An Overview of Solvent Extraction Processes Developed in Europe for Advanced Nuclear Fuel Recycling, Part 2 — Homogeneous Recycling

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Abstract

The hydrometallurgical separation concepts for the recycling of irradiated nuclear fuels developed in Europe are presented and discussed. Whilst Part 1 of the review focused on concepts for heterogeneous recycling of minor actinides, this article focuses on group recycling of transuranic actinides, which would support homogeneous recycling scenarios. Most of these concepts were developed within European collaborative projects and involve solvent extraction processes separating all the actinides (U-Cm) in two cycles. The first cycle uses a monoamide extractant to recover uranium leaving all the transuranic actinides in the aqueous raffinate with the fission products. The second cycle aims for a group recovery of the transuranium elements and several strategies have been proposed for this stage. In this review article, the various solvent extraction processes are summarised and the key features of the process schemes are compared.

***Keywords**. Nuclear fuel, homogeneous recycling, actinides, solvent extraction, GANEX*

Introduction

Nuclear power reactors provide a safe, low-carbon and non-intermittent production of electricity. In 2019, 26.7% of the EU's total net electricity generation was generated by 109 nuclear power reactors across 16 member countries [1]. However, whilst the potential contribution nuclear energy can make towards a sustainable, low carbon future is being increasingly recognised [2], the challenges remain related to safe, secure, long term management of the spent nuclear fuels (SNF) that are highly radioactive over long timescales [3]. Altogether, close to 58,000 tHM SNF had been produced and stored by the end of 2016 in the EU [4-7] whilst globally, around 10,000 tonnes of SNF are generated per year [8]. Although SNF can be interim stored safely for extended periods, ultimately there are only two options for spent fuel management (SFM): direct disposal or recycling. Direct disposal in a deep geological repository (DGR), called the open or once through fuel cycle, is the accepted strategy for many countries such as Finland, Sweden, Germany and the United States [9-10]. SNF recycling, based on reprocessing to recover re-usable nuclear materials and fabrication of new fuels from the reprocessed products, has been implemented industrially in some countries, e.g. France, Russia, UK and Japan. This is referred to as the closed nuclear fuel cycle and there are variations on the closed fuel cycle depending on which materials are recycled and whether the materials are recycled once or multiple times [11]. The advantages of recycling have been described elsewhere but, as might be expected, relate to improved use of natural resources, less wastes with reduced radiotoxicity for disposal leading to a smaller DGR and a smaller environmental footprint for nuclear energy [3, 9, 12-16].

Europe has a long experience of reprocessing SNF with facilities of varying scales in Belgium, France, Germany, Russia and the UK [17]. France and the UK have operated commercial scale reprocessing plants at La Hague and Sellafield, respectively, with more than 36,000 and 65,000 tonnes of used nuclear fuel reprocessed at these sites [18-19]. All these reprocessing programmes have used or still use the PUREX process [20-22] to separate fissionable materials, uranium and plutonium, from irradiated fuel. Uranium and plutonium can be recycled in present-day light water reactors (LWRs) either as reprocessed uranium oxide (RepU) fuels or mixed oxide (MOX) fuels.

Advanced fuel cycles, however, offer the prospect of multi-recycling of U and Pu which can substantially increase the benefits in terms of uranium utilisation and resource preservation [9]. [2312]. Compared to other fuel cycle options, SNF multi-recycling in advanced fuel cycles has potential advantages of comprehensively addressing issues related to sustainability, such as public acceptance, proliferation resistance, flexibility for reprocessing of non-oxide and high-burnup fuels and the most efficient use of the DGR. The latter is supported by recycling minor actinides (MA = Np, Am, Cm) to reduce the heat loading and radiotoxicity of the final wastes [9, 16, 24-25].

The multi-recycling of uranium, plutonium and MA advanced nuclear fuel cycles can be via either homogeneous or heterogeneous routes, see Figure 1 [26-27]. In heterogeneous recycling (often termed the partitioning and transmutation or P&T scenario), uranium, plutonium and potentially neptunium [28] are recovered, usually by the PUREX process for the production of MOX fuels [29]. The other MA, americium and curium, are then recovered from the PUREX high level waste (HLW) stream and converted to MA fuels or targets which can be transmuted in the reactor or accelerator driven system (ADS). In this scenario, the (U,Pu) and MA fuels are separated in different stages in the reprocessing plant and the refabricated fuels are distributed heterogeneously in the reactor core.

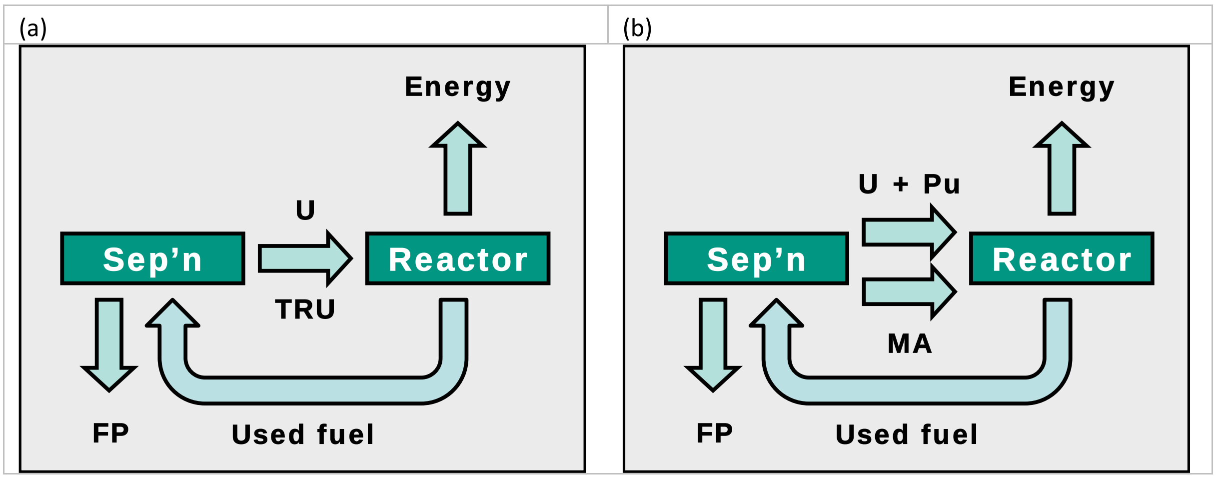

Figure 1: Schematic illustration of (a) homogeneous and (b) heterogeneous recycling. FP = fission products (redrawn from ref. [27])

In the homogeneous recycling option, uranium and the transuranic elements (TRU = Np, Pu, Am, Cm) are contained within a single fuel type and distributed homogeneously throughout the reactor core. These fuels typically have between 1 – 5 wt% MA compared to 10-20 wt% MA in the MA fuel in the heterogeneous recycle scenario [30]. The homogeneous mode with grouped actinide recycling is beneficial in that there is no pure stream of plutonium, this adds additional barriers against risks of proliferation[11]. Whilst the homogeneous route is perhaps more straightforward with regards to fuel fabrication and reactor physics, the separations chemistry is more complicated than the heterogeneous reprocessing. Therefore, advanced fuel cycle R&D programmes commonly pursue both heterogeneous and homogeneous options [9, 11, 26, 30].

The development of the chemical separations processes needed for the reprocessing (or partitioning) of the actinides is widely recognised as a key enabler of advanced fuel cycle technologies. In Europe, the development of the chemical separations required for such strategies was triggered by two French waste management acts (1991 and 2006) [31-32] and has found support from EURATOM-funded research programmes since the early 1990s. Continuously evolving from initially small programmes, a sequence of programmes dedicated to developing actinide separation processes and the related chemistry was executed: NEWPART (1997–1999) [33-34], PARTNEW (2000–2003) [35], EUROPART (2004–2007) [36], ACSEPT (2008–2012) [37], SACSESS (2013–2016) [38-40], and the latest programme, GENIORS (2017–2021) [41]. These programmes have made substantial progress in developing the separation technologies for both LWR and FR spent fuel recycling towards the point at which they can be deployed and our previous paper [27] discussed the actinide separation processes developed in Europe addressing heterogeneous recycling. This paper reviews and assesses the respective processes for homogeneous recycling, once again focusing on the development in Europe.

Recycling strategies

The discussion so far has focused on how multi-recycling in FRs can derive optimum benefits from nuclear energy generation related to sustainability and waste management and how this multi-recycling can be achieved either in a heterogeneous or homogeneous mode. The heterogeneous recycling mode is primarily related to the aqueous reprocessing (hydrometallurgical) routes, involving:

a) An initial separation of U and Pu using the PUREX process or some variation thereof. If desirable, neptunium can be recovered with the U and Pu relatively easily [28].
b) A new extraction process to recover either americium and curium or americium alone from the aqueous HLW stream.

The different strategies for heterogeneous recycling of MA are described in the preceding paper [27]. Homogeneous recycling, on the other hand, can be achieved either by an aqueous route or by a non-aqueous pyrometallurgical processing of SNF in high temperature molten salt media [42-43]. Indeed, pyro-processing is well suited to homogeneous recycling of FR fuels (metals, nitrides, oxides), being resilient to radiation from high burn up and short cooled FR fuels, based on electrorefining or reductive extraction that is adapted to the metal fuels often considered for FRs and naturally producing a low purity mixed actinide product [44]. However, pyro-processing is generally a low throughput batch process and, as such, was originally developed as part of the Integral Fast Reactor programme in the United States [45]. Further discussion of the pyrochemical routes for homogeneous recycling are beyond the scope of this paper but the interested reader is referred to references [11, 42, 46-49].

Aqueous separation processes for homogeneous recycling

The basic requirement for homogeneous recycling is that it requires the recovery of the TRU elements as a group. Uranium could be co-recovered with the TRU or separated on its own in a dedicated solvent extraction cycle (or other process such as crystallisation [11, 50]). From this initial assumption, some secondary characteristics of the process become evident as well:

- A new extractant is required since tributyl phosphate (TBP), as used in the PUREX process, is not able to extract trivalent minor actinides.
- Adherence to the “CHON principle[1]” of degradable ligands in the process is preferred, ideally for both phases.
- Efficient extraction of TRU actinide ions in oxidation states III (Am, Cm), IV (Pu, Np) and VI (Np, potentially U and Pu) is required.
- The process must be able to cope with high concentrations of plutonium (~10 times that of the conventional PUREX process for thermal oxide fuel reprocessing) without third phase or precipitate formation. Also, with high plutonium concentrations, methods avoiding Pu recovery by reductive stripping (as used in the PUREX process) are preferred due to potential re-oxidation of Pu(III) by nitrous acid and the consequent need for excessive levels of reductants, such as U(IV), to maintain plutonium in the trivalent state [51].
- Minimisation or preferably elimination of hazardous reagents, such as hydrazine, is advisable.
- At some point in the process there must be selectivity in either the organic or aqueous phases for trivalent actinides over trivalent lanthanides otherwise effective decontamination from lanthanides (which are neutron poisons in the reactor) will not be achievable.
- Fast chemical and/or mass transfer kinetics are required for compatibility with next generation solvent extraction equipment such as centrifugal contactors [52].

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[1] Ligands that contain carbon, hydrogen, oxygen and nitrogen only and, therefore, should be fully decomposable to gases.

- Ligands, particularly in the organic phase, must be sufficiently stable towards radiolysis and hydrolysis and extractants must be sufficiently soluble in the diluent to enable extraction of rather high concentrations of TRU elements.

In Europe, substantial challenges were met in early projects, NEWPART, PARTNEW and EUROPART, developing ligands that were able to achieve the challenging An(III)/Ln(III) separation [53-54] and this led to defining and testing 'reference' processes for heterogeneous recycling in the later projects, namely ACSEPT and SACSESS [43, 55-56]. The learning from these early projects was exploited, initially in the ACSEPT project, to start development of a European option for homogeneous recycling [57]. This pan-European development was in parallel to French efforts and indeed the first strategies for homogeneous recycling were developed by the French Alternative and Atomic Energies Commission (CEA) and tested in their ATALANTE facility at Marcoule [43, 58-60]. The process was termed GANEX (Grouped ActiNide Extraction) and, as of today, three GANEX options exist for homogeneous recycling and a fourth process variant for heterogeneous recycling has also been reported. These four GANEX-variants fall into three basic strategies, depending on how they recover the TRU actinides, as indicated in Figure 2:

1) Co-extraction of TRU and lanthanides followed by selective stripping of TRU
2) Selective extraction of TRU
3) Co-extraction of TRU and lanthanides followed by selective and sequential stripping of, firstly, Np and Pu and then trivalent MA

All three strategies presume an initial separation of most or all of the uranium to reduce the volume and complexity of the TRU recovery cycle. Figure 2 also indicates the types of ligands (O- or N-donor ligands in organic or aqueous phases) proposed for each strategy.

In brief, the GANEX process was first developed by the CEA and designed as a 2-cycle solvent extraction process, where the bulk uranium is extracted in the primary stage (GANEX-1) [61], while the TRU/fission product separation is achieved in the secondary GANEX-2 stage – this has been termed CEA-GANEX [59]. In the ACSEPT project alternatives to CEA-GANEX were investigated and the EURO-GANEX cycle was developed and tested [62-64] as well as the initial formulation of the Chalmers-GANEX (CHALMEX) [65-68]. In the CEA-GANEX and the EURO-GANEX processes, the actinides (An) and lanthanides (Ln) are co-extracted from the GANEX 1st cycle (GANEX-1) raffinate. The actinide/fission product separation is achieved through subsequent selective stripping. In the CHALMEX process, the An/Ln separation occurs by the selective extraction of An [65-67]. It is clear that the CHALMEX option, at least superficially, offers a simpler and more elegant solution to the challenge of recovering TRU actinides as a group. However, it is concomitantly more challenging from the process chemistry perspective and, for reasons that will become apparent later, the EURO-GANEX is considered to be the current reference process for the GANEX 2nd cycle (GANEX-2).

The individual processes will be briefly described below, focusing on aspects such as their basic principles, development status (technology readiness), upstream and downstream compatibilities, generation of secondary wastes and process safety. In line with our previous review [27], 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, together with their molecular structures, are explained in the Appendix.

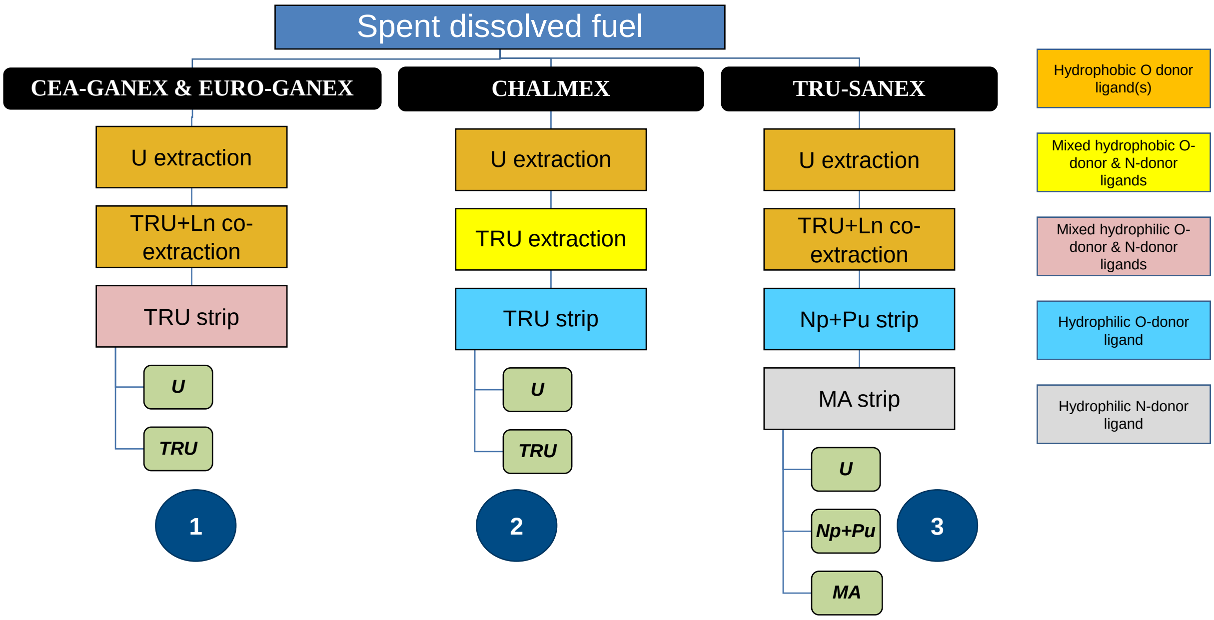

Figure 2: A schematic overview of GANEX solvent extraction processes for homogeneous recycling developed in Europe. The colour scheme indicates the kind of extracting or complexing agents used (see legend)

Uranium extraction (GANEX-1 cycle)

The GANEX 1st cycle is common for all the variants of the GANEX processes and is aimed at the bulk recovery of uranium from a dissolved spent nuclear fuel solution. This is necessary as a high purity uranium product is required to enable tuning of the U/TRU ratios in the final fuel. It also reduces the volume (mass) of material that must be processed in the next cycle and simplifies the chemistry – since uranium is present as the very stable, linear, hexavalent dioxo-cation, UO_2^{2+}, which is quite different to the other An^{3+} and An^{4+} cations. The uranium separation is achieved by a solvent consisting of a *N,N*-dialkylamide that is selective for U(VI), *N,N*-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) in an aliphatic diluent such as hydrogenated tetrapropylene (TPH) or Exxsol D-80. *N,N*-dialkylamides have several advantages including adherence to the CHON-principle, high hydrolytic and radiolytic stability and a high loading capacity for uranium. DEHiBA degrades into carboxylic acids and secondary amines, which have little to no effect on the separation of uranium from the raffinate. DEHiBA delivers high values for $D_{U(VI)}$, high U(VI)/Pu(IV) separation factors (~80) without need of redox agent, and high decontamination factors (DF) for most fission products in nitric acid media [43, 61, 69-70].

Two laboratory scale hot tests with SNF have been performed on the GANEX-1 cycle. The flowsheet was initially developed at the CEA in France and tested in lab-scale mixer-settlers in the ATALANTE facility at Marcoule with thermal oxide fuel [43, 61, 71]. Later, the flowsheet was adjusted by use of the CEA's PAREX model [72] and tested in centrifugal contactors at the Joint Research Centre (JRC) in Karlsruhe at the end of the ACSEPT project [43, 64]. In both cases the aim was to generate the highly active (HA) raffinate stream for testing the GANEX-2 cycle although CEA have looked further at the optimisation of the GANEX-1 cycle, particularly the scrubbing step. Nevertheless, both tests gave good results that are summarised in Table 1. The flowsheet for the JRC hot test was based on dissolved FR fuel and so had a different U:Pu ratio in the feed. The results of the JRC test with respect to Np, Pu and Tc decontamination were not as good as the CEA test. This is probably attributable to the use of short residence time centrifugal contactors and fewer scrubbing stages in the JRC test. Optimisation of the hydrazine scrubbing is evidently required. As with the PUREX process [73], technetium (Tc) co-extraction with uranium was also a significant factor and accounted for in the PAREX model [74]. The technical maturity for this cycle has been assessed through application of the widely used technology readiness level (TRL) assessment by the OECD-NEA [75]. Although it is noted that this assessment was made at the "system level" and so parts of the process (so-called "critical technology elements") may actually be at a lower level, GANEX-1 was assessed to be at TRL 5 (which was defined as "*Technology component or process step validated at bench scale under relevant conditions. Process models developed. Proof of principle hot tests using spent fuel*" [11, 75]).

Table 1: Key properties and results from the GANEX-1 hot tests at CEA and JRC [43, 61, 64]

Property	**CEA hot test**	**JRC hot test**
U in feed (g/L)	176	103.1
Pu in feed (g/L)	2.5	22.7
U in raffinate (%)	<0.002	0.06
Pu in U product (%)	0.024	0.38
Np in U product (%)	0.33	5.8
Tc in U product (%)	2.4	24.5
Contactor type	Mixer-settlers	Centrifugal contactors
Total stages	28	32

GANEX-2 cycle scheme 1: selective actinide stripping

The most developed formulation of the GANEX 2nd cycle is given in Scheme 1. This involves the co-extraction of TRU actinides and the trivalent lanthanides (together with some problematic fission products such as Mo, Zr, Tc, Fe) from the GANEX-1 aqueous raffinate. The co-extraction of the lanthanides is inevitable if an O-donor ligand is used as the extracting agent due to the chemical similarity of the trivalent actinides and lanthanides. The actinides are then selectively stripped from the organic phase by suitable hydrophilic ligands containing a soft donor ligand (usually N-donors). The lanthanides remain in the organic phase and are stripped in the next stage before the lean solvent is recycled.

CEA-GANEX

The GANEX-2 cycle was first proposed by CEA based on an adaptation of their DIAMEX-SANEX process [58-59]; this being a process already developed and tested for separation of minor actinides [31, 76]. Therefore, the organic phase was based on the combination of the malonamide *N,N*'-dimethyl-*N,N*'-dioctyl-2-(2-hexylethoxy) malonamide (DMDOHEMA) and di-(2-ethylhexyl)phosphoric acid (HDEHP) diluted in an aliphatic diluent (TPH). N-(hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was added to the aqueous feed and the scrub solution to suppress fission product extraction (specifically palladium) but molybdenum and technetium (as well as Zr, Fe) were nevertheless co-extracted with the TRU actinides. A dedicated scrubbing section was thus added to the flowsheet to scrub molybdenum and technetium at pH 2-3; pH adjustment was with citric acid. The actinide stripping section was also operated at pH 3 using a solution of HEDTA, citric acid and hydroxyurea. Hydroxyurea was added as a reducing agent for Np(VI) – plutonium being stablilised in the tetravalent state in the presence of HEDTA and citric acid. At this high pH, lanthanides were retained in the organic phase by complexation with HDEHP. The lanthanides and other residual contaminants (zirconium, iron) were finally stripped from the solvent with a mixture of TEDGA and oxalic acid before the solvent recycling [43].

This CEA-GANEX cycle has been tested with SNF at the Atalante facility (Marcoule, France) [59]. A LWR fuel was used (the aqueous raffinate from their GANEX-1 hot test described above) and the flowsheet test was performed in 48 stages of miniature mixer-settlers in a hot cell. Losses of TRU actinides were <0.5% with generally good fission product decontamination factors obtained. The exceptions were some middle lanthanide elements which contaminated the actinide product. Using their PAREX solvent extraction simulation capabilities [31], this was later shown to be due to an under-estimation of some of the fission product concentrations in the feed and simulations were run that predicted how this could be rectified in future. The CEA-GANEX was, therefore, the first process demonstration of the GANEX concept and was shown to be a viable option for the GANEX-2 cycle.

EURO-GANEX

European projects had already made substantial progress in developing processes for An(III) recovery, particularly based on applications of the diglycolamide extractants – mainly *N,N,N′,N′*-tetra-n-octyl-diglycolamide (TODGA) [55, 77-79]. Adapting these developments for the GANEX-2 cycle was seen as the logical place to start with early work based on a combination of TODGA and TBP [80]. However, in experiments with process concentrations of plutonium (as opposed to trace spiked solutions) precipitates were observed with TODGA and its dodecyl analogue (TDdDGA) alone in diluent or with TBP, octanol and *N,N*-dihexyloctanamide (DHOA) as phase modifiers [81]. Addition of the malonamide DMDOHEMA, was found to provide sufficient capacity for plutonium before a conventional third phase was observed (up to 35 g/L with 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA with extraction from 3 mol/L HNO_3); no precipitation occurred with DMDOHEMA [81] which acts as a co-extractant [82]. Screening of different TODGA:DMDOHEMA ratios settled on 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in an odourless kerosene diluent as the most suitable formulation. The third phase boundary was later defined as a function of nitric acid concentration showing this solvent had sufficient capacity for plutonium concentrations of ≥10 g/L for $[HNO_3] \leq 6$ mol/L [83]. Consequently, 10 g/L Pu was set as the target for future flowsheet design.

Spiked batch distribution experiments confirmed the expected efficient co-extraction of Pu(IV), Am(III) and Ln(III) [83]. Spiked batch distribution experiments also confirmed the sulphonated bistriazinyl pyridine ligand (SO_3-Ph-BTP), 2,6-bis(1,2,4-triazin-3-yl)-pyridine, developed for selective stripping of An(III) from Ln(III) in the i-SANEX process [84-85] also worked for the EURO-GANEX solvent [63]. Further experiments with process concentrations of Pu(IV) (1-10 g/L) defined suitable acid and SO_3-Ph-BTP concentration ranges that would deliver good separation factors whilst maintaining $D_{Pu,Am}<1$ and $D_{Eu}>1$. A second hydrophilic molecule, acetohydroxamic acid (AHA), was added as this was expected to act as a complexant for Pu(IV) [81, 86] and reductant for Np(VI) [87] but it was also shown to promote stripping with the SO_3-Ph-BTP although the reasons for this effect are still unclear.

Fission product decontamination is a key challenge with any reprocessing flowsheet and the EURO-GANEX process is no exception. CDTA (trans-1,2-diaminocyclohexane-*N,N,N,N′*-tetraacetic acid), developed for the i-SANEX cycle, was also shown to hold back zirconium and palladium in the aqueous phase when applied to the EURO-GANEX system [88]. E.g. for 0.05 mol/L CDTA, 3 mol/L HNO_3, 17 g/L Pu, D_{Zr} and D_{Pd} decreased from 11.3 to 1.2 and 250 to 0.05 respectively whilst D_{Pu} remained sufficiently high (35). Further data on problematic fission and corrosion products were reported, specifically focusing on Fe, Sr, Tc, Mo, Ru [63]. Iron showed a steep increase in distribution ratio above 1 mol/L HNO_3 due mainly to extraction with DMDOHEMA. Strontium showed a maximum in D_{Sr} around 2 mol/L HNO_3 whereas for technetium extraction, primarily due to TODGA, D_{Tc} decreased across the HNO_3 range but remained >>1 even at 4 mol/L HNO_3. Similarly, D_{Mo} was above 1 across the HNO_3 range although there was some reduction in a HA raffinate (HAR) simulant compared with the single component solution and with CDTA. Ruthenium distribution ratios were less than one but varied with mixing time of the solutions and are likely to be affected by changes in speciation. In fact, TODGA-based flowsheet trials often report some retention of ruthenium in the organic phase [78-79]. Ruthenium PUREX chemistry, for comparison, is known to be very complicated [89-90].

The behaviour of neptunium in the EURO-GANEX system was given specific attention due to the known complexity of neptunium solvent extraction and redox chemistry [28, 91]. The order of extractability of the different neptunium oxidation states was shown to be Np(IV)>Np(VI)>1>Np(V) on extraction from <3 mol/L HNO_3 [92]. Of particular interest was that whilst Np(IV) and (VI) were quite stable, the Np(V) oxidation state proved to be very unstable in the organic phase with respect to disproportionation, a feature which it was realised could be exploited in flowsheet design. An increased rate of Np(V) disproportionation in the organic phase compared to the aqueous phase was similarly seen in earlier studies in TBP [93].

A flowsheet was designed and tested using a surrogate feed with realistic concentrations of plutonium (10 g/L) in the feed [62]. 16 centrifugal contactor stages of extract-scrub were followed by 12 stages of TRU actinide stripping and 4 stages of lanthanide stripping. CDTA was added to the feed (0.05 mol/L) which was 5 mol/L HNO_3 to promote neptunium disproportionation and extraction. A double strip was employed to selectively strip TRU from Ln(III) using 0.5 mol/L AHA with two different concentrations of SO_3-Ph-BTP to minimise Ln(III) stripping in low plutonium stages. Plutonium was well controlled through the flowsheet with a DF of ~14,000 but ~30% neptunium was lost to the HA raffinate and the TRU product contained ~7% of europium (used as an exemplar lanthanide). A flowsheet model developed in the CEA's PAREX simulation code was validated from this test and used to refine the flowsheet design ready for a hot test. The hot test was run at the end of the ACSEPT project at the JRC, Karlsruhe, using a feed from dissolving spent Dounreay Fast Reactor (DFR) fuels [64]. Following the GANEX-1 cycle, the EURO-GANEX cycle was run in two parts using a 16 stage miniature centrifugal contactor cascade contained in a hot cell. Changes from the surrogate test included raising the feed acidity to 5.9 mol/L HNO_3 to promote neptunium oxidation to Np(VI), reducing the scrubbing stages and simplifying the strip to a single solution (1 mol/L AHA + 0.055 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3). The trial was very successful in demonstrating the EURO-GANEX concept – 99.9% Np, Pu and Am ions were recovered with 0.06% lanthanide contamination. The improved neptunium extraction in the initial extract-scrub was attributed to the flowsheet changes plus the nitrous acid generated from radiolysis catalysing the Np(V) oxidation most effectively [28, 94-95].

The subsequent European SACSESS project was focused on the safety of the reference separation processes, including EURO-GANEX [38-39]. One of the objectives for the SACSESS project was to perform a process safety review of the EURO-GANEX flowsheet under normal and potential maloperation conditions. For this purpose, a safety assessment methodology was developed based on the experience of the project collaborators across Europe and this methodology [96] was then utilised to carry out a review of the EURO-GANEX flowsheet at a SACSESS project meeting based on a workshop style approach [38]. A key maloperation identified was the loss of scrub acid from the initial extract-scrub contactor as this was likely to cause the accumulation of plutonium, americium and other species across the contactor leading to potential criticality or radiological hazards within the plant. Therefore, an experimental simulation of this maloperation was carried out in laboratory scale centrifugal contactors [97]. Following the establishment of steady state with the flowsheet under normal operating conditions, the scrub acid was reduced to 0.05 mol/L (from 0.5 mol/L). Surprisingly, plutonium accumulation was not observed, and the plutonium remained in the solvent product with almost no change to the profile. The organic phase, however, did change colour from red-brown to green and UV-vis absorption spectroscopy confirmed a change in the solvent phase speciation and that the process was reversible. This effect was proposed to be caused by hydrolysis of Pu(IV) due to the low acidity, that was then limited in its extent by the solvent shell around the hydrolysed plutonium preventing it from polymerising to form a colloid, as occurs in the aqueous phase [98]. It was concluded that the EURO-GANEX process was robust to at least this type of maloperation and, whilst wider studies are obviously needed, this is a potentially advantageous, if unexpected, feature of the system.

The resistance of the EURO-GANEX system against radiation has also been addressed during SACSESS and GENIORS [99-101] projects, by performing a wide variety of gamma irradiation experiments to simulate the most relevant process conditions. The studies demonstrated that although there is an important reduction in TODGA and DMDOHEMA concentration after 1 MGy adsorbed gamma dose, the system retains excellent extraction performance after 500 kGy and is still sufficient after 1 MGy, without compromising lanthanide loading capacity (i.e. the limiting organic concentration, LOC). A total of 14 degradation compounds (DCs) were identified, nine from TODGA and five from DMDOHEMA, leading to a complicated mixture where at least three of those compounds could form insoluble aggregates. Regarding fission products, the irradiated EURO-GANEX solvent only showed a slight increase in fission product extraction, with the exception of zirconium and palladium. However, irradiation of CDTA containing aqueous phases, up to relatively low doses (5-50 kGy), indicated a loss of the masking ability for zirconium and palladium due to the formation of some insoluble products. There was also some loss of selectivity in actinide stripping (in 1 mol/L HNO_3) from a loaded and irradiated (1 MGy) EURO-GANEX solvent and retention of residual lanthanides in the solvent requiring more stages for back extraction of lanthanides into dilute nitric acid in the lanthanide strip. Most of the effects were explained by the extraction properties of DCs formed on irradiation [101-103]. In general, it was found that the aqueous phase containing SO_3-Ph-BTP and AHA was less stable to radiolysis than the organic solvent but, as the aqueous phase is not recycled, the results indicate that after a low-moderate absorbed dose (40-50 kGy) the concentration of SO_3-Ph-BTP remaining is still enough to preserve an effective An/Ln separation if other factors such as AHA hydrolysis and pH are controlled [100, 104-105]. Furthermore, the studies to date do not show any evidence of effects due to DCs of SO_3-Ph-BTP or AHA. Whilst further studies are still needed, particularly in the presence of plutonium, the long term operation of the EURO-GANEX system with irradiated nuclear fuels seems realistic, particularly when the impacts of the solvent clean-up process are considered; although improvements to the masking agent strategy for zirconium and palladium may be necessary.

GANEX-2 cycle scheme 2: selective actinide extraction

The simplest formulation of the GANEX 2nd cycle is given in Scheme 2. This involves the selective extraction of TRU actinides leaving the trivalent lanthanides as well as all other fission products in the GANEX-2 aqueous raffinate. This is only possible by judicious choice of extractants; particularly avoiding O-donor ligands such as diglycolamides that can co-extract lanthanides, but also finding extractants that have capacity to extract the larger amounts of Pu(IV) ions present. Following extraction, the actinides are then stripped group-wise from the organic phase by suitable hydrophilic O-donor ligands before the lean solvent is recycled.

The CHALMEX process

The CHALMEX process was developed by Chalmers University of Technology (Sweden), as an alternative strategy for the GANEX 2nd cycle [65-68, 106-112]. The objective was to develop a simpler process, which could reduce the number of process steps, potentially reducing costs of a recycling plant [38]. While significantly less developed than the strategies outlined for Scheme 1, the CHALMEX process has shown promising results in its actinide/lanthanide separation characteristics.

By combining the well-known extractant TBP with 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine ($CyMe_4$-BTBP), the solvent can theoretically extract the actinides with oxidation states ranging from +III to +VI, without the co-extraction of lanthanides and fission products and without redox control of plutonium [65-67]. While the process chemistry of TBP is well established after decades of use in the PUREX process, the chemistry of CyMe$_4$-BTBP is less well-known. It has been found to be stable towards both hydrolysis and radiolysis, but a complete mapping of degradation products formed under process conditions is lacking and studies are in progress [113-115]. Both alpha and gamma-radiation induced degradations of CyMe$_4$-BTBP have been investigated [66]. It has been established that the ligand degrades readily when subjected to both types of radiation but extraction properties remain almost unaffected when irradiated in contact with nitric acid. It has also been suggested that the stability of the extractant towards radiolysis is dependent on the diluent having a similar shape: for cyclic extractant molecules, a cyclic diluent leads to higher radiolysis resistance, at least at low irradiation doses [116]. CyMe$_4$-BTBP is also the reference molecule for the regular (r) and 1-cycle (1c) SANEX processes [117-119] and has gone through hot tests on genuine spent nuclear fuel with good results [43, 55-56].

Phenyl trifluoromethyl sulfone (FS-13) is used as a diluent in the process. Both Russian and American research efforts have focused on its use as a diluent in the UNEX (Universal Solvent Extraction) process [120-126]. FS-13 is chemically inert and stable towards both hydrolysis and radiolysis. A major advantage of the diluent is its high density (~1.4 g/cm^3), which resolves any phase separation/inversion issues experienced in systems with more similar densities between organic and aqueous phases. Other advantageous chemical and physical properties include low aqueous solubility, low viscosity and it is non-toxic. FS-13 has a relative permittivity of approximately 30.8 F/m at 298 K [127] and high dielectric constants have been shown to beneficial for americium extraction as it increases the solubility of CyMe$_4$-BTBP and hence the distribution ratio of Am. The separation factor of Am/Eu, however, increases exponentially with decreasing relative permittivity[128].

The initial feasibility studies of the CHALMEX process were promising. A good separation factor of the actinides from the lanthanides was seen within only 10 minutes of contacting ($SF_{Am/Eu}$ = 160, $SF_{Pu/Eu}$ = 210, $SF_{Np/Eu}$ = 3.5). All fission products that were extracted, except samarium and zirconium, were extracted by CyMe$_4$BTBP and the most problematic fission products extracted included Ag, Cd, Mo Zr and Pd. The extraction of some corrosion products (Ni, Co, Mn) was also found to be an issue [65, 108].

To prevent the extraction of some of these fission products, different strategies were considered including pre-extraction, scrubbing and suppression. Pre-extraction is generally undesired due to the increase in final waste volume it would produce by adding another process stage. Both scrubbing and suppression are more attractive choices as they can be combined with already existing process steps. Finally, it was concluded that a combination of the masking agents bimet and D-mannitol added directly to the GANEX-1 raffinate successfully reduced the extraction of Mo, Zr and Pd [65, 106]. Palladium was then of concern as it is known to precipitate when in contact with a pure cyclic ketone (or rather the presence of enol impurities) [129], such as the original diluent of choice, cyclohexanone [65, 67, 106]. No such reaction is known for cyclic sulfones like FS-13. Gluco-lactone can be added to the acid scrub step to back-extract any molybdenum or zirconium [107].

The process feasibility has been demonstrated by batch scale tests [108] and the solvent has been tested for use in centrifugal contactors in single stage centrifugal contactor experiments [107]. Elemental calculations on number of ideal, counter-current process stages have been performed with promising results: a 99.9% recovery of Am was estimated using 3 extraction stages followed by 3 scrubbing stages and 2 stripping stages. However, to date, no counter-current flowsheet tests have been carried out.

GANEX-2 cycle scheme 3: split actinide stripping

The third application of the GANEX strategy for the 2nd cycle is given in Scheme 3. This is basically a variation of Scheme 1. It involves the co-extraction of TRU actinides and the trivalent lanthanides from the GANEX-1 aqueous raffinate. The actinides are then selectively stripped from the organic phase by suitable hydrophilic ligands but, in this case, a split stripping strategy is adopted whereby firstly the multi-valent TRU ions (Np, Pu) are stripped and then the trivalent MA are stripped (Am, Cm). This gives two products that can be used for heterogeneous recycling or re-combined for homogeneous recycling. The lanthanides remain in the organic phase and are stripped in the next stage before the lean solvent is recycled. This strategy is included in this review of homogeneous recycling since it is a straight forward variation of the GANEX concept rather than a specific MA separation from PUREX HAR; options that were discussed in the preceding paper [27].

TRU-SANEX

Earlier papers in the development of the EURO-GANEX cycle had reported stripping of TRU actinides from the EURO-GANEX solvent with AHA and SO_3-Ph-BTP both independently and together [63, 81]. The mixture of the two reagents was the optimum combination for grouped stripping of Np-Cm. However, it was clear that, at low acidity, AHA could strip Pu(IV) and Np(IV), by complexation, and Np(VI), by reduction to Np(V), without interacting with the trivalent ions, whilst SO_3-Ph-BTP was designed to selectively strip the trivalent actinides from trivalent lanthanides. These selectivities are nicely illustrated by a comparison of reported stability constants – data have previously been reported for a wide range of actinide and lanthanide AHA complexes (e.g. $\log\beta_1$ values of 6.19, 5.85, 7.94, 4.83 and 14.2 for Eu(III), Am(III), U(VI), Np(V) and Pu(IV) respectively) and for curium and europium SO_3-Ph-BTP complexes ($\log\beta_3$ (Cm) = 12.2; $\log\beta_3$ (Eu) = 10.2) [86, 130-134]. This raised the interesting possibility of adapting the EURO-GANEX flowsheet to produce separate (Np, Pu) and (Am, Cm) products by separate sequential strip sections using firstly AHA and then SO_3-Ph-BTP (the AHA strip needs to be first since the SO_3-Ph-BTP will strip tetravalent as well as trivalent actinides). This variation was termed "TRU-SANEX" to highlight its hybrid nature between the GANEX and SANEX processes [135]. Results from a flowsheet test confirmed the concept with only small cross-contamination between the two products. Interestingly, <10% neptunium was lost to the aqueous raffinate which is less than the simulant EURO-GANEX test (~30%) but not as good as the hot test (<0.1%). Since the extract-scrub-section in the TRU-SANEX test was based on the hot test, this gives a rough indication of the impact of (a) the flowsheet changes and (b) radiolytically generated nitrous acid in promoting neptunium conversion to extractable Np(VI) and Np(IV) oxidation states.

Comparing the process schemes

Looking at the different process schemes (Figure 2), Scheme 2 appears the simplest since it selectively extracts the actinides at the initial extract-scrub stage. However, all three schemes are based on two cycles of solvent extraction and each cycle contains extraction, scrubbing and stripping stages, spent solvent regeneration cycles and various auxiliary equipment; for example, the engineering design may include evaporators, buffer storage or conditioning tanks, reagent tanks, connecting pipework, etc. Also, the solvent extraction process is only one part of the reprocessing plant – upstream and downstream processes for fuel preparation, dissolution, product finishing and waste management must also be considered in order to make a proper evaluation of the 'simplicity' of any particular separation process. Beyond the assessment of the technologies themselves, other factors also affect the choice of separation process such as: technology readiness; safety; environmental impacts (particularly on the DGR); proliferation resistance and physical security challenges; socio-economic benefits, including public acceptability; national policies and fuel cycle scenarios [9]. 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. However, in the context of this article we can highlight certain features of the different processes for each scheme that enable comparisons at the technical level.

GANEX-1

The process based on the monoamide DEHiBA for selective uranium extraction has been tested twice now with SNF [61, 64]. Good results have been obtained although the slightly worse recoveries and decontamination factors in the JRC hot test, which used centrifugal contactors, point to some kinetic issues with the hydrazine scrubbing stage for technetium, neptunium and plutonium control [64]. Also, the rather low uranium saturation in the JRC hot test leads to excessive solvent and aqueous flows that should be minimised from the waste management perspective.

Nevertheless, whilst optimisation challenges remain, the concept is considered to be proven. Further physico-chemical data needed for building predictive process models are outstanding needs (see for example [73]).

Scheme 1 (CEA-GANEX and EURO-GANEX)

Two processes have been demonstrated with SNF – CEA-GANEX and EURO-GANEX – which confirm the technical feasibility of options that meet the challenging goals related to developing advanced reprocessing options for homogeneous recycling [43]. These two cycles are compared in Table 3. The EURO-GANEX option offers some significant advantages, notably:

- Actinide stripping in the acidic region (no need for pH adjustment)
- No phosphate wastes from the solvent management
- Compatibility with centrifugal contactors has been demonstrated at the lab scale

Note that both CEA-GANEX and EURO-GANEX meet the requirement to avoid plutonium reduction despite the addition of reducing agents[2] [136].

However, in its current form the EURO-GANEX cycle also has various drawbacks:

- The sulphonated BTP reagent in the aqueous phase adds to waste volumes and is incompatible with vitrification processes for HLW immobilisation
- The combination of two extractants in the organic phase complicates solvent formulation, clean up and recycling and process simulation.
- Incomplete control of some fission products; notably molybdenum, technetium and ruthenium.
- No solvent clean up process has been developed yet for used solvent recycling.

Table 2: Comparison of key features of CEA-GANEX and EURO-GANEX cycles (data from [43, 59, 64])

	CEA-GANEX	**EURO-GANEX**
Developed by	CEA (France)	ACSEPT project (FP7)
Date of hot test	2008	2013

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[2] In EURO-GANEX, AHA can reduce Pu(IV) to Pu(III), most probably via hydroxylamine which is a product of the acid hydrolysis of AHA, but excess AHA stabilises Pu(IV) and the reduction reaction occurs too slowly under process conditions to be of any practical concern, at least under normal operations. In CEA-GANEX, Pu(IV) is stabilised by HEDTA and citric acid despite the addition of hydroxyurea. Both AHA and hydroxyurea act as reducing agents for Np(VI) ions in these GANEX-2 cycles.

Fuel for hot test	LWR	DFR
Pu content in HAF	≈2 g/L	10 g/L
Equipment	Mixer-settlers	Centrifugal contactors
No. of stages	48	32
CHON?	Aqueous phase only	Organic phase only
Organic phase	DMDOHEMA + HDEHP	TODGA + DMDOHEMA
Diluent	Industrial (TPH)	Industrial (Exxsol D-80)
FP scrubbing/holdback	Citric acid (Mo,Tc) HEDTA (Pd)	CDTA (Zr,Pd)
Actinide strip	pH 3	0.5 mol/L HNO_3
Actinide strip agents	HEDTA + citric acid + hydroxyurea	AHA + SO_3-Ph-BTP
Pu stripping	Complexation	Complexation
Ln(III) decontamination	5% in An product	<0.06 % in An product
Np recovery	~99%	99.90%
TRL (at system level) [75]	4-5	4-5

Scheme 2 (the CHALMEX process)

The CHALMEX process has to date been developed at the fundamental level. Latest studies have moved into the process development side through single stage centrifugal contactor experiments and a ‘flowsheet’ simulation by sequential batch experiments. Clearly, the process flowsheet needs testing in a counter-current mode with a realistic simulant before it can be compared directly with the Scheme 1 options. The CyMe$_4$BTBP, although very successful in selectively extracting MA, is also known to have slow kinetics and low solubility in diluents. These issues are partially addressed by use of the FS-13 diluent but it is unclear whether this is suitable for industrial applications. As in the EURO- and CEA-GANEX processes, the CHALMEX process combines two extractants in the organic phase, of which the well-known TBP molecule degrades into problematic byproducts that can complicate the solvent management. CHALMEX also relies on a series of aqueous phase ligands (bimet, D-mannitol and gluco-lactone) of which one (bimet) contains sulphur.

Scheme 3 (the TRU-SANEX process)

As has been emphasised already, this is a relatively simple adaptation of EURO-GANEX and so does not have, *per se*, pressing, unique R&D needs. However, an innovative and potentially transformative development would be if this Scheme could be extended to a “TRU-EXAm” mode; that is recovery of (Np, Pu) followed by Am alone – leaving curium in one of the waste streams.

Outlook

The GANEX-1 cycle is necessary and has wider applicability for uranium recovery. Flowsheet optimisation, basic data generation and process simulation that lead to process scale up are obvious future directions. R&D needs for the EURO-GANEX process are also quite clear and the GENIORS project is already looking at a CHON replacement for the SO_3-Ph-BTP ligand [137-138] and a modified DGA ligand that could replace the combined TODGA and DMDOHEMA organic phase [139]. CHALMEX would benefit from a focus on flowsheet testing and a safety review, similar to that trialled on the EURO-GANEX process in the SACSESS project [38]. All processes need solvent recycling capabilities and integration with upstream (fuel dissolution) and downstream (product finishing) stages. More in-depth safety studies, such as gas generation and thermal stability of proposed solvents, are also an essential next stage. Process modelling and simulation capabilities [140-141] are another generic need in order to more efficiently design flowsheets and also to probe sensitivities to process upsets [142].

Conclusions

As with the heterogeneous recycling option, several solvent extraction processes addressing homogeneous recycling have been developed and demonstrated in Europe. These essentially fall into three schemes for separating the TRU actinides, all of which are preceded by a common uranium extraction cycle. The following conclusions are drawn, based on the current state of the art:

The principles of the uranium extraction (GANEX-1) cycle have been demonstrated although work is still required to optimise the process, prove the decontamination factors (particularly in short residence time centrifugal contactors) and move towards process scale up, underpinned by process models and simulation with comprehensive sets of basic physico-chemical data.

Scheme 2 appears the most complex to develop into a working process, although it is potentially the most elegant concept with the fewest number of stages. However, in its current form (the CHALMEX process) it uses a mixed organic phase, various aqueous phase complexants and a fluorinated diluent. Significant further work is required to take this option towards a process demonstration with SNF and a design that is industrially deployable.

Two promising options exist for Scheme 1, both of which have been tested with SNF and demonstrate good results. Nevertheless, questions remain around both CEA-GANEX and EURO-GANEX. For the CEA-GANEX process, testing with elevated Pu content fuels, the compatibility with centrifugal contactors (particularly in the stripping stages) and the need for a high pH strip are concerns. For the EURO-GANEX process, the replacement of the SO_3-Ph-BTP ligand with a CHON ligand, simplification of the organic phase to a single extractant and verification of DFs for some problematic fission products are key R&D directions. The big advantage of the EURO-GANEX cycle is it has been proven for actinide stripping in the acidic region.

Scheme 3 is just a variant on the EURO-GANEX cycle and, whilst further testing would be needed to confirm the DFs for this TRU-SANEX cycle, its development can be assumed to be at a similar status to the EURO-GANEX cycle. Whether a heterogeneous recycling option that was based on GANEX rather than PUREX chemistry is advantageous would depend on extraneous factors related to the deployment of advanced fuel cycles in a particular country.

For nearly all separation processes, significant quantities of experimental data and experience have already been accumulated – particularly the CEA-GANEX and GANEX-1 cycles – such that now addressing the outstanding key technology gaps should become the main focus, e.g. process scale up, integration with upstream and downstream stages and solvent management (recycling within the process and solvent destruction at end of life). No processes yet have complete suites of validated process models readily available for flowsheet design in normal and off-normal (maloperation) operations, although some simulations have been performed (notably within the CEA's PAREX code which is a mature and proprietary code for modelling solvent extraction operations in nuclear fuel reprocessing plant [72]).

So far, the developments discussed in this review have been pursued on the laboratory scale only. There are clearly important knowledge gaps that need to be filled before these processes would be ready for possible industrial applications. As well as those already noted, safety studies, including gas generation and impacts of maloperations; scale up; process monitoring and control technologies are certainly desirable to raise the technological readiness of the process. The likely disadvantages of TRU fuels with their higher activities and masses, due to the combined plutonium and MA content, in the recycle fuel fabrication plant must be considered in order to optimise the whole recycle system rather than parts of the system. Beyond, technology readiness, how these processes fit into advanced, sustainable, economic and proliferation-resistant nuclear fuel cycles, supporting future low carbon generation, must be analysed [11].

Acknowledgements

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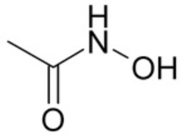
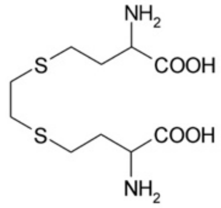
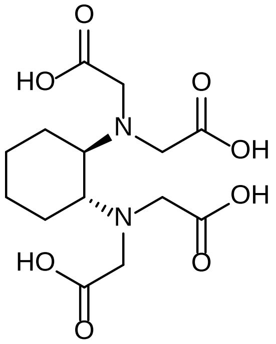
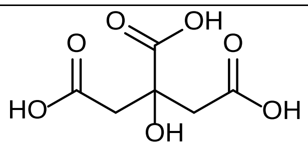
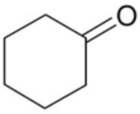
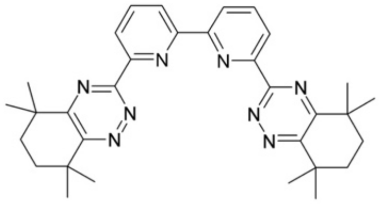
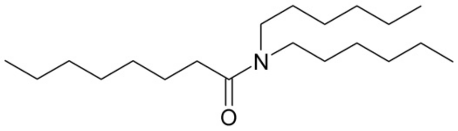
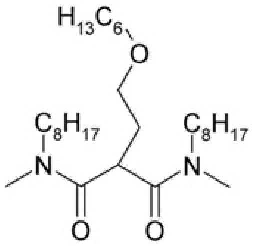
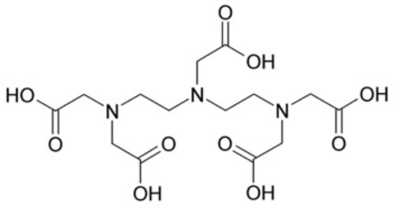
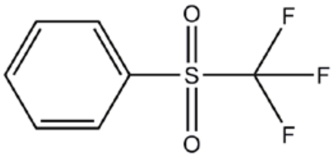
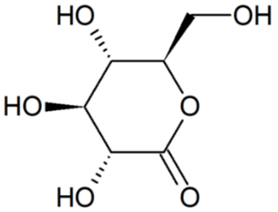
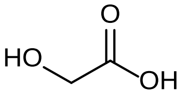
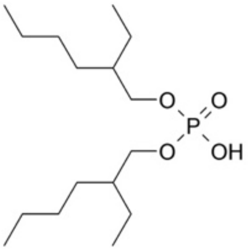
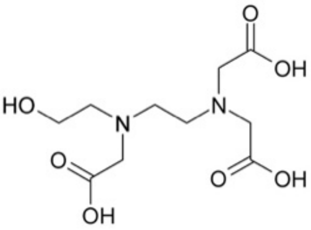
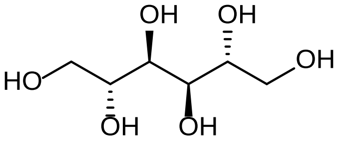
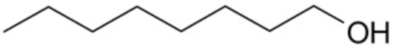
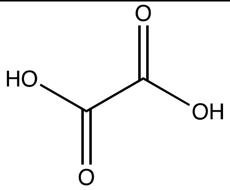
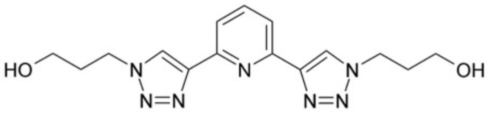
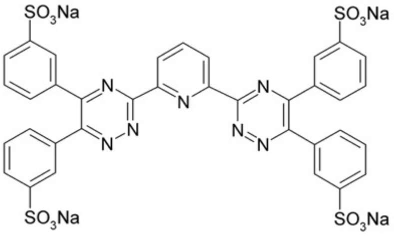
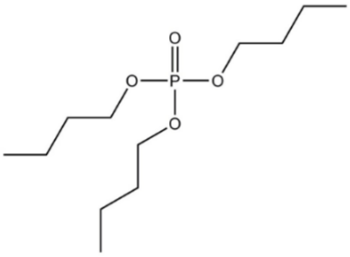
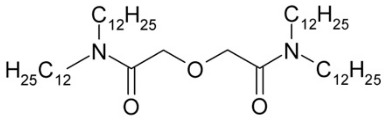
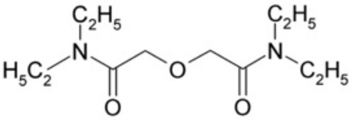
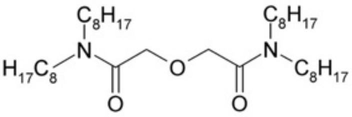
Table of process ligands

Compound	Acronym	Name
	AHA	Acetohydroxamic acid
	bimet	(2S,2’S)-4,4’-(ethane-1,2-diylbis(sulfanediyl))bis(2-aminobutanoic acid)
	CDTA	trans-1,2-Diaminocyclohexane-*N,N*,*N’,N’*-tetraacetic acid
	Citric acid	(2-Hydroxypropane-1,2,3-tricarboxylic acid)
	Cyclohexanone	Cyclohexanone
	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
	DHOA	Di-*n*-hexyl *n*-octaneamide
	DMDOHEMA	*N,N*’-dimethyl-*N,N*’-dioctyl-2-(2-hexyloxy-ethyl)-malonamide

	DTPA	diethylenetriaminepentaacetic acid
	FS-13	(Trifluoromethyl)sulfonyl benzene
	Gluco-lactone	Gluco-lactone
	Glycolic acid	2-Hydroxyethanoic acid
	HDEHP	Di-(2-ethylhexyl)phosphoric acid
	HEDTA	N-(hydroxyethyl)ethylenediaminetriacetic acid
	Mannitol	D-mannitol
	Octanol	1-Octanol
	Oxalic acid	Oxalic acid

	PTD	2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]-pyridine
	SO$_3$-Ph-BTP	2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)-pyridine tetrasodium salt
	TBP	Tributyl phosphate
	TDdDGA	*N,N,N′,N′*-tetra-*n*-dodecyl diglycolamide
	TEDGA	*N,N,N′,N′*-tetraethyl diglycolamide
	TODGA	*N,N,N′,N′*-tetra-n-octyl diglycolamide

References

1. Nuclear energy statistics. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Nuclear_energy_statistics (accessed 24 June).

2. Bouckaert, S.; Pales, A. F.; McGlade, C.; Remme, U.; Wanner, B.; Varro, L.; D'Ambrosio, D.; Spencer, T.; Abergel, T.; Arsalane, Y.; Bains, P.; Menendez, J. M. B.; Connelly, E.; Crow, D.; Dasgupta, A.; Delmastro, C.; Goodson, T.; Gouy, A.; Hugues, P.; Lee, L.; Levi, P.; Mandova, H.; Millot, A.; Olejarnik, P.; Paoli, L.; Papadimoulis, F.; Papapanagiotou, S.; Pavan, F.; Petropoulos, A.; Pośpiech, R.; Staas, L.; Tattini, J.; Teter, J.; Tonolo, G.; Vass, T.; Wetzel, D. *Net Zero by 2050 - A Roadmap for the Global Energy Sector*; International Energy Agency (IEA): Paris, France, 2021; pp 1-224.

3. *Management of spent nuclear fuel and its waste*; The European Academies' Science Advisory Council (EASAC): Brussels, 2014; pp 1-40.

4. Eurostat Electricity production, consumption and market overview. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_production,_consumption_and_market_overview#Electricity_generation (accessed 28/7/21).

5. World Nuclear Association Nuclear Power in the European Union. https://www.world-nuclear.org/information-library/country-profiles/others/european-union.aspx (accessed 28/7/21).

6. *Report From The Commission To The Council And The European Parliament On Progress Of Implementation Of Council Directive 2011/70/Euratom And An Inventory Of Radioactive Waste And Spent Fuel Present In The Ommunity's Territory And The Future Prospects. Second Report*; European Commission: Brussels, 2019; pp 1-18.

7. Electricity generation statistics - first results. https://ec.europa.eu/eurostat/statistics-explained/index.php?oldid=443430 (accessed 17/7/21).

8. *Nuclear Technology Review, 2019*; International Atomic Energy Agency: Vienna, 2019; pp 1-49.

9. Eynde, G. V. d.; Pedoux, S.; Trtilek, R.; Fritz, L.; Evans, C.; Mathonnière, G.; Werf, J. V. d.; Lucibello, P.; Suzuki, K.; Sano, T.; Takeda, S.; Nam, H.-o.; Khasperskaya, A.; Rakitskaya, T.; Zhurbenko, E.; Dixon, B.; McCaughey, W.; Gonzalez-Espartero, A.; León, S. B. y.; Henderson, D.; Ko, W. I.; Goto, H. *Strategies and Considerations for the Back End of the Fuel Cycle*; OECD-NEA: 2021; pp 1-72.

10. Kazimi, M.; Moniz, E. J.; Forsberg, C. W.; Ansolabehere, S.; Deutch, J. M.; Driscoll, M. J.; Golay, M. W.; Kadak, A. C.; Parsons, J. E.; Regalbuto, M.; Apostolakis, G.; Hejzlar, P.; Shwageraus, E. *The Future of the Nuclear Fuel Cycle: An Interdisciplinary MIT Study*; Massachusetts Institute of Technology: Cambridge, USA, 2011; pp 1-258.

11. Collins, E. D.; DelCul, G. D.; Spencer, B. B.; Jubin, R. T.; Maher, C.; Kim, I.-T.; Lee, H.; Fedorov, Y. S.; Saprykin, V. F.; Beznosyuk, V. I.; Kolyadin, A. B.; Baron, P.; Miguirditchian, M.; Sorel, C.; Morita, Y.; Taylor, R.; Khaperskaya, A.; Hill, C.; Malmbeck, R.; Law, J.; de Angelis, G.; Boucher, L.; Xeres, X.; Mendes, E.; Inoue, T.; Glatz, J. P.; Kormilitsyn, M.; Uhlíř, J.; Ignatiev, V.; Serp, J.; Delpech, S. *State-of-the-art report on the progress of nuclear fuel cycle chemistry*; OECD-NEA: Paris, France, 2018; pp 1-300.

12. Behar, C., Energy for the future: Generation IV fast reactors and the closed fuel cycle. *Nuclear Future* **2014,** *10*, 23-25.

13. Poinssot, C.; Bourg, S.; Ouvrier, N.; Combernoux, N.; Rostaing, C.; Vargas-Gonzalez, M.; Bruno, J., Assessment of the environmental footprint of nuclear energy systems. Comparison between closed and open fuel cycles. *Energy* **2014,** *69* (0), 199-211.

14. Wigeland, R.; Taiwo, T.; Ludewig, H.; Todosow, M.; Halsey, W.; Gehin, J.; Jubin, R.; Buelt, J.; Stockinger, S.; Jenni, N. K.; Oakley, B. *Nuclear Fuel Cycle Evaluation and Screening – Final Report* Fuel Cycle Research and Development, United States Department of Energy: Idaho National Laboratory, 2014; pp 1-51.

15. Marivoet, J.; Milot, J.-F.; Salvatores, M.; Saturnin, A.; Zaetta, A.; Geckeis, H.; Gompper, K.; Oigawa, H.; Taiwo, T.; Wigelund, R.; Choi, Y.-J. *Potential benefits and impacts of advanced nuclear fuel cycles with actinide partitioning and transmutation*; OECD-NEA: Paris, 2011; pp 1-78.

16. Serp, J.; Poinssot, C.; Bourg, S., Assessment of the Anticipated Environmental Footprint of Future Nuclear Energy Systems. Evidence of the Beneficial Effect of Extensive Recycling. *Energies* **2017,** *10* (9).

17. Dey, P. K.; Giroux, M.; Khaperskaya, A.; Laidler, J.; Machiels, A.; Masson, M.; Storrer, F.; Uchiyama, G.; Participants; Bakhtyar, S.; Bohe, A.; Bychkov, A.; Godun, O.; Inoue, T.; Jackson, D.; Jung, I. H.; Koch, L.; Kormilitsyn, V.; Law, J.; Maurin, M.; Ospina-Esperon, C.; Osipenko, A.; Sheng, X.; Tulackova, R. *Spent Fuel Reprocessing Options*; International Atomic Energy Agency: Vienna, 2008; pp 1-151.

18. Orano The world leader in recycling used nuclear fuels. https://www.orano.group/en/nuclear-expertise/from-exploration-to-recycling/world-leader-in-recycling-used-nuclear-fuels (accessed 17/7/21).

19. Benedicic, J., Life without reprocessing – the end of an era. *Nuclear Future* **2017,** *13* (2), 34-39.

20. Denniss, I. S.; Jeapes, A. P., Reprocessing irradiated fuel. In *The Nuclear Fuel Cycle*, Wilson, P. D., Ed. Oxford Science Publications: Oxford, 1996.

21. Herbst, R. S.; Baron, P.; Nilsson, M., Standard and advanced separation: PUREX processes for nuclear fuel reprocessing. In *Advanced separation techniques for nuclear fuel reprocessing and radioactive waste treatment*, Nash, K. L., Lumetta, G. J., Ed. Woodhouse Publishing Ltd.: Oxford, 2011; pp 141-175.

22. Taylor, R., The Chemical Basis for Separating Recycling Materials by Hydro-Processes. In *Encyclopedia of Nuclear Energy*, Greenspan, E., Ed. Elsevier: Oxford, 2021; pp 450-464.

23. Collins, E. D.; DelCul, G. D.; Renier, J. P.; Spencer, B. B. *Preliminary Multicycle Transuranic Actinide Partitioning-Transmutation Studies*; Oak Ridge National Laboratory: 2007; pp 1-66.

24. Nishihara, K.; Nakayama, S.; Morita, Y.; Oigawa, H.; Iwasaki, T., Impact of Partitioning and Transmutation on LWR High-Level Waste Disposal. *Journal of Nuclear Science and Technology* **2008,** *45* (1), 84-97.

25. Nishihara, K.; Oigawa, H.; Nakayama, S.; Ono, K.; Shiotani, H., Impact of Partitioning and Transmutation on High-Level Waste Disposal for the Fast Breeder Reactor Fuel Cycle. *Journal of Nuclear Science and Technology* **2010,** *47* (12), 1101-1117.

26. Delpech, M.; Salvatores, M.; Zaetta, A.; Maschek, W.; Romanello, V.; Glinatsis, G.; Mizuno, T.; Bays, S.; Hoffman, E.; Taiwo, T. A.; Wigeland, R.; Choi, Y.-J. *Homogeneous versus heterogeneous recycling of transuranics in fast nuclear reactors*; OECD-NEA: Paris, 2012; pp 1-95.

27. Geist, A.; Adnet, J.-M.; Bourg, S.; Ekberg, C.; Galán, H.; Guilbaud, P.; Miguirditchian, M.; Modolo, G.; Rhodes, C.; Taylor, R., An overview of solvent extraction processes developed in Europe for advanced nuclear fuel recycling, part 1 — heterogeneous recycling. *Separation Science and Technology* **2021,** *56*, 1866-1881.

28. Taylor, R. J.; Gregson, C. R.; Carrott, M. J.; Mason, C.; Sarsfield, M. J., Progress towards the Full Recovery of Neptunium in an Advanced PUREX Process. *Solvent Extraction and Ion Exchange* **2013,** *31* (4), 442-462.

29. Herbst, R. S.; Baron, P.; Nilsson, M., 6 - Standard and Advanced Separation: PUREX Processes for Nuclear Fuel Reprocessing. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, Nash, K. L.; Lumetta, G. J., Eds. Woodhead Publishing: 2011; pp 141-175.

30. Chauvin, N.; Minato, K.; Ogata, T.; Pouchon, M. A.; Pasamehmetoglu, K. O.; Choi, Y. J.; Massara, S.; Cornet, S.; Sommers, J. *State-of-the-art Report on Innovative Fuels for Advanced Nuclear Systems*; OECD-NEA: Paris, 2014; pp 1-198.

31. Lecomte, M. E., *Treatment and recycling of spent nuclear fuel: actinide partitioning - application to waste management* CEA Saclay: Paris, 2008.

32. Madic, C.; Lecomte, M.; Baron, P.; Boullis, B., Separation of long-lived radionuclides from high active nuclear waste. *Comptes Rendus Physique* **2002,** *3* (7), 797-811.

33. Madic, C.; Hudson, M. J.; Liljenzin, J.-O.; Glatz, J.-P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R. *New Partitioning Techniques for Minor Actinides. Final Report*; European Commission (NEWPART project): Luxembourg, 2000.

34. Madic, C.; Hudson, M. J.; Liljenzin, J.-O.; Glatz, J.-P.; Nannicini, R.; Facchini, A.; Kolarik, Z.; Odoj, R., Recent achievements in the development of partitioning processes of minor actinides from nuclear wastes obtained in the frame of the NEWPART European programme (1996–1999). *Progress in Nuclear Energy* **2002,** *40* (3), 523-526.

35. Madic, C.; Testard, F.; Hudson, M. J.; Liljenzin, J.-O.; Christiansen, B.; Ferrando, M.; Facchini, A.; Geist, A.; Modolo, G.; Espartero, A. G.; De Mendoza, J. *PARTNEW—New Solvent Extraction Processes for Minor Actinides. Final Report*; France, 2004.

36. Madic, C.; Ouvrier, N., EUROPART: EUROpean research program for the PARTitioning of minor actinides from high active wastes arising from the reprocessing of spent nuclear fuels. *Radiochimica Acta* **2008,** *96* (4-5), 183-185.

37. Bourg, S.; Hill, C.; Caravaca, C.; Rhodes, C.; Ekberg, C.; Taylor, R.; Geist, A.; Modolo, G.; Cassayre, L.; Malmbeck, R.; Harrison, M.; de Angelis, G.; Espartero, A.; Bouvet, S.; Ouvrier, N., ACSEPT--Partitioning technologies and actinide science: Towards pilot facilities in Europe. *Nuclear Engineering and Design* **2011,** *241*, 3427-3435.

38. Bourg, S.; Guilbaud, P.; Mendes, E.; Ekberg, C.; Gibilaro, M.; Soucek, P.; Modolo, G.; Geist, A.; Boo, E.; Duplantier, B.; Rhodes, C.; Taylor, R.; Harrison, M.; Flint, L.; Bell, K.; Sharrad, C.; Hanson, B. *SACSESS: Final Report*; CEA: France, 2016; pp 1-35.

39. Geist, A.; Taylor, R.; Ekberg, C.; Guilbaud, P.; Modolo, G.; Bourg, S., The SACSESS Hydrometallurgy Domain — An Overview. *Procedia Chemistry* **2016,** *21*, 218-222.

40. Bourg, S.; Geist, A.; Narbutt, J., SACSESS – the EURATOM FP7 project on actinide separation from spent nuclear fuels. *Nukleonika* **2015,** *60*, 809-814.

41. Bourg, S.; Geist, A.; Adnet, J.-M.; Rhodes, C.; Hanson, B. C., Partitioning and transmutation strategy R&D for nuclear spent fuel: the SACSESS and GENIORS projects. *EPJ Nuclear Sci. Technol.* **2020,** *6*, 35.

42. Lewin, R. G.; Harrison, M. T., 15 - International developments in electrorefining technologies for pyrochemical processing of spent nuclear fuels. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 373-413.

43. Modolo, G.; Geist, A.; Miguirditchian, M., 10 - Minor actinide separations in the reprocessing of spent nuclear fuels: recent advances in Europe. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 245-287.

44. Glatz, J.-P.; Malmbeck, R.; Souček, P.; Claux, B.; Meier, R.; Ougier, M.; Murakami, T., 26 - Development of Pyrochemical Separation Processes for Recovery of Actinides from Spent Nuclear Fuel in Molten LiCl-KCl. In *Molten Salts Chemistry*, Lantelme, F.; Groult, H., Eds. Elsevier: Oxford, 2013; pp 541-560.

45. Till, C. E.; Chang, Y. I., *Plentiful energy: the story of the Integral Fast Reactor*. CreateSpace: Amazon, 2011.

46. Koyama, T., 10 - Nuclear engineering for pyrochemical treatment of spent nuclear fuels. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, Nash, K. L.; Lumetta, G. J., Eds. Woodhead Publishing: Oxford, 2011; pp 269-310.

47. Koyama, T.; Iizuka, M., 18 - Pyrochemical fuel cycle technologies for processing of spent nuclear fuels: Developments in Japan. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 457-519.

48. Lee, H., 16 - Oxide electroreduction and other processes for pyrochemical processing of spent nuclear fuels: Developments in Korea. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 415-436.

49. Souček, P.; Malmbeck, R., 17 - Pyrochemical processes for recovery of actinides from spent nuclear fuels. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 437-456.

50. Minato, K., 22 - Development of closed nuclear fuel cycles in Japan. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 565-578.

51. Miles, J. H., Separation of plutonium and uranium. In *Science and Technology of Tributyl Phosphate*, Schulz, W. W.; Burger, L. L.; Navratil, J. D.; Bender, K. P., Eds. CRC Press: Boca Raton, Florida, 1990; Vol. III, pp 11-54.

52. Hanson, B., 6 - Process engineering and design for spent nuclear fuel reprocessing and recycling plants. In *Reprocessing and Recycling of Spent Nuclear Fuel*, Taylor, R., Ed. Woodhead Publishing: Oxford, 2015; pp 125-151.

53. Geist, A.; Hill, C.; Modolo, G.; Foreman, M. R. S. J.; Weigl, M.; Gompper, K.; Hudson, M. J., 6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl) [2,2′]bipyridine, an Effective Extracting Agent for the Separation of Americium(III) and Curium(III) from the Lanthanides. *Solvent Extraction and Ion Exchange* **2006,** *24* (4), 463-483.

54. Panak, P. J.; Geist, A., Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands. *Chemical Reviews* **2013,** *113* (2), 1199-1236.

55. Modolo, G.; Wilden, A.; Geist, A.; Magnusson, D.; Malmbeck, R., A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate. *Radiochimica Acta* **2012,** *100* (8-9), 715-725.

56. Modolo, G.; Wilden, A.; Kaufholz, P.; Bosbach, D.; Geist, A., Development and demonstration of innovative partitioning processes (i-SANEX and 1-cycle SANEX) for actinide partitioning. *Progress in Nuclear Energy* **2014,** *72*, 107-114.

57. Taylor, R.; Bourg, S.; Glatz, J.-P.; Modolo, G., Development of actinide separation processes for future nuclear fuel cycles in Europe. *Nuclear Future* **2015,** *11* (4), 38-43.

58. Miguirditchian, M.; Chareyre, L.; Hérès, X.; Hill, C.; Baron, P.; Masson, M. In *GANEX: Adaptation of the DIAMEX-SANEX Process for the Group Actinide Separation*, Proc. GLOBAL 2007, Advanced Nuclear Fuel Cycles and Systems, Boise, Idaho, American Nuclear Society: Boise, Idaho, 2007; pp 550-552.

59. Miguirditchian, M.; Roussel, H.; Chareyre, L.; Baron, P. In *HA demonstration in the Atalante facility of the GANEX 2nd cycle for the grouped TRU extraction*, GLOBAL 2009, Paris, France, American Nuclear Society: Paris, France, 2009; p 9378.

60. Miguirditchian, M., Héres, X., Chareyre, L., Baron, P. Grouped separation of actinides from a highly acidic aqueous phase. WO2007/118904 A1, 2007.

61. Miguirditchian, M.; Sorel, C.; Camès, B.; Bisel, I.; Baron, P., Extraction of uranium (VI by N,N-di(2-ethylhexyl)isobutyramide (DEHIBA): from the batch experimental data to the countercurrent process. In *Solvent extraction: fundamentals to industrial applications. Proceedings ISEC 2008 International Solvent Extraction conference*, Moyer, B. A., Ed. Can. Inst. Min. Metall. Pet.: Montreal, Canada, 2008; pp 721-726.

62. Carrott, M.; Bell, K.; Brown, J.; Geist, A.; Gregson, C.; Hères, X.; Maher, C.; Malmbeck, R.; Mason, C.; Modolo, G.; Müllich, U.; Sarsfield, M.; Wilden, A.; Taylor, R., Development of a new flowsheet for co-separating the transuranic actinides: the "EURO-GANEX" process. *Solvent Extraction and Ion Exchange* **2014,** *32*, 447-467.

63. Carrott, M.; Geist, A.; Hères, X.; Lange, S.; Malmbeck, R.; Miguirditchian, M.; Modolo, G.; Wilden, A.; Taylor, R., Distribution of plutonium, americium and interfering fission products between nitric acid and a mixed organic phase of TODGA and DMDOHEMA in kerosene, and implications for the design of the "EURO-GANEX" process. *Hydrometallurgy* **2015,** *152*, 139-148.

64. Malmbeck, R.; Magnusson, D.; Bourg, S.; Carrott, M.; Geist, A.; Hérès, X.; Miguirditchian, M.; Modolo, G.; Müllich, U.; Sorel, C.; Taylor, R.; Wilden, A., Homogenous recycling of transuranium elements from irradiated fast reactor fuel by the EURO-GANEX solvent extraction process. *Radiochimica Acta* **2019,** *107* (9-11), 917-929.

65. Aneheim, E.; Ekberg, C.; Foreman, M. R. S. J., A TBP/BTBP-Based GANEX Separation Process – Part 3: Fission Product Handling. *Solvent Extraction and Ion Exchange* **2013,** *31* (3), 237-252.

66. Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. S. J.; Grűner, B.; Hájková, Z.; Kvičalová, M., A TBP/BTBP-based GANEX Separation Process—Part 2: Ageing, Hydrolytic, and Radiolytic Stability. *Solvent Extraction and Ion Exchange* **2011,** *29* (2), 157-175.

67. Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. S. J.; Retegan, T.; Skarnemark, G., A TBP/BTBP-based GANEX Separation Process. Part 1: Feasibility. *Solvent Extraction and Ion Exchange* **2010,** *28* (4), 437-458.

68. Halleröd, J.; Ekberg, C.; Aneheim, E., Phenyl trifluoromethyl sulfone as diluent in a grouped actinide extraction process: extraction properties of the solvent components TBP and CyMe4-BTBP. *Journal of Radioanalytical and Nuclear Chemistry* **2016,** *307* (3), 1711-1715.

69. Pathak, P. N.; Veeraraghavan, R.; Prabhu, D. R.; Mahajan, G. R.; Manchanda, V. K., Separation Studies of Uranium and Thorium Using Di-2-Ethylhexyl Isobutyramide (D2EHIBA). *Separation Science and Technology* **1999,** *34* (13), 2601-2614.

70. Condamines, N.; Musikas, C., The extraction by N,N-dialkylamides. II. Extraction of actinide cations. *Solvent Extraction and Ion Exchange* **1992,** *10*, 69-100.

71. Miguirditchian, M.; Sorel, C.; Camès, B.; Bisel, I.; Baron, P.; Espinoux, D.; Calor, J.-N.; Viallesoubranne, C.; Lorrain, B.; Masson, M. In *HA Demonstration in the Atalante Facility of the GANEX 1st Cycle for the Selective Extraction of Uranium from HLW*, GLOBAL, Paris, France, GLOBAL: Paris, France, 2009; pp 1032-1035.

72. Bisson, J.; Dinh, B.; Huron, P.; Huel, C., PAREX, A Numerical Code in the Service of La Hague Plant Operations. *Procedia Chemistry* **2016,** *21*, 117-124.

73. Moeyaert, P.; Dumas, T.; Guillaumont, D.; Solari, P. L.; Lefebvre, C.; Thevenet, A.; Sorel, C.; Moisy, P., Modeling and Speciation Study of Uranium(VI) and Technetium(VII) with TBP. *Solvent Extraction and Ion Exchange* **2021,** *39* (3), 305-327.

74. Moeyaert, P.; Dumas, T.; Guillaumont, D.; Kvashnina, K.; Sorel, C.; Miguirditchian, M.; Moisy, P.; Dufrêche, J.-F., Modeling and Speciation Study of Uranium(VI) and Technetium(VII) Coextraction with DEHiBA. *Inorganic Chemistry* **2016,** *55* (13), 6511-6519.

75. Baron, P.; Cornet, S. M.; Collins, E. D.; DeAngelis, G.; Del Cul, G.; Fedorov, Y.; Glatz, J. P.; Ignatiev, V.; Inoue, T.; Khaperskaya, A.; Kim, I. T.; Kormilitsyn, M.; Koyama, T.; Law, J. D.; Lee, H. S.; Minato, K.; Morita, Y.; Uhlíř, J.; Warin, D.; Taylor, R. J., A review of separation processes proposed for advanced fuel cycles based on technology readiness level assessments. *Progress in Nuclear Energy* **2019,** *117*, 103091.

76. Baron, P. *National Programmes in Chemical Partitioning: A Status Report*; Nuclear Energy Agency, Organisation for Economic Cooperation and Development: Paris, 2010; pp 1-120.

77. Modolo, G.; Asp, H.; Schreinemachers, C.; Vijgen, H., Development of a TODGA based Process for Partitioning of Actinides from a PUREX Raffinate Part I: Batch Extraction Optimization Studies and Stability Tests. *Solvent Extraction and Ion Exchange* **2007,** *25* (6), 703-721.

78. Modolo, G.; Asp, H.; Vijgen, H.; Malmbeck, R.; Magnusson, D.; Sorel, C., Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from a Simulated PUREX Raffinate, Part II: Centrifugal Contactor Runs. *Solvent Extraction and Ion Exchange* **2008,** *26* (1), 62-76.

79. Magnusson, D.; Christiansen, B.; Glatz, J.-P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C., Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate -- Part III: Centrifugal Contactor Run using Genuine Fuel Solution. *Solvent Extraction and Ion Exchange* **2009,** *27* (1), 26-35.

80. Brown, J.; Carrott, M. J.; Fox, O. D.; Maher, C. J.; Mason, C.; McLachlan, F.; Sarsfield, M. J.; Taylor, R. J.; Woodhead, D. A., Screening of TODGA/TBP/OK solvent mixtures for the grouped extraction of actinides. *IOP Conference Series: Materials Science and Engineering* **2010,** *9* (1), 012075.

81. Brown, J.; McLachlan, F.; Sarsfield, M. J.; Taylor, R. J.; Modolo, G.; Wilden, A., Plutonium loading of prospective grouped actinide extraction (GANEX) solvent systems based on diglycolamide extractants. *Solvent Extraction and Ion Exchange* **2012,** *30*, 127-141.

82. Berthon, L.; Paquet, A.; Saint-Louis, G.; Guilbaud, P., How Phase Modifiers Disrupt Third-phase Formation in Solvent Extraction Solutions. *Solvent Extraction and Ion Exchange* **2021,** *39* (2), 204-232.

83. Bell, K.; Carpentier, C.; Carrott, M.; Geist, A.; Gregson, C.; Hérès, X.; Magnusson, D.; Malmbeck, R.; McLachlan, F.; Modolo, G.; Müllich, U.; Sypula, M.; Taylor, R.; Wilden, A., Progress Towards the Development of a New GANEX Process. *Proc. Chem.* **2012,** *7*, 392-397.

84. Geist, A.; Müllich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T., Actinide(III)/Lanthanide(III) Separation Via Selective Aqueous Complexation of Actinides(III) using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-Yl)-Pyridine in Nitric Acid. *Solvent Extraction and Ion Exchange* **2012,** *30* (5), 433-444.

85. Wilden, A.; Modolo, G.; Kaufholz, P.; Sadowski, F.; Lange, S.; Sypula, M.; Magnusson, D.; Müllich, U.; Geist, A.; Bosbach, D., Laboratory-Scale Counter-Current Centrifugal Contactor Demonstration of an Innovative-SANEX Process Using a Water Soluble BTP. *Solvent Extraction and Ion Exchange* **2015,** *33* (2), 91-108.

86. Carrott, M. J., Fox, O. D., Maher, C. J., Mason, C., Taylor, R. J., Sinkov, S. I., Choppin, G. R., Solvent Extraction Behavior of Plutonium (IV) Ions in the Presence of Simple Hydroxamic Acids. *Solvent Extraction and Ion Exchange* **2007,** *25* (6), 723-745.

87. Carrot, M. J.; Gregson, C. R.; Taylor, R. J., Neptunium extraction and stability in the GANEX solvent: 0.2 M TODGA / 0.5 M DMDOHEMA / kerosene. *Solvent Extraction and Ion Exchange* **2013,** *31*, 463-482

88. Sypula, M.; Wilden, A.; Schreinemachers, C.; Malmbeck, R.; Geist, A.; Taylor, R.; Modolo, G., Use of polyaminocarboxylic acids as hydrophilic masking agents for fission products in actinide partitioning processes. *Solvent Extraction and Ion Exchange* **2013,** *3*, 748-764.

89. Moeyaert, P.; Miguirditchian, M.; Masson, M.; Dinh, B.; Hérès, X.; De Sio, S.; Sorel, C., Experimental and modelling study of ruthenium extraction with tri-n-butylphosphate in the purex process. *Chemical Engineering Science* **2017,** *158*, 580-586.

90. Pruett, D. J., Extraction chemistry of fission products. In *Science and Technology of Tributyl Phosphate*, Schulz, W. W.; Burger, L. L.; Navratil, J. D., Eds. CRC Press: Boca Raton, 1990; Vol. III, pp 81-122.

91. Drake, V. A., Extraction chemistry of neptunium. In *Science and technology of tributyl phosphate*, Schulz, W. W.; Burger, L. L.; Navratil, J. D.; Bender, K. P., Eds. CRC Press Inc.: Boca Raton, Florida, 1990; Vol. III. Applications of tributyl phosphate in nuclear fuel reprocessing, pp 123-146.

92. Carrott, M. J.; Gregson, C. R.; Taylor, R. J., Neptunium extraction and stability in the GANEX solvent (0.2 M TODGA / 0.5 M DMDOHEMA / kerosene). *Solvent Extr. Ion Exch.* **2013,** *31* (5), 463-482.

93. Sarsfield, M. J., Taylor, R. J., Maher, C. J., Neptunium(V) disproportionation and cation–cation interactions in TBP/kerosene solvent. *Radiochimica Acta* **2007,** *95*, 677-682.

94. Moulin, J. P. *Oxidation – reduction kinetics of neptunium in nitric acid solution*; Fontenay-aux-Roses, France, 1978.

95. Precek, M.; Paulenova, A.; Tkac, P.; Knapp, N., Effect of Gamma Irradiation on the Oxidation State of Neptunium in Nitric Acid in the Presence of Selected Scavengers. *Separation Science and Technology* **2010,** *45* (12-13), 1699-1705.

96. Flint, L. *Production of SACSESS combined safety methodology: Delivery of the SACSESS combined safety assessment methodology*; National Nuclear Laboratory: Preston, 2014.

97. Carrott, M. J.; Maher, C. J.; Mason, C.; Sarsfield, M. J.; Whittaker, D.; Taylor, R. J., Experimental test of a process upset in the EURO-GANEX process. *Separation Science and Technology* **2021,** *in preparation*.

98. Ockenden, D. W.; Welch, G. A., 653. The preparation and properties of some plutonium compounds. Part V. Colloidal quadrivalent plutonium. *Journal of the Chemical Society (Resumed)* **1956,** (0), 3358-3363.

99. Sánchez-García, I.; Galán, H.; Perlado, J. M.; Cobos, J., Stability studies of GANEX system under different irradiation conditions. *EPJ Nuclear Sci. Technol.* **2019,** *5*, 19.

100. Sánchez-García, I.; Galán, H.; Perlado, J. M.; Cobos, J., Development of experimental irradiation strategies to evaluate the robustness of TODGA and water-soluble BTP extraction systems for advanced nuclear fuel recycling. *Radiation Physics and Chemistry* **2020,** *177*, 109094.

101. Galán, H.; Núñez, A.; Espartero, A. G.; Sedano, R.; Durana, A.; de Mendoza, J., Radiolytic Stability of TODGA: Characterization of Degraded Samples under Different Experimental Conditions. *Procedia Chemistry* **2012,** *7*, 195-201.

102. Galan, H.; Zarzana, C. A.; Wilden, A.; Nunez, A.; Schmidt, H.; Egberink, R. J. M.; Leoncini, A.; Cobos, J.; Verboom, W.; Modolo, G.; Groenewold, G. S.; Mincher, B. J., Gamma-radiolytic stability of new methylated TODGA derivatives for minor actinide recycling. *Dalton Transactions* **2015,** *44* (41), 18049-18056.

103. Hubscher-Bruder, V.; Mogilireddy, V.; Michel, S.; Leoncini, A.; Huskens, J.; Verboom, W.; Galan, H.; Nunez, A.; Cobos, J.; Modolo, G.; Wilden, A.; Schmidt, H.; Charbonnel, M. C.; Guilbaud, P.; Boubals, N., Behaviour of the extractant Me-TODGA upon gamma irradiation: quantification of degradation compounds and individual influences on complexation and extraction. *New J. Chem.* **2017,** *41* (22), 13700-13711.

104. Peterman, D.; Geist, A.; Mincher, B.; Modolo, G.; Galán, M. H.; Olson, L.; McDowell, R., Performance of an i-SANEX System Based on a Water-Soluble BTP under Continuous Irradiation in a γ-Radiolysis Test Loop. *Industrial & Engineering Chemistry Research* **2016,** *55* (39), 10427-10435.

105. Sánchez-García, I.; Bonales, L. J.; Galán, H.; Perlado, J. M.; Cobos, J., Radiolytic degradation of sulphonated BTP and acetohydroxamic acid under EURO-GANEX process conditions. *Radiation Physics and Chemistry* **2021,** *183*, 109402.

106. Aneheim, E.; Ekberg, C.; Foreman, M. R. S., Aqueous complexation of palladium to prevent precipitation and extraction in a group actinide extraction system. *Hydrometallurgy* **2012,** *115-116*, 71-76.

107. Authen, T. L. CHALMEX FS-13 investigations for process implementation. Chalmers University of Technology, Gothenburg, Sweden, 2020.

108. Authen, T. L.; Wilden, A.; Halleröd, J.; Schneider, D.; Kreft, F.; Modolo, G.; Ekberg, C., Batch Tests for Optimisation of Solvent Composition and Process flexibility of the CHALMEX FS-13 Process. *Solvent Extr. Ion Exch.* **2021,** *39* (1), 1-17.

109. Authen, T. L.; Wilden, A.; Schneider, D.; Kreft, F.; Modolo, G.; Foreman, M. R. S.; Ekberg, C., Batch flowsheet test for a GANEX-type process: the CHALMEX FS-13 process. *Solvent Extr. Ion Exch.* **2021,** *DOI:10.1080/07366299.2021.1890372*.

110. Halleröd, J.; Ekberg, C.; Authen, T.; Bertolo, L.; Lin, M.; Grüner, B.; Švehla, J.; Wagner, C.; Geist, A.; Panak, P.; Aneheim, E., On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based GANEX System Containing CyMe4-BTBP and TBP. *Solvent Extraction and Ion Exchange* **2018,** *36* (4), 360-372.

111. Halleröd, J.; Ekberg, C.; Kajan, I.; Aneheim, E., Solubility Thermodynamics of $CyMe_4$-BTBP in Various Diluents Mixed with TBP. *Journal of Solution Chemistry* **2018,** *47* (6), 1021-1036.

112. Halleröd, J.; Ekberg, C.; Löfström-Engdahl, E.; Aneheim, E., Development of the Chalmers Grouped Actinide Extraction Process. *Nukleonika* **2015,** *60* (4), 829-835.

113. Schmidt, H.; Wilden, A.; Modolo, G.; Bosbach, D.; Santiago-Schübel, B.; Hupert, M.; Švehla, J.; Grüner, B.; Ekberg, C., Gamma Radiolysis of the Highly Selective Ligands CyMe4BTBP and CyMe4BTPhen: Qualitative and Quantitative Investigation of Radiolysis Products. *Procedia Chemistry* **2016,** *21*, 32-37.

114. Schmidt, H. W., A.; Modolo, G.; Švehla, J.; Grüner, B.; Ekberg, C., Gamma radiolytic stability of CyMe4BTBP and effect of nitric acid. *Nukleonika* **2015,** *60*, 879-884.

115. Holger Schmidt, A. W., Giuseppe Modolo, Dirk Bosbach, Beatrix Santiago-Schübel, Michelle Hupert, Bruce J. Mincher, Stephen P. Mezyk, Jaroslav Švehla, Bohumir Grüner and Christian Ekberg, Gamma and pulsed electron radiolysis studies of CyMe4BTBP and CyMe4BTPhen: identification of radiolysis products and effects on the hydrometallurgical separation of trivalent actinides and lanthanides. *Radiation Physics and Chemistry* **2021,** *accepted*.

116. Retegan, T.; Ekberg, C.; Englund, S.; Fermvik, A.; Foreman, M. R. S.; Skarnemark, G., The behaviour of organic solvents containing C5-BTBP and CyMe4-BTBP at low irradiation doses. *Radiochimica Acta* **2007,** *95*, 637-642.

117. Wilden, A.; Modolo, G.; Schreinemachers, C.; Sadowski, F.; Lange, S.; Sypula, M.; Magnusson, D.; Geist, A.; Lewis, F. W.; Harwood, L. M.; Hudson, M. J., Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe4BTBP and TODGA as 1-cycle SANEX Solvent Part III: Demonstration of a Laboratory-Scale Counter-Current Centrifugal Contactor Process. *Solvent Extraction and Ion Exchange* **2013,** *31* (5), 519-537.

118. Wilden, A.; Schreinemachers, C.; Sypula, M.; Modolo, G., Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe4BTBP and TODGA as 1-cycle SANEX Solvent. *Solvent Extraction and Ion Exchange* **2011,** *29* (2), 190-212.

119. Magnusson, D.; Geist, A.; Wilden, A.; Modolo, G., Direct Selective Extraction of Actinides(III) from PUREX Raffinate Using a Mixture of CyMe4-BTBP and TODGA as 1-cycle SANEX Solvent PART II: Flow-sheet Design for a Counter-Current Centrifugal Contactor Demonstration Process. *Solvent Extraction and Ion Exchange* **2013,** *31* (1), 1-11.

120. Herbst, R. S.; Law, J. D.; Todd, T. A.; Romanovskiy, V. N.; Smirnov, I. V.; Babain, V. A.; Esimantovskiy, V. N.; Zaitsev, B. N., Development Of The Universal Extraction (Unex) Process For The Simultaneous Recovery Of Cs, Sr, And Actinides From Acidic Radioactive Wastes. *Separation Science and Technology* **2003,** *38* (12-13), 2685-2708.

121. Kumar, S.; Muthukumar, M.; Sinha, P. K.; Kamachi Mudali, U.; Natarajan, R., PVT properties of UNEX/HCCD-PEG diluent phenyl trifluoromethyl sulfone (FS-13) and experimental measurement of vapour pressure in 283.15–363.15 K range. *Journal of Radioanalytical and Nuclear Chemistry* **2011,** *289* (1), 247-249.

122. Law, J. D.; Herbst, R. S.; Todd, T. A.; Romanovskiy, V. N.; Babain, V. A.; Esimantovskiy, V. M.; Smirnov, I. V.; Zaitsev, B. N., The Universal Solvent Extraction (Unex) Process. Ii. Flowsheet Development And Demonstration Of The Unex Process For The Separation Of Cesium, Strontium, And Actinides From Actual Acidic Radioactive Waste. *Solvent Extraction and Ion Exchange* **2001,** *19* (1), 23-36.

123. Luther, T. A.; Herbst, R. S.; Peterman, D. R.; Tillotson, R. D.; Garn, T. G.; Babain, V. A.; Smirnov, I. V.; Stoyanov, E. S.; Antonov, N. G., Some aspects of fundamental chemistry of the Universal Extraction (UNEX) process for the simultaneous separation of major radionuclides (cesium, strontium, actinides, and lanthanides) from radioactive wastes. *Journal of Radioanalytical and Nuclear Chemistry* **2006,** *267* (3), 603-613.

124. Romanovskiy, V. N.; Smirnov, I. V.; Babain, V. A.; Todd, T. A.; Herbst, R. S.; Law, J. D.; Brewer, K. N., The Universal Solvent Extraction (Unex) Process. I. Development Of The Unex Process Solvent For The Separation Of Cesium, Strontium, And The Actinides From Acidic Radioactive Waste. *Solvent Extraction and Ion Exchange* **2001,** *19* (1), 1-21.

125. Rzhekhina, E. K.; Karkozov, V. G.; Alyapyshev, M. Y.; Babain, V. A.; Smirnov, I. V.; Todd, P. A.; Law, J. D.; Herbst, R. S., Reprocessing of spent solvent of the UNEX process. *Radiochemistry* **2007,** *49* (5), 493-498.

126. Sinha, P. K.; Kumar, S.; Kamachi Mudali, U.; Natarajan, R., Thermal Stability of UNEX/HCCD-PEG Diluent FS-13. *Journal of Radioanalytical and Nuclear Chemistry* **2011,** *289* (3), 899-901.

127. SpringerMaterials Interactive, Dielectric Constant of Phenyl trifluoromethyl sulfone (pure). Springer-Verlag Berlin Heidelberg Release 2017: Online, 2017.

128. Ekberg, C.; Löfström-Engdahl, E.; Aneheim, E.; Foreman, M. R. S.; Geist, A.; Lundberg, D.; Denecke, M.; Persson, I., The structures of CyMe$_4$-BTBP complexes of americium(III) and europium(III) in solvents used in solvent extraction, explaining their separation properties. *Dalton Transactions* **2015,** *44* (42), 18395-18402.

129. Bartholomew, C. H.; Farrauto, R. J., *Fundamentals of industrial catalytic processes*. 2. ed. ed.; Wiley Interscience: Hoboken, New Jersey, 2006.

130. Sinkov, S.; Choppin, G., Acetohydroxamic Acid Complexes with Trivalent f-Block Metal Cations. *Journal of Nuclear Science and Technology* **2002,** *39* (sup3), 359-362.

131. Sinkov, S. I.; Choppin, G. R.; Taylor, R. J., Spectrophotometry and Luminescence Spectroscopy of Acetohydroxamate Complexes of Trivalent Lanthanide and Actinide Ions. *Journal of Solution Chemistry* **2007,** *36* (6), 815-830.

132. Taylor, R. J.; Sinkov, S. I.; Choppin, G. R., Complexation of lanthanides and actinides by aceto-hydroxamic acid. In *Solvent extraction: fundamentals to industrial applications, Proc. ISEC 2008 International Solvent Extraction conference*, Moyer, B. A., Ed. Can. Inst. Min. Metall. Pet.: Montreal, 2008; pp 527-531.

133. Taylor, R. J.; Sinkov, S. I.; Choppin, G. R.; May, I., Solvent Extraction Behavior of Neptunium (IV) Ions between Nitric Acid and Diluted 30% Tributyl Phosphate in the Presence of Simple Hydroxamic Acids. *Solvent Extraction and Ion Exchange* **2007,** *26* (1), 41-61.

134. Ruff, C. M.; Müllich, U.; Geist, A.; Panak, P. J., Complexation of Cm(iii) and Eu(iii) with a hydrophilic 2,6-bis(1,2,4-triazin-3-yl)-pyridine studied by time-resolved laser fluorescence spectroscopy. *Dalton Transactions* **2012,** *41* (48), 14594-14602.

135. Carrott, M.; Maher, C.; Mason, C.; Sarsfield, M.; Taylor, R., "TRU-SANEX": A variation on the EURO-GANEX and i-SANEX processes for heterogeneous recycling of actinides Np-Cm. *Separation Science and Technology* **2016,** *51* (13), 2198-2213.

136. Carrott, M. J., Fox, O. D., LeGurun, G., Jones, C. J., Mason, C., Taylor, R. J., Andrieux, F. P. L., Boxall, C., Oxidation–reduction reactions of simple hydroxamic acids and plutonium(IV) ions in nitric acid. *Radiochimica Acta* **2008,** *96* (6), 333-343.

137. Macerata, E.; Mossini, E.; Scaravaggi, S.; Mariani, M.; Mele, A.; Panzeri, W.; Boubals, N.; Berthon, L.; Charbonnel, M.-C.; Sansone, F.; Arduini, A.; Casnati, A., Hydrophilic Clicked 2,6-Bis-triazolyl-pyridines Endowed with High Actinide Selectivity and Radiochemical Stability: Toward a Closed Nuclear Fuel Cycle. *Journal of the American Chemical Society* **2016,** *138* (23), 7232-7235.

138. Mossini, E.; Macerata, E.; Wilden, A.; Kaufholz, P.; Modolo, G.; Iotti, N.; Casnati, A.; Geist, A.; Mariani, M., Optimization and Single-Stage Centrifugal Contactor Experiments with the Novel Hydrophilic Complexant PyTri-Diol for the i-SANEX Process. *Solvent Extraction and Ion Exchange* **2018,** *36* (4), 373-386.

139. Malmbeck, R.; Magnusson, D.; Geist, A., Modified Diglycolamides for Grouped Actinide Separation. *Journal of Radioanalytical and Nuclear Chemistry* **2017,** *314* (3), 2531-2538.

140. Chen, H.; Taylor, R.; Jobson, M.; Woodhead, D.; Masters, A., Development and Validation of a Flowsheet Simulation Model for Neptunium Extraction in an Advanced PUREX Process. *Solvent Extraction and Ion Exchange* **2016,** *34* (4), 297-321.

141. Chen, H.; Taylor, R. J.; Jobson, M.; Woodhead, D. A.; Boxall, C.; Masters, A. J.; Edwards, S., Simulation of Neptunium Extraction in an Advanced PUREX Process—Model Improvement. *Solvent Extraction and Ion Exchange* **2017,** *35* (1), 1-18.

142. McLachlan, F.; Taylor, R.; Whittaker, D.; Woodhead, D.; Geist, A., Modelling of Innovative SANEX Process Maloperations. *Procedia Chemistry* **2016,** *21*, 109-116.