## Chapter 1

# Aqueous Reprocessing of Used Nuclear Fuel

Jack D. Law
*Idaho National Laboratory*
*Idaho Falls, ID 83415-3870, USA*
*jack.law@inl.gov*

## 1. Introduction

Aqueous technologies for used nuclear fuel reprocessing have historically been utilized to recover uranium (U) and plutonium (Pu) from irradiated nuclear reactor fuel for recycle. The purpose for reprocessing used fuel has been to recover unused U and Pu in the used fuel elements. This results in gaining more energy from the original U and contributes to the national energy security of the country reprocessing their fuel. Also, reprocessing results in a reduction in volume of high-level waste for disposal, and the radiotoxicity is lower and reduces more rapidly than with used nuclear fuel.

With aqueous technologies, the used nuclear fuel is typically mechanically chopped into small pieces and leached into an acidic solution. The resulting dissolver product is chemically processed to separate actinides for recycle to a reactor. The remaining metals and fission products are treated for disposal as a high-level waste. The primary aqueous separation method utilized to accomplish the required separation is solvent extraction, although precipitation has been used initially in the US defense industry for the recovery of Pu for weapons.

The plutonium uranium reduction extraction (PUREX) process is the most common solvent extraction technology utilized in the USA and internationally for the separation of U and Pu from used nuclear fuel. Variations in the PUREX process are being developed and implemented to prevent the separation of pure Pu. Additionally, advanced aqueous separation technologies are being developed in the USA and internationally for the separation and recycle/transmutation of minor actinides.

## 2. Solvent Extraction

Solvent extraction is the primary technology utilized in aqueous used nuclear fuel reprocessing. First, used nuclear fuel from a reactor, after some amount of decay storage, is leached with an acidic solution. The resulting aqueous solution is separated from the remaining fuel cladding and then chemically processed via solvent extraction to separate the components of interest, typically U and/or Pu.

Solvent extraction within used nuclear fuel reprocessing utilizes an organic phase containing an extractant, in contact with the aqueous dissolver product via mixing, to extract the components of interest into the organic phase. Typically, this process is carried out by intimately mixing the two immiscible phases, allowing for the selective transfer of solute(s) from one phase to the other, then allowing the two phases to separate. The component of interest is subsequently removed from the organic phase to an aqueous phase via back-extraction. In order for effective processing, the two phases must be immiscible, have enough of a density difference to allow rapid disengagement, be of an appropriate viscosity to be transported through process equipment, limited solubility of the organic phase in the aqueous phase to maintain the extractant concentration over long-term use, and the organic phase must have sufficient hydrolytic and radiolytic stability to allow for long-term reuse to minimize organic waste volumes.

One of the primary advantages of solvent extraction processes is the ability to operate in a continuous, countercurrent manner with multiple contacting/separating stages to achieve the desired removal efficiency of the components being extracted. This allows for continuous operation instead of batch operation. Countercurrent operation is shown graphically for an extraction section of a U/Pu separation flowsheet in Figure 1.

In this flow diagram, the aqueous dissolver product feed stream containing the components to be extracted enters at one end of the process ($A_{N+1}$), and the fresh solvent (organic) stream enters the other end ($O_0$). The aqueous and organic steams flow countercurrently from stage to stage where they are intimately mixed and separated, and the final products are the solvent loaded with the desired components (e.g., U and Pu), $O_N$, leaving stage $N$ and the aqueous raffinate, $A_1$, depleted in U and Pu leaving stage 1.

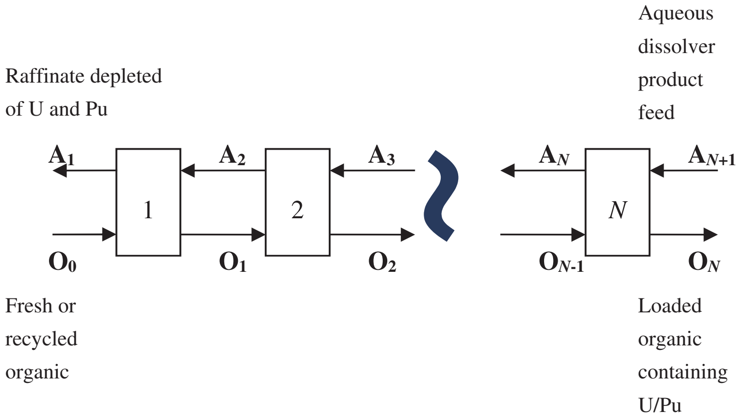

**Figure 1.** Countercurrent — Multistage extraction process flow diagram.

Following an extraction section, scrub, strip, and solvent wash sections are typically employed. The purpose of the scrub section is to back extract (scrub) to the extraction section any metals/fission products (e.g., Zr) that may have co-extracted along with the desired components. The strip section is utilized to back-extract the desired components (e.g., U and Pu) into an aqueous phase where they will ultimately be re-enriched and converted into an oxide form for recycle to a reactor, typically as MOX fuel. The solvent wash section is utilized to remove any hydrolytic or radiolytic degradation products from the solvent and prepare the solvent for recycle to the extraction section, thus minimizing organic waste volumes.

## 3. Solvent Extraction Equipment

Solvent extraction equipment has been utilized in the nuclear industry since the implementation of the PUREX process for the separation of Pu and U from fission products for weapons production in the 1950s [1]. This technology was later implemented for the reprocessing of used nuclear fuel from commercial power reactors. PUREX-based solvent extraction processing has been and continues to be utilized worldwide including France, Japan, Russia, the UK, and the USA. Additionally, considerable research in the development of advanced separation processes is ongoing, requiring the use of solvent extraction equipment. In these efforts, solvent extraction equipment is utilized to efficiently mix and separate the aqueous and organic phases to facilitate separation of the species of interest. The solvent extraction equipment is designed for countercurrent flow to facilitate high separation efficiencies and continuous operation.

To support operation in a radioactive environment, solvent extraction equipment must be remotely operable and maintainable, resistant to high radiation fields, capable of continuous countercurrent operation, and be critically safe for certain applications. In addition, desirable attributes include the ability to accommodate solids, a small process footprint, and operational flexibility (continuous long-term operation or frequent start–stop operation). The three main types of solvent extraction equipment used in industrial-scale reprocessing facilities and in fuel cycle research laboratories include (1) columns, (2) mixer-settlers, and (3) centrifugal contactors. A brief description of each type of equipment follows. More detailed description of these type of equipments can be found in literature [2, 3].

### 3.1. *Columns*

Packed columns and pulse columns with sieve plates or trays are the typical type of solvent extraction column utilized in the nuclear industry. Packed columns contain packing material (e.g., Raschig Rings) to create mixing of the two phases as they flow counter currently. The phases disengage at either the top or the bottom of the column depending upon whether the column is operated in an aqueous or organic continuous mode. Pulsed columns with trays or plates were developed to increase the mixing intensity of the phases and, thus, decrease the height requirement of the column. The mechanical energy applied to the column via pulsing with air facilitates the formation of small droplets for mass transfer. A photograph of an operating pulsed column used to support laboratory testing is shown in Figure 2.

### 3.2. *Mixer-settlers*

A mixer-settler contains a small mixing chamber and a larger settling chamber. The two immiscible phases enter the mixing chamber containing an impeller. This dispersion that forms flows into the settling chamber where the two phases separate by gravity. A system of weirs allow for the light phase to flow over the higher weir and the heavy phase to flow under the lower weir. Multiple mixer-settlers are configured for countercurrent flow to achieve high separation efficiency. A photo of several mixer-settlers is shown in Figure 3.

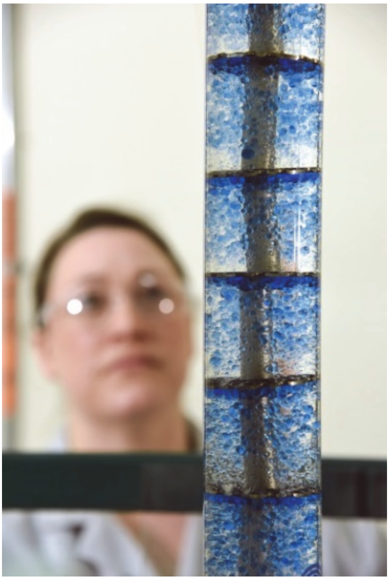

**Figure 2.** Operating lab-scale pulsed column at Idaho National Laboratory.

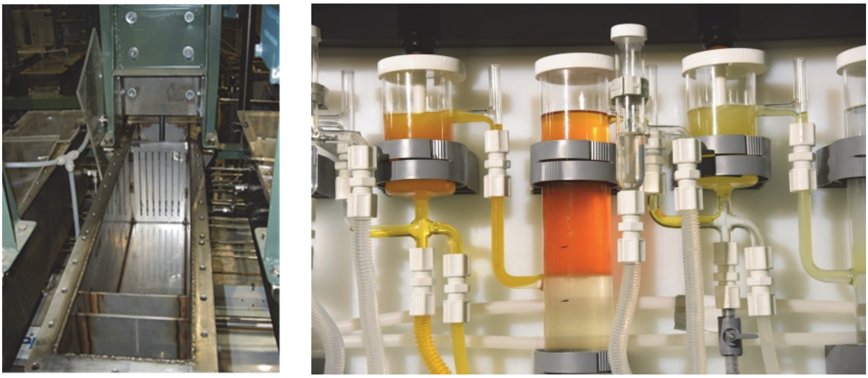

**Figure 3.** Industrial and lab-scale mixer-settlers.

### 3.3. *Centrifugal contactors*

Centrifugal contactors consist of a hollow rotor that rotates within a cylindrical housing utilizing a motor mounted above the housing. The aqueous and organic feed solutions enter a stage near the top of the housing and are mixed as they flow downward. For annular centrifugal contactors, the

**Figure 4.** Operating 5 cm centrifugal contactor with plastic housing.

shear forces between the spinning rotor and the stationary housing mix the two phases. Other contactor designs utilize alternative methods of mixing such as mixing pins attached to the bottom of the spinning rotor. When the mixture enters the spinning rotor through an opening at its base, the spinning rotor acts as a centrifuge with the heavy phase going to the rotor wall. A series of weirs allow the separated heavy and light phases to flow out of the contactors as separate streams. Multiple centrifugal contactors are configured for countercurrent flow to achieve high separation efficiency. An operating centrifugal contactor is shown in Figure 4.

## 4. Reprocessing History

Aqueous reprocessing technologies were first utilized at the Hanford Site during the Manhattan Project for the recovery of Pu-239 by using a bismuthate phosphate precipitation process [1]. Recovery transitioned to solvent extraction processes that allowed for continuous instead of batch operation, as well as the concurrent recovery of U and Pu. Also, the purpose of the reprocessing of used fuel transitioned from defense purposes to commercial use for the recycle of U and Pu.

The first solvent extraction process implemented was the reduction oxidation (REDOX) process [1]. The process was developed and tested at Argonne National Laboratory and Oak Ridge National Laboratory, and the first REDOX plant operated at Hanford. The REDOX process utilizes Methyl isobutyl ketone (hexone) to extract uranyl nitrate and Pu nitrate. U(VI) and Pu(IV) are co-extracted then the Pu is reduced to Pu(III) by using ferrous sulfamate and selectively stripped from the U. One disadvantage of this process is the required addition on aluminum nitrate to increase the nitrate concentration. Also, hexone is a flammable and volatile solvent.

The BUTEX process was developed by British scientists at Chalk River Laboratory [4]. This process utilized dibutyl carbitol as the extractant and used nitric acid as a salting agent instead of aluminum nitrate, thus reducing the problem of larger waste volumes due to the addition of $Al(NO_3)_3$. This process was implemented at the Windscale plant at the Sellafield Site in the UK for the reprocessing of used fuel.

Aqueous reprocessing transitioned to the PUREX process in the 1950s [1]. The PUREX process was developed by Knolls Atomic Power Laboratory and tested at ORNL. A modified PUREX production-scale plant was used in Idaho at the Idaho Chemical Processing Plant beginning in 1953. This process utilized hexone as an extractant in the first cycle and PUREX in the second and third cycles. The PUREX process was utilized on a production scale at Savannah River in the F-Canyon in 1954 [5]. It has been used at the Savannah River Site since 1955 in the H-Canyon facility [5]. It replaced the REDOX process at Hanford in 1956. From here, the use of the PUREX process expanded within the USA and internationally.

## 5. PUREX Process

The PUREX process has historically been the primary aqueous separation process utilized worldwide for the reprocessing of used nuclear fuel. Table 1 lists historical, current, and in-construction reprocessing facilities utilizing the PUREX process or a variant.

The front-end of the PUREX-based reprocessing consists of chopping the used fuel into small pieces; leaching the used fuel from the cladding using a nitric acid solution; separation of the fuel cladding pieces, spacers, and other fittings; chemical adjustment; and filtration of this dissolver product. This dissolver product is then fed to a first cycle of solvent extraction where the U and Pu are separated from the dissolver product and subsequently separated from each other. Several additional cycles of solvent extraction are used to further purify the U and Pu. The resulting U and/or Pu product

Table 1. Historical PUREX reprocessing facilities.

| Facility | Country | Operation | Capacity (MTHM/yr) | Comments |
|---|---|---|---|---|
| Savannah River F, H-Canyon [5] | USA | 1955–present | 5–10 MT/yr | Recovered Pu, U, and Np from weapon production reactors |
| Hanford [6] | USA | 1956–1972, 1983–1988 | 8.3 MT/day design up to 20 actual | Recovered Pu, U, and Np from Hanford production reactors |
| UP1 Magnox-Marcoule [7] | France | 1958–1997 | 960 MT/yr | Fuel from Pu production reactors — later, power reactors |
| B20 — Sellafield | UK | 1964–present | 1500 MT/yr | Magnox fuel [6] |
| Trombay [8, 9] | India | 1964–1973, 1983–present | 60 MT/yr | Research reactor fuel [10] |
| West Valley [8, 10] | USA | 1966–1972 | 300 MT/yr | First plant in USA to process commercial fuel |
| Morris, IL [8, 10] | USA | NA | 300 MT/yr | Construction halted prior to ops. F volatility polishing |
| Barnwell, SC [8, 10] | USA | NA | 1500 MT/yr | Shutdown during startup testing US reprocessing policy change |
| UP2 Magnox-LaHague [7] | France | 1966–1976 | 800 MT/yr | Magnox fuel then converted into oxide fuel |
| Tokai [8] | Japan | 1975–2014 | 210 MT/yr design, 100 actual | Boiling water reactor (BWR) and pressurized water reactor (PWR) fuel, adv. thermal reactor fuel |

| | | | | |
|---|---|---|---|---|
| UP2 Oxide-LaHague [5] | France | 1976–present | 800 MT/yr design, 400 actual | Commercial light water reactor (LWR) fuel |
| RT1 Mayak [8] | Russia | 1976–present | 400 MT/yr | VVER-440 fuel, preparing to expand to VVER-1000 fuel |
| UP3 Oxide-LaHague [7] | France | 1989–present | 800 MT/yr | Commercial LWR fuel for foreign countries |
| Thorp [8] | UK | 1994–present | 1200 MT/yr | Foreign and domestic fuel. Planned shutdown in 2018 |
| KARP-Kalpakkam [9] | India | 1996–present | 100 MT/yr | Reprocesses oxide fuels from PHWRs |
| Jiuquan [11] | China | 2010–present | 50 MT/yr | Pilot scale facility |
| PREFRE-2 Tarapur [9] | India | 2011–present | 100 MT/yr | Oxide fuels from PHWRs |
| Rokkasho [6] | Japan | 2018 | 800 MT/yr | Planned startup in 2018. PUREX process variant |
| New [12] | China | 2025–2030 | 800 MT/yr | AREVA contract to design, 2030 target |

is converted into an oxide form. In commercial fuel reprocessing, the Pu oxide product, with or without U, is recycled to a reactor as mixed oxide (MOX) fuel in light water reactors (LWRs). About 50 reactors in Europe and Japan are licensed to use MOX fuel with around 30 actually doing so.

The PUREX process utilizes 20–40 vol% tributyl phosphate (TBP) in a hydrocarbon diluent (typically kerosene or $n$-dodecane) to extract U and Pu from the dissolver product. The PUREX process is effective in extracting actinides in the +4 and +6 oxidation state. U, as U(VI) is extracted as follows:

$$UO_2^{2+} + 2NO_{3^-} + 2TBP \leftrightarrow UO_2(NO_3)_2 \cdot 2TBP \tag{1}$$

The chemical equilibria for the actinides in the +4 oxidation state is

$$An^{4+} + 4NO_{3^-} + 2TBP \leftrightarrow An(NO_3)_4 \cdot 2TBP \tag{2}$$

In the PUREX process, Pu is present as Pu(IV) and is co-extracted with the U. Other actinides and lanthanides present in the +3 or lower oxidation state are not extracted with the PUREX process, thus allowing for an efficient separation. Neptunium is another actinide that can be maintained as Np(VI), if desired, and co-extracted with the U and Pu.

## 6. PUREX Process Variants

Numerous modifications to the standard PUREX process have been or are currently being developed. The primary purpose of these variations is to prevent the production of a pure Pu stream due to concerns with proliferation. With the standard PUREX process, a pure U stream and a pure Pu stream are produced. Theft or diversion of the reactor-grade Pu for weapons use has been a concern under these conditions. While no separations process can be made proliferation-proof, modifications to the PUREX process can effectively reduce the proliferation risk. Table 2 lists several PUREX process variants that have been or are currently being developed.

### 6.1. *COEX$^{TM}$ process*

The co-extraction (COEX$^{TM}$) process, developed in France by AREVA, utilizes variants of the PUREX process chemistry to allow some of the extracted U to follow the Pu, resulting in three streams; a U/Pu product, a U product, and a raffinate waste solution containing fission products and minor actinides [13]. This is accomplished using a reducing agent, such as U(IV) nitrate or hydroxylamine nitrate to reduce the Pu(IV) to

**Table 2.** PUREX process variants.

| Technology | Country | Variation |
|---|---|---|
| COEX$^{TM}$ | CEA/AREVA France | No separation of pure Pu |
| UREX | Department of Energy (DOE), USA | Single cycle U and technetium (Tc) separation, lower acidity |
| Co-decontamination | DOE, USA | No separation of pure Pu |
| NUEX | Energy Solutions | No separation of pure Pu |
| NNL advanced process | National Nuclear Laboratory, UK | Single cycle, no separation of pure Pu |
| NEXT process | JAEA, Japan | Combines crystallization with PUREX process, no separation of pure Pu |
| Simplified PUREX | Russia | Thermochemical decladding of the used fuel assemblies instead of chopping. Operated at lower acidity |
| PARC process | India | Tc and Np are extracted by TBP along with the U and Pu. Single cycle |

Pu(III) and back-extract this Pu while only partially reducing and back-extracting the U(VI). Additionally, this multi-cycle process includes the use of a co-conversion process to produce a U/Pu oxide product. At no point during the process is pure Pu separated.

### 6.2. *UREX*

The uranium extraction (UREX) process is a variant of the PUREX process that was developed by the US Department of Energy (DOE) as a method to separate U, without co-extracting Pu [14, 15]. Co-extraction of Pu and Np is prevented by introduction of a complexant/reductant, such as acetohydroxamic acid (AHA) in the scrub feed. The complexation of Pu and Np are enhanced in the UREX process through the use of low-acidity feed and scrub solutions, as well as to enhance the extractability of technetium. Development of the UREX process has progressed to the point of demonstrations with actual used nuclear fuel using 2-cm centrifugal contactors, with good results [14].

### 6.3. *Co-decontamination process*

The co-decontamination process is a variant of the PUREX process that is being developed by the US DOE as a method of co-extracting U and Pu, with no separation of pure Pu [16]. There are several variants of this process with similar goals that utilize various reductants. Previously, a co-decontamination process has been demonstrated with actual used nuclear fuel at the laboratory scale. With these tests, it has been demonstrated that a U–Pu–Np product can be produced which contains approximately 10% Pu–Np and, in a second test, which contains approximately 30% Pu–Np [15]. Recent focus of development of the co-decontamination process is being pursued through a multi-year experimental study to evaluate the technological capability to control the preparation of U/Pu product [18]. To this end, the process being developed, after co-extraction of U and Pu via standard PUREX process chemistry, uses hydrazine-stabilized U(IV) as a Pu reductant. An excess of the reductant will produce a U/Pu nitrate solution at a flexible range of U/Pu ratios, dependent upon process goals. This ratio is determined by adjusting the flow rate in the back-extraction section, the purpose of which is to remove excess U in the solvent and produce the desired product ratio. The co-decontamination process is under active development by the US DOE, with flowsheet testing planned in the 2018 timeframe [18].

### 6.4. *NUEX process*

The new uranium extraction (NUEX) process is a PUREX process variant that was designed by EnergySolutions as a potential near-term reprocessing flowsheet for application in the USA for used LWR fuel [17, 19]. This process modifies the PUREX process flowsheet utilized in the Thorp reprocessing facility at the Sellafield Site in the UK to produce a U/Pu/Np product and prevent the production of a pure Pu stream. This is accomplished through modifications to the three cycle PUREX process by replace the U(IV)/$N_2H_4$ reductant from the THORP flowsheet with AHA. This would result in partitioning U from U/Pu by complexation rather than reduction, resulting in U and U/Pu/Np products. Technetium is also separated and recovered with this process.

### 6.5. *NNL advanced process*

The National Nuclear Laboratory in the UK is developing a simplified flowsheet variant of the PUREX process for the reprocessing of GenIV fuel [17]. The process consists of a single cycle flowsheet that utilizes a hydroxamic acid complexant, much like the NUEX process described previously. Research and development to date have indicated that the use of AHA (1) results in a high decontamination factor for Pu in the U product stream, (2) the U decontamination factor in the Pu product stream can be maintained low enough to result in a U/Pu product instead of pure Pu, (3) Np is separated with the U/Pu product stream, (4) technetium (Tc) mostly follows the U but more R&D is needed, (5) process kinetics allow the use of centrifugal contactors as the separation equipment, and (6) AHA degradation to acetic acid is an issue relative to recycle of nitric acid within a facility.

### 6.6. *NEXT process*

The new extraction system for transuranic (TRU) recovery (NEXT) is being developed by the Japan Atomic Energy Agency (JAEA) for the reprocessing of fast reactor fuel [20, 21]. The process combines PUREX process chemistry with crystallization. First, U is partially recovered (approximately 70%) by crystallization of uranyl nitrate hexahydrate from the used fast reactor fuel dissolver product accomplished by lowering the temperature. The resulting uranyl nitrate hexahydrate crystals are washed with nitric acid to further decontaminate them from TRU elements and fission products. The crystals can then be further treated in a crystal purification step [21]. U/Pu/Np is recovered from the mother liquor via PUREX process chemistry without the need for multiple cycles of purification. Further recovery of Am and Cm is obtained through the use of extraction chromatography. The PUREX solvent extraction portion of this process has been demonstrated with actual fast reactor (JOYO) irradiated MOX fuel dissolved in nitric acid by using laboratory-scale centrifugal contactors. With this test, it was shown that Np is recovered with the U and Pu [20].

### 6.7. *Simplified PUREX process*

The simplified PUREX process is being developed in Russia as a next-generation reprocessing with the goal of reducing the volume of low-level waste generated [22]. The simplified PUREX process, compared with classical PUREX, implements thermo-chemical (dry) operations in the head-end of the process. This is accomplished through thermochemical decladding of the used fuel assemblies instead of chopping. Low-temperature voloxidation of the fuel is performed to release volatile fission products prior to dissolution and to generate a more quickly dissolvable $U_3O_8$ form. The end result is a more concentrated dissolver product, relative to U concentration in a lower nitric acid concentration feed, resulting the generation of less liquid waste. One variant of the simplified PUREX process dissolves the SNF, after voloxidation, with a $\mathrm{TBP} \cdot n\mathrm{HNO}_3$ adduct in a supercritical fluid for extraction [22].

### 6.8. *PARC process*

The partitioning conundrum key (PARC) process is a PUREX process variant being developed by JAEA [23]. With this process, Tc and Np are extracted by TBP along with the U and Pu in a co-extraction step. Extracted Np and Tc are separated from the U/Pu stream via selective reduction of Np(VI) to Np(V) by using normal-butyraldehyde in the presence of U(VI) and Pu(IV) and high acid scrubbing of technetium. The U and Pu can then be separated from each other resulting in four product streams — Tc, Np, Pu, and U products. Second and third cycles of PUREX purification are not required. Further processing of the raffinate to separate Am and Cm can then be performed using adsorption techniques with TODGA and alkyl-BTP solvents [23].

## 7. Advanced Reprocessing Technologies

Reprocessing technologies for the separation of minor actinides from lanthanides are expected to be an important part of future advanced reprocessing for used nuclear fuel. The recovery and transmutation, in a fast reactor or potentially LWR or Boiling water reactors (BWRs) [24], of long-lived minor actinides to short-lived fission products would reduce the long-term heat load and radiotoxicity of used fuel or high-level waste resulting from reprocessing. Transmutation is accomplished by irradiation in an intense neutron field to form short-lived fission products. The main focus for minor actinide recycle is the separation of Am and Cm from used fuel. There are two main approaches, homogenous and heterogeneous recycles. In the homogeneous recycle, the minor actinides are combined with the U and Pu in fast reactor nuclear fuel. In the heterogeneous recycle, the minor actinides are manufactured into targets, which are subsequently transmutated in the reactor. Minor actinide separation has become a key R&D area worldwide in the development of advanced reprocessing technologies. Many, but not all, of the areas of development are presented below.

### 7.1. *TRUEX/TALSPEAK process*

The Transuranic Extraction/Trivalent Actinide Lanthanide from Separation with Phosphorus Reagent Extraction from Aqueous Komplexes (TRUEX/TALSPEAK) process is a two cycle solvent extraction process in which the trivalent actinides and lanthanides are first co-extracted from the high-acidity raffinate of a PUREX-based U/Pu separation process raffinate by using the transuranic extraction (TRUEX) process. The actinide/lanthanide product stream from the TRUEX process is then treated using the TALSPEAK process to separate the actinides from the lanthanides.

The TRUEX process was developed by Argonne National Laboratory [25] and consists of an octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) extractant in an aliphatic diluent. The CMPO extracts the trivalent actinides and lanthanides from the acidic raffinate of the upfront U/Pu separation process. TBP is added as a solvent modifier to prevent the third phase formation. The TRUEX solvent typically consists of 0.2 mol/L CMPO and 1.4 mol/L TBP in *n*-dodecane. In the TRUEX process, trivalent actinides and lanthanides are co-extracted from the PUREX raffinate. Once extracted, the actinides and lanthanides are effectively stripped using low-acidity nitric acid. Alternatively, an aqueous solution consisting of diethylenetriaminepentaacetic acid (DTPA) in a lactate buffer at pH 5 is used to facilitate separation in the subsequent TALSPEAK process. This actinide/lanthanide strip product can then be fed directly into the TALSPEAK process with only minor adjustments.

The TALSPEAK process was developed at Oak Ridge National Laboratory (ORNL) [26]. This process functions based on the higher affinity of polyaminocarboxylate ligands for trivalent actinides compared with the trivalent lanthanides. DTPA is added to the aqueous phase, resulting in selective complexation of the actinides, holding them in the aqueous phase while the lanthanides are extracted into the organic phase by using bis-(2-ethylhexyl)phosphoric acid (HDEHP). The aqueous phase is buffered with lactic acid to control the pH and also to improve the extraction kinetics [27]. The TRUEX/TALSPEAK process has been demonstrated at the laboratory-scale by using actual used nuclear fuel. In these tests, the TRUEX and TALSPEAK testing followed an upfront UREX process [28]. Results from these tests indicated >99.99% recovery of Pu, Np, and Cm and 99.97% recovery of Am [28].

### 7.2. *TRUEX/advanced TALSPEAK*

The TALSPEAK process is very sensitive to aqueous solution pH. In order to reduce the dependence of the process performance on the pH, and thereby obtain more predictable extraction behavior, and, additionally, to obtain more rapid extraction kinetics, the advanced TALSPEAK process is currently being developed in the USA by the DOE. For the advanced TALSPEAK process, some adjustments are made to the TRUEX process. Primarily, the DTPA/lactate stripping solution is replaced with a (HEDTA)/citric acid stripping solution which is compatible with the advanced TALPSEAK process. The advanced TALSPEAK flowsheet is a modified version to the TALSPEAK flowsheet that utilizes a 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]) extractant instead of HDEHP and utilizes an aqueous feed composition of (HEDTA)/citric acid instead of DTPA/lactate [29].

Recently, as a collaboration between the US DOE and Forschungszentrum (FZ) Jülich in Germany, an advanced TALSPEAK flowsheet test was performed at Jülich facilities by using a radio-traced feed simulant and 24 stages of 1-cm annular centrifugal contactor manufactured by the Institute of Nuclear Energy Technology (INET) in Beijing, China. Results of these recent tests are yet to be published but separation goals were met.

### 7.3. *ALSEP process*

The most recent focus in the USA for development of a minor actinide separation process center on simplification to a single process as opposed the two process TRUEX/TALSPEAK system. The primary simplified process being developed is the actinide–lanthanide separation (ALSEP) concept which consists of $N,N,N',N'$-tetraoctyldiglycolamide (TODGA) or $N,N,N',N'$-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) as extractants combined with (mono-2-ethylhexyl ester [2-ethylhexylphosphonic acid] (HEH[EHP]) for the co-extraction of trivalent actinides and lanthanides [30]. Scrub sections with nitric acid and citrate are used to back-extract Mo. A citrate-buffered DTPA solution in the pH range of 2.5–4 is used to selectively strip the actinides from the solvent, and a solution of tetraethyldiglycolamide (TEDGA) in nitric acid is used to strip the lanthanides from the solvent.

Proof-of-principle testing of the ALSEP concept has been completed using radio-traced feed streams [30]. These tests have resulted in separation factors of the minor actinides from the lanthanides in the range of 20–40. ALSEP development continues with the development of stripping agents (i.e., modified polyaminocarboxylate chelates) that exhibit enhanced kinetics [31] with a near-term goal of laboratory-scale flowsheet testing in centrifugal contactor equipment using radio-traced simulant leading to a laboratory-scale demonstration with actual dissolved used nuclear fuel.

### 7.4. *Am(VI) extraction*

Another approach being developed in the USA by the DOE-NE Sigma Team for Advanced Actinide Recycle (STAAR) is through the exploitation of higher oxidation states of Am. The approach is to use a strong oxidant (standard potential of 1.7 V for the Am(III)/Am(VI) redox couple) to oxidize Am(III) to Am(VI), leaving the lanthanides as Ln(III) (with the exception of Ce) and extracting the Am(VI). The most mature process being developed in the USA uses sodium bismuthate [32]. The solid sodium bismuthate oxidizes Am(III) to Am(VI) and 1 M diamylamylphosphonate (DAAP) in *n*-dodecane extracts the Am(VI). The sodium bismuthate also oxidizes Ce(III) to Ce(IV) and the DAAP co-extracts the Ce(IV). A selective strip using dilute $HNO_3$ or $H_2O_2$ is accomplished based on the large difference in stability between Am(VI), which is unstable, and Ce(VI), which is stable. This process has been tested using a radio-traced simulant in 5-cm centrifugal contactors with a resulting removal efficiency of 62% compared with a batch contact removal efficiency of 65% obtained immediately prior to the radio-tracer test. These results demonstrated that Am(VI) can remain oxidized long enough to accomplish a separation by using solvent extraction in engineering-scale equipment. Recent research focuses on developing the selective stripping and testing of alternative extractants such as butyramides [33].

### 7.5. *Group hexavalent actinide precipitation*

Another promising approach being developed by the US DOE-NE STAAR program focuses on a group separation of all actinides from U to Am in the hexavalent form [34]. This process would forgo a required upfront PUREX-type process to separate and Pu prior to the minor actinide separation process, thus further simplifying the overall reprocessing flowsheet. The main challenge to such a process is the oxidation and stability of Am(VI). Sodium bismuthate has been shown to be an effective oxidant for Am [32]. As such, the concept behind this group hexavalent actinide separation process is to oxidize U, Pu, Np, and Am to the hexavalent state using sodium bismuthate. The solution is then cooled to 2C, resulting in co-crystallization of the hexavalent actinides. Results to date indicate near proportional removal in the range of 61–71% with a single crystallization [34]. Multiple recrystallizations have the potential to significantly increase the recovery of the hexavalent actinides. Study of the fission products Zr, Cs, Ce, and Nb indicates that Nb is separated significantly (12%). The fission products Nb, and to a lesser extent Zr, Cs, and Ce showed some separation under the highly oxidizing conditions created with the sodium bismuthate [34].

### 7.6. *DIAMEX/SANEX process*

The diamide extraction (DIAMEX)/selective actinide (SANEX) process, developed in France in collaboration with European researchers, is a two-step process which would follow a PUREX type U/Pu separation process. First, the lanthanides and trivalent actinides are separated from the remaining fission products (DIAMEX), and then the trivalent actinides are separated from the lanthanides in the SANEX process [35].

The DIAMEX process uses a malonamide, such as 1 M *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-hexylethoxy-malonamide (DMDOHEMA) in a hydrogenated tetrapropylene, to co-extract the lanthanides and trivalent actinides [36]. After scrubbing with a $HNO_3$/oxalic acid/HEDTA scrub and a second 1 M $HNO_3$ scrub, the actinides and lanthanides are back-extracted into a 0.3 $HNO_3$ stream. This strip product is feed for the SANEX process.

The SANEX process uses an extractant consisting of 15 mM 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2′]bi-pyridine (CyMe4-BTBP) and 0.25 M DMDOHEMA in an octanol diluent [35]. The acidity of the aqueous feed from the DIAMEX process is increased to 2 M $HNO_3$. A dilute $HNO_3$ scrub is used to back-extract the lanthanides and 0.5 M glycolic acid at pH 4 is used to strip the actinides from the solvent.

The DIAMEX and SANEX processes are relatively well developed. The DIAMEX process has been tested with simulated and actual used nuclear fuel solutions in a variety of equipment — mixer-settlers, pulse columns, and centrifugal contactors [17, 36]. The SANEX process has been demonstrated in laboratory-scale centrifugal contactors with actual used fuel solutions [35].

### 7.7. *DIAMEX-SANEX/HDEHP process*

A single-step process has been developed by the French CEA by combining bis-(2-ethylhexyl)phosphoric acid (HDEHP) with the DMDOHEMA from the DIAMEX/SANEX process to co-extract the lanthanides and trivalent actinides and selectively strip first the actinides and then the lanthanides [17, 37]. The HEDTA holds the lanthanides in the organic phase during the actinide strip. The actinide strip solution uses HEDTA and citric acid to back-extract the actinides followed by dilute nitric acid to back-extract the lanthanides. Zr, Mo, and Fe co-extract with this process, requiring a citric acid strip prior to the actinide strip, to remove the Mo, and an oxalic acid/nitric acid strip to remove the Zr and Fe [17]. Simulant testing and hot testing with actual used fuel solution (ATALANTE facility) have been successfully performed using laboratory-scale equipment [17].

### 7.8. *I-SANEX*

The innovative selective actinide separation (I-SANEX) process uses TODGA and octanol in a TPH diluent to extract the minor actinides and lanthanides from a PUREX raffinate [38]. A series of two scrub solutions back-extract Mo, Zr, Sr, and $HNO_3$ from the solvent. Trans-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetic acid (CDTA) is added to the feed and scrub as a complexing agent for Zr and Pd. Selective stripping of the actinides from the lanthanides is accomplished using $SO_3$–Ph–BTP in $HNO_3$ to back-extract the actinides and citric acid solution buffered to pH 3 to back-extract the lanthanides. This process has been demonstrated at the laboratory scale by using centrifugal contactors and radio-traced PUREX raffinate simulant [38]. Results of the testing indicate >99.9% recovery of the Am(III), Cm(III), and Ln(III) with <0.1% contamination of the actinide product with lanthanides. The scrub section was effective in back-extraction of Mo, Zr, and Sr. Ruthenium was found to extract (16%) and mostly remained in the solvent, requiring further research.

### 7.9. *1-Cycle SANEX*

The one-cycle selective actinide separation (1-Cycle SANEX) process uses $CyMe_4BTBP$ and TODGA in a TPH/1-octanol diluent to extract the minor actinides from a PUREX raffinate [38]. Scrub solutions consisting of oxalic acid and $HNO_3$ are used to back-extract Zr and residual lanthanides and -cysteine in $HNO_3$ is used to back-extract Pd(II). The minor actinides are then stripped using a solution of glycolate at pH 4. This process has been demonstrated at the laboratory scale by using centrifugal contactors and radio-traced PUREX raffinate simulant [38]. Results of the testing indicate >99.8% recovery of Am(III), >99.4% recovery for Cm(III), and satisfactory decontamination of the actinide product from fission products and lanthanides. Slow extraction kinetics and limited loading capacity of the organic phase are issues requiring further research [38].

### 7.10. *CEA-GANEX and Euro-GANEX processes*

The group actinide extraction (GANEX) process was developed by the French CEA. This process supports homogenous recycle of actinides by first separating a pure U product in the first cycle solvent extraction process that uses DEHiBA (*N*,*N*-di-(ethyl-2-hexyl)isobutyramide) as a U(VI) extractant, followed by the second cycle in which the TRU is separated together for recycle. DEHiBA is used instead of TBP due to increased selectivity for U(VI) over Pu(IV) and its high loading capacity for U. This portion of the CEA-GANEX process has been demonstrated at the Atalante facility, using actual used nuclear fuel dissolved in nitric acid, with good results [39].

The second cycle of the CEA-GANEX process uses *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) and HDEHP extractants to co-extract the actinides and lanthanides, and a few other extractable fission products (Mo, Ru, Tc) [40]. The Mo, Ru, and Tc are stripped from the solvent prior in a series of two strip sections. The actinides and lanthanide are then selectively stripped using a mixture of HEDTA and citric acid at pH 3 for the actinides and a TEDGA/oxalic acid/nitric acid solution to strip the lanthanides. This second cycle of the CEA-GANEX process was demonstrated at the Atalante facility, using actual used nuclear fuel dissolved in nitric acid, with good actinide recovery but higher than expected contamination of the actinide product with lanthanides [17, 40].

As part of the European Union Actinide Recycling by Separation and Transmutation (ACSEPT) and Safety of Actinide Separation processes (SACSESS) programs, the EURO-GANEX process was developed [41]. This process consists of a first cycle as described above, followed by a second cycle that utilizes TODGA and *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexyloxyethyl) malonomide (DMDOHEMA) extractants. CDTA is used in the extraction/scrub aqueous phase to suppress Zr and Pd extraction. The TRU and lanthanides are selectively stripped using $SO_3$–Ph–BTP, AHA, and $HNO_3$ to back-extract the actinides and dilute nitric acid to back-extract the lanthanides [17, 41]. Testing of the process with fast reactor carbide fuel that was oxidized and dissolved in nitric acid, and processed in a U-extraction cycle, was performed at the European Joint Research Centre Institute of TransUranium elements (ITU). Results were positive — good recovery of Am, Np, and Pu (>99%) with very little lanthanide contamination (<0.1%) [41].

### 7.11. *Japan — DGA extraction process*

Diglycolamide (DGA) extractants are being developed in Japan for the separation of minor actinides from used nuclear fuel [42]. One of the more promising DGA's is *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA).

TODGA effectively extracts Am, Cm, and rare earth elements at acidities greater than 1 M $HNO_3$. Back-extraction can be accomplished at low acidity. The third phase formation was noted with the extraction of Nd. To alleviate this issue, *N*,*N*,*N*′,*N*′-tetradodecyldiglycolamide (TDdDGA) was developed [42]. Alternative methods to address the third phase formation include the addition of *N*,*N*-dihexyloctanamide (DHOA) to the TODGA/dodecane solvent, or through the use of TBP or octanol as a phase modifier [43, 44]. Also, Russian researchers at the Khlopin Radium Institute have developed several alternative polar-fluorinated diluents for DGA extractants that increase the extraction capability of TODGA for Am and Eu [17].

Countercurrent flowsheet testing with HLW simulant in mixer-settler equipment has been performed in Japan by using TDdDGA in *n*-dodecane [45]. With the flowsheet tested, minor actinides and lanthanides are extracted by the TDdDGA and back-extracted, together, using dilute $HNO_3$. Zirconium and Pd extraction is suppressed through the use of HEDTA and $H_2O_2$ in the feed and scrub. Separation of the minor actinides from the lanthanides is then accomplished using extraction chromatography. The countercurrent flowsheet test of the TRU recovery step achieved >99.99% recovery of Am and 62% recovery of Np [45].

### 7.12. *Diamides of dipicolinic acid*

Diamides of dipicolinic acid (DPA) are being investigated in Russia and other countries for the separation of actinides and lanthanides from used fuel [46, 47]. Mixtures of cobalt dicarbollide and DPA in an FS-13 diluent have been investigated in Russia. The study included *N*,*N*,*N*′,*N*′-tetrabutyldipicolinic acid (TBDPA) and the *ortho*, *meta*, and *para* isomers of *N*,*N*-diethyl-*N*′,N′-ditolyl diamides. Results indicate that the *ortho*-position is the most favorable and the ethyl-tolyl isomer Et(o)TDPA has good selectivity between the heavy and light lanthanides [46]. In the Czech Republic, *N*,*N*′-diethyl-*N*,*N*′-di-meta-tolyldipicolinamide (Et(m)TDPA) was found to have the high Am extractability while maintaining good Am(III)/Eu(III) selectivity [47].

Alternatively, at the Khlopin Radium Institute, dipyridyl-dicarboxylic acid in polar fluorinated diluents has been studied [48]. Diamides of 2,2-dipyridyl-6,6-dicarboxylic acid can be used for the separation of minor trivalent actinides from lanthanides with good separation factors (>10) obtained.

### 7.13. *EXAm*

The extraction of americium (EXAm) process is being developed in France by the CEA for the recovery of only Am, as the main contributor to long-term heat generation and radiotoxicity, from PUREX raffinate [49, 50]. The solvent consists of DMDOHEMA and HDEHP in TPH. TEDGA is used as a complexing agent to maintain Cm and heavy lanthanides in the aqueous phase, thus improving the Am/Cm selectivity. Molybdenum, Pd, and Ru are stripped from the solvent by using citric acid and NaOH prior to stripping of the Am. A selective strip is then employed which first back-extracts Am using DTPA at a low acidity and then back-extracts the lighter lanthanides by using oxalic acid and TEDGA.

Hot testing of the EXAm process has been performed using actual PUREX raffinate [49]. Greater than 99% of the Am was extracted with a decontamination factor of >500 relative to Cm. Approximately 0.7% of the extracted Am was lost to the Mo strip effluent. Good decontamination from the light lanthanides was obtained for the Am product.

Recent efforts have focused on operation of the EXAm process by using a concentrated PUREX raffinate [50]. These efforts have included countercurrent flowsheet testing with simulants and actual PUREX raffinate to produce $AmO_2$ pellets for irradiation testing. These tests resulted in an acceptable Am product; however, there was a 10% loss of Am to the raffinate.

## 8. Summary

Historically, there is a great deal of experience with aqueous separation technologies for the separation of U and Pu from used nuclear fuel. Much of this experience is based on the use of the PUREX process on an industrial-scale for decades. As countries move forward with development of advanced separation processes, considerable effort has focused on modified PUREX processes in which there is not a pure Pu product. Additionally, a great deal of progress has been made in development of aqueous separation processes for the separation and recycle of minor actinides from used nuclear fuel. This is the primary area of ongoing research and development in the nuclear separations community with several processes having been demonstrated with actual used nuclear fuel in laboratory-scale equipment.

## References

1. M. S. Gerber, The plutonium production story at the Hanford site: Processes and facilities history, report WHC-MR-0532, Westinghouse Hanford Company (1998).

2. M. F. Simpson and J. D. Law, Nuclear fuel reprocessing, In *Encyclopedia of Sustainability Science and Technology*, R. A. Meyers ed., Springer, New York, pp. 7142–7156 (2012).
3. F. Drain, R. Vinoche, and J. Duhamet, 40 years of experience with liquid-liquid extraction equipment in the nuclear industry, In *Proc. Waste Management 2003*, Tucson, AZ, USA (2003).
4. C. H. Castano, Nuclear fuel reprocessing, In *Nuclear Energy Encyclopedia: Science, Technology, and Applications*, T. B. Kingrey ed., Wiley, Hoboken, New Jersey, pp. 121–126 (2011).
5. T. F. Severynse, Nuclear material processing at the Savannah River Site, report WSRC-MS-98-00515, Westinghouse Savannah River Company (1998).
6. M. S. Gerber, A brief history of the PUREX and $UO_3$ facilities, report WHC-MR-0437, Westinghouse Hanford Company (1993).
7. M. Schneider and Y. Marignac, Spent nuclear fuel reprocessing in France, A research report of the International Panel on Fissile Materials, Research Report No. 4, International Panel on Fissile Materials (2008).
8. A. G. Croff, R. G. Wymer, L. L. Tavlarides, J. H. Flack, and H. G. Larson, Background, status, and issues related to the regulation of advanced spent nuclear fuel recycle facilities: ACNW&M white paper (Nureg-1909), Advisory Committee on Nuclear Waste and Materials, U.S. Nuclear Regulatory Commission (2008).
9. R. Natarajan and B. Raj, Technology development of fast reactor fuel in India, *Curr. Sci.* **108**(1), 30–38 (2015).
10. J. H. Saling and A. W. Fentiman eds., *Radioactive Waste Management*, 2nd edition, CRC Press, New York (2001).
11. H. Zhang, Chinese reprocessing and nuclear security issues, In *Proc. Institute of Nuclear Materials Management 55th Annual Meeting*, Atlanta, GA, USA (2014).
12. F. Fiori and Z. Zhou, Sustainability of the Chinese nuclear expansion: The role of ADS to close the nuclear fuel cycle, *Prog. Nucl. Energy* **83**, 123–134 (2015).
13. P. Baron, Process for reprocessing a spent nuclear fuel and of preparing a mixed uranium-plutonium oxide, US Patent US 2007/0290178 Al (2007).
14. C. Pereira, G. F. Vandegrift, M. C. Regalbutto, A. Bakel, D. Bowers, A. V. Gelis, A. S. Hebden, L. E. Maggos, D. Stepinski, Y. Tsai, and J. J. Laidler, Lab-scale demonstration of the UREX+1a process using spent fuel, In *Proc. Waste Management 2007*, Tucson, AZ, USA (2007).
15. T. S. Rudisill and M. C. Thompson, Demonstration of the use of formohydroxamic acid in the UREX process, *Separ. Sci. Technol.* **50**(18), 2823–2831 (2015).
16. E. D. Collins, D. E. Benker, W. D. Bond, D. O. Campbell, and B. B. Spencer, Development of the UREX+ co-decontamination solvent extraction process, In *Proc. Global 2003*, New Orleans, LA, USA (2003).
17. P. Baron *et al.*, Organization for Economic Co-operation and Development Nuclear Energy Agency, State-of-the-art report on progress on separation

chemistry, minor actinide separation and perspectives for future R&D, OECD/NEA, Paris, France, in press, https://www.oecd-nea.org/science/pubs/2018/7267-soar.pdf (2018).

18. J. Bresee, P. Paviet, and T. Todd, Nuclear separations process control and accountability, In *Proc. 14th Information Exchange Meeting on Partitioning and Transmutation (IEMPT'14)*, San Diego, CA, USA (2016).
19. S. T. Arm and E. J. Butcher, Treatment and disposal of process wastes arising from the recycle of spent nuclear fuel in the USA, In *Proc. Waste Management 2009*, Phoenix, AZ, USA (2009).
20. M. Nakahara, Y. Sano, Y. Koma, M. Kamiya, A. Shibata, T. Koizumi, and T. Koyama, Separation of actinide elements by solvent extraction using centrifugal contactors in the NEXT process, *J. Nucl. Sci. Technol.* **44**(3), 373–381 (2007).
21. M. Nakahara, Separation of uranyl nitrate hexahydrate crystal from dissolver solution of irradiated fast neutron reactor fuel, In *Advances in Crystallization Processes*, Y. Mastai ed., InTech (2012).
22. V. V. Bondin, P. M. Gavrilov, Y. A. Revenko, B. Y. Zilberman, B. N. Romanovskij, Y. S. Fedorov, A. Y. Shadrin, E. G. Kudryavcev, and A. V. Haperskaja, Simplified PUREX process — Perspective SNF reprocessing technology for the plant of the next generation, In *Proc. GLOBAL 2007*, Boise, ID, USA, pp. 1484–1489 (2007).
23. G. Uchiyama, H. Mineo, T. Asakura, S. Hotoku, M. Llzuka, S. Fujisaki, H. Isogai, Y. Itoh, M. Sato, and N. Hosoya, Long-lived nuclide separation for advancing back-end fuel cycle process, *J. Nucl. Sci. Technol.* **39**(Suppl. 3), 925–928 (2002).
24. IAEA, Status of minor actinide fuel development, IAEA Nuclear Energy Series No. NF-T-4.6 (2010).
25. E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandegrift, and W. W. Schulz, The TRUEX process — A process for the extraction of the transuranic elements from nitric acid wastes utilizing modified PUREX solvent, *Solv. Extr. Ion Exch.* **3**(1–2), 75–109 (1985).
26. B. F. Weaver and F. A. Kappelmann, Preferential extraction of lanthanides over trivalent actinides by monoacidic organophosphates from carboxylic acids and from mixtures of carboxylic acids and aminopolyacetic acids, *J. Inorg. Nucl. Chem.* **30**(1), 263–272 (1968).
27. P. R. Danesi and C. Cianetti, Kinetics and mechanism of the interfacial mass transfer of Eu(III) in the system: Bis(2-ethylhexyl)phosphoric acid, n-dodecane-NaCl, lactic acid, polyaminocarboxylic acid, water, *Sep. Sci. Technol.* **17**(7), 969–984 (1982).
28. C. Pereira, G. F. Vandegrift, M. C. Regalbuto, A. Bakel, D. Bowers, A. V. Gelis, A. S. Hebden, L. E. Maggos, D. Stepinski, Y. Tsai, and J. J. Laidler, Lab-scale demonstration of the UREX+1a process using spent fuel, In *Proc. Waste Management 2007*, Tucson, AZ, USA (2007).
29. G. J. Lumetta, A. J. Casella, B. M. Rapko, T. G. Levitskaia, N. K. Pence, J. C. Carter, C. M. Niver, and M. R. Smoot, An advanced TALSPEAK concept using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as the extractant, *Solv. Extr. Ion Exch.* **33**(3), 211–223 (2015).

30. G. J. Lumetta, A. V. Gelis, J. C. Carter, C. M. Niver, and M. R. Smoot, The actinide-lanthanide separation concept, *Solv. Extr. Ion Exch.* **32**(4), 333–347 (2014).
31. T. Grimes, C. Heathman, S. Jansone-Popova, V. Bryantsev, S. Srinivasan, M. Nakase, and P. Zalupski, Thermodynamic, spectroscopic, and computational studies of f-element complexation by N-hydroxyethyl-diethylenetriamine-N,N′,N″,N‴-tetraacetic Acid, *Inorg. Chem.* **56**(3), 1722–1733 (2017).
32. B. J. Mincher, R. D. Tillotson, T. G. Garn, V. Rutledge, J. D. Law, and N. C. Schmitt, The solvent extraction of Am(VI) using centrifugal contactors, *J. Radioanal. Nucl. Chem.* **307**(3), 1833–1836 (2016).
33. B. J. Mincher, T. S. Grimes, R. D. Tillotson, and J. D. Law, Am(VI) extraction final report: FY16, report FCRD-MRWFD-2016-000327, Idaho National Laboratory (2016).
34. J. D. Burns and B. A. Moyer, Group hexavalent actinide separations: A new approach to used nuclear fuel recycling, *Inorg. Chem.* **55**(17), 8913–8919 (2016).
35. D. Magnusson, B. Christiansen, M. R. S. Foreman, A. Geist, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, and C. Sorel, Demonstration of a SANEX process in centrifugal contactors using the CyMe4-BTBP molecule on a genuine fuel solution, *Solv. Extr. Ion Exch.* **27**(2), 97–106 (2009).
36. G. Modolo, H. Vijgen, D. Serrano-Purroy, B. Christiansen, R. Malmbeck, C. Sorel, and P. Baron, DIAMEX counter-current extraction process for recovery of trivalent actinides from simulated high active concentrate, *Separ. Sci. Technol.* **42**(3), 439–452 (2007).
37. C. Hill, Overview of recent advances in An(III)/Ln(III) separation, In *Ion Exchange and Solvent Extraction: A Series of Advances*, *Volume 19*, B. A. Moyer edn., CRC Press (2009).
38. G. Modolo, A. Wilden, P. Kaufholz, D. Bosbach, and A. Geist, Development and demonstration of innovative partitioning processes (i-SANEX and 1-cycle SANEX) for actinide partitioning, *Prog. Nucl. Energy* **72**, 107–114 (2014).
39. M. Miguirditchian, C. Sorel, I. Bisel, B. Cames, P. Baron, D. Espinoux, J. N. Calor, C. Viallesoubranne, C. Lorrain, and M. Masson, HA demonstration in the Atalante facility of the GANEX 1st cycle for the selective extraction of Uranium from HLW, In *Proc. GLOBAL 2009*, Paris, France (2009).
40. M. Miguirditchian, H. Roussel, L. Chareyre, P. Baron, D. Espinoux, C. N. Calor, C. Viallesoubranne, B. Lorrain, and M. Masson, HA demonstration in the Atalante facility of the Ganex 2nd cycle for the grouped TRU extraction, In *Proc. GLOBAL 2009*, Paris, France (2009).
41. R. Taylor, M. Carrott, H. Galan, A. Geist, X. Hères, C. Maher, C. Mason, R. Malmbeck, M. Miguirditchian, G. Modolo, C. Rhodes, M. Sarsfield, and A. Wilden, The EURO-GANEX process: Current status of flowsheet development and process safety studies, *Procedia Chem.* **21**, 524–529 (2016).
42. Y. Sasaki, Y. Kitatsuji, Y. Tsubata, Y. Sugo, and Y. Morita, Separation of Am, Cm and lanthanides by solvent extraction with hydrophilic and lipophilic organic ligands, *Solv. Extr. Res. Dev. Jpn.* **18**, 93–101 (2011).

43. G. Modolo, H. Asp, H. Vijgen, R. Malmbeck, D. Magnusson, and C. Sorel, Demonstration of a TODGA/TBP process for recovery of trivalent actinides and lanthanides from a PUREX raffinate, In *Proc. GLOBAL 2007*, Boise, ID, USA, pp. 1111–1116 (2007).
44. A. Geist and G. Modolo, TODGA process development: an improved solvent formulation, In *Proc. GLOBAL2009*, Paris, France (2009).
45. Y. Morita and T. Kimura, Development of separation process for transuranium elements and some fission products using new extractants and adsorbents, actinide and fission product partitioning and transmutation, In *Proc. 11th OECD/NEA Information Exchange Meeting (IEMPT)*, San Francisco, USA, pp. 235–244 (2012).
46. M. Y. Alyapyshev, V. A. Babain, R. S Herbst, J. D Law, and A. Paulenova, Extraction of lanthanoids with diamides of dipcolinic acid from nitric acid solutions II. Synergistic effect of ethyl-tolyl derivates and dicarbollide cobalt, *Solv. Extr. Ion Exch.* **31**(2), 184–197 (2013).
47. M. Bubenıkova, J. Rais, P. Selucky, and J. Kvıcala, Am(III) separation from acidic solutions by diamides of dipicolinic acid, *Radoichim. Acta* **101**, 753–759 (2013).
48. M. Y. Alyapyshev, V. A. Babain, L. I. Tkachenko, A. Paulenova, A. A. Popova, and N. E. Borisova, New diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid for actinide-lanthanide separation, *Solv. Extr. Ion Exch.* **32**(2), 138–152 (2014).
49. C. Rostaing, C. Poinssot, D. Warin, P. Baron, and B. Lorrain, Development and validation of the EXAm separation process for single Am recycling, *Procedia Chem.* **7**, 367–373 (2012).
50. V. Vanel, M-J. Bollesteros, C. Marie, M. Montuir, V. Pacary, F. Antegnard, S. Costenoble, and V. Boyer-Deslys, Consolidation of the EXAm process: Towards the reprocessing of a concentrated PUREX raffinate, *Procedia Chem.* **21**, 190–197 (2016).