An Overview of Solvent Extraction Processes Developed in Europe for Advanced Nuclear Fuel Recycling, Part 1 — Heterogeneous Recycling

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Abstract. The hydrometallurgical separation concepts for the heterogeneous recycling of irradiated nuclear fuel developed in Europe are presented and discussed. Most of these concepts were developed within European collaborative projects and involve solvent extraction processes separating trivalent minor actinides (with a focus on americium) from the raffinate solution from processes such as PUREX (Plutonium Uranium Reduction Extraction) or an evolution of PUREX. Depending on the process chemistry applied, process schemes each consisting of one, two or three solvent extraction cycles are required to obtain a pure americium product. The various solvent extraction processes are briefly introduced. The most suitable choices are selected, and the process schemes are compared to one another.

Keywords. Nuclear fuel, heterogeneous recycling, actinides, solvent extraction, processes

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Introduction

Nuclear power contributed 10.3% of the global electricity generation in 2017, according to the International Energy Agency (IEA). Per year this requires approximately 65,000 tons of natural uranium to fabricate nuclear fuel and produces approximately 10,000 tons of irradiated nuclear fuel.

Irradiated nuclear fuel from reactors must be managed by interim storage to reduce the radioactivity and heat generated followed by (a) encapsulation and final disposal in a deep geological repository or (b) reprocessing to enable recycle of valuable materials to produce new fuel, with final disposal of the residual high level waste (HLW) plus secondary (intermediate level) wastes from reprocessing.

In contrast to conventional fuels (coal, gas oil, etc.) which are burnt completely, nuclear fuel is consumed only to a small extent. The irradiated nuclear fuel unloaded from a typical light water reactor (burn-up of 40 GWd/t) contains 95% fertile U-238, residual fissile U-235 (0.8 %), fission products (3-4%) and approximately 1% transuranium elements (TRU: neptunium, plutonium, americium and curium). With a "once-through" fuel cycle (i.e. a fuel cycle without reprocessing and recycling), natural uranium utilisation is less than 0.7%.[1] Recycling the useful components, most notably uranium and plutonium, results in an improved utilisation of resources of approximately 1%. A dramatic increase in natural uranium utilisation is achievable by deploying multiple recycling in fast reactors, a concept fundamentally demonstrated in the United States and elsewhere as early as the 1950s.[2]

In France, for example, the stockpile of depleted uranium (approximately 300,000 tons) would render further uranium mining unnecessary for centuries if plutonium multi-recycling was pursued.[1, 3-5] Consequently, the overall ecological impact of electricity generation by nuclear fission would also be reduced.[1]

In addition, recycling americium would significantly reduce the burden of HLW long term management and optimise the utilisation of a final deep geological repository: the decay heat of HLW determines how densely the HLW containers can be packed in a final repository. This decay heat is initially governed by fission products and after approximately 60 years by americium. Thus, removing americium from the HLW and storing the remaining HLW (for approximately 100 years for short lived fission products to decay) before emplacing it in a final repository would significantly increase a geological repository's capacity or reduce its size required to accommodate a given amount of HLW.[6]

Many countries deploying nuclear electricity generation have pursued R&D programmes to develop advanced nuclear fuel cycle strategies.[7] In Europe, the development of the chemical separations required for such strategies was triggered by two French waste management acts (1991and 2006) and has found support from EURATOM-funded research programmes since the early 1990's. Continuously evolving from initially small programmes,[8-9] a sequence of programmes dedicated to developing actinide separation processes and the related chemistry was executed: NEWPART (1997–1999),[10] PARTNEW (2000–2003),[11] EUROPART (2004–2007),[12] ACSEPT (2008–2012),[13] SACSESS (2013–2016).[14]

Now, well into the current programme, GENIORS (2017–2021),[15-16] we take the opportunity to sum up the development of actinide separation processes developed in Europe for heterogeneous recycling strategies. Processes for homogeneous recycling will be summarised in Part 2 (see below for a definition of homogeneous and heterogeneous recycling).

Recycling strategies

Taking full advantage of the benefits described above requires multiple recycling of the TRU, most notably plutonium and americium, in reactors with a fast neutron spectrum.[17] Recycling actinides requires separating them from fission products and, depending on the recycling strategy, from one another.

Homogeneous and heterogeneous recycling

Homogeneous recycling describes a fuel cycle in which TRU are contained together in the fuel and homogeneously distributed in the reactor core. *Heterogeneous recycling,* in contrast, relies on MOX driver fuel (containing uranium, plutonium and optionally, neptunium) with dedicated targets containing americium (or potentially americium and curium) distributed in specific locations in the core.

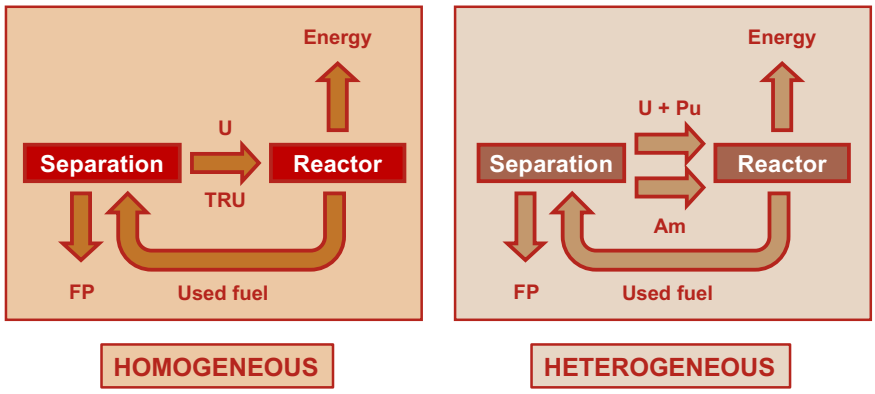

Figure 1. Schematic illustration of homogeneous and heterogeneous recycling. FP = fission products.

The reactors and fuels aspects related to heterogeneous and homogeneous recycling have been compiled and compared against one another in a publication by the OECD-NEA.[17] As far as separation processes are concerned, heterogeneous recycling requires generating separate product streams containing uranium, plutonium (and possibly neptunium) on one hand and americium (or americium and curium) on the other hand. While such separations are suitable for homogeneous recycling, too, dedicated separation processes addressing homogeneous recycling are being developed nevertheless. Such processes typically separate uranium in a first step, followed by a second step co-separating the TRU.[18-22]

The required separations are achievable using either **non-aqueous (pyrometallurgical)**[23-24] or **aqueous (hydrometallurgical)** processes. The latter, usually using solvent extraction-based processes, has successfully been applied for separating uranium and plutonium: the PUREX process is applied at the industrial scale, see the reprocessing plants at La Hague (France) and at Sellafield (UK).[25]

Aqueous separation processes for heterogeneous recycling

Heterogeneous recycling requires separating uranium, plutonium and neptunium from americium and curium and from the fission and corrosion products in a first step. This is achieved e.g. by the well-established PUREX process (or by evolutionary PUREX designs,[26-28] allowing a co-recovery and a co-management of U and Pu). Uranium, plutonium and — following some modifications to the process, also neptunium[29-30] — are routed to the product streams. Americium and curium, having a very low affinity for tri-*n*-butyl phosphate (TBP, the extractant used in the PUREX process) are directed to the raffinate solution (high level liquid waste, HLLW), together with fission and corrosion products. To recover americium (or americium and curium) from this solution in a second step, a suite of solvent extraction processes has been developed internationally.[7, 31-36] The chemical

similarity of americium and curium (typically being trivalent cations in solution, An(III)) and the "fission lanthanides" (Ln(III) = La(III)–Dy(III)) require a demanding process chemistry.

In Europe, substantial challenges were met in early projects, NEWPART, PARTNEW and EUROPART,[10-12] developing ligands and potential processes to achieve the challenging An(III)/Ln(III) separation.[37-39] Following the extraordinary successes of these projects, later projects, ACSEPT and SACSESS,[13-14] focused on defining and testing 'reference' processes. The selection of such reference processes was dominated by the process chemistry, i.e. considering properties such as separation factors, radiolytic stability, kinetics etc. These choices demanded completely incinerable extractants *(CHON,*[8] to minimise the generation of solid waste) being able to process solutions containing elevated concentrations of nitric acid (in order to prevent dilution or denitration steps). In most cases, laboratory-scale solvent extraction flow-sheet tests confirmed the performance of these references processes.

More recently, in SACSESS and GENIORS,[14-15] these reference processes are being assessed, focusing on the overall complexity and the associated engineering issues. These issues (safety, solvent clean up, choice of contactors and scalability, interfacing with other parts of the process etc.) determine whether a process has the potential for being industrialised. At the current stage of R&D, simpler processes are assumed to be more economic to deploy, largely due to the capital and operational expenditure associated with the downstream processing of complex and multiple waste streams. Future projects are enabled to efficiently focus limited resources on the most promising options and their optimisation, to a point at which industry can take over implementation.

Over the course of the collaborative European projects the emphasis has shifted from the co-recovery of americium and curium to recovering only americium. This reflects the increasing sophistication and fundamental understanding of the separation processes, that are enabling more challenging separations to be attempted, as well as the realisation that, whilst curium causes significant problems with target fabrication and irradiation, the majority of the benefits to the HLW disposal in the geological repository can be obtained by the recycling of americium alone. Figure 2 therefore gives an overview of aqueous post-PUREX processes for heterogeneous recycling which were developed in Europe, and how these processes connect to obtain an americium product.

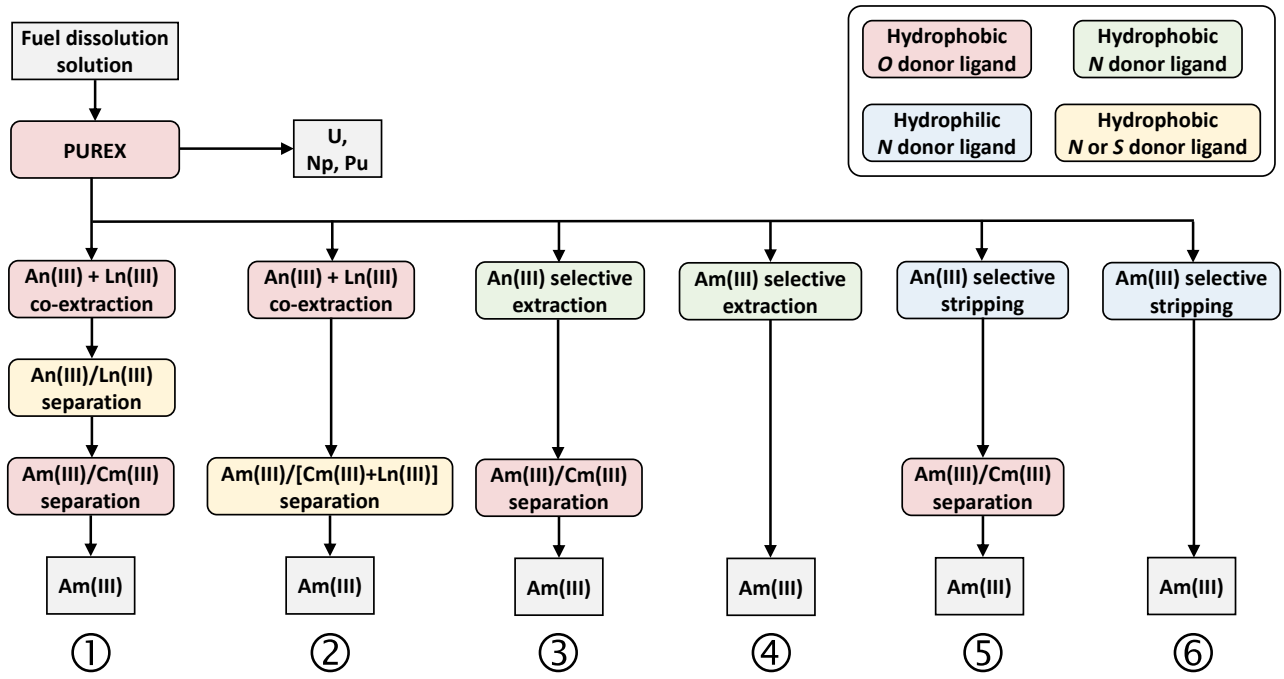

Figure 2. A schematic overview of post-PUREX solvent extraction processes for heterogeneous recycling developed in Europe. The colour scheme indicates the kind of extracting or complexing agents used (see legend).

The individual processes are represented by boxes in Figure 2. They are briefly described below, focusing on aspects such as upstream and downstream compatibility and generation of secondary waste. Decontamination factors achieved in lab-scale process demonstration trials are not reported (stricter purity requirements can quite easily be met by e. g. increasing the number of stages); such data are found in the original literature. Acronyms for extracting and complexing agents are explained in the Appendix.

An(III) and Ln(III) co-extraction

Earlier schemes for separating An(III) from HLLW were based on a process co-separating An(III) and chemically similar fission lanthanides(III), Ln(III), from HLLW, separating them from other fission products and corrosion products.

Processes known as DIAMEX were developed, using malonamide extracting agents such as DMDOHEMA.[40-43] These processes are directly compatible with the PUREX process, requiring no feed adjustment such as adjustment of the nitric acid concentration between PUREX and DIAMEX solvent extraction cycles. The product solution contains An(III) and Ln(III) in dilute nitric acid. The raffinate contains non-lanthanide fission products and corrosion products plus some complexing agents (added to prevent the co-extraction of Fe, Zr, Mo and Pd) in nitric acid. The raffinate is suitable for further treatment by vitrification.

Diglycolamide extracting agents[44-47] were later proposed[48-50] to co-extract An(III) and Ln(III). Spiked[51] and hot[52] process tests† using a solvent containing 0.2 mol/L TODGA + 0.5 mol/L TBP in TPH[53] were performed using 32 stages of centrifugal contactors. The raffinate solution, containing non-lanthanide fission products and corrosion products plus complexing agents, is suitable for vitrification. The product solution contains An(III) and Ln(III) in 0.01 mol/L HNO_3.

An(III)/Ln(III) separation

The product solution from above processes, containing Am(III), Cm(III), Ln(III) (more exactly, Y(III) and the "fission lanthanides", La(III)–Dy(III)) in nitric acid, is subjected to further processes to obtain a pure Am(III) + Cm(III) fraction. Since An(III) and Ln(III) are chemically similar they cannot be separated using usual extracting agents which co-ordinate via oxygen donor atoms. Separation is based on the fact that An(III) form slightly stronger complexes with soft donor atoms than Ln(III).[54-55] Thus, extracting agents coordinating via nitrogen or sulphur donor atoms are used to extract An(III) preferentially over Ln(III) by processes known as SANEX (selective actinide extraction).

A breakthrough was achieved in 1999 with the development of aromatic dithiophosphinic acids[56] and of alkylated 2,6-bis(1,2,4-triazin-3-yl)-pyridines (BTP),[57] both ligand families enabling the selective extraction of An(III) from acidic solutions.

A spiked test was performed in a 24-stage centrifugal contactor setup using a solvent comprising $(ClPh)_2$-PSSH acid and TOPO in *tert*-butyl benzene.[58] This process requires a feed acidity of ≤ 0.5 mol/L, making it directly compatible to An(III)-Ln(III) co-extraction processes. The product solution contains An(III) in 1.5 mol/L HNO_3, the raffinate contains Ln(III) in 0.6 mol/L HNO_3 and is suitable for vitrification. The sulphur and phosphorus content of the solvent is a drawback, giving rise to secondary waste from solvent clean-up.

Process tests using BTP extracting agents were less successful due to the limited chemical and radiolytic stability of early BTP compounds.[59] Following numerous less successful approaches,[60-63] a modification to the BTP structure was made to develop the bis-triazinyl bipyridine (BTBP) ligand $CyMe_4$-BTBP. This compound was more chemically and radiolytically stable than the BTPs.[64-65] Spiked[66] and hot[67] tests using $CyMe_4$-BTBP were performed in 20 or 16-stage centrifugal contactor

† Here we refer to spiked tests as experiments using a simulant solution containing a representative selection of actinides and fission products. Spiked tests may be conducted either with trace or realistic concentrations of actinides; fission products are replaced with the stable elements to avoid high beta/gamma dose rates. Spiked tests can usually be conducted in designated radiochemical fume hoods or glove boxes. Hot tests refer to experiments with dissolved fuels or targets after irradiation in a reactor. These solutions are highly active and require shielded cells due to the beta/gamma radiation levels.

setups. Highly pure Am(III) + Cm(III) product solutions were obtained, containing only small fractions of the Ln(III) inventory. This process requires a feed nitric acid concentration of 1.3–2 mol/L, making it directly compatible to An(III)-Ln(III) co-extraction processes following feed nitric acid concentration adjustment by addition of concentrated nitric acid. The product solution contains An(III) in a 0.5 mol/L glycolate solution, the raffinate contains Ln(III) in ≈ 1 mol/L HNO_3 and is suitable for vitrification. However, the relatively slow kinetics of $CyMe_4$-BTBP requires larger equipment.

Am(III)/Cm(III) separation

Processes yielding an An(III) product solution containing both americium and curium require an additional separation if only americium is to be recycled (curium isotopes do not significantly contribute to long-term heat generation and radiotoxicity). Due to the similar chemical behaviour of Am(III) and Cm(III), most extracting agents have a low selectivity (with most of the compounds studied showing a separation factor of approximately 1.6[65, 68-69]).

Despite this low selectivity, separation is achieved by using a sufficient number of stages. Indeed, a successful Am(III)/Cm(III) separation test was performed using the extracting agent DMDOHEMA in a 56-stage centrifugal contactor setup.[70] This process requires a feed nitric acid concentration in the range of 3 mol/L. The impact of any complexing agents present in the feed solution (coming from an upstream process) would have to be assessed. The raffinate solution (Cm(III) in nitric acid) is suitable for vitrification. The product solution is Am(III) in dilute nitric acid.

A different approach exploits the fact that in contrast to Cm(III), Am(III) can be oxidised to higher valences, enabling separation by common extracting agents.[71] This approach was studied at the CEA[72-73] but abandoned later due to issues with upstream compatibility and with quantitatively oxidising and extracting Am due to parasitic reactions. Nevertheless, new processes based on this concept are currently under development in the USA.[74-77]

Separation of Am(III) from Cm(III) and Ln(III)

Extracting only Am(III) from the product solution of an An(III)-Ln(III) co-extraction process requires a solvent preferentially extracting Am(III) over Cm(III) and Ln(III) — the other fission and the corrosion products already being separated in the upstream process. A synergistic system comprising $(ClPh)_2PSSH$ and T2EHP yields an exceptionally high Am(III)/Cm(III) separation factor of $SF_{Am(III)/Cm(III)} \approx 7$ and Am(III)/Ln(III) separation factors > 1000.[78] This system was successfully applied with a 24-stage flow-sheet.[79] However, this process requires a feed nitric acid concentration of < 0.1 mol/L; additionally, 0.5 mol/L $NaNO_3$ is added to warrant satisfactory phase separation in

the extraction section. The product solution contains Am(III) in ≈ 0.7 mol/L HNO_3, the raffinate contains Cm(III) and lanthanides(III) in ≈ 0.1 mol/L HNO_3 + 0.15 mol/L $NaNO_3$. The nitrate salt content may require adapting the formulation of the glass in the vitrification process. The sulphur and phosphorus content of the solvent is a drawback, giving rise to secondary waste from solvent clean-up.

Selective An(III) extraction

During EUROPART, omitting a prior An(III)-Ln(III) co-extraction process and extracting Am(III) and Cm(III) directly from HLLW was proposed. However, developing and demonstrating such a process took several more years.

A solvent containing $CyMe_4$-BTBP and TODGA in a kerosene/octanol diluent directly extracts Am(III) and Cm(III) from HLLW.[80] The co-extraction of Zr(IV) and Mo(VI) is suppressed by adding oxalic acid to the feed. A flow-sheet was developed[81] and tested[82] using a spiked surrogate feed solution. This flow-sheet manages co-extracted Pd(II) in a selective Pd(II) stripping section using L-cysteine before stripping Am(III) and Cm(III) using a glycolate solution. Ni(II) and Cd(II), which are also co-extracted, stay in the organic phase, requiring additional solvent treatment.

This process known as 1-cycle SANEX directly uses HLLW as a feed solution; nitric acid concentration adjustment is not required. The product solution contains An(III) in a 0.5 mol/L glycolate solution, the raffinate contains fission products and oxalic acid in ≈ 2 mol/L HNO_3. A second raffinate solution is generated, containing Pd(II) + 10 mmol/L L-cysteine in 1 mol/L HNO_3. The sulphur content of this solution due to L-cysteine may pose problems during vitrification. A drawback is the rather slow kinetics, in common with the An(III)/Ln(III) separation processes using $CyMe_4$-BTBP.[66-67]

Selective Am(III) extraction

Based on the experience with the 1-cycle SANEX process[80-82] a solvent extraction system was developed[83] to extract only Am(III) directly from HLLW. It uses another variant of the BTP/BTBP ligand family, $CyMe_4$-BTPhen,[84] in combination with the water soluble diglycolamide, TEDGA. Exploiting the Am(III)/Cm(III) selectivity of $CyMe_4$-BTPhen and the reverse selectivity of TEDGA in a "push-pull"[85] system allows preferentially extracting Am(III) over Cm(III) and Ln(III), similarly to the $(ClPh)_2PSSH$ and T2EHP system.[78] The major difference being the $CyMe_4$-BTPhen and TEDGA system's direct compatibility with a PUREX HLLW. Bimet[86-87] is added to the aqueous feed phase to suppress Pd(II) and Ag(I) co-extraction. With Am(III)/Cm(III) separation factors in the range of 2–5, depending on experimental conditions, this system has the potential to extract only

Am(III) from HLLW. As with the 1c-SANEX process, slow kinetics and incompatibility with vitrification due to the sulphur containing Bimet are unfavourable. Consequently, no priority was given to developing and testing a flow-sheet using this system.

Selective An(III) stripping

Based on the TALSPEAK process[88-89] developed at Oak Ridge National Laboratory, USA, in the 1960's, various processes were developed using chemistry that places selectivity for An(III) over Ln(III) in the aqueous phase rather than using selective extracting agents in the organic phase. These processes use aqueous solutions containing aminopolycarboxylates such as DTPA or HEDTA to strip An(III) from a solvent loaded with An(III) and Ln(III). To make extraction from HLLW viable, neutral extracting agents such as CMPO, DMDOHEMA or TODGA are used. Ln(III) must remain in the organic phase under the low acidity conditions required to strip An(III) using aminopolycarboxylates. This is achieved either by adding an acidic extracting agent to the solvent or by adding nitrate salt to the aminopolycarboxylate solution.

TALSPEAK-based processes such as TRUSPEAK,[90] advanced TALSPEAK,[91-93] ALSEP,[94-95] SETFICS,[96-97] DIAMEX-SANEX[70] and *i*-SANEX[98] have been developed and tested. TALSPEAK chemistry is continuously being improved in the USA by synthesising systematically modified aminopolycarboxylates.[99-100]

To avoid the addition of an acidic extracting agent or of nitrate salt, stripping agents coping with nitric acid concentrations sufficient to keep Ln(III) in the TODGA solvent were developed in Europe. This marked a significant advance in the potential for industrialisation of this type of process as it removes the reliance on buffering and careful pH control needed when using aminopolycarboxylates.

SO_3-Ph-BTP was shown to be a useful An(III) stripping agent,[69] combining excellent selectivity with efficiency in nitric acid. A successful spiked process test was performed using a 32 stages centrifugal contactor setup.[101]

Due to concerns with the sulphur content of SO_3-Ph-BTP, an improved system was developed. This system uses PTD to strip actinides(III).[102] A flow-sheet for a centrifugal contactor run has been calculated;[103] a counter-current flow-sheet test is planned for the near future.

By using TODGA as extracting agent, these two processes are compatible with HLLW without requiring feed adjustment. The raffinate solutions are suitable for vitrification. Product solutions are Am(III) and Cm(III) in nitric acid containing either SO_3-Ph-BTP or PTD. However, SO_3-Ph-BTP

gives rise to sulphur-containing solid waste, which should be avoided. PTD, on the other hand, is a *CHON* compound, allowing for its destruction to gaseous products.

Selective Am(III) stripping

Some of the concepts involving selective stripping of An(III) (see *Selective An(III) stripping* above) were modified in order to obtain a pure Am(III) product solution.

The EXAm process[104-106] developed at the CEA is based on the DIAMEX-SANEX process,[70] making use of TEDGA to achieve a sufficient Am(III)/Cm(III) selectivity *($SF_{Am(III)/Cm(III)} \approx 2.6$)*. A successful hot test was performed in mixer-settler batteries. A further hot EXAm test was performed at the CEA, using a concentrated HLLW feed solution. Approximately 2.5 g americium was recovered and converted into $(U,Am)O_2$ to be irradiated in a materials test reactor.[106-107]

To replace aminopolycarboxylates with stripping agents that remain efficient at elevated acidity, two further systems were developed:

- The EURO-EXAm system uses a TODGA solvent to co-extract An(III) and Ln(III); TPAEN is used to selectively strip Am(III) from the loaded solvent.[108-110] Unfortunately, precipitation problems were encountered during counter-current centrifugal contactor runs.[111]

- Am(III) is also selectively stripped from a TODGA solvent by SO_3-Ph-BTBP[112] or SO_3-Ph-BTPhen[113] — a system termed the AmSel process. However, these systems have not yet been applied in process demonstration tests.

The above processes directly use HLLW as the feed solution, requiring no prior nitric acid concentration adjustment. The raffinate solutions are compatible with vitrification. The EXAm product solution contains Am(III), DTPA and malonate. The EURO-EXAm product solution contains Am(III) and TPAEN in $HNO_3/NaNO_3$. The product solution from a TODGA/SO_3-Ph-BTBP AmSel process would be Am(III) and 10–20 mmol/L SO_3-Ph-BTBP in ≈ 0.8 mol/L HNO_3. However, the sulphur content in the product solution would create a waste problem.

Comparing the process schemes ①–⑥

Looking at the different process schemes to separate Am(III) from HLLW (Figure 2), schemes ④ and ⑥ appear the simplest (adding one solvent extraction cycle to PUREX), scheme ① the most complex (adding three solvent extraction cycles), schemes ②, ③ and ⑤ intermediate (two additional solvent extraction cycles). However, each solvent extraction cycle contains extraction, scrubbing and

stripping stages, spent solvent regeneration cycles and various auxiliary processes. The arrows connecting the solvent extraction cycle in reality are more than a simple pipe; buffer tanks, feed adjustment, addition or destruction of auxiliary chemicals may be required to connect the solvent extraction cycles to one another. Thus, evaluating the different process schemes requires consideration of many aspects which have economic implications to the viability of the flowsheet at an industrial scale, such as the number of stages required to achieve certain decontamination factors, waste generation, upstream and downstream compatibility, solvent clean-up, safety of operation etc.

Scheme ①

This scheme adds three solvent extraction processes to the PUREX process: An(III)-Ln(III) co-extraction from the HLLW solution, An(III)/Ln(III) separation, and Am(III)/Cm(III) separation.

The DMDOHEMA[40] and TODGA[52] based processes have similar performance. Hence, no clear recommendation is made as to which process is most favourably used to co-extract An(III) and Ln(III). However, a selection may be made depending on which process is used to separate Am(III) from Cm(III), see below.

To separate An(III) from Ln(III), the $CyMe_4$-BTBP process is the European reference process. Whether to add TODGA[66] or DMDOHEMA[67] as the phase transfer catalyst should be decided based on which extracting agent is used in the first and third solvent extraction processes, in order to minimise the number of extracting agents in use. However, the relatively slow kinetics of these processes requires larger equipment. Finding a solvent extraction system with faster kinetics but otherwise comparable performance would greatly help. The PTEH extracting agent developed recently[114] appears promising.

The DMDOHEMA process[70] is suitable to separate Am(III) from Cm(III). To make this process more compact (i.e. reduce the number of stages), the addition of TEDGA should be considered, which would help in increasing the Am(III)/Cm(III) selectivity, see the EXAm process.[104-105]

A possibly promising direction of research would be developing an Am(III)/Cm(III) separation process using TODGA (which extracts Cm(III) slightly better than Am(III)) as extracting agent and searching for water soluble complexing agents with the reverse selectivity.

In conclusion, scheme ① appears the most complex. However, using the same extracting agent in the first and in the third solvent extraction cycles would reduce the number of solvent clean-up cycles to two. This way, this scheme would be less complex than it appears at first sight.

Scheme ②

This scheme adds two solvent extraction processes to the PUREX process, one process to co-extract An(III) and Ln(III) and one to separate Am(III) from Cm(III) and the lanthanides(III).

Regarding the first process, again, both the DMDOHEMA[40] and TODGA[52] based processes appear similarly suitable.

Using the $(ClPh)_2$-PSSH + T2EHPH system[79] to separate Am(III) from Cm(III) and Ln(III) is not optimal since it uses a mixture of an acidic and a neutral extracting agent; furthermore, both are non-*CHON*. Alternative processes based on $CyMe_4$-BTBP or $CyMe_4$-BTPhen may be a possibility.[83] However, besides not having been developed and demonstrated, such processes will suffer from slow kinetics.

In any case, scheme ② involves two different solvents, requiring two solvent clean-up cycles.

Scheme ③

This scheme adds two solvent extraction processes, An(III) extraction from HLLW and Am(III)/Cm(III) separation. The bottleneck of this scheme is the extraction of An(III) from HLLW[80-82] for two reasons: (a) the slow kinetics will require comparatively large equipment; (b) the use of sulphur-containing Pd(II) stripping or masking agents continuously routes sulphur to the raffinate, creating issues with vitrification.

Scheme ④

This scheme adds a single solvent extraction process to the PUREX process. This process directly extracts only Am(III) from the HLLW solution. The only chemical system developed so far[83] shares the drawbacks of the direct An(III) extraction process[80-82] (see scheme ③) regarding kinetics and sulphur-containing waste. Furthermore, a flow-sheet based on this system has not yet been developed and tested.

Scheme ⑤

This scheme adds two solvent extraction cycles to the PUREX process. The first one would most favourably use the PTD system[102-103] to separate actinides(III) from the HLLW solution, assuming the planned spiked test is successful. Regarding the second process (Am(III)/Cm(III) separation), see the discussion on scheme ①. Again, developing a TODGA-based Am(III)/Cm(III) separation system

would be beneficial since the PTD system[102-103] also uses TODGA: only one solvent clean-up cycle would be necessary to regenerate the solvent from both cycles.

Scheme ⑥

This scheme is very compact as it adds only one solvent extraction cycle to the PUREX process. However, so far no Am(III) selective stripping process without more or less substantial drawbacks is available, see *Selective Am(III) stripping.*

Conclusions and outlook

Several solvent extraction processes addressing heterogeneous recycling have been developed and demonstrated in Europe. Based on the most promising of these solvent extraction processes, six schemes for separating americium from PUREX HLLW were compared to one another. The following conclusions are drawn, based on the current state of the art:

Scheme ① appears the most complex. However, using the same extracting agent in the first and in the third solvent extraction cycles reduces the number of solvent clean-up cycles to two. This way, this scheme is less complex than it appears at first sight. The second solvent extraction cycle (An(III)/Ln(III) separation) benefits from using PTEH[114] due to its faster kinetics.

Scheme ② appears promising but so far has only been demonstrated using an extraction system which is not *CHON* compliant.

Schemes ③ and ④ create a sulphur-containing raffinate solution. This is expected to cause problems with the vitrification of these solutions.

Scheme ⑤ appears a promising option given that a process selectively stripping An(III) using PTD will be successfully demonstrated. Finding an Am(III)/Cm(III) separation system based on the use of TODGA makes scheme ⑤ rather compact, adding two solvent extraction cycles with a common solvent clean-up.

Scheme ⑥ appears promising as it adds only one additional solvent extraction cycle. Unfortunately, the systems available for developing such a process so far have drawbacks of varying significance and much more R&D is still required to develop a viable option.

So far, the developments discussed in this review have been pursued on the laboratory scale only. There are clearly a number of knowledge gaps that need to be filled before these processes would be ready for industrialisation, specifically these include:

- The thermal stability of the proposed solvents needs to be assessed to exclude safety hazards, e. g. with any downstream evaporation processes.
- Downstream effects must be studied in detail, e. g. the effect chemicals such as aqueous phase complexing agents may have on precipitation processes to obtain a solid actinide product.
- Solvent regeneration steps must be optimised in order to allow for a continuous recycling and re-use of the solvent.

Finally, demonstrating the most promising of the above process schemes — including the interfaces between the individual processes — using a genuine PUREX HLLW feed solution is certainly desirable to raise the technological readiness of the process.[36]

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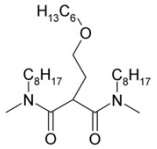
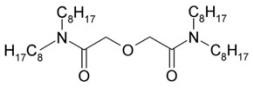
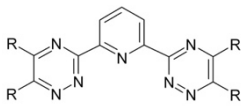
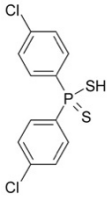
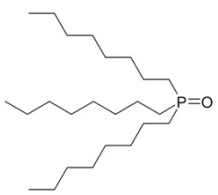
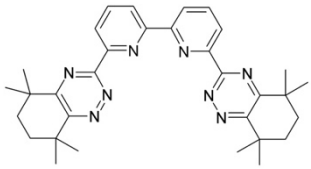
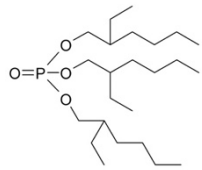
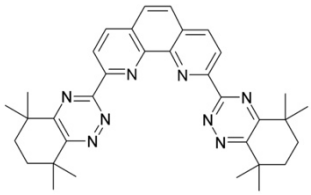
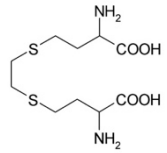
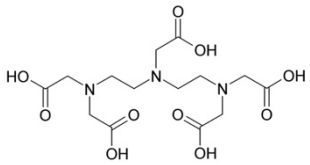
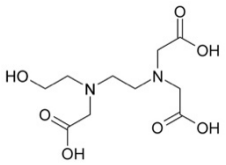
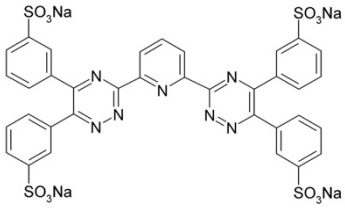
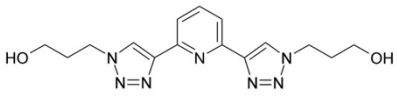
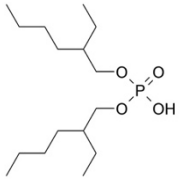
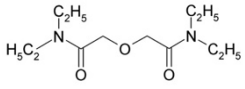
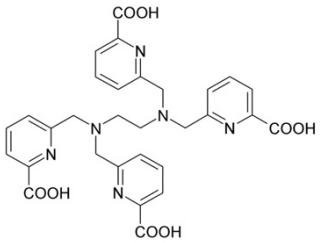
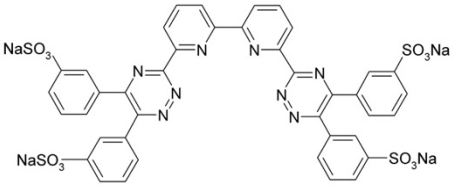
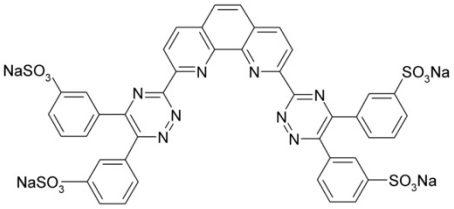
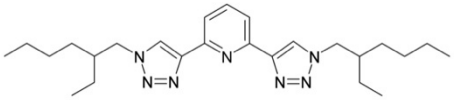
Appendix: list of compounds

The structures and names of extracting and complexing agents mentioned in the report are given in below table, in order of appearance in the text.

Compound	Acronym	Name
	DMDOHEMA	*N*,*N*'-dimethyl-*N*,*N*'-dioctyl-2-(2-hexyloxy-ethyl)-malonamide
	TODGA	*N,N,N',N'*-tetra-*n*-octyl diglycolamide
	BTP	2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridine
	$(ClPh)_2PSSH$	bis(chlorophenyl)dithiophosphinic acid
	TOPO	tri-*n*-octylphosphine oxide

Compound	Acronym	Name
	$CyMe_4$-BTBP	6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine
	T2EHP	tris(2-ethylhexyl) phosphate
	$CyMe_4$-BTPhen	2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-1,10-phenanthrolin
	bimet	(2S,2'S)-4,4'-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)
	DTPA	diethylenetriaminepentaacetic acid
	HEDTA	*N*-(hydroxyethyl)ethylenediamine-triacetic acid
	SO_3-Ph-BTP	2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-pyridine tetrasodium salt
	PTD	2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine
	HDEHP	bis(2-ethylhexyl)phosphate
	TEDGA	*N,N,N',N'*-tetraethyl diglycolamide

Compound	Acronym	Name
	TPAEN	*N,N,N′,N′*-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine
	SO_3-Ph-BTBP	6,6’-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-2,2’-bipyridine tetrasodium salt
	SO_3-Ph-BTPhen	2,9-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline tetrasodium salt
	PTEH	2,6-bis[1-(2-ethylhexyl)-1,2,3-triazol-4-yl]pyridine