A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate

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Summary. The selective partitioning (P) of long-lived minor actinides from highly active waste solutions and their transmutation (T) to short-lived or stable isotopes by nuclear reactions will reduce the long-term hazard of the high-level waste and significantly shorten the time needed to ensure their safe confinement in a repository. The present paper summarizes the on-going research activities at Forschungszentrum Jülich (FZJ), Karlsruher Institut für Technologie (KIT) and Institute for Transuranium Elements (ITU) in the field of actinide partitioning using innovative solvent extraction processes. European research over the last few decades, *i.e.* in the NEWPART, PARTNEW and EUROPART programmes, has resulted in the development of multi-cycle processes for minor actinide partitioning. These multi-cycle processes are based on the co-separation of trivalent actinides and lanthanides (*e.g.* by the DIAMEX process), followed by the subsequent actinide(III)/lanthanide(III) group separation in the SANEX process. The current direction of research for the development of innovative processes within the recent European ACSEPT project is discussed additionally.

This paper is focused on the development of flow-sheets for recovery of americium and curium from highly active waste solutions. The flow-sheets are verified by demonstration processes, in centrifugal contactors, using synthetic or genuine fuel solutions. The feasibility of the processes is also discussed.

1. Introduction

Nuclear power constantly produces used nuclear fuel which contains, apart from the mainly short-lived fission products, a significant amount of the higher actinides neptunium (Np), plutonium (Pu), americium (Am) and curium (Cm), which are responsible for the long-term radiotoxicity of the used fuel. At present, two management options are considered worldwide: the open cycle, where the used fuel is directly sent to long term storage in a deep geological repository and

the closed fuel cycle including reprocessing and fabrication of new fuel.

Therefore, the protection of the biosphere from highly radiotoxic used nuclear fuel constituents over very long timescales is extremely important. The used nuclear fuel and the highly active waste from reprocessing needs to be stored for a very long time (over 100 000 a) in a well-shielded deep geological repository until its radiotoxicity has reached natural background level.

Closing the fuel cycle is an important objective to ensure the sustainability of nuclear energy, and reducing the radiotoxicity of used nuclear fuel is an important objective to increase the public acceptance of nuclear energy. The latter objective can be attained by recovering the long-lived elements from the used fuel and converting them into short-lived or stable nuclides by irradiation in a dedicated reactor. This strategy is referred to as the partitioning (P) and transmutation (T) strategy [1].

It has been shown in many studies that the radiotoxicity inventory can be reduced up to a factor of 10 if all plutonium is recycled and fissioned. Reduction factors higher than 100 can be obtained if, in addition, the minor actinides (Np, Am, Cm) are recycled. P and T also decreases the amount of highly active waste for a final disposal and the long-term heat production. This makes a smaller and more efficient storage facility possible [2].

Plutonium, which is the main contributor to the long-term radiotoxicity, can already be recovered by the PUREX process, as commercially operated in France and the UK. With some modifications, neptunium can also be recovered (advanced PUREX) [3–5]. Up to now, solvent extraction processes have been the reference technology for fuel processing at commercial scale for more than 60 years and the reasons for this are multiple. Solvent extraction processes are able to provide extremely high separation yields, considering both recovery and purification yields without generating a significant amount of secondary waste, which is very important in nuclear industry.

In order to achieve a significant reduction in the radiotoxicity of used nuclear fuel, there is a need to recover and

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transmute also Am and Cm. However, these trivalent minor actinides are not industrially separated. They are channelled into the high active raffinate (HAR) of the PUREX process together with the fission and activation products. The PUREX raffinate is industrially vitrified and prepared for final disposal. Unfortunately, the trivalent minor actinides cannot be extracted with tributylphosphate (TBP) within the PUREX process [6], requiring additional processes for their separation. The high neutron-capture cross-sections of the lanthanides would hinder an efficient transmutation of the trivalent minor actinides, and therefore, the two groups of elements have to be separated. The chemical similarity of trivalent actinides (An) and lanthanides (Ln) combined with the unfavourable mass ratio necessitate very demanding and complex process steps.

Processes developed over the last 20 years are predominantly based on the combined extraction of An(III) and Ln(III) from the PUREX raffinate followed by their subsequent group separation. A distinction is made between two process variants, described in detail in recent reviews [1, 7–9].

The multi-cycle processes, on the one hand, make use of different extractants for every single process. Following the joint co-separation of An(III) + Ln(III) from the fission product solution, *e.g.* using the TRUEX (USA), TRPO (China) or DIAMEX (France) processes, the next process step involves the joint back-extraction of trivalent An + Ln. This is followed by a selective An(III)/Ln(III) separation process using a highly selective extractant, *e.g.* CyMe$_4$BTBP [10]. One of the most promising options for the removal of MA is the DIAMEX-SANEX concept.

In the single-cycle processes, on the other hand, An(III) + Ln(III) are simultaneously separated. Following an An(III)/Ln(III) co-extraction step, the trivalent actinides are selectively back-extracted (stripped) from the loaded organic phase, *e.g.* using a hydrophilic polyaminocarboxylic acid such as diethylenetriaminepentaacetic acid (DTPA). The most important developments in terms of this process include the reversed TALSPEAK (USA), DIDPA (Japan) and SETFICS (Japan) processes [6].

This paper provides an overview of important process developments for An(III) separation achieved within the scope of European collaborative projects from the 4th to the 7th EU Framework Programmes [11–13]. Particular attention will be devoted to developments at FZJ, KIT and ITU which were made possible through close cooperation with other partners in the EU projects. The strategy employed
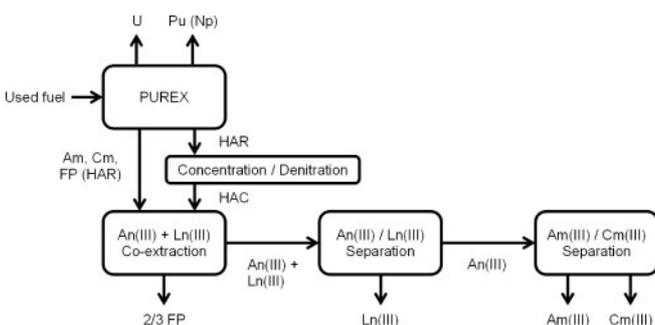
for the multi-cycle separation studied within the NEWPART, PARTNEW and EUROPART projects is shown in Fig. 1.

2. Multi-cycle processes

2.1 An(III) + Ln(III) co-extraction using diamide-based solvents (DIAMEX)

The acronym DIAMEX stands for DIAMide EXtraction and is used for many different processes, using a diamide-based solvent.

During the 1980s, the family of malonamides was developed for the extraction of minor actinides from high level liquid waste solutions. From the multitude of synthesized compounds, dimethyldibutyltetradecylmalonamide (DMDBTDMA, Fig. 2), was found to have the most promising properties for use in liquid-liquid extraction processes. A great improvement over the formerly used phosphorus-based extractants was the complete combustibility of the solvent, containing only carbon, hydrogen, oxygen and nitrogen (CHON principle) [14]. The DIAMEX process was successfully tested using real waste solution for the first time in 1993 in the CEA's Fontenay-aux-Roses research centre [14] and it was continuously further developed within European collaborative projects (3rd, 4th and 5th Framework Programmes). In the EU's 4th Framework Programme (NEWPART), FZJ was involved in the development of an optimized DIAMEX process in cooperation with ENEA Saluggia and Politechnico di Milano (PoliMi). This new DIAMEX process used 1 mol/L DMDBTDMA in TPH (hydrogenated tetrapropylene, an aliphatic diluent) as solvent instead of 0.5 mol/L or 0.65 mol/L used in previous tests [11]. Increasing the diamide concentration from 0.5 to 1.0 mol/L significantly increased the capacity of the solvent. This in turn decreased the tendency to third-phase formation and also allowed the process to be conducted at higher HNO$_3$ concentrations. In order to prevent the co-extraction of Zr and Mo, oxalic acid was used as masking agent. It was added to the feed (PUREX raffinate) in advance and to the scrubbing solution during the process. A spiked test (*i.e.* synthetic PUREX raffinate with ^{241}Am, ^{152}Eu and ^{137}Cs tracers) was successfully tested in 1998 at Forschungszentrum Jülich in a 16-step mixer-settler set-up [15]. The corresponding flow-sheet was developed with the aid of a computer model at PoliMi. In this test, more than 99.99% Am(III) and Ln(III) were recovered, and a high decontamination factor from the fission products including Mo and Zr was achieved.

In the NEWPART project [16], 26 different malonamides were synthesized and tested towards their suitability for An(III) extraction. In addition, intensive studies were conducted on hydrolysis and radiolysis stability. Molecule optimizations ultimately led to a new DIAMEX reference molecule: the *N,N'*-dimethyl-*N,N'*-dioctyl-2-hexylethoxymalonamide (DMDOHEMA, Fig. 2).

Its suitability for use in the process was demonstrated in a range of hot tests using genuine fuel solutions, both at CEA in Marcoule and at the ITU in Karlsruhe.

Currently, during reprocessing in the PUREX process, the high active raffinate (HAR) is concentrated and then denitrated for subsequent vitrification. The volume of the product, which is known as high active concentrate (HAC),
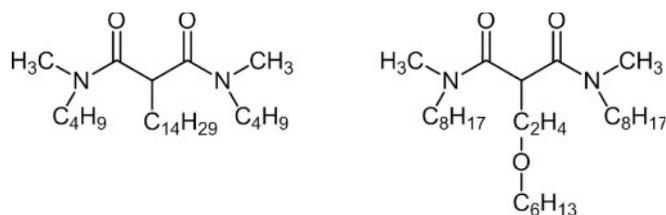

Fig. 1. European partitioning strategy for the separation of all actinides from used fuel.

Fig. 2. Structures of DMDBTDMA (left) and DMDOHEMA (right).

is reduced by a factor of 15 compared to HAR. As a result, the high active process flows to be processed are also reduced, as is the size of the processing unit. In the PARTNEW project, three partners (ITU, CEA and FZJ) were collaborating on the development of a DIAMEX process for separating An(III) from HAC. As a result of the very high metal concentrations in HAC, the question arose as to how the co-extraction of certain transition metals (Zr, Mo, Pd, *etc.*) together with the trivalent actinides and lanthanides could be avoided. Such co-extraction would inevitably lead to third-phase formation and the failure of the separation process. Against this background, cold concentration and denitration experiments were performed with simulated HAR solutions. In these optimization experiments, parameters were developed leading to a successful hot demonstration (concentration-denitration) [17]. For the hot tests, a genuine fuel solution was used as the basis to prepare a HAC with a concentration factor of 11 and a final acidity of 4 mol/L. The loss of actinides in the accruing precipitation was very low at < 0.04%.

In batch extraction experiments, the thermodynamic distribution data were determined for the DIAMEX process and a 16-stage flow-sheet was generated using computer code calculations. In order to minimize the risks during a hot test (third-phase formation, precipitation, *etc.*), a cold DIAMEX test was first performed at FZJ, using a centrifugal contactor battery. A simulated HAC solution (identical metal concentrations to real HAC) was used with the radionuclide tracers ^{241}Am, ^{244}Cm, ^{134}Cs and ^{152}Eu. The solvent consisted of 1 mol/L DMDOHEMA in TPH. The aim of the DIAMEX test was to separate > 99% of the An(III) together with the Ln(III) and to achieve high decontamination factors in relation to the other HAC elements. As can be inferred from the findings of Modolo *et al.*, these ambitious goals were achieved in a 16-step process [18].

In this DIAMEX-HAC process, five extraction stages were sufficient to obtain Am and Cm decontamination factors (DF$_{feed/raffinate}$) higher than 5000 and for the co-extracted lanthanides decontamination factors between 1100 and 4500. Co-extraction of Zr, Mo, and Pd was prevented by using oxalic acid and N-(2-hydroxyethyl)-ethylenediamine-N,N',N'-triacetic acid (HEDTA). The back-extraction comprising 4 stages was also efficient and the recoveries of the actinides were higher than 99.8%. They could be even further improved by minor process flow-sheet optimisations. The experimental steady-state concentration profiles of important solutes were determined and compared with model calculations and good agreement was generally obtained [18].

Based on the positive results of the spiked tests, a hot DIAMEX experiment was successfully performed in the hot cell facility at ITU using a genuine fuel solution. The findings are discussed in detail in Serrano-Purroy et al. [19]. Almost identical results were generated with the same flow-sheet as was used in the spiked test. With the exception of Tc (97.8% remained in the solvent), most of the non-lanthanide fission products were not extracted. Here, oxalic acid and HEDTA also very effectively prevented the co-extraction of Mo, Zr and Pd. The studies described here on the development of a new partitioning process very clearly demonstrate the transferability of simulated process conditions to real process conditions. This was shown both for the preparation of HAC as well as for the subsequent DIAMEX test. This makes optimization experiments both easier and cheaper as compared to only hot-cell optimization experiments.

2.2 An(III) + Ln(III) co-extraction using TODGA-based solvents

In the early 1990s, Stephan *et al.* [20] reported on the extraction of different metals using multi-dentate ligands such as diglycolamides (DGA). The DGA substance class also satisfies the CHON principle and during the late 1990s, Japanese scientists recognized that these ligands are particularly suitable for extracting An(III) from acidic waste solutions [21].

Extensive extraction studies were performed with this very promising substance class [22–24]. The change from a bi-dentate ligand (*e.g.* malonamide) to a tri-dentate diglycolamide significantly increased the affinity for trivalent actinides and lanthanides.

Different DGAs were synthesized and N,N,N',N'-tetra-octyl-diglycolamide (TODGA, Fig. 3) was found to have the best properties in terms of extraction, solubility in aliphatic solvents and process stability. The tri-dentate TODGA extractant exhibits even higher affinity for trivalent actinides and lanthanides than the reference diamide DMDOHEMA, and could therefore be an interesting alternative to the diamide-based processes.

However, TODGA has a tendency for third phase formation in aliphatic solvents such as *n*-dodecane, particularly at high HNO$_3$ concentrations [25].

Within the scope of the PARTNEW project, the aggregation behaviour of TODGA was studied in *n*-dodecane. With the aid of small-angle X-ray and neutron scattering experiments, it was shown that the reason for the third-phase formation was the van der Waals interaction between self-aggregated polar cores of spherical reverse micelles at low temperatures [26]. Numerous basic studies with TODGA and related compounds can be found in the literature nowadays. Around the year 2001 almost no information existed on process development studies including process demonstrations. This motivated Modolo *et al.* to develop a continuous reversible partitioning process, which was successfully tested for the first time in 2003 in centrifugal contactors at Forschungszentrum Jülich [27].
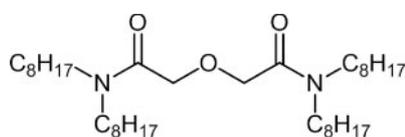

Fig. 3. Chemical structure of TODGA.

However, high oxalic acid concentrations of up to 0.4 mol/L had to be added to the PUREX raffinate in order to suppress the extraction of Zr and Mo on the one hand and to supress third-phase formation on the other. At such high oxalic acid concentrations, a slow precipitation of the trivalent actinide- and lanthanide-oxalates was observed in the used feed solution and during the scrubbing steps of the continuous process, leading to some An(III) losses.

Following this, Modolo *et al.* optimized the partitioning process and suggested a new continuous process in which the extractant was a mixture of 0.2 mol/L TODGA and 0.5 mol/L TBP in TPH [28]. The addition of TBP not only improved the hydrodynamic properties but also increased the loading capacity of the extractant and reduced the tendency to third-phase formation. In 2006, Forschungszentrum Jülich performed two tests in centrifugal extractors in cooperation with the Institute for Transuranium Elements (ITU) and CEA Marcoule [29].

In the second test run (Fig. 4) using 28 stages (4 extraction, 12 scrubbing and 12 back-extraction stages), 99.99% of the actinides and lanthanides were selectively extracted from a PUREX raffinate and back-extracted to the aqueous product solution. Problems were caused only by Ru, which was

partly co-extracted (10% of initial amount) and remained in the spent solvent.

Based on these encouraging results, a hot process test was run at the end of 2006 in ITU's centrifugal contactor battery with almost identical results (Fig. 5) [30]. Very high feed decontamination factors were obtained for Am and Cm (DF ∼ 40 000) and the recovery of these elements was higher than 99.99%. Only Y and a small part of Ru was routed to the product fraction together with the lanthanides and the MA. The collected actinide/lanthanide fraction had an acidity of 0.13 mol/L HNO$_3$ and could be used for a subsequent An(III)/Ln(III) separation process. The acidity can be easily adjusted to cope with the requirements of the subsequent process.

In summary, it was shown that the solvent composed of TODGA and TBP in an aliphatic solvent is particularly suitable for separating An(III) from a process solution containing numerous fission products. This was demonstrated with a synthetic and a genuine PUREX raffinate with an optimized flow-sheet. The main objective (> 99.9% actinide separation) and a high fission product decontamination factor were achieved. The results are comparable with those obtained for the DIAMEX processes developed in France and within European projects [31].
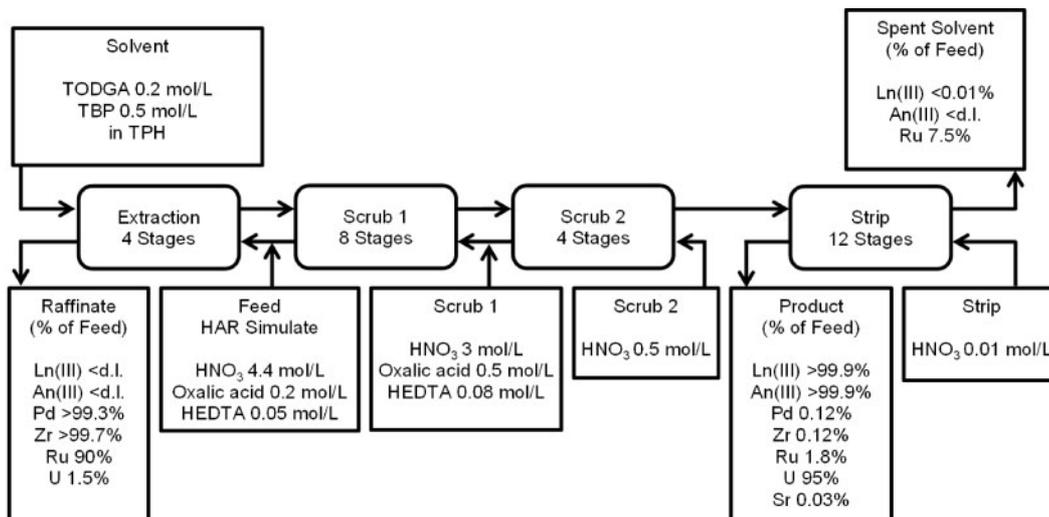

Fig. 4. Flow-sheet and main results of the spiked TODGA-based process carried out at FZJ/Jülich in 2006 [29].
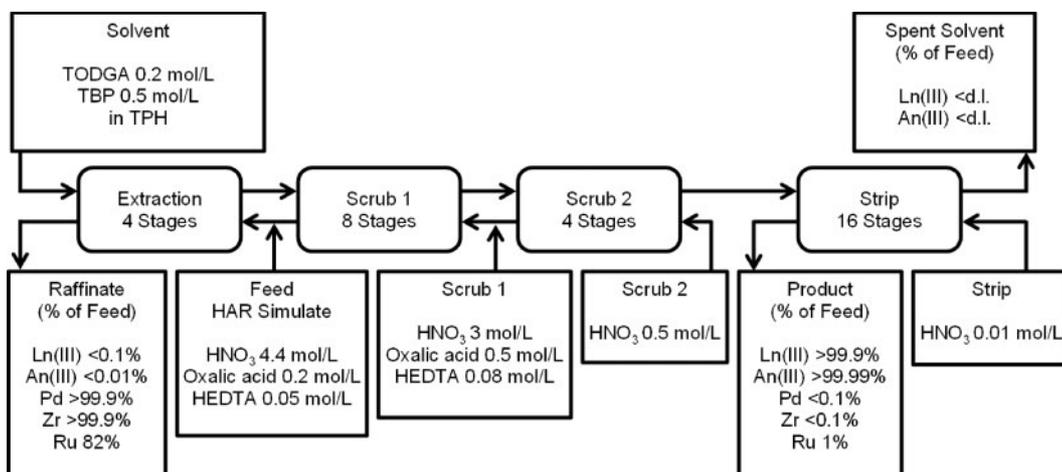

Fig. 5. Flow-sheet and main results of the hot TODGA-based process carried out at ITU in 2006 [30].

Finally, TBP was replaced by 1-octanol, making the TODGA solvent CHON compliant. A solvent consisting of 0.2 mol/L TODGA + 5 vol.-% 1-octanol in kerosene was shown to have good performance with respect to loading and 3rd phase formation [32]. This solvent is currently used for further process development.

3. Regular SANEX

The extraction systems described above separate the trivalent actinides together with the lanthanides from most of the fission products (*e.g.* Cs, Sr, Mo, Zr, *etc.*) present in the PUREX raffinate (HAR). For an efficient transmutation of the minor actinides, the lanthanides should be separated because of their large neutron-capture cross-sections. As a result of the chemical similarity of both element groups, group separation is only possible using highly selective extractants or complexants containing soft donor atoms, such as N, S or Cl, as they evidently have a stronger interaction with trivalent actinides than with the lanthanides [6].

Many extraction systems with relatively low An(III)/Ln(III) separation factors are described in the literature [8]. These systems, however, are of little interest for technical application, because a large number of stages would be needed to obtain the desired high decontamination factors. Systems with a high selectivity are also described, but they are extremely complex (*e.g.* high salt loads leading to secondary waste), or they are incompatible with the partitioning processes described previously (*i.e.* PUREX and DIAMEX processing prior to the An(III)/Ln(III) separation) [1].

The SANEX concept (Selective ActiNide EXtraction) aiming at selectively extracting trivalent actinides, was first proposed by Musikas *et al.* [33]. In the early 1980s, they discovered two selective An(III)/Ln(III) extraction systems comprising soft N- or S-donor atoms, which subsequently formed the basis for the development of more efficient extractants. This triggered work on finding CHON compliant N-donor extracting agents which could separate Am(III) and Cm(III) with high selectivity over Ln(III) from solutions containing up to 1 mol/L nitric acid.

The first breakthrough was achieved when Kolarik *et al.* tested alkylated bis-triazinyl-pyridines (BTP, Fig. 6) as selective An(III) extracting agents [34]. BTP were the first compounds to directly extract trivalent actinide nitrates from up to 1 mol/L nitric acid with excellent selectivity over lanthanides; an Am(III)/Eu(III) separation factor of approx. 150 was achieved. Counter-current SANEX tests with real highly active feed solutions have shown promising results [35, 36], but the first-generation BTPs have low stabilities with respect to hydrolysis and radiolysis [11, 36, 37]. Following the identification of the mechanism of hydrolytic
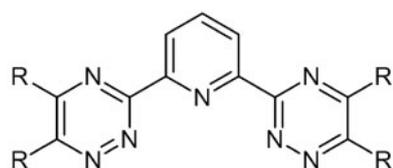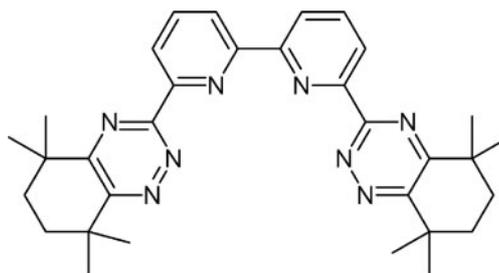

Fig. 7. 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridine (CyMe₄BTBP).

degradation [11, 36, 37], CyMe₄BTP which is resistant towards hydrolysis has been developed [11, 38]. Unfortunately, the actinide(III) distribution ratios were extremely high, and back-extraction was impossible.

Finally, a new class of heterocyclic N-donor SANEX ligands was developed by Foreman *et al.* [38, 39], namely 6,6′-bis(5,6-dialkyl)-[1,2,4]-triazin-3-yl)-[2,2′]-bipyridines (BTBPs). A summary of the extraction properties of the reference molecule CyMe₄BTBP (Fig. 7) can be found in Geist *et al.* [10, 40]. The slow extraction kinetics was significantly improved with a phase transfer catalyst, such as the malonamide DMDOHEMA or the diglycolamide TODGA [41]. However, continuous tests on extraction and back-extraction using a single centrifugal contactor showed that even at low process flow-rates, equilibrium values could not be achieved [42].

Despite this, in the beginning of 2008, a hot test was successfully conducted for this SANEX process at ITU, Karlsruhe (Fig. 8) [43]. The continuous counter-current process, in which An(III) were separated from Ln(III), was carried out in laboratory centrifugal contactors using an optimized flow-sheet involving a total of 16 stages. The process was divided into 9 stages for extraction from a 2 mol/L nitric acid feed solution, 3 stages for lanthanide scrubbing, and 4 stages for actinide back-extraction. Excellent feed decontamination factors for Am (7000) and Cm (1000) were obtained and the recoveries of these elements were higher than 99.9%. More than 99.9% of the lanthanides were directed to the raffinate except Gd for which 0.32% was recovered in the product.

At Forschungszentrum Jülich, Modolo *et al.* developed an alternative process [41]. The extractant comprised 0.015 mol/L CyMe₄BTBP in 1-octanol. However, instead of 0.25 mol/L DMDOHEMA, only 0.005 mol/L TODGA were used to improve the extraction kinetics. This system showed comparably good extraction properties and the process was successfully demonstrated in Jülich in February 2008.

In this 20-stage process with 12 extraction steps, 4 scrubbing steps and 4 back-extraction steps, > 99.9% Am(III), > 99.7% Cm(III) and > 99.9% Cf(III) were separated, and the product fraction contained less than 0.1% of the initial lanthanides (Fig. 9).

The SANEX process variant developed at Forschungszentrum Jülich appears to be very promising for two reasons: replacing DMDOHEMA with TODGA increases the solubility of the BTBPs, and the regeneration of the extractant is easier. The low flow-rate (in both processes, CyMe₄BTBP/DMDOHEMA or CyMe₄BTBP/TODGA), caused by the slow kinetics, is a drawback in an industrial
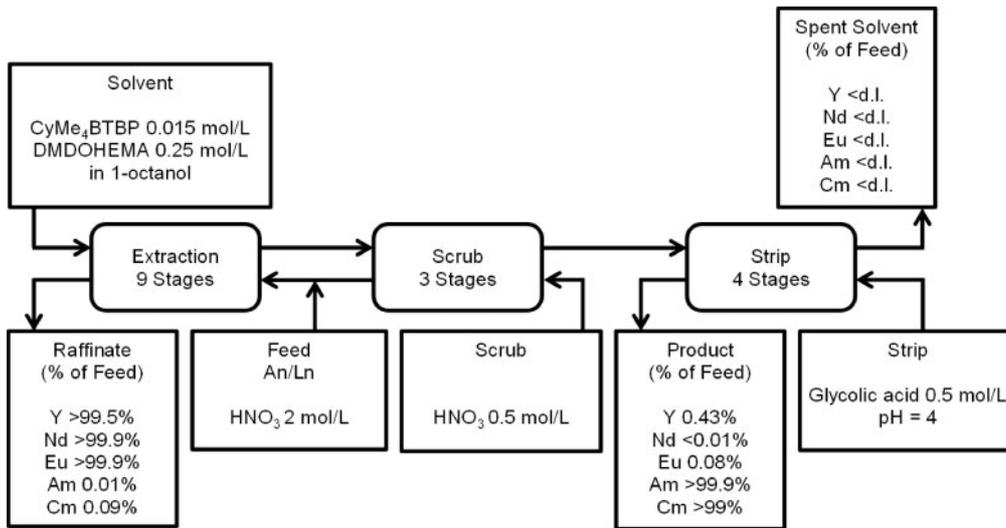

Fig. 6. 2,6-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)pyridine (BTP).

Fig. 8. Flow-sheet and main results of the hot SANEX CyMe₄BTBP/DMDOHEMA process carried out at ITU/Karlsruhe in 2008 [43].
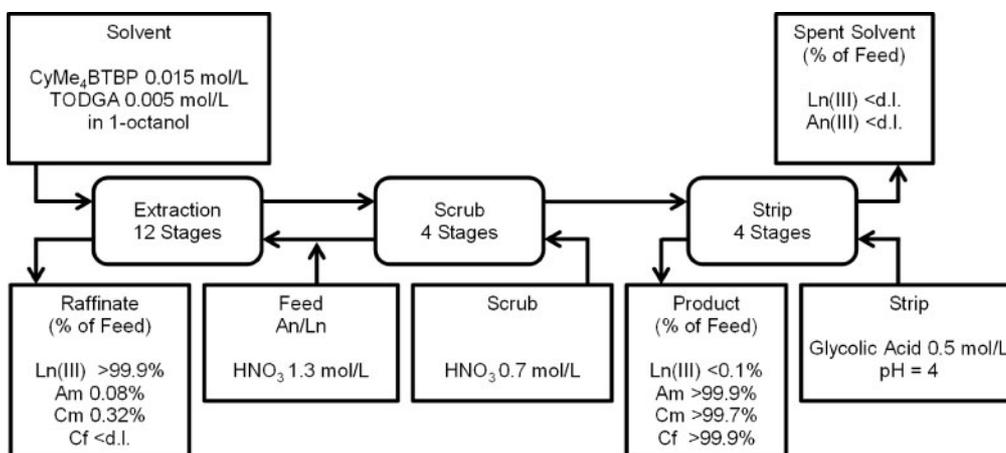

Fig. 9. Flow-sheet and main results of the spiked SANEX CyMe₄BTBP/TODGA process carried out at FZJ/Jülich in 2008 [41].
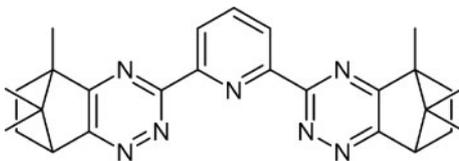

Fig. 10. Bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)-pyridine (CA-BTP).

process in which large amounts of waste are supposed to be treated. In addition, the limited loading capacity of the organic phase will be a problem in the treatment of wastes with high MA content [44]. Whether these problems can be solved without modifying the extracting agent remains still to be investigated.

Recently, a new BTP, CA-BTP (Fig. 10) [45] was developed, having good stability but faster kinetics and improved solubility as compared to CyMe₄BTBP. However, this compound has not yet been used in a continuous counter-current test.

4. Americium/curium separation by the LUCA process

The separation of adjacent trivalent actinides represents an even more challenging task than the An(III)/Ln(III) sepa-

ration. In principle, both elements could be transmuted together in a fast reactor or ADS system. However, due to the high decay heat and neutron emission of curium, any dry or wet fabrication process will require remote handling and continuous cooling in neutron shielded hot cells. The development of a simple, compact and robust fabrication process appears to be a great challenge [46]. Therefore, an effective method for separating Am from Cm prior to re-fabrication is a major prerequisite for the discussion of further fuel cycle scenarios [47]. It is known that separating Am(III) from Cm(III) is a very difficult task due to the very similar properties of these elements. Numerous techniques, including high-pressure ion exchange, extraction chromatography, and solvent extraction using *e.g.* di(2-ethyl-hexyl)phosphoric acid (HDEHP) have been utilized for Am(III)/Cm(III) separation and purification [1, 6, 8]. However, the Am/Cm separation factors were low and did not exceed 3, necessitating a large number of stages in order to obtain a pure product. The best separation of transplutonium elements has been obtained using methods based on the different oxidation states of the separated elements (*e.g.* Am(IV or VI)/Cm(III)) [48].

The synergistic mixture (Fig. 11) composed of bis(4-chlorophenyl)-dithiophosphinic acid [(ClPh)₂PSSH] and tris(2-ethylhexyl) phosphate (TEHP) shows a very high affinity for An(III) over Ln(III). Am(III)/Eu(III) separation
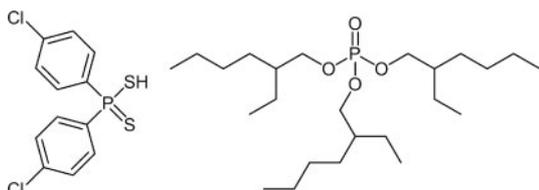
Fig. 11. Synergistic mixture of (ClPh)$_2$PSSH (left) and TEHP (right) used in the LUCA process.

factors > 3000 are achieved. Surprisingly high Am(III)/ Cm(III) separation factors of 6–10 were also reported by Modolo *et al.* [49]. Based on the extraordinary extraction properties of the above mentioned synergistic mixture, the LUCA process [50, 51] was invented for the selective recovery of Am(III) from an aqueous nitric acid solution containing trivalent actinides (*i.e.* Am(III), Cm(III) and Cf(III)) and trivalent lanthanides.

LUCA is the acronym for "Lanthaniden Und Curium Americum separation". Optimization studies were carried out to define the best conditions for extraction, scrubbing and stripping. In addition to batch extraction studies, a single-stage extraction experiment was conducted to obtain more data on the system kinetics, and to generate data required for the flow-sheet calculations.

After the data were collected, a 24-stage flow-sheet was designed, and the final assessment was performed in a counter-current test using miniature centrifugal contactors [51]. The results of this counter current test (Fig. 12) showed, that the difficult recovery of Am(III) is possible from an acidic solution containing a mixture of trivalent actinides (Am(III), Cm(III) and Cf(III)) and Eu(III) as a lanthanide representative. The LUCA process can be used after a co-extraction process (*e.g.* after DIAMEX) for the selective extraction of Am(III), leaving Cm(III) together with the lanthanides in the raffinate fraction. Alternatively, the process can also be run after a SANEX process for mutual Am/Cm separation.

In the future, we plan to optimize the formulation of the extractant composition, *e.g.* by changing the diluent. Oxidation of the ligand, which is still an issue at high HNO$_3$ acidities, can be suppressed by adding HNO$_2$ scavengers or using hydrochloric acid as a stripping medium.

5. One-cycle process

Within the current European research project ACSEPT (Actinide reCycling by SEParation and Transmutation), the development of new extractants and innovative separation processes with a reduced number of cycles is envisaged [52]. A single process is advantageous in comparison to a multi-cycle process as it would make the complete advanced reprocessing of nuclear waste easier and more economical. Therefore, two concepts based on the PUREX process are being studied: the "innovative-SANEX"-concept and the "1-cycle SANEX" concept.

In the "innovative-SANEX"-concept, an An(III)/Ln(III) co-extraction is followed by the selective stripping of the An(III) using selective hydrophilic complexing agents and the subsequent stripping of the Ln(III) to recycle the solvent (Fig. 13).

In the "1-cycle SANEX" concept, the direct and selective extraction of the trivalent actinides by a highly selective solvent system is desired (Fig. 13). This is a complicated task since the feed solution will include a wide range of elements with varied concentrations. The separation will also be carried out at a relatively high acidity (> 2 mol/L HNO$_3$).

6. Innovative-SANEX

The innovative-SANEX (*i*-SANEX) process is under development at the French CEA and in the framework of the European ACSEPT project [52, 53] to simplify the DIAMEX/*r*-SANEX process. It is basically a DIAMEX process with selective back-extraction of An(III) from the loaded organic phase. This concept is based on the reverse TALSPEAK process [54, 55]. An(III) and Ln(III) are co-extracted from the PUREX raffinate in a DIAMEX-like process, *e.g.* using TODGA (Fig. 3) as extracting agent [23, 28, 29]. A hydrophilic complexing agent selective for An(III) over Ln(III) such as DTPA (diethylenetriaminepentaacetic acid) is used for back-extracting An(III) from the loaded organic phase. To keep the trivalent lanthanides in the organic phase, a nitrate salt must be added to the selective stripping solution. Another option is to add a second extracting agent (such as HDEHP, bis(2-ethylhexyl)phosphate) to the organic
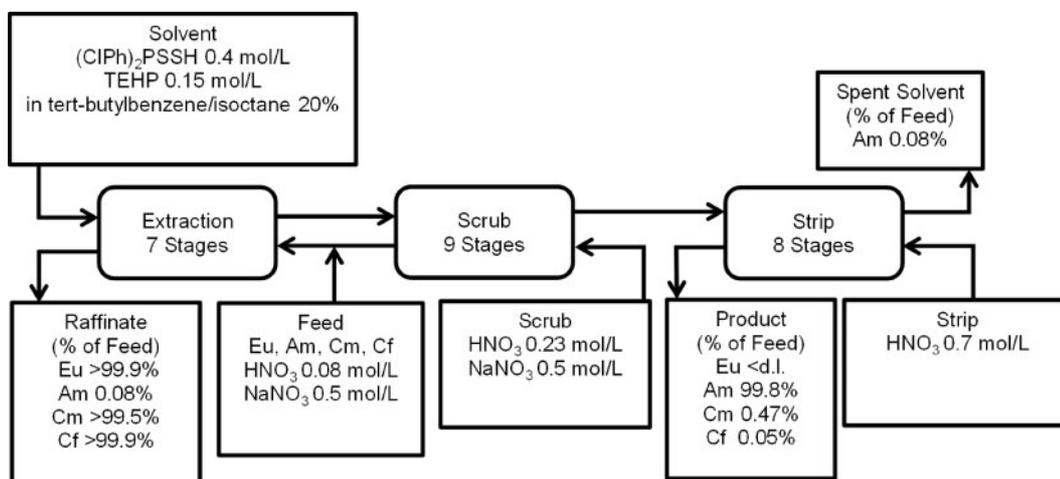

Fig. 12. Flow-sheet and main results of the LUCA process for Am/Cm separation carried out at FZJ/Jülich in 2008 [51].
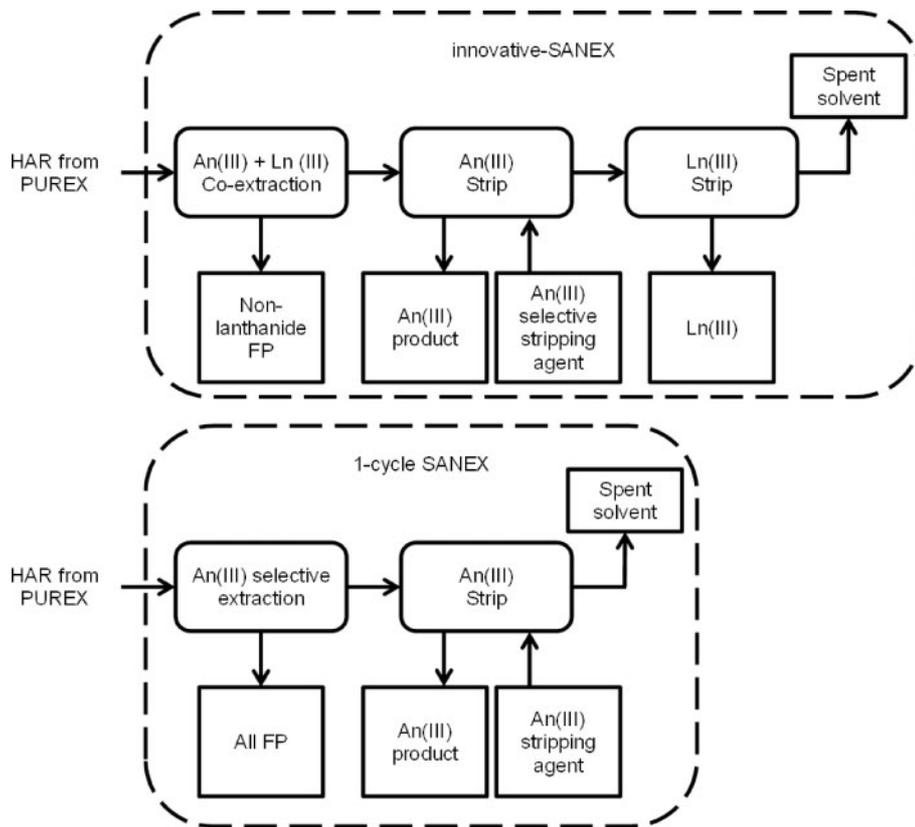
phase to keep the lanthanides in the organic phase at low
acidity [56].

A drawback of *i*-SANEX processes developed so far
[57, 58] is the limited acidity range (pH $\approx$ 3) in which
the An(III) complexing agents are effective, meaning that
buffering agents need to be added to the aqueous phase
used for actinide back-extraction. The required addition of
a nitrate salt or a second extracting agent is another disad-
vantage considering secondary waste generation. Geist *et al.*
have synthesised recently a hydrophilic BTP, 2,6-bis(5,6-
di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine (SO$_3$-Ph-BTP,
Fig. 14) [59], and tested it for its ability of selectively
suppressing the extraction of An(III) from nitric acid solu-
tions [60, 61].

When co-extracting Am(III), Cm(III) and Ln(III) from
nitric acid into a TODGA solvent, adding SO$_3$-Ph-BTP to
the aqueous phase suppresses Am(III)+Cm(III) extraction
while Ln(III) are still extracted. Separation factors in the
range of 1000 are achieved. The investigations have shown
that SO$_3$-Ph-BTP remains active in nitric acid solutions up
to 6 mol/L. This means that buffering or salting-out agents
do not need to be added to the aqueous phase; nitric acid is
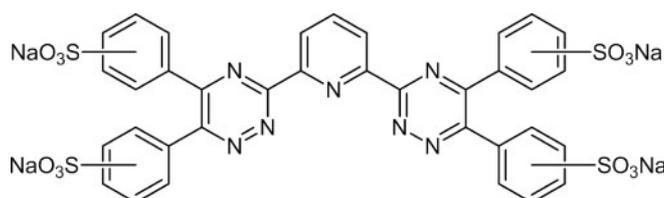used to keep the Ln(III) in the TODGA solvent. These prop-

erties make SO$_3$-Ph-BTP a suitable candidate for *i*-SANEX
process development.

A SO$_3$-Ph-BTP i-SANEX process test is planned for the
near future. Before doing so, single-stage centrifugal contac-
tor tests to determine the kinetic data required for calculating
the final flow-sheet will be performed.

7. 1-cycle SANEX

Another concept studied within the ACSEPT project is the
1-cycle SANEX concept, aiming at the selective extraction
of the trivalent actinides directly from a PUREX raffinate
solution.

A system using an organic phase comprising 0.015 mol/L
CyMe$_4$BTBP (Fig. 7) and 0.005 mol/L TODGA (Fig. 3)
in a mixture of 40% TPH and 60% 1-octanol was pro-
posed after gathering data from batch experiments [62].
CyMe$_4$BTBP has good properties for the separation of
An(III) from Ln(III), as already discussed above [10].
A drawback is, however, the slow extraction kinetics which
can be improved with the addition of phase transfer reagent,
e.g. TODGA [41].

A common problem in any of the advanced partition-
ing processes is the unwanted co-extraction of some fission
and corrosion products. Often, the co-extraction can be sup-
pressed by complexation of the elements in the aqueous feed
solution prior to extraction, using selective masking agents.
For example, oxalic acid for masking Zr and Mo as well
as HEDTA (N-(2-hydroxyethyl)-ethylenediamine N,N',N'-
triacetic acid) for masking Pd were used in the DIAMEX
process [63, 64]. Oxalic acid was also shown to be effective
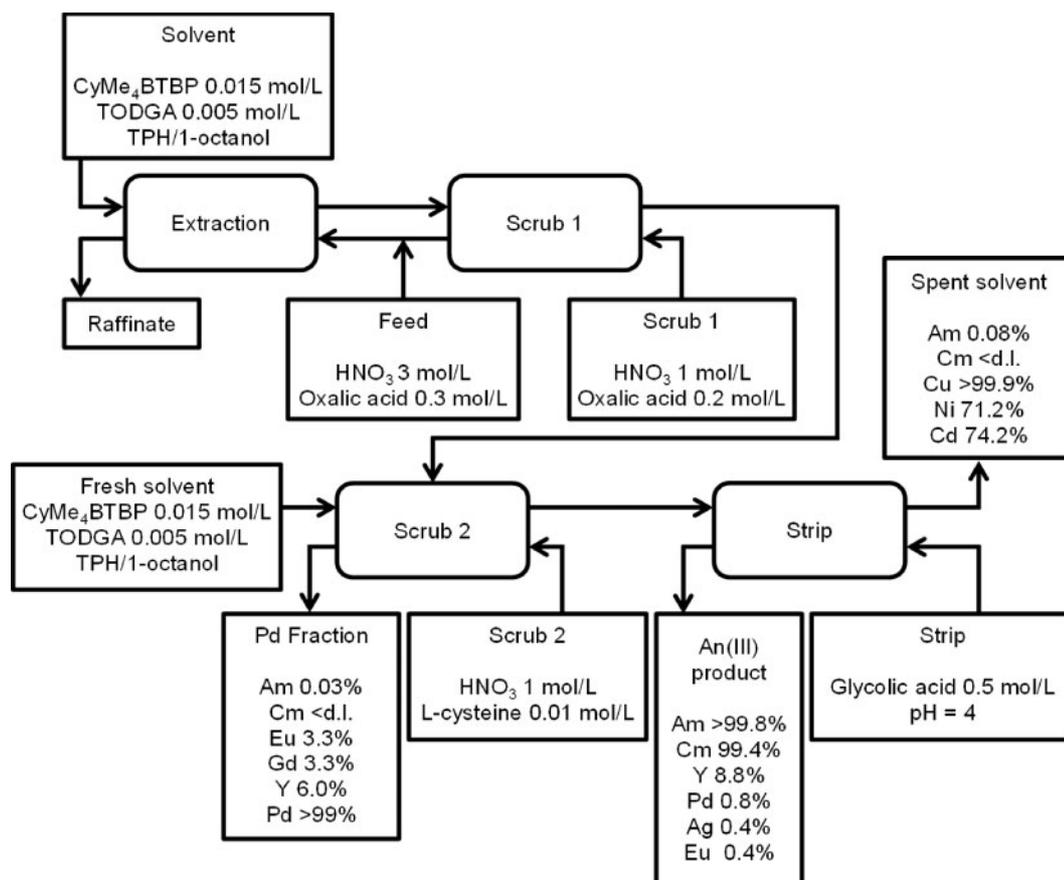in the 1-cycle SANEX process for masking of Zr and Mo,

Fig. 14. 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine (SO$_3$-
Ph-BTP).

Fig. 15. Flow-sheet and main results of the spiked 1-cycle SANEX process carried out at FZJ/Jülich in 2011.

but HEDTA did not have the desired effect on the masking of Pd. Therefore, the alternative Pd-stripping agent L-cysteine (an amino acid) was introduced [62].

The results from single stage centrifugal contactor tests were used to design and develop a flow-sheet. A battery of 16 centrifugal contactors was available in the laboratory, but the calculations showed that it would not be possible to run the whole test in just 16 stages. Therefore, a 32-stage flow-sheet was developed, as shown in Fig. 15. The flow-rates to be used in the spiked countercurrent test and the number of stages for the individual sections were optimized by computer-code calculations. The computer-code development and methodology were presented recently [65, 66].

In a full continuous counter-current centrifugal contactor test using a simulated HAR solution containing trace amounts of Am and Cm, the lab-scale applicability of the developed 1-cycle SANEX process was demonstrated. The minor actinides were recovered to > 99.4% and separated from the other elements in just a single process. The minor actinides were efficiently stripped to the product fraction by a glycolate solution with minor contamination of the product with Y, Pd, Ag and some of the trivalent lanthanides being observed. This process represents a significant improvement in advanced nuclear fuel partitioning processes with respect to the direct selective recovery of Am and Cm from a PUREX raffinate becoming possible. However, some drawbacks of the proposed process are the slow kinetics and the low solubility of the reagent in the solvent. Both aspects warrant further studies.

8. Conclusion

Used fuel from nuclear power plants has to be managed in a safe manner, respectful of the environment and socially acceptable to the public. Amongst the different strategies studied to manage safely the long-lived radioactive waste, partitioning and transmutation allows a reduction of the amount, the radiotoxicity and the thermal power of these wastes, leading to an optimal use of the geological repository sites.

Research on partitioning in the European Union (EU) is at such an advanced stage that serious consideration is being given to the industrialization of some hydrometallurgical separation processes. The leading nation here is France with its ambitious R&D programme on partitioning and transmutation. After decades of research in this area, separating minor actinides (americium and curium) from the PUREX raffinate still poses just as a big a challenge as in the past.

Several aqueous partitioning processes were selected and developed up to the demonstration level on the laboratory scale. The feasibility of some multi-cycle processes (*e.g.* DIAMEX, TODGA, SANEX) was even demonstrated on the laboratory scale using genuine fuel solutions.

The challenge now is to optimize the developed processes in terms of their transferability towards industrial process maturity. This will only be possible in the form of a large international project, and is being addressed in the current EU project ACSEPT [52].

Within the framework of this international project, the focus is also on developing innovative processes. The objectives include simplifying processes developed in the past

and reducing the number of cycles. The direct separation of trivalent actinides from the fission product solution (1-cycle SANEX) seems to be possible, as shown in this paper. However, some drawbacks of the proposed process are the slow kinetics and the low solubility of the reagent in the solvent. Both aspects and a hot demonstration need to be further studied.

Implementation of an innovative SANEX process would also result in a simplification of the processes required for trivalent actinide separation. A combination of An(III) + Ln(III) co-extraction by a diamide or diglycolamide solvent (*e.g.* TODGA) and subsequent selective stripping of An(III) by a strong hydrophilic complexing agent (*e.g.* SO₃-Ph-BTP) seems to be a promising process for the separation of Am(III) and Cm(III) from a PUREX raffinate solution.

All innovative separation processes described in this paper are based on solvent extraction, which benefit from the experience gained over 60 years R&D in actinide separation science.

As shown above, these processes involved new extracting or complexing organic molecules and new diluents. It is clear that the mechanistic understanding of the chemical and physical reactions involved (thermodynamic and kinetics) needs to be improved further.

This knowledge is important to develop multi-scale models to be used in a simulation code, which is an indispensable tool to operate such processes in a safe manner. In addition, these processes require a comprehensive study of the multiform safety issues that any chemical process requires under operation or mal-operation conditions. Last but not least, the long term operation of the solvent (hydrolysis and radiolysis), its recycling, cleaning and the management of the secondary waste, need to be studied.

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