium by Means of Electrolysis” (SESAME) process, Am(III) is oxidized to Am(IV) electrochemically on a platinum anode in the presence of hydrophilic lacunary polyanionic ligands (LHPA) that have high affinity for tetravalent cations and are stable in acidic media. The further oxidation of Am(IV) to Am(V) is thermodynamically disfavored in nitric acid, therefore Ag(I) (in the form of silver nitrate) is added to the solution, which serves a redox-mediator or “holding oxidant”. The Ag (I→II) oxidation is rapid on the platinum anode, and the Ag(II) is an oxidizer strong enough to convert Am(IV) to Am(V) and subsequently Am(V) to the AmO₂²⁺ americyl-ion. The extraction of the oxidized Am(VI) was possible with TBP. Due to the presence of fission products from the transition metal group in PUREX HAR, several versions of the process have been investigated, each based on a different head-end process and thus different feed solution composition. As the fission products such as Ru, Mo, Zr and Cs interfere with the oxidation, the Am(III) oxidation was envisaged to be performed on a DIAMEX product (see above in Section 4), instead of the PUREX HAR itself. The role of the LHPA is to reduce the redox potential of the Am(IV)/Am(III) couple, by stabilizing Am(IV) as a complex. As stabilizing LHPA, α-SiW₁₁O₃₉⁸⁻ silicotungstate (SiW) and α₂-P₂W₁₇O₆₁¹⁰⁻ phosphotungstate (PW) complexants were studied. In the presence of 2 molar equivalents of LHPA and 0.01 mol L⁻¹ AgNO₃, quantitative oxidation of Am(III) was possible at E = 1.92 V / SHE. The oxidized americyl ion (AmO₂²⁺) is released from the binding of the lacunary polyanions (Eq. (3)) due to the large structural change of the cation and is stable enough in nitric acid solution so that solvent extraction with TBP can be performed (Eq. (5)). The equilibrium distribution ratio (*D*_{Am} = 2) from a 5 mol L⁻¹ HNO₃ feed were achieved within a few seconds, but slowly decreased for contact times longer than 30 s. Such decrease in distribution ratio can be attributed to self-reduction of Am(VI → III) taking place either in the organic or aqueous phase.

Although the SESAME process was promising due to the selectivity, it had several shortcomings. After a hot test by CEA, whereby only 80% of the americium was recovered, this research approach was abandoned [93]. It turned out during the experiments that the Am(IV)/LHPA ratio needed to be carefully controlled during the course of the extraction, since if Am(III) was oxidized to the *bis* complexes: Am(IV)(SiW)₂ or Am(IV)(PW)₂, then the second oxidation step to Am(VI) did not take place Eqs. (3)–(5) [94]. The control of the molar ratio of the metal ion and the LHPA complexant would be difficult in a continuous process, since

the extraction of Am(VI) is foreseen from the same solution, therefore the concentration of Am(IV) will be a function of the oxidation of Am(III) to Am(IV), the oxidation of Am(IV) to Am(VI), and the extraction of Am(VI) by TBP. This dynamic equilibrium could be controlled, if there would be a method to sequester or separate the LHPA at a similar rate as the extraction of Am(VI), however, no such method has been proposed so far. Other redox-active fission product metal ions such as Ce(III)/Ce(IV) or Ru(III)/Ru(IV/VIII) are also going to interfere with the oxidation, unless they are preliminarily separated from the feed solution in advance.



3.2. Bismuthate-based chemical oxidation methods

In the early 1970's a research group at Tohoku University in Japan investigated the chemistry of higher valence states of americium [95,96, 108,109]. They reported a successful quantitative oxidation at 90–95 °C of Am(III) in acidic environment exploiting NaBiO₃. The pentavalent Am was found to be extractable by 0.1 mol L⁻¹ TTA in isobutanol from a feed solution buffered at pH 3.

In the United States, the use of NaBiO₃ as a powerful, acid-compatible oxidizing agent for oxidation of Am(III) to Am(V) or Am(VI) was investigated in detail in Idaho National Laboratory by the research group of Bruce J. Mincher [98–100]. Sodium bismuthate is a commercially available powder which is stable under ambient conditions. The color can vary from pale through pink to dark reddish-brown. The darker color usually indicated a lower remaining fraction of the pentavalent bismuth. Pentavalent bismuthate has long been known as a useful oxidizer in liquid-phase oxidations of organic compounds [110]. This oxidizing agent is very useful in organic synthesis procedures since the oxidation reaction can be visually followed, as the insoluble BiO₃⁻ completely reacts, the slurry clears out and turns into a transparent homogenous Bi(III) solution [111].

A further advantage of this reagent in the case of Am(III) oxidation, is that with the selection of the reaction temperature the final oxidation state of Am can be reliably chosen. If the reaction is conducted at room temperature, the oxidation results in quantitative oxidation to Am(VI), while at 85–90 °C, it yields completely Am(V) [100]. Moreover, the compatibility of this reagent with high (up to 6 mol L⁻¹) HNO₃ concentrations makes it an interesting candidate to perform the Am(III) oxidation prior to its solvent extraction by extractants selective for tetra- or hexavalent actinides. The most common neutral phosphonate extractants are only effective at higher acidities. With the PUREX solvent (30 vol.% TBP in *n*-dodecane), Am(VI) showed only a modest distribution ratio (~2.5) at 2–4 mol L⁻¹ HNO₃ feed acidity. Mincher et al. found that the addition of HClO₄ in the aqueous feed is necessary to prevent the reduction of oxidized americium upon contact with the organic phase composed of 30 vol.% TBP in *n*-dodecane [100]. Perchloric acid is deemed to enhance the dissolution of Bi(V) which then acts as a “holding oxidant”. The reduction of Am(VI) by the solvent also implies that for a reliable continuous process, very short contact times need to be ensured.

Subsequent to basic TBP extraction studies, the *in situ* oxidation of Am(III) to AmO₂²⁺ was integrated with the TRUEX process by Mincher et al. [98]. The TRUEX process is a modified version of the PUREX process for the treatment of nuclear effluent from earlier defense programs containing high concentration of chlorides besides the nitrate salts [112]. The TRUEX process is based on a solvent containing octyl-phenyl-*N,N*-diisobutyl carbamoyl methyl phosphine oxide

(CMPO) and TBP in Isopar L diluent. Am(V) was found to be stable for several days in a 4 mol L⁻¹ HNO₃ solution, thus the stability of this oxidation state is more interesting for industrial process development. Neither CMPO, nor TBP has appreciable affinity for the complexation of the low charge density pentavalent AmO₂²⁺ (such as AmO₂²⁺ or NpO₂²⁺). In principle, the pentavalent americium and neptunium could in this way be group-separated from trivalent Ln(III) and An(III) as well as from the major actinides. However, the reduced bismuthate Bi(III)-ions strongly compete with Ln(III) for complexation by CMPO. This competition suppresses the distribution ratios of the Ln(III) by a factor of 5. The other redox-active metal ions, such as Np, Pu and Ce, if present at the stage of Am(III) oxidation would be also oxidized to their highest stable oxidation state (Np(VI), Pu(VI) and Ce(IV)), imposing the necessity to add a considerably higher amount of oxidant than required for the Am(III) oxidation alone (this way further aggravating the Bi(III) vs. Ln(III) competition). In a simulated feed solution (composed of Cs⁺, Sr²⁺, La-Gd³⁺, Zr⁴⁺ and Ba²⁺ - ions), the highest $SF_{Eu/Am}$ was only 5, at acidities in the region of 6 mol L⁻¹ HNO₃. The authors suggested that at 4 mol L⁻¹ HNO₃ all solid bismuthate dissolved and remained active.

The difficulties experienced with the TRUEX-based separation directed the INL group to investigate the possibility of Am(VI) extraction by alternative extractants. Two promising candidate compounds were identified: dibutylbutylphosphonate (DBBP) and diamylamylphosphonate (DAAP) [99,101]. These molecules are soluble at sufficiently high concentration in alkane diluents and they overcome disadvantages of TBP when used in Am(VI) extraction as they don't require the addition of perchloric acid to stabilize Am(VI). Both compounds show a sufficiently high distribution ratio for Am(VI) extraction from a 4 mol L⁻¹ HNO₃ feed: $D_{Am} \sim 3.6$ and ~ 5.3 for DBBP and DAAP, respectively, compared to ~ 2.5 with TBP. The Ce(III) / Ce(IV) redox couple, as expected, interfered with the Am(VI) extraction, though Ce(IV) was not completely extracted. A fraction of the Ce(IV) precipitated on the still present solid NaBiO₃ powder. Prior to the solvent extraction the aqueous feed needed to be filtered from the suspended undissolved oxidant, thus a fraction of the Ce(IV) is mechanically removed together with the oxidant from the system. A similar activity loss can also be expected to occur with Cm(III), due to adsorption on the solid oxidant [113]. The back extraction of americium from the loaded organic phase can be easily performed. Addition of dilute H₂O₂ in 1 mol L⁻¹ HNO₃ solution reduces Am(VI) to Am(III), while the Ce(IV) to Ce(III) reduction is considerably slower, thus an effective separation can be achieved with short contact times. Besides tracer-spiked experiments, spiked simulated raffinate solutions and feed solutions containing macro-concentration of Am(III) and Ce (III) were also conducted to prove the concept of this method. In both cases the selective Am(VI) extraction and back-extraction could be performed with success, only Ru and Zr showing additional interference to Ce(IV).

The screening of three *N,N*-dialkyl amides in *n*-dodecane diluent: *N,N*-di-(2-ethylhexyl)butyramide (DEHBA), *N,N*-di-(2-ethylhexyl)isobutyramide (DEHIBA) and *N,N*-dihexyloctanamide (DHOA) extractants for the extraction of bismuthate-oxidized Am-feed solution showed that DEHBA provides the highest affinity for Am(VI) ($D_{Am} = 4.5$ - 5.5 from 6 to 7 mol L⁻¹ HNO₃) [102]. These extractants are all compatible with the CHON principle and therefore the spent solvent can be treated in an incineration facility without generating a solid by-product.

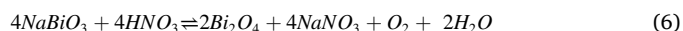
In a later proof-of principle experiment single-stage extraction and two-stage back-extraction of the bismuthate-oxidized Am(VI) was tested with *N,N*-di-(2-ethylhexyl)butyramide (DEHBA) in dodecane from a highly acidic feed using 3D-printed PMMA centrifugal contactors [103]. The suspension formed by bismuthate was allowed to settle before the feed solution (containing only ²⁴³Am and ¹³⁹Ce tracers) was introduced into the centrifugal contactor to prevent the build-up of solid particles inside the equipment. This small-scale test proved to be fruitful; important finding is that the centrifugal contactor can handle such small amount of fine solid particles. As the deposition of the solids on the rotor were clearly visible, a suitable filtration system (one that does not

reduce Am(VI)) needs to be elaborated. The stage efficiency for the extraction was remarkably high (95-100%), but the selective Am-stripping from Ce was less successful due to the co-reduction of the two oxidized ions although the rate of reduction of Am(VI) and Ce(IV) was expected to be different.

The bismuthate oxidation method is very promising notwithstanding the remaining difficulties with upscaling to a continuous process. Main challenges are the need to handle undissolved solid NaBiO₃ particles in a solvent extraction equipment and the co-oxidation and co-extraction of Ru, Ce and Zr with Am(VI). The former requires the design of a solvent extraction equipment that can tolerate the presence of undissolved solid fines or a suitable filtration step, while the latter necessitates further chemical studies to mitigate chemical interferences. The Ru interference with the redox reaction based separations is particularly troublesome as the oxidation product RuO₄ has a high affinity for most aliphatic diluents (hexane, heptane, dodecane) and its extraction is quantitative within a few seconds of phase contact. The extracted compound is prone to undergo reduction to RuO₂ which manifests itself as a black precipitate sitting on the interphase or on the walls of the containing vessel. This issue was addressed by a dedicated solid/liquid extraction study conducted with Imbiber beads® impregnated with either toluene or 4-heptanone by Richards and Mincher [114]. This strategy thus aims at the selective Ru extraction ahead of the Am(III) oxidation step. The authors found that the use of impregnated beads can achieve more than 99% extraction of the RuO₄ within the course of a few minutes.

3.3. Bismuthate and perxenate-based chemical oxidation methods

The sodium bismuthate and sodium perxenate chemistry has also been studied in Russia. In a recent study Kulyako et al. have shown that the reaction of solid sodium bismuthate with dilute to high concentration of nitric acid solutions results in the reduction of the acidity and the adsorption of actinides on the surface of the oxidant [104]. In the authors' interpretation, the acid is partially consumed in a reaction as described in Eq. (6). For this reason, less than 4% of the originally present Am is extracted by 30% TBP in Isopar M from a 3 mol L⁻¹ HNO₃, if no further precautions are taken. Keeping the contact time short (~ 15 s), using TOPO synergist and adding HClO₄ to the feed solution allowed the extraction of nearly 90% of the initially present Am. The short contact times are mandated by the rapid reduction of the Am(VI) extracted in the organic phase. The adsorption of the trivalent Am(III) to the solid NaBiO₃ renders the re-oxidation of Am(III) ineffective even with the addition of fresh amounts of oxidants.



From a dilute nitric acid solution (0.1 mol L⁻¹ HNO₃) of Am(III) and Cm(III) the combination of two oxidants (100 mg NaBiO₃ and 40 mg Na₄XeO₆ per mL of feed) resulted in the solution to become alkaline (pH 10 as a result of Eqs. (7) and (8)) and a simultaneous quantitative and selective oxidation of Am(III) into a tetravalent form. The Am(IV)XeO₆ form is thought to be stable against hydrolysis even in alkaline solutions. The trivalent Cm(III) and a fraction of Am(III) was found to be bound to the solid oxidants. This would require again a subsequent filtration step prior to a conditioning in the final waste form. This second method is similar to the INL methodology in the usage of a solid oxidant and it probably can be developed further as a powerful tool to perform analytical scale separations of Am(III) from Cm(III) present in relatively pure and mildly acidic solutions. On larger scale applications, such as minor actinide partitioning directly from spent nuclear fuel treatment process liquors (e.g. PUREX HAR) the possible interferences of the fission products (especially that of the abundantly present Ru) must be anticipated.



3.4. Copper(III) periodate oxidation of Am(III)

The feasibility of the oxidation of Am(III) to Am(VI) with the use of a large (10-fold or more) excess of $\text{KNa}_4\text{Cu}(\text{HIO}_6)_2$ was tested by Sinkov and Lumetta at various acidities (ranging from 0.25 mol L^{-1} to $3.5 \text{ mol L}^{-1} \text{ HNO}_3$) [105]. Similarly to bismuthate, the oxidant can be stored for months at ambient temperature and conditions without any noticeable loss of oxidation. The solubility of Cu(III) periodate in acidic aqueous solutions is much better than sodium bismuthate, allowing the development of a hybrid system containing an oxidation and a subsequent solvent extraction step without the presence of undissolved solid. The Cu(III)-ions are complexed by two orthoperiodate ions in aqueous solutions in the form of $[\text{Cu}(\text{H}_2\text{IO}_6)_2]^{5-}$ and this complex form impedes to some extent reactions with water and dissolved oxygen [115]. Under acidic conditions, the orthoperiodate ions get protonated and dissociate allowing Am(III) and Cu(III) to enter into a redox-reaction.

With the Cu(III) periodate, the Am(III) to Am(VI) oxidation proceeded with fast kinetics and spectroscopic studies showed that at acidities below $1 \text{ mol L}^{-1} \text{ HNO}_3$ the periodate ions complex the Am(VI). The Am(III) oxidation occurred with high efficiency ($> 98\%$) with a 10-fold molar excess (corresponding to 3.33-fold excess of the oxidant) for acid solutions containing $0.25 - 3 \text{ mol L}^{-1} \text{ HNO}_3$. At higher nitric acid concentrations, the oxidation yield was not completely reproducible and generally lower (76.8–95.0%). A 20:1 Cu(III):Am(III) molar ratio was necessary to reach a quantitative oxidation of Am(VI) at $3.5 \text{ mol L}^{-1} \text{ HNO}_3$. The liquid-liquid extraction of americium ions generated via orthoperiodate oxidation was also tested with DAAP [115]. The distribution ratio of Am oxidized by Cu(III) periodate reached a maximum around 1–1.8 when extracting from a $1 \text{ mol L}^{-1} \text{ HNO}_3$ feed solution with 1 mol L^{-1} DAAP in *n*-dodecane and a $SF_{\text{Am/Cm}} \approx 5.4 - 6.4$ in the case of 2–4 mol L^{-1} initial feed acidities. The direct addition of the oxidant to a simulated PUREX HAR solution resulted in the formation of a white precipitate, due to the formation of Zr(IV), Sn(IV) and Ru(IV) – containing insoluble compounds. Besides, the Mo(VI) and Sm(III) concentrations also decreased in the solution, probably due to the formation of poorly soluble complexes. Ce(III) underwent oxidation to Ce(IV) and precipitated as CeHIO_6 . The $D_{\text{Am}} (\approx 0.40 \pm 0.03)$ was considerably lower than from simple acidic solutions. Especially the Ce(IV) precipitation is indicative of similar redox-interferences that can be expected in solutions containing Th(IV) or Pu(IV), therefore the use of Cu(III) periodate is probably better suited for applications on An(III)+Ln(III) or An(III)-only feed solutions instead of a direct addition to the PUREX HAR.

4. Separation of americium based on column chromatography

Solid-liquid separation methods are different from liquid-liquid extraction methods in the sense that one phase is immobilized, thus not capable of constantly ensure the outflow of material from the system, only the mobile phase is able to do that. Due to this, chromatography is inherently a batch process, in comparison to the liquid-liquid extraction that can be operated both in batch and in continuous modus. Metal ions from a solution can be loaded on a column, followed by a sequential elution with a suitable eluent. In the last step, the solid phase requires re-generation or other chemical conditioning before it is used again.

A chromatographic separation method for removing Am from a PUREX-type raffinate is very challenging similarly to liquid-liquid extraction methods. Most chromatographic methods were tested on feed solutions with much more simple matrices such as An(III) mixtures or An(III)/Ln(III) mixtures. The interference caused by fission products with most of the methods described below requires a preliminary purification step for simplifying the matrix of a PUREX HAR solution.

4.1. Chromatographic methods based on preferential complexation

The methods discussed in this section are based on the slightly higher affinity for Am(III) over Cm(III)/Ln(III) of one or more functional groups covalently bonded to a styrene-divinylbenzene polymer, extractants immobilized on an inert support, or complexants dissolved in a mobile phase (Table 3). The large number of theoretical plates achievable with long chromatographic columns can provide a nearly baseline separation of the various An(III) ions.

The first methods for the separation of Am(III) from Cm(III) and/or the Ln(III), which were based on cation exchange, were elaborated during the Manhattan Project [125]. Scientists at the University of California used Dowex-50 (composed of sulfonated divinyl benzyl copolymer) resin with various concentrations of HCl ($3 - 12 \text{ mol L}^{-1}$) [116–118]. An(III) ions tend to form negatively charged complexes with Cl^- ions at high concentrations. The strength of the complexes can be exploited during the elution from a loaded ion-exchange resin.

The elution of a mixture of Pu(III)/Am(III)/Cm(III) loaded on a column filled with Dowex-50 cation exchange resin with $3 - 9 \text{ mol L}^{-1}$ HCl eluents yielded separated fractions in the sequence of Cm(III) → Am(III) → Pu(III). When the eluent HCl concentration is 12 mol L^{-1} or higher, the order of elution is reversed: Pu(III) → Am(III) → Cm(III).

Explanation of the order of elution at lower chloride concentrations is more related to the effective hydrated ionic radii of the An(III) ions and less to their tendency of chloride complex formation. As Cm(III) is the most compact in the series, this ion will have higher charge density and therefore accommodate a larger hydration shell around itself than the others. This larger hydration shell (i.e. larger distance between the nuclei) only allows a weaker ionic interaction between the negatively charged functional group of the resin and the positively charged An(III).

Explanation for the reversed order of elution at concentrated (12 mol L^{-1}) HCl solutions was given as a *progressive weakening* in the strength of the chloro-complexes caused by the spatial contraction of the 5f-orbitals. As the 5f orbitals of Cm(III) are smaller than those of Am(III) or Pu(III), they can hybridize with the electron orbitals of the chloride ions less effectively, than the larger orbitals of Am(III) or Pu(III). The An(III) ions with the largest ionic radius (Pu(III)) therefore form the strongest chloro-complex, while the An(III) ions with the smallest ionic radius (Cm(III)) form the weakest chloro-complexes under the same conditions.

The same chloride complexation was proven to allow gram scale purification of ^{242}Cm from irradiated ^{241}Am targets [119]. In this version, the target material is dissolved in $3 - 4 \text{ mol L}^{-1} \text{ NaOH}$, yielding a sludge containing the trivalent actinides and lanthanides. The sludge is dissolved in excess HCl; then evaporated to remove the bulk of the acid. Subsequently close to saturated (13.5 mol L^{-1}) LiCl solution is added at 90°C in 0.1 mol L^{-1} HCl and the resulting solution was loaded on a strongly basic anion exchange resin such as Dowex-1 or Dowex-2 (polystyrene-based polymer carrying quaternary amine functional groups). The negatively charged chloro-complexes of the Ln(III) and An(III) are retained on the column. The Ln(III) can be first selectively rinsed off using concentrated LiCl in dilute HCl. The An(III) can afterwards be co-eluted by concentrated HCl and dilute nitric acid. For a subsequent Am(III)/Cm(III) separation, the eluate is evaporated and re-dissolved in 1 mol L^{-1} HCl. In this matrix, the solution can be loaded on a sulfonated

Table 3

Summary of chromatographic methods based on preferential complexation of Am(III) over Cm(III).

Origin	Resin/Complexant	Reference
US	Dowex-50/ Cl^-	[116–119]
US	Dowex-50 W X8 / NTA	[120,121]
Russia	DMDBDDEMA	[122]
Japan	TODGA/DOODA(C2) or DOODA(C8)/TEDGA	[123]
Japan	Tertiary pyridine/ $\text{CH}_3\text{OH} + \text{HNO}_3$	[124]

cation exchange resin and the individual fractions of Am(III) can be eluted by pouring through either α -hydroxy-isobutyric acid (α -HIBA) or lactic acid at pH 4.5. If the chlorides are not a problem for the product's further use, concentrated HCl would also work. The subsequent application of acidic, buffered and acidic loading and elution cycles allowed the achievement of 99.99% purity of 1.44 g ^{242}Cm . While this method is excellent for radionuclide production purposes, the recovery is only 60%. Such losses would be unacceptable for larger-scale industrial spent fuel recycling processes. This strategy would pose a significant problem for the downstream waste conditioning process, since it introduces large quantities of chloride ions that are incompatible with the generally implemented vitrification processes for HLW [126]. In addition, the spent resin is a problematic waste form, very difficult to bring in compliance with current waste acceptance criteria of radioactive waste treatment facilities. Furthermore, resin degradation due to radiolysis (i. e. hydrogen formation) is a potential explosion hazard. An example of resin degradation is the 1976 incident at the Hanford site. The underlying reason was probably the radiolysis of the resin material by the large amount of ^{241}Am loaded on a large volume ion-exchange column [127].

Later in the 1960's scientists at the Savannah River National Laboratory developed further the cation exchange chromatographic Am(III)/Cm(III) separation method. They achieved gram-scale (up to 65 g) separations of Cm(III) using high pressure liquid chromatography and DTPA in the eluent [120,121]. The high pressure allows significantly reduced residence time of the radionuclides on the resin, which helps to minimize radiation damage and the equally acute heat dissipation problem encountered with high activity solutions. According to the flow sheet, the An(III)/Ln(III) separation was achieved on a Dowex 50W-X8 resin, converted to its Zn^{2+} -form with $0.5 \text{ mol L}^{-1} \text{ Zn}(\text{NO}_3)_2$ and rinsed until the effluent pH raised to 5. At this pH, the An(III) ions can be eluted with a DTPA solution (curium eluting ahead of americium), followed by loading the An(III) product on a cation exchange resin in a $2 \text{ mol L}^{-1} \text{ HNO}_3$ feed and effecting the Am(III)/Cm(III) separation by eluting with nitriloacetic acid (NTA) at pH = 7 and 80°C .

Nearly half a century after the elaboration of the initial chromatographic separation methods Myasoedov *et al.* used a two-layer coil column for counter-current solid-liquid extraction to separate Am(III) from Cm(III) aqueous solutions with high concentrations of HNO_3 [122]. In their set-up, the stationary phase was composed of N,N' -dimethyl- N,N' -dibutyldecylethoxy-malonamide (DMDBDEMA) in hydrogenated tetrapropene (TPH). The mobile phase was a $3 \text{ mol L}^{-1} \text{ HNO}_3$ containing the metal ions to be separated. Although the selected malonamide has only a modest separation factor for the Am(III)/Cm(III) couple ($SF_{\text{Am/Cm}} = 1.6 - 1.7$) the selected method allowed a nearly baseline separation of the two adjacent actinide ions showing that the batch results can be transferred to a continuous process. These recovery values represent a major advancement in comparison with the traditional chromatographic methods as shown above, and are promising for the separation of Am(III) from an An(III) feed, previously separated from a more complex HAR.

Usuda *et al.* tested an extraction chromatography method for the separation of Am(III) from Cm(III) using an impregnated porous silica/polymer support [123]. Two combinations of a lipophilic extractant (impregnated on a support) and a hydrophilic complexant were explored for the separation of Am(III) from Cm(III) and Eu(III):

- (i) TODGA in combination with N,N,N',N' -tetraethyl-3,6-dioxaoctanediamide (DOODA(C2) in dilute HNO_3), and
- (ii) N,N,N',N' -tetraoctyl-3,6-dioxaoctanediamide (DOODA(C8)) in combination with TEDGA in $3 \text{ mol L}^{-1} \text{ HNO}_3$.

The extractant-impregnated beads were filled in columns, loaded with trivalent metal ions (^{241}Am , ^{243}Cm and ^{152}Eu) in an aqueous solution of HNO_3 . The columns were subsequently eluted with the eluent solution containing the hydrophilic complexant. The first combination

(TODGA_{org}/DOODA(C2)_{aq}) gave $SF_{\text{Am/Cm}} = 3.9$, and $SF_{\text{Cm/Eu}} = 8.7$, and rather pure fractions: Am-fraction: 97.1% Am, 0.26% Cm and 0.03% Eu; Cm-fraction: 2.62% Am, 97.8% Cm and 0.07% Eu. In the case of the second ligand combination (DOODA(C8)_{org}/TEDGA_{aq}) the order of elution was reversed compared to the previous combination and each fraction was cross contaminated with the other two tracers. The separation factors were also lower compared to the first ligand combination; $SF_{\text{Am/Cm}} = 2.2$ and $SF_{\text{Cm/Eu}} = 2.8$.

Suzuki *et al.* used a tertiary pyridine resin and a nitric acid/methanol mixture for the elution of Am(III) and Cm(III) from the loaded resin [124]. At high methanol volume fractions (e.g. 80 vol.%) with $1 \text{ mol L}^{-1} \text{ HNO}_3$, the Am(III) and Cm(III) elution peaks were nearly base line separated (Am(III) eluting ahead of Cm(III)). The method is simple and does not require expensive complexants or extractants. However, the use of a mixture of short chain length alcohols and nitric acid is less safe due to potential unwanted chemical reactions. The authors found that the separation is mainly depending on the methanol content of the mobile phase and less on the acid concentration. The exact reason for this was not elucidated in the paper, but one can hypothesize that by lowering the water content, the hydration of both the resin and the metal ions is considerably decreased, resulting in smaller hydration shell radii. Consequently the overlap of the orbitals of the pyridine non-binding electrons with the 5f-orbitals of An(III) is less hindered by the hydration shell in comparison with the fully hydrated ions. As the ionic charge density increases along the An(III) contraction, the strength of interaction between the N-donor atoms and the An(III) 5f orbitals should increase, hence the faster elution of Am(III) compared to Cm(III). This study is probably the first example on the use of a soft-donor compound for the Am(III)/Cm(III) separation, preceding the solvent extraction methods.

4.2. Chromatographic methods based on the selective oxidation of americium

These methods exploit the fact that unlike Cm(III), Am(III) can be oxidized to higher oxidation states. The Am(III)/Am(V) and Am(III)/Am(VI) redox couples require powerful oxidizing agents, which will also be consumed by other redox-active species present in the solution. The use of selective oxidants allows a much more effective chromatographic separation of Am(VI) from Cm(III) than what can be achieved between Am(III) and Cm(III). An overview of chromatographic methods based on selective americium oxidation is provided in Table 4.

To overcome the low separation factors achievable with the ion exchange or extraction chromatography, the selective oxidation of Am(III) to presumably Am(VI) using $0.025 \text{ mol L}^{-1} \text{ AgNO}_3$ and $0.185 \text{ mol L}^{-1} \text{ K}_2\text{S}_2\text{O}_8$ reagents in dilute nitric acid (0.025 mol L^{-1}) was tested both in liquid-liquid and solid-liquid extraction studies by Mason *et al.* [128]. The oxidation was performed with the Ag(I/II) redox-mediator, and the powerful peroxy-radical ion, that was capable of completely oxidizing Am(III) to Am(IV) at 50°C within 10 min. As a solvent 0.6 mol L^{-1} bis(2, 6-dimethyl-4-heptyl) phosphoric acid (HD(DIBM)P) in heptane was used in the liquid-liquid extraction studies and the undiluted HD(DIBM)P

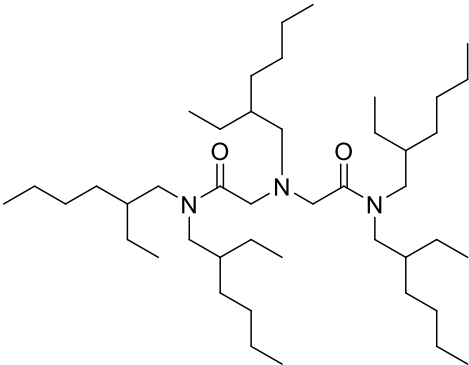
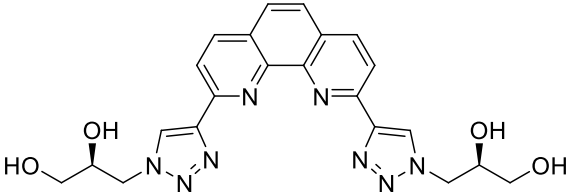
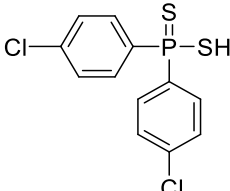
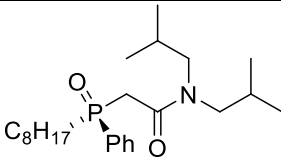
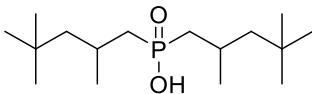
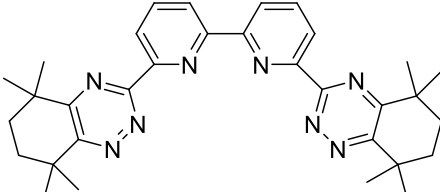
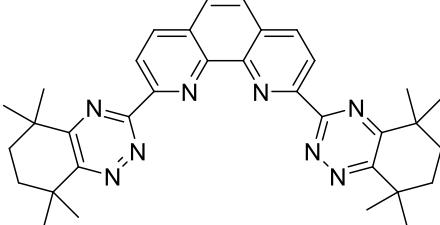
Table 4

Summary of experimental conditions for chromatographic methods based on selective americium oxidation.

Origin	Oxidant	Experimental conditions	Oxidation state of Am	Reference
US	$\text{AgNO}_3 + \text{K}_2\text{S}_2\text{O}_8$	50°C , dilute HNO_3	Am(IV)	[128, 129]
US	NaBiO_3	Ambient temperature, HNO_3	Am(VI)	[113]
US	$\text{Na}_2\text{S}_2\text{O}_8$	80°C , dilute HNO_3 , HClO_4 , UMOFs	Am(V)	[130]
US	$\text{Na}_4\text{XeO}_6 + \text{Ag(I/II)}$	Neutral pH or dilute HNO_3	Am(VI)	[97]

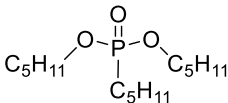
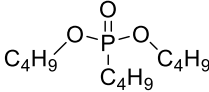
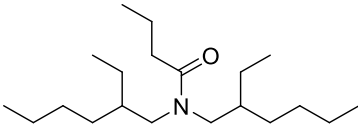
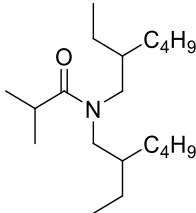
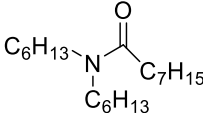
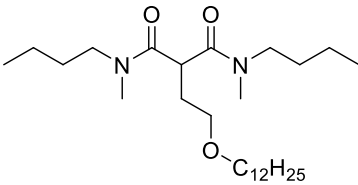
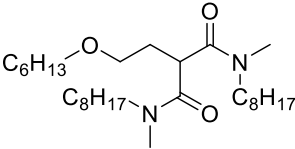
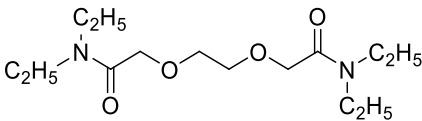
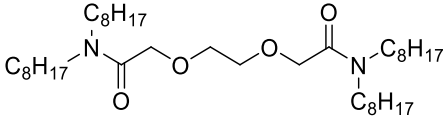
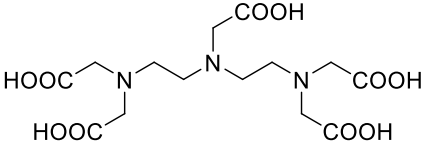
Table 5

Overview of chemical compounds discussed in this paper.

Compound	Acronym
	ADAAM(EH)
	BTrzPhen
	(ClPh) ₂ PSSH
	CMPO
	Cyanex-272
	CyMe ₄ BTBP
	CyMe ₄ BTPhen

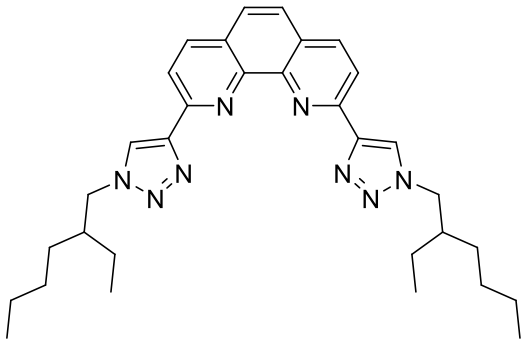
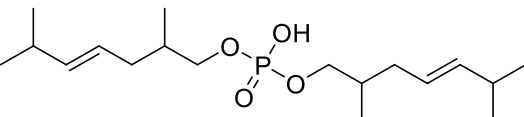
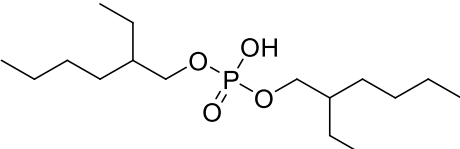
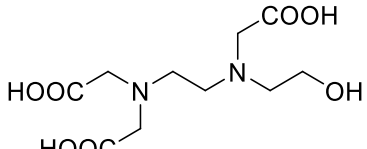
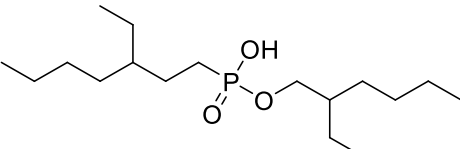
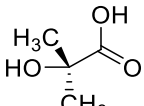
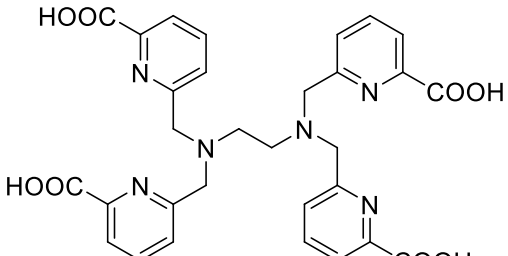
(continued on next page)

Table 5 (continued)

	DAAP
	DBBP
	DEHBA
	DEHiBA
	DHOA
	DMDBDDEMA
	DMDOHEMA
	DOODA(C2)
	DOODA(C8)
	DTPA

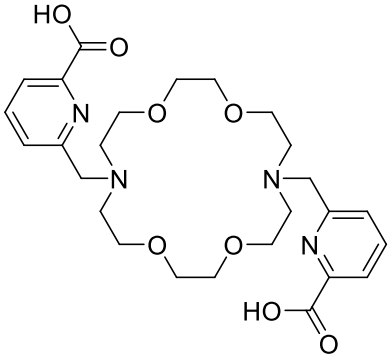
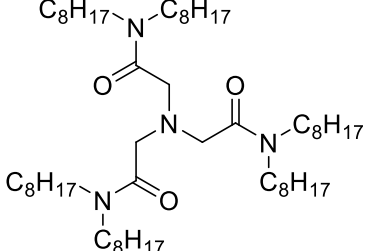
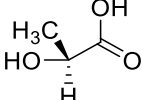
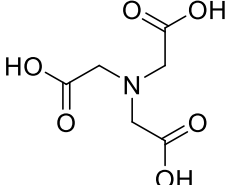
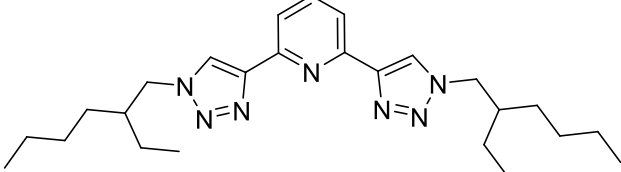
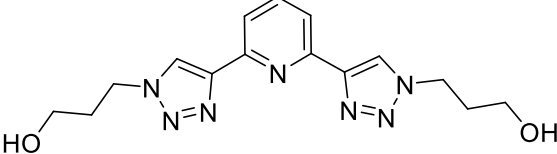
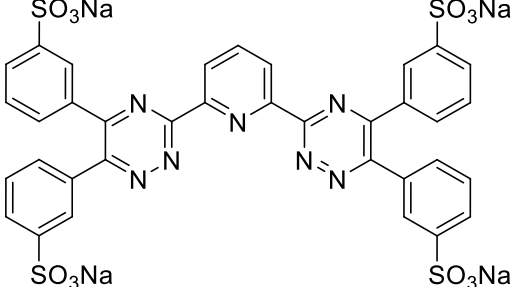
(continued on next page)

Table 5 (continued)

	EH-BTzPhen
	HD(DIBM)P
	HDEHP
	HEDTA
	HEH[EHP]
	α -HIBA
	H ₄ TPAEN

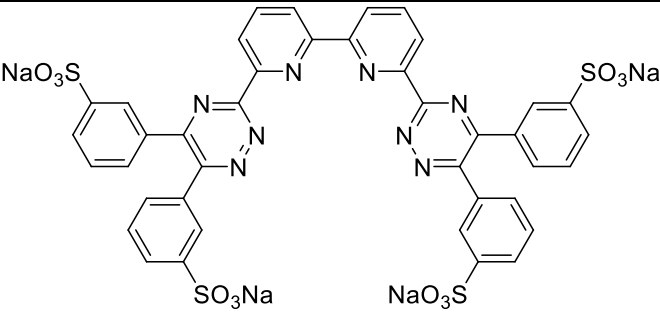
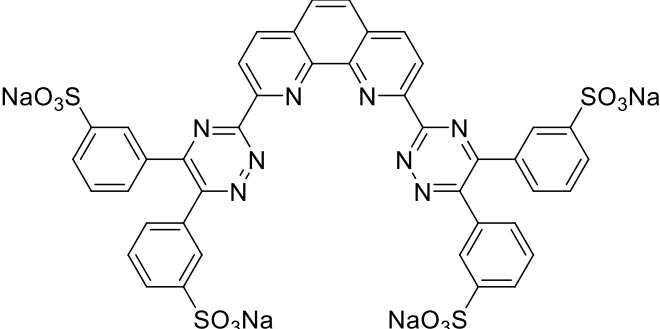
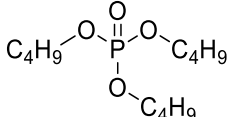
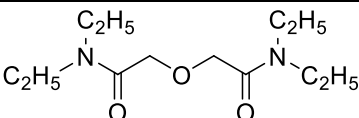
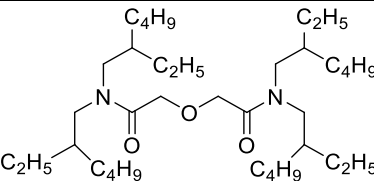
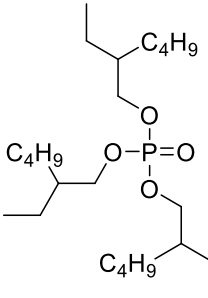
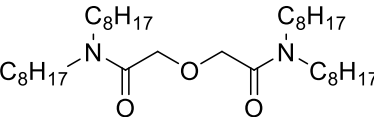
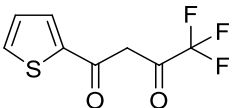
(continued on next page)

Table 5 (continued)

	H ₂ bp18c6
	HONTA/ NTAamide(C8)
	Lactic acid
	NTA
	PTEH
	PTD
	SO ₃ -Ph-BTP

(continued on next page)

Table 5 (continued)

	SO ₃ -Ph-BTPBP
	SO ₃ -Ph-BTPhen or TS-BTPhen
	TBP
	TEDGA
	TEHDGA
	TEHP
	TODGA
	TTA

dispersed on a silica carrier was used in extraction chromatography [128,129]. This extractant is selective for hexavalent actinides at low acidities with very low affinity for trivalent actinides and lanthanides. The method allowed the attainment of a Am/Cm decontamination factor exceeding 1200. The loaded organic phase can be stripped by mixing it with 1 mol L⁻¹ HNO₃ with 2 vol.% H₂O₂ that ensures the rapid and quantitative reduction of high valence forms of americium. The peroxo-disulphate ion or its decomposition product was found to complex the Cm(III) ions, and it was also incompatible with the acidities typical for PUREX HAR; since it generates H₂O₂ that reduces back the Am(VI) to its trivalent state.

Richards and Sudowe used the NaBiO₃ oxidant to generate Am(VI) in situ inside a column filled with Celite carrier containing homogeneously dispersed NaBiO₃ [113]. Hexavalent americium was completely eluted with 0.1 mol L⁻¹ HNO₃, while the Cm(III) fraction was recovered by eluting the column with 2 mol L⁻¹ HNO₃. The method allowed a high Am(VI)/Cm(III) separation factor of ~ 90 with recoveries of 97 and 98% for Am and Cm, respectively. Notwithstanding the engineering difficulties it would take to implement this method on an industrial scale to separate Am from spent fuel treatment raffinates, probably this is one of the most compact and efficient ways to date to separate Am from Cm for analytical purposes.

A common limitation of the methods based on the selective oxidation of americium is that it is only selective with respect to most Ln(III) and Cm(III). Besides other actinides (U, Pu, Np) redox-active, abundant fission products (Ce and Ru in particular) would be co-oxidized with Am(III), unless removed completely from the feed solution prior to the Am(III) oxidation step. The interference caused by the multiple ruthenium species was addressed by a strategy that aims at the selective Ru extraction ahead of the Am(III) oxidation step as referred above [114]. The redox-interference caused by the presence of Ce(III) can be mitigated by any An(III)/Ln(III) group separation technique prior to the selective Am(III) – oxidation.

Pentavalent americium was separated from simple make up solutions containing americium and curium in nitric or perchloric acid with the use of Zr(IV) or Sn(IV)-pillared phosphate phosphonate unconventional metal organic frameworks (UMOFs) [130]. These metal (IV) pillared UMOFs act as ion exchange materials with a high affinity for binding highly charged ions, but negligible binding of mono and divalent cations. It was found that the addition of such UMOFs to the reaction mixture and hypochlorite ions to the still warm solution upon oxidizing Am(III) to AmO₂⁺ by Na₂S₂O₈ at 80 °C stabilizes Am(V) against reduction for a long time. By this method 95% of the original pentavalent americium remained present after 5 days of storage. The use of UMOFs with pentavalent americium allowed Am(V)/Cm(III) separation factors up to 20. The ion exchange material can be loaded into columns and the retained Am(V) can be probably eluted after adding a reducing agent as eluent. Further studies are certainly necessary for assessing the potential for upscaling.

Holcomb has shown that a reactive noble gas compound, solid sodium perxenate is able to rapidly oxidize Am(III) to Am(VI) in neutral or basic solutions [97]. However, below pH 7, the Xe(VIII) → Xe(VI) reduction in aqueous media was instantaneous. The addition of Ag(I) allowed the in situ generation of Ag(II) (argentic ion) which can act as a “holding oxidant” that keeps Am(VI) oxidized even in the presence of nitric acid. The Am(VI)/Cm(III)+Ln(III) separation was performed by passing through the solution through a column filled with CaF₂ that retains completely the trivalent An(III) and Ln(III). The trivalent *f*-elements form insoluble fluoride precipitates on the surface of the CaF₂ filling, preventing their co-elution with the hexavalent americium.

5. Discussion and outlook

Different chemical separation methods were covered in the previous sections, each with their individual advantages and disadvantages. Several americium selective hydrometallurgical separation methods

described in this review are promising to be considered for lab-scale hot demonstration and maybe pilot scale application in shielded facilities. Chromatographic separation methods can provide very high decontamination factors and are therefore often used for smaller scale separations or analytical purposes. Different combinations of extractant/complexant and support enable a wide choice of chromatography columns suitable for many separation tasks, and many of them are commercially available and easy to use. The use of oxidizing agents can even further increase the selectivity of the separation systems. Larger scale applications, however, are currently not described for irradiated nuclear fuel recycling, as a continuous operation of chromatographic separation methods is demanding, especially if it needs to be operated remotely. Also, no successful direct separation of americium from a PUREX raffinate was described. Liu et al. tested an isohexyl-BTP/SiO₂-P extraction resin for the direct separation of MA from HLLW, but found strong interference of Pd(II) [131]. Usually, a series of chromatographic separations using different extractants/complexants and supports needs to be used to achieve the required decontamination from fission products. Degradation of the chromatography resin (e.g., by radiolysis, hydrolysis, or aging) can cause practical problems like blocking, gas bubble or crud formation, and reduced separation performance. Disposal of larger volumes of used resins or chromatography columns towards solid waste streams would require further treatment and conditioning. Further research and development would be required for larger scale use of chromatographic separation methods for Am separation from PUREX raffinate. Among the selective oxidation methods, the oxidation of Am(III) to Am(VI) by copper(III) periodate seems to be the most promising, as the oxidant is dissolved (as opposed to the bismuthate oxidation method). The effect of the introduction of a considerable amount of non-radioactive transition metals such as bismuth or copper into the process and the waste matrix needs to be studied. The redox-interference of certain elements (Ce and Ru) and precipitation observed with periodate ions suggest that probably the application of the method directly on the PUREX HAR is too ambitious, and might rather be applied on an Am(III)+Cm(III) or an An(III)+Ln(III) feed.

Liquid-liquid extraction methods are widely used, also in used nuclear fuel treatment, and have proven to be mature even on the industrial scale (e.g., the PUREX process). Recent developments aim at increasing the selectivity of the chemical separation system using selective Am oxidation methods, combination of lipophilic and hydrophilic ligands with opposite selectivity, or development of new ligands with high Am(III) selectivity.

The selective Am oxidation is a promising approach, that can provide very high selectivity for higher americium oxidation states over trivalent curium and lanthanides. However, strong oxidizing agents are needed, and Am(IV/V/VI) is usually unstable in acidic solutions and requires stabilization or fast extraction. Several different oxidizing agents were recently tested (Ag(II), NaBiO₃, Na₄XeO₆, Cu(III) periodate, or electrochemical methods) with each of them showing certain benefits and drawbacks. For an Am separation from PUREX raffinate, the biggest challenge is to mitigate unwanted oxidation, sorption, precipitation or extraction of other redox-sensitive metal ions (fission or corrosion products, e.g., Ru, Ce and Zr which are most abundant). The formation of insoluble particles (e.g., NaBiO₃), or corrosion due to the strong oxidation potential, need to be addressed and require further research and development. Nevertheless, if the limitations are considered in the process design, further upscaling towards demonstration experiments seems worthwhile.

The combination of lipophilic and hydrophilic ligands with opposite selectivity, and the development of new ligands with high Am(III) selectivity progressed significantly recently and several promising processes were developed, including Am(III) selective separation processes from PUREX raffinate. These processes can be run in conventional counter-current set-ups, like pulsed columns or mixer-settlers, but recently centrifugal contactors are tested more often. Centrifugal contactors can provide a compact process design and relatively low

footprint. The cost of the low footprint however is the usually short contact time, compared to pulsed columns and mixer settler, which imposes fast chemical kinetics of the solvent system. However, the chemical systems tested for high-selectivity Am(III) separations often show relatively slow chemical kinetics. Nevertheless, several process demonstrations on the laboratory scale successfully used commercially available miniature centrifugal contactors with good results. To overcome the issue of short contact times, Gelis et al. designed and 3D printed complex multi-stage contactor modules with internal channels to increase the residence time, and successfully tested them in an ALSEP process [132]. Recently, the development of new highly selective ligands composed only of C, H, O, and N (the CHON principle) was followed. The use of corrosive halogenides (via fluorinated or chlorinated compounds) could cause corrosion or other problems, while sulfur could interfere with sintering of the Am-product as well as the vitrification of the raffinate issued from the process. In addition, halogenides, sulfur and phosphor elements are not allowed in many radioactive waste processing facilities (related to incompatibility with the incineration installations). Within the European research framework, selective Am (III) back-extraction from an An(III)+Ln(III)-loaded organic phase using a CHON-compliant complexant is followed, e.g., with the novel ProH-BPTD molecule [133].

The laboratory scale process demonstrations showed that even with modest separation factors, a reasonable number of stages can be sufficient to achieve a pure Am product from a PUREX-type raffinate. The 2010 hot test of the French EXAm process on a genuine PUREX raffinate achieved a decontamination factor of 500 of the Am product with respect to Cm [134].

Further use of the separated Am (target and fuel fabrication specifications), scale-up issues and economics need to be addressed before a decision can be made on the most suitable separation method and process design. Nevertheless, currently solvent extraction processes seem to be most mature and have most promising perspectives.

CRedit authorship contribution statement

P. Zsabka: Conceptualization, Writing – review & editing. **A. Wilden:** Conceptualization, Writing – review & editing. **K. Van Hecke:** Conceptualization, Writing – review & editing. **G. Modolo:** Conceptualization, Writing – review & editing. **M. Verwerft:** Conceptualization, Writing – review & editing. **T. Cardinaels:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors have no competing interests to declare.

Data availability

No data was used for the research described in the article.

References

- [1] Boundary conditions for separation and conditioning, Report, E. Weetjens, J. Govaerts, J. Perko, K. Van Hecke, K. Govers, SCK CEN, 2019, pp. 1–52., Report No.: SCK CEN/33517036.
- [2] Status and Trends in Spent Fuel and Radioactive Waste Management, Report, IAEA Nuclear Energy Series, IAEA, Vienna, Austria, 2022, pp. 1–102. NW-T-1.14 (Rev.1).
- [3] RED-IMPACT Impact of Partitioning, Transmutation and Waste Reduction Technologies on the Final Nuclear Waste Disposal, Report, D. Greneche, B. Quiniou, L. Boucher, M. Delpech, E. Gonzalez, F. Alvarez, M.A. Cuñado, G. Serrano, J.L. Cormenzana, W. Kuckshinrichs, R. Odoj, W. von Lensa, J. Wallenius, D. Westlén, C. Zimmermann, J. Marivoet, in *Schriften des Forschungszentrums Jülich Reihe Energie & Umwelt /Energy & Environment*, Vol. 15 (Eds.: W. von Lensa, R. Nabbi, M. Rossbach), Forschungszentrum Jülich GmbH Institut für Energieforschung (IEF) Sicherheitsforschung und Reaktortechnik (IEF-6), Jülich, Germany, 2008.
- [4] K. Nishihara, S. Nakayama, Y. Morita, H. Oigawa, T. Iwasaki, Impact of partitioning and transmutation on LWR high-level waste disposal, *J. Nucl. Sci. Technol.* 45 (2008) 84–97.
- [5] F. Hirano, S. Sato, T. Kozaki, Y. Inagaki, T. Iwasaki, T. Ohe, K. Kato, K. Kitayama, S. Torikai, Y. Niibori, S. Nagasaki, Thermal impact on geological disposal of hull and end piece wastes resulting from high-burn-up operation of LWR and introduction of MOX fuels into LWR, *J. Nucl. Sci. Technol.* 46 (2009) 443–452.
- [6] Minor Actinide Burning in Thermal Reactors, A report by the working party on scientific issues of reactor systems - organisation for economic co-operation and development, report. Minor Actinide Burning in Thermal Reactors, OECD Publishing, Paris, 2014.
- [7] B. Vezzoni, F. Gabrielli, A. Rineiski, A. Schwenk-Ferrero, V. Romanello, W. Maschek, C. Fazio, M. Salvatores, Plutonium and minor actinides incineration options using innovative Na-cooled fast reactors: impacting on phasing-out and on-going fuel cycles, *Prog. Nucl. Energy* 82 (2015) 58–63.
- [8] Management and Disposal of High-Level Radioactive Waste, Global Progress and Solutions, Report, OECD-NEA, Paris, 2020. Report Nr. 7532.
- [9] Strategies and Considerations, For the Back End of the Fuel Cycle, OECD-NEA, Boulogne-Billancourt, 2021. ReportReport Nr.7469.
- [10] J. Serp, C. Poinssot, S. Bourg, Assessment of the anticipated environmental footprint of future nuclear energy systems. evidence of the beneficial effect of extensive recycling, *Energies* 10 (2017) 1445–1464.
- [11] R. Taylor, W. Bodel, L. Stamford, G. Butler, A review of environmental and economic implications of closing the nuclear fuel cycle—part one: wastes and environmental impacts, *Energies* 15 (2022) 1433.
- [12] R. Taylor, W. Bodel, G. Butler, A review of environmental and economic implications of closing the nuclear fuel cycle—part two: economic impacts, *Energies* 15 (2022) 2472.
- [13] H. Hayashi, H. Hagiya, S.Y. Kim, Y. Morita, M. Akabori, K. Minato, Separation and recovery of Cm from Cm–Pu mixed oxide samples containing Am impurity, *J. Radioanal. Nucl. Chem.* 296 (2013) 1275–1286.
- [14] A. Geist, J.M. Adnet, S. Bourg, C. Ekberg, H. Galán, P. Guilbaud, M. Miguiditchian, G. Modolo, C. Rhodes, R. Taylor, An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, part 1 — Heterogeneous recycling, *Sep. Sci. Technol.* 56 (11) (2020) 1866–1881.
- [15] S. Pillon, J. Somers, S. Grandjean, J. Lacquement, Aspects of fabrication of curium-based fuels and targets, *J. Nucl. Mat.* 320 (2003) 36–43.
- [16] S.A. Ansari, P. Pathak, P.K. Mohapatra, V.K. Manchanda, Aqueous partitioning of minor actinides by different processes, *Sep. Purif. Rev.* 40 (2011) 43–76.
- [17] Eurapor: European Research programme for partitioning of minor actinides within high active wastes issuing from the reprocessing of spent nuclear fuels, Conference Paper, C. Madic, M.J. Hudson, P. Baron, N. Ouvrier, C. Hill, S. Bourg, F. Arnaud, A.G. Espartero, J.F. Desreux, G. Modolo, R. Malmbeck, G.d. Angelis, J. Uhlir, Information Exchange Meeting, Nimes (France); 25–29 Sep 2006., Organisation for Economic Co-Operation and Development - Nuclear Energy Agency, Nuclear Energy Agency of the OECD (NEA), 2007.
- [18] G. Modolo, A. Wilden, A. Geist, D. Magnusson, R. Malmbeck, A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate, *Radiochim. Acta* 100 (2012) 715–725.
- [19] A. Geist, R. Taylor, C. Ekberg, P. Guilbaud, G. Modolo, S. Bourg, The SACSESS hydrometallurgy domain — an overview, *Procedia Chem.* 21 (2016) 218–222.
- [20] T. Lyseid Authen, J.-M. Adnet, S. Bourg, M. Carrott, C. Ekberg, H. Galán, A. Geist, P. Guilbaud, M. Miguiditchian, G. Modolo, C. Rhodes, A. Wilden, R. Taylor, An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, Part 2 — Homogeneous recycling, *Sep. Sci. Technol.* 57 (2022) 1724–1744.
- [21] State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry, Report, OECD-NEA, in Nuclear Science, OECD, 2018. NEA No. 7267.
- [22] M.J. Hudson, L.M. Harwood, D.M. Laventine, F.W. Lewis, Use of soft heterocyclic N-donor ligands to separate actinides and lanthanides, *Inorg. Chem.* 52 (2013) 3414–3428.
- [23] Z. Kolarik, Recent trends in the search for new extractants, *Miner. Process. Extr. Metall. Rev.* 21 (2000) 89–141.
- [24] P.J. Panak, A. Geist, Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligands, *Chem. Rev.* 113 (2013) 1199–1236.
- [25] A. Geist, P.J. Panak, Recent progress in trivalent actinide and lanthanide solvent extraction and coordination chemistry with triazinylpyridine N donor ligands, *Solvent Extr. Ion Exch.* 39 (2021) 128–151.
- [26] P. Matveev, P.K. Mohapatra, S.N. Kalmykov, V. Petrov, Solvent extraction systems for mutual separation of Am(III) and Cm(III) from nitric acid solutions. A review of recent state-of-the-art, *Solvent Extr. Ion Exch.* 39 (2021) 679–713.
- [27] P. Baron, S.M. Cornet, E.D. Collins, G. DeAngelis, G. Del Cul, Y. Fedorov, J. P. Glatz, V. Ignatiev, T. Inoue, A. Khaperskaya, I.T. Kim, M. Kormilitsyn, T. Koyama, J.D. Law, H.S. Lee, K. Minato, Y. Morita, J. Uhlir, D. Warin, R. J. Taylor, A review of separation processes proposed for advanced fuel cycles based on technology readiness level assessments, *Prog. Nucl. Energy* 117 (2019), 103091.
- [28] H. Boussier, R. Malmbeck, G. Marucci, The European pyrometallurgical processing research program PYROREP: main issues, *Global 2003: Global 2003: Atoms for Prosperity: Updating Eisenhower's Global Vision for Nuclear Energy* (2003) 966–975.
- [29] Status and Trends, Pyroprocessing of Spent Nuclear Fuels, Report, IAEA, Vienna, Austria, 2021, pp. 1–150. IAEA-TECDOC-1967.

- [30] M.J. Hudson, An introduction to some aspects of solvent extraction chemistry in hydrometallurgy, *Hydrometallurgy* 9 (1982) 149–168.
- [31] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533–3539.
- [32] Separation of Actinides and Long-lived Fission Products from High-level Radioactive Wastes (A review), Report, Z. Kolarik, Kernforschungszentrum Karlsruhe, Institut für Heisse Chemie, Karlsruhe, 1991, pp. 1–64. KfK 4945.
- [33] Z. Kolarik, U. Müllich, F. Gassner, Selective extraction of Am(III) over Eu(III) by 2,6-ditriazolyl- and 2,6-ditriazinylpyridines, *Solv. Extr. Ion Exch.* 17 (1999) 23–32.
- [34] New partitioning techniques for minor actinides. Final Report, NEWPART, C. Madic, M.J. Hudson, J.O. Liljenzin, J.P. Glatz, R. Nannicini, A. Facchini, Z. Kolarik, R. Odoj, European Commission Brussels, 2000, Project report EUR 19149.
- [35] Partnew - New solvent extraction processes for minor actinides - final report, C. Madic, F. Testard, M.J. Hudson, J.O. Liljenzin, B. Christiansen, M. Ferrando, A. Facchini, A. Geist, G. Modolo, A. Gonzalez-Espartero, J.d. Mendoza, France, 2004, Report No.: CEA-R-6066.
- [36] F.W. Lewis, L.M. Harwood, M.J. Hudson, Synthesis of Ligands For Use in Actinide Extraction Patent, The University of Reading, 2009. VolWO2011077081A1 (Ed.: WO).
- [37] G.R. Choppin, Comparative solution chemistry of the 4f and 5f elements, *J. Alloys Compd.* 223 (1995) 174–179.
- [38] Ed. M.J. Hudson, F.W. Lewis, L.M. Harwood, M. Harmata, *Strategies and Tactics in Organic Synthesis*, 9, Academic Press, 2013, pp. 177–202. Ed.
- [39] P.W. Huang, C.Z. Wang, Q.Y. Wu, J.H. Lan, Z.F. Chai, W.Q. Shi, Quantum chemical studies of selective back-extraction of Am(III) from Eu(III) and Cm(III) with two hydrophilic 1,10-phenanthroline-2,9-bis-triazolyl ligands, *Radiochim. Acta* 108 (2020) 517–526.
- [40] G. Modolo, R. Odoj, Method for separating trivalent americium from trivalent curium, European Patent EP1664359A1 (2003).
- [41] G. Modolo, P. Kluxen, A. Geist, Demonstration of the LUCA process for the separation of americium(III) from curium(III), californium(III), and lanthanides (III) in acidic solution using a synergistic mixture of bis(chlorophenyl) dithiophosphinic acid and tris(2-ethylhexyl)phosphate, *Radiochim. Acta* 98 (2010) 193–201.
- [42] S. Chapron, C. Marie, V. Pacary, M.T. Duchesne, G. Arrachart, S. Pellet-Rostaing, M. Miguiditchian, Separation of americium by liquid-liquid extraction using diglycolamides water-soluble complexing agents, *Procedia Chem.* 21 (2016) 133–139.
- [43] S. Chapron, C. Marie, G. Arrachart, M. Miguiditchian, S. Pellet-Rostaing, New insight into the americium/curium separation by solvent extraction using diglycolamides, *Solv. Extr. Ion Exch.* 33 (2015) 236–248.
- [44] M.C. Charbonnel, C. Berthon, L. Berthon, N. Boubals, F. Burdet, M.T. Duchesne, P. Guibaud, N. Mabilé, S. Petit, N. Zorz, Complexation of Ln(III) and Am(III) with the Hydrosoluble TEDGA: speciation and thermodynamics studies, *Procedia Chem.* 7 (2012) 20–26.
- [45] M.J. Bollesteros, J.N. Calor, S. Costenoble, M. Montuir, V. Pacary, C. Sorel, F. Burdet, D. Espinoux, X. Hérés, C. Eysseric, Implementation of americium separation from a PUREX raffinate, *Procedia Chem.* 7 (2012) 178–183.
- [46] V. Vanel, M.J. Bollesteros, C. Marie, M. Montuir, V. Pacary, F. Antégnard, S. Costenoble, V. Boyer-Deslys, Consolidation of the EXAm process: towards the reprocessing of a concentrated PUREX raffinate, *Procedia Chem.* 21 (2016) 190–197.
- [47] M. Miguiditchian, V. Vanel, C. Marie, V. Pacary, M.C. Charbonnel, L. Berthon, X. Hérés, M. Montuir, C. Sorel, M.J. Bollesteros, S. Costenoble, C. Rostaing, M. Masson, C. Poinssot, Americium recovery from highly active PUREX raffinate by solvent extraction: the EXAm process. a review of 10 years of R&D, *Solv. Extr. Ion Exch.* 38 (2020) 365–387.
- [48] P. Baron, M. Lecomte, B. Boullis, N. Simon, D. Warin, Separation of the Long Lived radionuclides: Current status and Future R&D Program in France, Conference Paper, New Orleans, United States, 2003. *GLOBAL 2003*.
- [49] N. Boubals, C. Wagner, T. Dumas, L. Chanac, G. Manie, P. Kaufholz, C. Marie, P. J. Panak, G. Modolo, A. Geist, P. Guibaud, Complexation of actinide(III) and lanthanide(III) with HTPAEN for a separation of americium from curium and lanthanides, *Inorg. Chem.* 56 (2017) 7861.
- [50] V. Vanel, C. Marie, P. Kaufholz, M. Montuir, N. Boubals, A. Wilden, G. Modolo, A. Geist, C. Sorel, Modeling and flowsheet design of an am separation process using TODGA and H₄TPAEN, *Proc. Chem.* 21 (2016) 223–230.
- [51] S. Gracia, G. Arrachart, C. Marie, S. Chapron, M. Miguiditchian, S. Pellet-Rostaing, Separation of Am (III) by solvent extraction using water-soluble H₄tpaen derivatives, *Tetrahedron* 71 (2015) 5321–5336.
- [52] S. Lange, A. Wilden, G. Modolo, F. Sadowski, M. Gerdes, D. Bosbach, Direct selective extraction of trivalent americium from PUREX raffinate using a combination of CyMe₄BTPhen and TEDGA—a feasibility study, *Solv. Extr. Ion Exch.* 35 (2017) 161–173.
- [53] C. Wagner, U. Müllich, A. Geist, P.J. Panak, Selective extraction of Am(III) from PUREX raffinate: the AmSel system, *Solv. Extr. Ion Exch.* 34 (2016) 103–113.
- [54] P. Weßling, M. Maag, G. Baruth, T. Sittel, F.S. Sauerwein, A. Wilden, G. Modolo, A. Geist, P.J. Panak, Complexation and extraction studies of trivalent actinides and lanthanides with water-soluble and CHON-compatible ligands for the selective extraction of americium, *Inorg. Chem.* 61 (2022) 17719–17729.
- [55] M.P. Jensen, R. Chiarizia, I.A. Shkrob, J.S. Ulicki, B.D. Spindler, D.J. Murphy, M. Hossain, A. Roca-Sabio, C. Platas-Iglesias, A. de Blas, T. Rodríguez-Blas, Aqueous complexes for efficient size-based separation of americium from curium, *Inorg. Chem.* 53 (2014) 6003–6012.
- [56] M.P. Jensen, R. Chiarizia, J.S. Ulicki, B.D. Spindler, D.J. Murphy, M.M. Hossain, A. Roca-Sabio, A. de Blas, T. Rodríguez-Blas, Solvent extraction separation of trivalent americium from curium and the lanthanides, *Solv. Extr. Ion Exch.* 33 (2015) 329–345.
- [57] Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, Novel extractant, NTAamide, and its combination with TEDGA for mutual separation of Am/Cm/Ln, *Solv. Extr. Ion Exch.* 32 (2014) 179–188.
- [58] H. Suzuki, Y. Tsubata, T. Kurosawa, M. Shibata, T. Kawasaki, S. Uraba, T. Matsumura, Highly practical and simple ligand for separation of Am(III) and Eu(III) from highly acidic media, *Anal. Sci.* 32 (2016) 477–479.
- [59] H. Suzuki, Y. Tsubata, T. Matsumura, High-performance alkyl diamide amine and water-soluble diamide ligand for separating of Am(III) from Cm(III), *Anal. Sci.* 33 (2017) 239–242.
- [60] H. Suzuki, Y. Tsubata, T. Kurosawa, H. Sagawa, T. Matsumura, Continuous extraction and separation of Am(III) and Cm(III) using a highly practical diamide amine extractant, *J. Nucl. Sci. Technol.* 54 (2017) 1163–1167.
- [61] G. Modolo, S. Nabet, Thermodynamic study on the synergistic mixture of Bis (chlorophenyl)dithiophosphinic acid and tris(2-ethylhexyl)phosphate for separation of actinides(III) from lanthanides(III), *Solv. Extr. Ion Exch.* 23 (2005) 359–373.
- [62] G. Modolo, S. Seekamp, Hydrolysis and radiation stability of the alina solvent for actinide(III)/lanthanide(III) separation during the partitioning of minor actinides, *Solv. Extr. Ion Exch.* 20 (2002) 195–210.
- [63] X. Heres, P. Baron, Increase in the separation factor between americium and curium and/or between lanthanides in a liquid-liquid extraction process, Patent WO/2011/012579, 2011.
- [64] J. Bisson, B. Dinh, P. Huron, C. Huel, A. Parex, Numerical code in the service of La Hague plant operations, *Procedia Chem.* 21 (2016) 117–124.
- [65] M.P. Jensen, R. Chiarizia, J.S. Ulicki, B.D. Spindler, D.J. Murphy, M.M. Hossain, A. Roca-Sabio, A. de Blas, T. Rodríguez-Blas, Solvent extraction separation of trivalent americium from curium and the lanthanides, *Solv. Extr. Ion Exch.* 33 (2015) 329–345.
- [66] A.V. Gelis, G.J. Lumetta, Actinide-lanthanide separation process-ALSEP, *Ind. Eng. Chem. Res.* 53 (2014) 1624–1631.
- [67] A.V. Gelis, P. Kozak, A.T. Breshears, M.A. Brown, C. Launier, E.L. Campbell, G. B. Hall, T.G. Levitskaia, V.E. Holfeltz, G.J. Lumetta, Closing the nuclear fuel cycle with a simplified minor actinide lanthanide separation process (ALSEP) and additive manufacturing, *Sci. Rep.* 9 (2019) 12842, 1.
- [68] A. Wilden, F. Kreft, D. Schneider, Z. Paparigas, G. Modolo, G.J. Lumetta, A. V. Gelis, J.D. Law, A. Geist, Countercurrent actinide lanthanide separation process (ALSEP) demonstration test with a simulated PUREX raffinate in centrifugal contactors on the laboratory scale, *Appl. Sci.* 10 (2020) 7217.
- [69] Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, T. Kimura, Extraction behavior of metal ions by TODGA, DOODA, MDOA, and NTAamide extractants from HNO₃-dodecane, *Solv. Extr. Ion Exch.* 31 (2013) 401–415.
- [70] F.W. Lewis, L.M. Harwood, M.J. Hudson, M.G. Drew, J.F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.H. Vu, J.P. Simonin, Highly efficient separation of actinides from lanthanides by a phenanthroline-derived bis-triazine ligand, *J. Am. Chem. Soc.* 133 (2011) 13093–13102.
- [71] J. Kondé, P. Distler, J. John, J. Švehla, B. Grüner, Z. Belčická, Radiation influencing of the extraction properties of the CyMe₄BTBP and CyMe₄BTPhen solvents with FS-13, *Procedia Chem.* 21 (2016) 174–181.
- [72] P. Distler, M. Mindová, J. John, V.A. Babain, M.Y. Alyapyshev, L.I. Tkachenko, E. V. Kenf, L.M. Harwood, A. Afsar, Fluorinated carbonates as new diluents for extraction and separation of f-block elements, *Solv. Extr. Ion Exch.* 38 (2020) 180–193.
- [73] P. Zsabka, K. Van Hecke, A. Wilden, G. Modolo, M. Hupert, V. Jaspers, S. Voorspoels, M. Verwerft, K. Binnemans, T. Cardinaels, Gamma radiolysis of TODGA and CyMe₄BTPhen in the ionic liquid tri-n-octylmethylammonium nitrate, *Solv. Extr. Ion Exch.* 38 (2020) 212–235.
- [74] P. Zsabka, K. Van Hecke, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans, T. Cardinaels, Selective extraction of americium from curium and the lanthanides by the lipophilic ligand CyMe₄BTPhen dissolved in aliquat-336 nitrate ionic liquid, *Solv. Extr. Ion Exch.* 38 (2020) 194–211.
- [75] F.W. Lewis, L.M. Harwood, M.J. Hudson, A. Afsar, D.M. Laventure, K. Šťastná, J. John, P. Distler, Separation of the minor actinides americium(III) and curium (III) by hydrophobic and hydrophilic BTPhen ligands: exploiting differences in their rates of extraction and effective separations at equilibrium, *Solv. Extr. Ion Exch.* 36 (2018) 115–135.
- [76] P. Distler, K. Stamborg, J. John, L.M. Harwood, F.W. Lewis, Modelling of the Am (III) – Cm(III) kinetic separation effect observed during metal ion extraction by bis-(1,2,4)-triazine ligands, *Sep. Sci. Technol.* 53 (2018) 277–285.
- [77] P. Zsabka, K. Van Hecke, L. Adriaenssens, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans, T. Cardinaels, Selective extraction of trivalent actinides using CyMe₄BTPhen in the ionic liquid aliquat-336 nitrate, *RSC Adv.* 11 (2021) 6014–6021.
- [78] S. Bourg, A. Geist, J. Narburt, The EURATOM FP7 project on actinide separation from spent nuclear fuels, *Nukleonika* 60 (2015) 809–814.
- [79] C. Marie, P. Kaufholz, V. Vanel, M.T. Duchesne, E. Russello, F. Faroldi, L. Baldini, A. Casnati, A. Wilden, G. Modolo, M. Miguiditchian, Development of a selective americium separation process using H₄TPAEN as water-soluble stripping agent, *Solv. Extr. Ion Exch.* 37 (2019) 313–327.
- [80] J. Borriani, A. Favre-Reguillon, M. Lemaire, S. Gracia, G. Arrachart, G. Bernier, X. Hérés, C. Hill, S. Pellet-Rostaing, Water soluble PDCA derivatives for selective Ln(III)/An(III) and Am(III)/Cm(III) separation, *Solv. Extr. Ion Exch.* 33 (2015) 224–235.

- [81] N. Chatterton, Y. Bretonnière, J. Pécaut, M. Mazzanti, An efficient design for the rigid assembly of four bidentate chromophores in water-stable highly luminescent lanthanide complexes, *Angew. Chem. Int. Ed.* 44 (2005) 7595–7598.
- [82] P. Kaufholz, G. Modolo, A. Wilden, F. Sadowski, D. Bosbach, C. Wagner, A. Geist, P.J. Panak, F.W. Lewis, L.M. Harwood, Solvent extraction and fluorescence spectroscopic investigation of the selective Am(III) complexation with TS-BTPhen, *Solv. Extr. Ion Exch.* 34 (2016) 126–140.
- [83] P. Kaufholz, F. Sadowski, A. Wilden, G. Modolo, F.W. Lewis, A.M. Smith, L. M. Harwood, TS-BTPhen as a promising hydrophilic complexing agent for selective Am(III) separation by solvent extraction, *Nukleonika* 60 (2015) 815–820.
- [84] The Selective Separation of Am(III) from Highly Radioactive PUREX Raffinate Kaufholz Doctoral thesis, P., RWTH Aachen, Jülich, Germany, 2017.
- [85] F.W. Lewis, L.M. Harwood, M.J. Hudson, A. Geist, V.N. Kozhevnikov, P. Distler, J. John, Hydrophilic sulfonated bis-1,2,4-triazine ligands are highly effective reagents for separating actinides(III) from lanthanides(III) via selective formation of aqueous actinide complexes, *Chem. Sci.* 6 (2015) 4812–4821.
- [86] E. Mossini, E. Macerata, A. Wilden, P. Kaufholz, G. Modolo, N. Iotti, A. Casnati, A. Geist, M. Mariani, Optimization and single-stage centrifugal contactor experiments with the novel hydrophilic complexant PyTri-Diol for the i-SANEX process, *Solv. Extr. Ion Exch.* 36 (4) (2018) 1–14.
- [87] E. Macerata, E. Mossini, S. Scaravaggi, M. Mariani, A. Mele, W. Panzeri, N. Boubals, L. Berthon, M.C. Charbonnel, F. Sansone, A. Arduini, A. Casnati, Hydrophilic clicked 2,6-bis-triazolyl-pyridines endowed with high actinide selectivity and radiochemical stability: toward a closed nuclear fuel cycle, *J. Am. Chem. Soc.* 138 (2016) 7232–7235.
- [88] A.C. Edwards, P. Mocilac, A. Geist, L.M. Harwood, C.A. Sharrad, N.A. Burton, R. C. Whitehead, M.A. Denecke, Hydrophilic 2,9-bis-triazolyl-1,10-phenanthroline ligands enable selective Am(III) separation: a step further towards sustainable nuclear energy, *Chem. Commun.* 53 (2017) 5001–5004.
- [89] P. Zsabka, T. Opsomer, K. Van Hecke, W. Dehaen, A. Wilden, G. Modolo, M. Verwerft, K. Binnemans, T. Cardinaels, Solvent extraction studies for the separation of trivalent actinides from lanthanides with a triazole-functionalized 1,10-phenanthroline extractant, *Solv. Extr. Ion Exch.* 38 (2020) 719–734.
- [90] W.H. Runde, B.J. Mincher, Higher oxidation states of americium: preparation, characterization and use for separations, *Chem. Rev.* 111 (2011) 5723–5741.
- [91] L. Donnet, J.M. Adnet, N. Faure, P. Bros, P. Brossard, F. Josso, Development of the SESAME process, Conference proceedings, in: Proceedings of the 5th International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mol, Belgium, 1998.
- [92] S. Picart, D. Chartier, L. Donnet, J.M. Adnet, Electrochemical oxidation of americium in nitric medium: study of reaction mechanisms, Report, CEA Saclay, Direction du Cycle du Combustible, 91 - Gif-sur-Yvette (France), 383 (2000) 192–197, Report No.: R-5892.
- [93] C. Poinssot, J.M. Adnet, S. Bourg, B. Boullis, E. Tournon, 1992-2017: 25 years of success story on minor actinides partitioning processes development, conference paper, in: Proceedings of the International Conference on Fast Reactors and Related Fuel Cycles Next Generation Nuclear Systems for Sustainable Development (FR17), Yekaterinburg, Russia, 2017.
- [94] C. Madic, M. Lecomte, P. Baron, B. Boullis, Separation of long-lived radionuclides from high active nuclear waste, *C. R. Phys.* 3 (2002) 797–811.
- [95] M. Hara, The chemistry of americium. I. a study of the preparation of Am (V) and its behavior by means of TTA extraction, *Bull. Chem. Soc. Jpn.* 43 (1970) 89–94.
- [96] M. Hara, S. Suzuki, The chemistry of americium. II. The behavior of Am(III), Am (V), and Am(VI) in column chromatography, with Bis(2-ethylhexyl)phosphoric acid used as the extractant, *Bull. Chem. Soc. Jpn.* 47 (1974) 635–638.
- [97] H.P. Holcomb, Analytical oxidation of americium with sodium perxenate, *Anal. Chem.* 37 (1965) 415.
- [98] B.J. Mincher, N.C. Schmitt, M.E. Case, A TRUEX-based separation of americium from the lanthanides, *Solv. Extr. Ion Exch.* 29 (2011) 247–259.
- [99] L. Martin, B. Mincher, N. Schmitt, Extraction of americium(VI) by a neutral phosphonate ligand, *J. Radioanal. Nucl. Chem.* 282 (2009) 523–526.
- [100] B.J. Mincher, L.R. Martin, N.C. Schmitt, Tributylphosphate extraction behavior of bismuthate-oxidized americium, *Inorg. Chem.* 47 (2008) 6984–6989.
- [101] B.J. Mincher, L.R. Martin, N.C. Schmitt, Diamylmethylphosphonate solvent extraction of Am(VI) from nuclear fuel raffinate simulant solution, *Solv. Extr. Ion Exch.* 30 (2012) 445–456.
- [102] K. McCann, B.J. Mincher, N.C. Schmitt, J.C. Braley, Hexavalent actinide extraction using N,N-Dialkyl amides, *Ind. Eng. Chem. Res.* 56 (2017) 6515–6519.
- [103] J.D. Law, B.J. Mincher, R.D. Tillotson, N.C. Schmitt, T.S. Grimes, Oxidation and extraction of Am(VI) using a monoamidic extractant in 3D printed centrifugal contactors, *J. Radioanal. Nucl. Chem.* 318 (2018) 35–41.
- [104] Y.M. Kulyako, D.A. Malikov, T.I. Trofimov, S.A. Perevalov, K.S. Pilyushenko, S. E. Vinokurov, B.F. Myasoedov, Separation of americium and curium in nitric acid solutions via oxidation of Am(III) by bismuthate and perxenate ions, *Radiochemistry* 62 (2020) 581–586.
- [105] S.I. Sinkov, G.J. Lumetta, Americium(III) oxidation by copper(III) periodate in nitric acid solution as compared with the action of Bi(V) compounds of sodium, lithium, and potassium, *Radiochim. Acta* 103 (2015) 541–552.
- [106] R.A. Penneman, T.K. Keenan, The Radiochemistry of Americium and Curium, The National Academies Press, Washington, DC, 1960.
- [107] L.B. Werner, Method For the Separation of Americium from Solutions Containing the same, Patent, United States of America, 1951 US Pat. 577,097.
- [108] H. Mitsuo, S. Shin, The Chemistry of Americium. III. The coprecipitation of Am (III), Am(V), and Am(VI) by some fluorides and phosphates 48 (1975) 1431–1435.
- [109] H. Mitsuo, S. Shin, The Chemistry of Americium. IV. The stability of Am(V) and Am(VI) in nitric acid solutions and in the solutions containing ozone gas fluoride, or phosphate ions, *Bull. Chem. Soc. Jpn.* 52 (1979) 1041–1045.
- [110] M. Postel, E. Duñach, Bismuth derivatives for the oxidation of organic compounds, *Coord. Chem. Rev.* 155 (1996) 127–144.
- [111] W. Rigby, Oxidations with sodium bismuthate: glycol fission and related reactions, *J. Chem. Soc.* (1950) 1907–1913.
- [112] E.P. Horwitz, W.W. Schulz, The TRANSuranium EXtraction (TRUEX) process: a vital tool for disposal of US defense nuclear waste, Report, United States, 1990, p. 9, CONF-900579–2.
- [113] J.M. Richards, R. Sudowe, Separation of americium in high oxidation states from curium utilizing sodium bismuthate, *Anal. Chem.* 88 (2016) 4605–4608.
- [114] J.M. Richards, B.J. Mincher, Selective partitioning of ruthenium from nitric acid media, *Solv. Extr. Ion Exch.* 35 (2017) 49–60.
- [115] K. McCann, D.M. Brigham, S. Morrison, J.C. Braley, Hexavalent americium recovery using copper(III) periodate, *Inorg. Chem.* 55 (2016) 11971–11978.
- [116] R.M. Diamond, K. Street, G.T. Seaborg, An ion-exchange study of possible hybridized 5f bonding in the actinides, *J. Am. Chem. Soc.* 76 (1954) 1461–1469.
- [117] K. Street, G.T. Seaborg, The separation of americium and curium from the rare earth elements, *J. Am. Chem. Soc.* 72 (1950) 2790–2792.
- [118] K.J. Street, Curium-Americium Separation and Purification process, Patent, 86, U. S. P. Office), United States of America, 1955, p. 739. Vol. US Pat. 2,711,362Ed.
- [119] G.H. Higgins, W.W.T. Crane, Large Scale Method For the Production and Purification of curium, Patent, U. S. P. Office), United States of America, 1959. VolUS Pat. 2,887,358Ed.
- [120] W.E. Hale, J.T. Lowe, Rapid, gram-scale separation of curium from americium and lanthanides by cation exchange chromatography, *Inorg. Nucl. Chem. Letters* 5 (1969) 363–368.
- [121] Simultaneous Recovery and Purification of Pm, Am and Cm by Use of Alternating DTPA and NTA Cation Exchange Flowsheets, E. J. Wheelwright, F. P. Roberts, L. A. Bray, G. L. Ritter and A. L. Bolt, USAEC Report BNWL-SA. 1492, Battelle Northwest Laboratory (March 6, 1968).
- [122] B.F. Myasoedov, T.A. Maryutina, M.N. Litvina, D.A. Malikov, Y.M. Kulyako, B. Y. Spivakov, C. Hill, J.M. Adnet, M. Lecomte, C. Madic, Americium(III)/curium (III) separation by countercurrent chromatography using malonamide extractants, *Radiochim. Acta* 93 (2005) 9–15.
- [123] S. Usuda, K. Yamanishi, H. Mimura, Y. Sasaki, A. Kirishima, N. Sato, Y. Niibori, Separation of Am and Cm by using TODGA and DOODA(C8) adsorbents with hydrophilic ligand - nitric acid solution, *J. Radioanal. Nucl. Chem.* 303 (2015) 1351–1355.
- [124] T. Suzuki, K. Otake, M. Sato, A. Ikeda, M. Aida, Y. Fujii, M. Hara, T. Mitsugashira, M. Ozawa, Separation of americium and curium by use of tertiary pyridine resin in nitric acid/methanol mixed solvent system, *J. Radioanal. Nucl. Chem.* 272 (2007) 257–262.
- [125] W.C. Johnson, L.L. Quill, F. Daniels, Rare earths separation developed on manhattan project, *J. Chem. Eng. News* 25 (1947) 2494.
- [126] M.I. Ojovan, W.E. Lee, Glassy wasteforms for nuclear waste immobilization, *Metall. Mater. Trans. A* 42 (2011) 837–851.
- [127] 1976 Hanford americium accident, Report, K.R. Heid, B.D. Breitenstein, H.E. Palmer, B.J. McMurray, N. Wald, United States, Report No. TID-28938, 1979.
- [128] G.W. Mason, A.F. Bollmeier, D.F. Peppard, Partition of oxidized americium from actinides(III) and lanthanides(III), *J. Inorg. Nucl. Chem.* 32 (1970) 1011–1022.
- [129] G.W. Mason, A.F. Bollmeier, D.F. Peppard, Separation of Americium and Curium, Patent, United States of America, 1973 US Pat. 3,743,696.
- [130] J.D. Burns, T.C. Shehee, A. Clearfield, D.T. Hobbs, Separation of americium from curium by oxidation and ion exchange, *Anal. Chem.* 84 (2012) 6930.
- [131] R. Liu, Y. Wei, Y. Xu, S. Usuda, S. Kim, H. Yamazaki, K. Ishii, Properties evaluation of isohexyl-BTP/SiO₂-P extraction resin for potential direct separation of minor actinides from HLLW, in: Proceedings of the Conference Proceedings, Makuhari, Japan, GLOBAL, 2011. Paper No. 357146.
- [132] A.V. Gelis, P. Kozak, A.T. Breshears, M.A. Brown, C. Launier, E.L. Campbell, G. B. Hall, T.G. Levitskaia, V.E. Holfeltz, G.J. Lumetta, Closing the nuclear fuel cycle with a simplified minor actinide lanthanide separation process (ALSEP) and additive manufacturing, *Sci. Rep.* 9 (2019) 12842.
- [133] P. Weßling, M. Maag, G. Baruth, T. Sittel, F.S. Sauerwein, A. Wilden, G. Modolo, A. Geist, P.J. Panak, Complexation and extraction studies of trivalent actinides and lanthanides with water-soluble and CHON compatible ligands for the selective extraction of americium, *Inorg. Chem.* 61 (2022) 17719–17729.
- [134] M. Miguiditchian, V. Vanel, C. Marie, V. Pacary, M.C. Charbonnel, L. Berthon, X. Hères, M. Montuir, C. Sorel, M.J. Bollesteros, S. Costenoble, C. Rostaing, M. Masson, C. Poinssot, Americium recovery from highly active PUREX raffinate by solvent extraction: the EXAm process. a review of 10 years of R&D, *Solv. Extr. Ion Exch.* 38 (2020) 365–387.