

Development and demonstration of innovative partitioning processes (i-SANEX and 1-cycle SANEX) for actinide partitioning

Andreas Wilden,*^a Giuseppe Modolo^a and Andreas Geist^b

^aForschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung, Nukleare Entsorgung
und Reaktortechnik (IEK-6), Germany

^bKarlsruher Institut für Technologie, Institut für Nukleare Entsorgung, Germany

Abstract

For the recovery of the trivalent actinides Am(III) and Cm(III) from PUREX raffinate, two innovative partitioning processes were developed within the European project ACSEPT. In the “innovative-SANEX” concept, trivalent actinides (An(III)) and lanthanides (Ln(III)) are co-extracted by a TODGA-based solvent, which is then subjected to several stripping steps: selective stripping of An(III) with the hydrophilic ligand SO₃-Ph-BTP, followed by subsequent stripping of Ln(III). A more challenging route studied also within our laboratories is the direct An(III) separation using a mixture of CyMe₄BTBP and TODGA, the so-called “1-cycle SANEX” process. Both processes have been successfully demonstrated using spiked simulate solutions in laboratory-scale miniature annular centrifugal contactors using 32-stages flow-sheets. The process development and results of the demonstration tests will be presented and discussed. Both processes showed a high recovery of An(III) with high fission-product decontamination factors. The safety of these processes is studied within the current European project SACSESS.

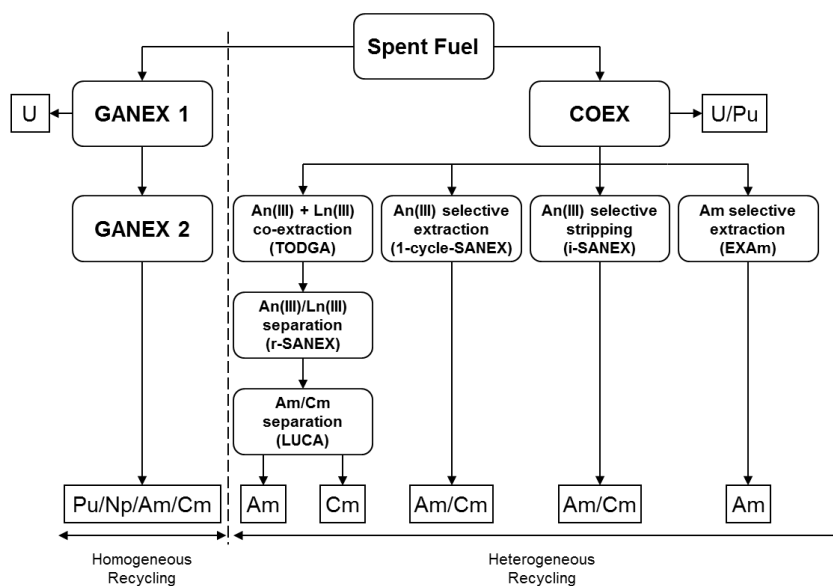
Introduction

The long-term management of used nuclear fuel and other long-lived highly active legacy wastes has been under investigation in various countries over the last 60 years. Amongst the different strategies studied to safely manage the long-lived radioactive waste, it has been found that partitioning and transmutation (P&T) to short-lived or stable elements allows a reduction of the amount, the radiotoxicity, and the thermal power of such wastes, leading to an optimal use of geological repository sites [1]. Plutonium and the minor actinides (MA) neptunium, americium, and curium are the main contributors to the long-term heat production and radiotoxicity of nuclear waste. Today, Pu is industrially reprocessed using the well-established PUREX process, which can be adapted for the partitioning of Np. This is not the case for Am and Cm. Several extraction processes have been developed worldwide for the separation and recovery of Am and Cm from highly active raffinates (HAR, e.g. the PUREX raffinate) [2].

European collaborative research has resulted in the development and demonstration of several multi-cycle separation processes within the framework of collaborative projects such as NEWPART, PARTNEW, and EUROPART [3-5]: e.g. DIAMEX, TODGA, ALINA, SANEX-BTBP, and LUCA. A review of these processes that were tested at Jülich and at ITU was recently published by Modolo et al. [6]. Within the recent European research project ACSEPT (Actinide reCYcling by SEParation and Transmutation) [7], the development of new extractants and innovative separation processes with a reduced number of cycles was envisaged. A schematic representation of the studied processes is given in Figure 1. A new approach, which was also studied within the ACSEPT project, is the GANEX (Grouped ActiNide EXtraction) concept (Figure 1, left) addressing the simultaneous partitioning of all transuranium (TRU) elements for their homogeneous recycling in advanced generation IV reactor systems. Different approaches have been proposed [8-11]. Single-cycle processes (Figure 1, right) are advantageous in comparison to multi-cycle processes as they would make the advanced reprocessing of nuclear waste easier and more economical. In France, the americium-selective extraction process “ExAm” was recently presented by the CEA [12] using the slight Cm(III) preference of the complexing agent TEDGA in the aqueous phase. A hot demonstration of this EXAm process was carried out in 2009 with very satisfactory results, such as an Am recovery of 98.5% and an Am/Cm DF of 500 [13].

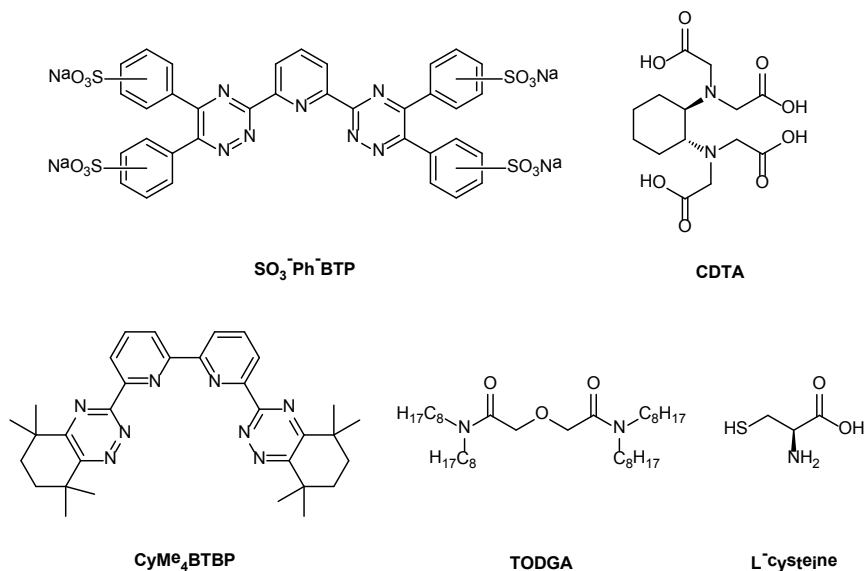
Two new advanced concepts based on the PUREX process have been studied in our laboratories: the innovative SANEX concept [14] and the 1-cycle SANEX concept [15]. In the 1-cycle SANEX concept, the direct and selective extraction of trivalent actinides from PUREX raffinate by a highly selective solvent system is required. This is a complicated task since the PUREX raffinate includes a wide range of elements with varying concentrations [15]. The separation of trivalent actinides from trivalent lanthanides is a particularly difficult task, due to the similar chemical properties of the two groups of elements. In the innovative SANEX process, An(III) and Ln(III) are co-extracted from a PUREX raffinate and the An(III) is separated from the Ln(III) in a selective stripping step, e.g. using a hydrophilic polyaminocarboxylic acid such as diethylenetriaminepentaacetic acid (DTPA) [16]. The most important developments of this kind of process include the reversed TALSPEAK (USA), DIDPA (Japan), SETFICS (Japan) and TODGA-SANEX (France) processes [17-18]. However, a common feature of these processes is complicated pH control during the important An(III) stripping step. The required addition of a nitrate salt or a second extracting agent is another disadvantage with respect to secondary waste generation.

Figure 1: European hydrometallurgical partitioning process strategy for the homogeneous and heterogeneous recycling of transuranium elements



At KIT, Geist et al. recently introduced the new hydrophilic complexing agent $\text{SO}_3\text{-Ph-BTP}$ (Figure 2) for the An(III) selective stripping step [11]. This molecule combines the high selectivity of the well-known BTP family of extractants with high solubility in aqueous phases. Ln(III)/An(III) separation factors in the range of 1000 were achieved. The selective stripping of An(III) now becomes possible, even at relatively high nitric acid concentrations of up to ≤ 1 mol/L HNO_3 .

Figure 2: Structures of ligands and complexants used in the innovative SANEX and 1-cycle SANEX processes



The present paper therefore summarizes recent achievements in the development and implementation of both processes, i.e. the innovative SANEX and the 1-cycle SANEX process and results from spiked counter-current tests run using centrifugal contactors are presented.

Experimental

The composition of the synthetic PUREX raffinate used as the feed solution for both processes is shown in Table 1.

Table 1: Composition of the synthetic PUREX raffinate solution (HAR) used as feed solution for the demonstration of the innovative SANEX and the 1-cycle SANEX processes

| Element | Concentration [mg/L] | Element | Concentration [mg/L] | Element | Concentration [mg/L] |
|-------------------|----------------------|---------|----------------------|---------|----------------------|
| ²⁴¹ Am | tracer | Ag | 9 | Pd | 102 |
| ²⁴⁴ Cm | tracer | Al | 2 | Rb | 67 |
| ¹⁵² Eu | tracer | Ba | 247 | Rh | 77 |
| Y | 78 | Cd | 19 | Ru | 368 |
| La | 209 | Cr | 80 | Sb | 4 |
| Ce | 480 | Cs | 449 | Se | 24 |
| Pr | 195 | Cu | 20 | Sn | 11 |
| Nd | 716 | Fe | 1979 | Sr | 156 |
| Sm | 146 | Mo | 642 | Te | 109 |
| Eu | 40 | Na | 2000 | Zr | 698 |
| Gd | 46 | Ni | 41 | | |

Computer code calculations

The flow sheets were optimized using batch data, single-stage centrifugal contactor experiments and data from previous TODGA processes [19-21] (for innovative SANEX) and CyMe₄BTBP processes (for 1-cycle SANEX) [22-23], respectively. Calculations were carried out using the SX Process program, described in [24], which is designed for centrifugal contactors with an emphasis on a simple model for the system's kinetics.

Results and Discussion

Batch studies and single-stage experiments

Solvent extraction batch studies were performed in a wide range of conditions (e.g. variable nitric acid concentrations, variable ligand concentrations) to construct a database of experimental equilibrium distribution ratios of actinides and all important fission products contained in a typical PUREX raffinate. Optimization studies were then carried out under different experimental conditions related to the flow sheets (extraction, scrubbing and stripping) presented in Figure 3 and Figure 6 using different selective masking and stripping agents to optimize the system formulation. Details can be found in [15] for the development of the 1-cycle SANEX process. Important solvent extraction data collected for the development of the innovative SANEX process can be found in [11].

Single-stage experiments were carried out in a single-stage centrifugal contactor setup described in [25]. The single-stage experiments were run while varying the organic/aqueous flow rates to determine the distribution ratios for some key elements as well as the stage efficiency. The kinetics data for the 1-cycle SANEX are discussed in [23]. The extraction with CyMe₄BTBP is rather slow, even when a phase transfer catalyst is used. Flow rates of 10 mL/h were used in a previously run BTBP test and were found to be

suitable for the 1-cycle SANEX test as well. Lower flow rates would give better stage efficiency but should be avoided due to adverse centrifugal contactor performance and since it takes a long time to reach the steady state.

Results from the single-stage experiments for the innovative SANEX process were recently reported in [26]. The experiments showed that the kinetics of the TODGA-based system for An(III)+ Ln(III) co-extraction and the SO₃-Ph-BTP system for selective An(III) stripping is fast, which is in agreement with earlier batch studies.

Results of the innovative SANEX demonstration test

An innovative SANEX process was designed using an organic phase comprising TODGA in TPH + 5 vol.-% 1-octanol and an aqueous phase containing SO₃-Ph-BTP for the selective strip. The flow sheet is shown in Figure 3.

Similar versions of the first part of the flow sheet (extraction, Scrub 1, Scrub 2, see Figure 3) have been tested successfully in a spiked TODGA/TBP demonstration process at Jülich [19] and in a hot TODGA/TBP demonstration process at the Institute for Transuranium Elements in Karlsruhe [20]. The TBP used as a modifier in the previous tests is a non-CHON compound, which is not desirable as it generates secondary solid waste. TBP can be replaced by 1-octanol (5 vol.-%) [27], which also reduces the nitric acid extraction and suppresses 3rd phase formation. Finally, a solvent comprising 0.2 mol/L TODGA in TPH/5 vol.-% 1-octanol was chosen. The results show that TODGA extracts An(III) and Ln(III) with the desired high efficiency and with good kinetics. In addition, we replaced the oxalic acid and HEDTA used in previous processes (e.g. DIAMEX and TODGA/TBP) for masking Zr and Pd by the hydrophilic complexing agent CDTA (Figure 2). The problem of co-extraction of fission and corrosion products, such as Zr, Mo, Sr, Ru, Fe or Pd, is well known and occurs in several innovative partitioning processes. Recently, it was found that CDTA can be used to efficiently mask Zr and Pd in the feed under GANEX, DIAMEX and innovative SANEX solvent extraction conditions, preventing those metal ions from being extracted from HAR simulant solutions [28]. In batch extraction studies, it was demonstrated that a relatively small concentration of CDTA (0.05 mol/L) was sufficient to complex Zr and Pd and to keep them in the aqueous phase, while the lanthanides and TRU were efficiently extracted. Hence, the challenge was here to prove the efficiency of CDTA under realistic process conditions in a counter-current test.

The results of the innovative SANEX process show that Am(III) + Cm(III) and Ln(III) were quantitatively extracted (>99.9%) and very high feed/raffinate decontamination factors were achieved with DF>10³. 0.05 mol/L CDTA was added to the feed to limit the co-extraction of Zr and Pd. The Scrub 1 and Scrub 2 steps proved to be very efficient for the back-extraction of Mo, Zr, and Sr, since the collected organic solvent (stage 16) contained only 0.07% Mo, 0.07% Zr and 0.27% Sr of the initial amounts. The behavior of Ru is very similar to that in earlier TODGA tests, since 16% was co-extracted. The experimental ²⁴¹Am and ¹⁵²Eu profiles for the complete test are shown in Figure 4 and Figure 5. The results of the selective back-extraction of An(III) (Figure 5) show that 6 stages were sufficient for An(III) stripping and only 4 stages were needed for complete Ln(III) stripping with citric acid solution. <0.1% of Am(III), Cm(III), and Eu(III) were found in the spent solvent after stripping.

Figure 3: Flow sheet of the innovative SANEX demonstration process

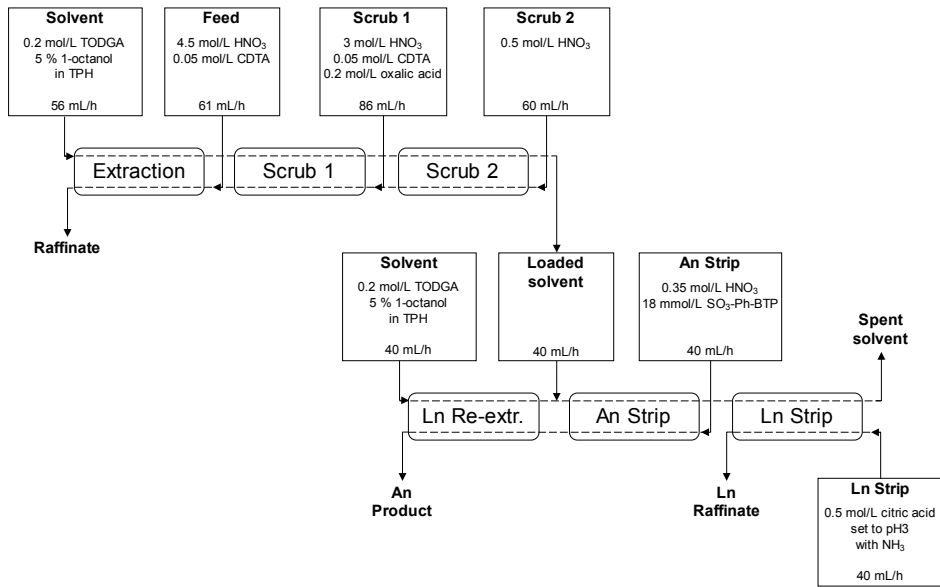


Figure 4: Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the innovative SANEX test: 1st day results

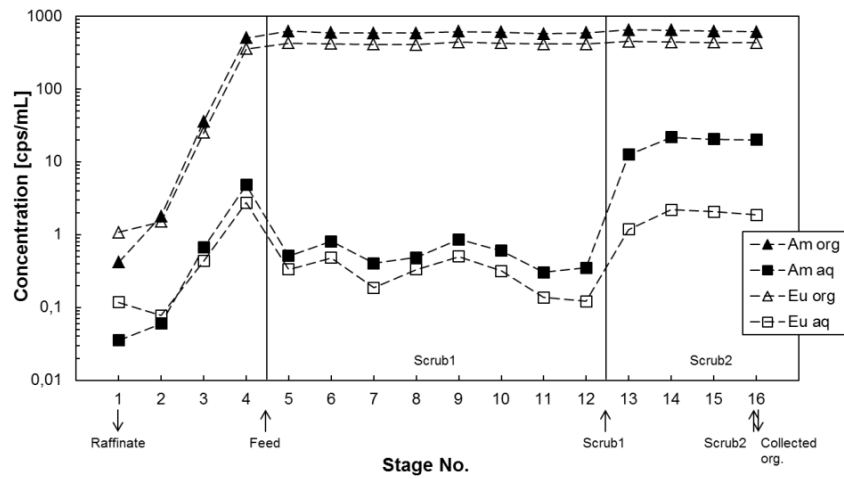
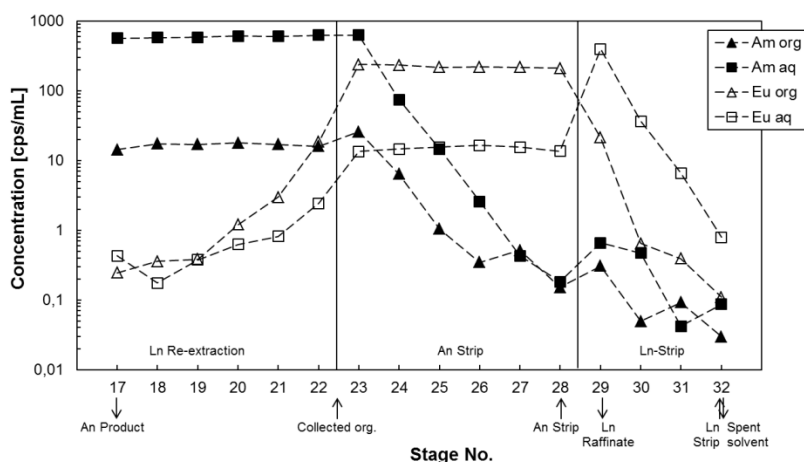


Figure 5: Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the innovative SANEX test: 2nd day results

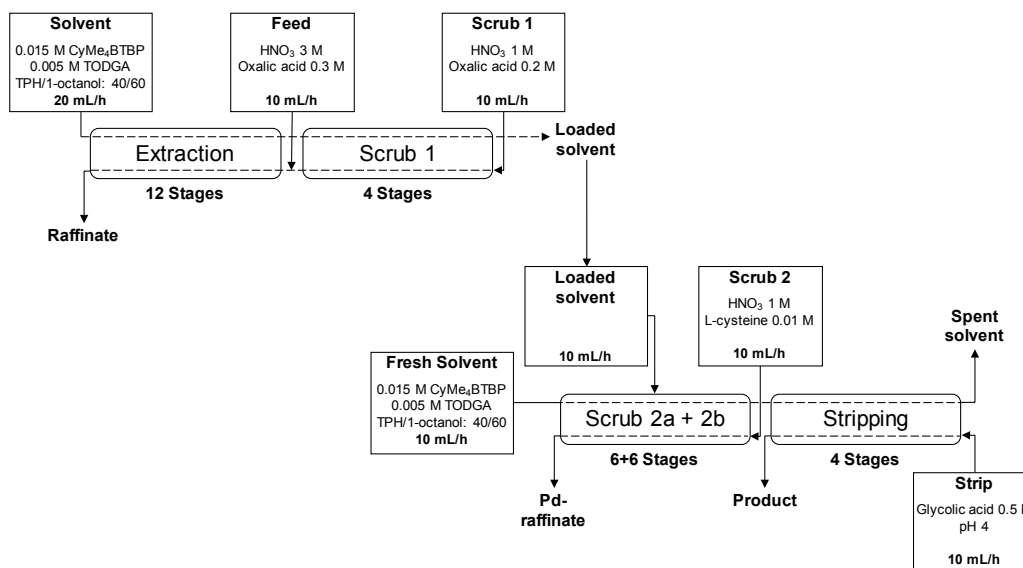


As expected, the spent solvent was contaminated with 12.8% Ru, thus requiring further investigations, either to avoid the extraction of Ru using special complexing agents or to regenerate the solvent by specific washing steps. The Am(III) + Cm(III) product was fairly clean and only contaminated with 0.34% Sr, 0.44% Ru and <0.1% Ln(III). >99.8% Am(III) and Cm(III) were recovered in the An product fraction. The hydrodynamic behavior of the solvent was excellent during the whole spiked test and no phase entrainment or 3rd phase formation was observed. Thanks to the promising results obtained in the spiked counter-current test, a hot demonstration is planned after re-calculation of the results to verify the computer-code models and further optimizations.

1-cycle SANEX

A single process directly using the PUREX raffinate would reduce the number of cycles, making the complete advanced partitioning process more economical and easier. CyMe₄BTBP (Figure 2) is the current European reference molecule for SANEX-type processes [29-30]. The extractant shows good extraction of An(III) with high separation from the Ln(III) and good hydrolytic and radiolytic stability. The good performance of the extractant has been demonstrated in several laboratory-scale process tests [22, 31]. A solvent comprising 0.015 mol/L CyMe₄BTBP and 0.005 mol/L TODGA in an aliphatic diluent (40% TPH + 60% 1-octanol) was recently proposed at Jülich to achieve the desired direct and selective extraction of the trivalent actinides from HAR, after gathering data from numerous batch experiments described in [15]. The results from single-stage centrifugal contactor tests were used to develop a 16 +16-stage flow sheet, which was designed at KIT-INE in Karlsruhe [23]. The flow sheet is shown in Figure 6.

Figure 6: Flow sheet of the 1-cycle SANEX demonstration process



The main results of this spiked test can be summarized as follows. High recovery yields for An(III) were found in the product fraction: >99.8% for Am(III) and >99.4% for Cm(III). The raffinate contained only 0.03% of the Am and 0.2% of the Cm(III) inventories, respectively. This could be improved by two additional stages in the extraction section. Satisfactory An(III)/Ln(III) decontamination was achieved and less than 1% of the initial amount of lanthanides was found in the An(III) product fraction. Satisfactory An(III)/fission product decontamination was achieved. Only 0.1% Mo, 0.8% Pd, and 8.8% Y followed the An(III) fraction. It should be noted, however, that the flow rates used in the implementation of the process were rather low, due to the slow extraction kinetics of the solvent. This is a drawback in an industrial process in which large amounts of waste are 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. Whether these problems can be solved without modifying the extracting agent remains still to be investigated. Recently, a new BTP, CA-BTP [32], was developed, showing good stability but faster kinetics and improved solubility as compared to CyMe₄BTBP. The new CyMe₄BTPhen molecule, developed at the University of Reading, could be an alternative option [33]. However, these compounds have not yet been implemented in a continuous counter-current process.

Conclusions

The separation processes described in this paper are based on solvent extraction studies which benefit from the experience gained over the last 15 years in European collaborative projects. Both spiked processes showed excellent performance for the recovery of An(III) from simulated HAR solution. The 1-cycle SANEX and innovative SANEX processes demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle. This is a great improvement over the former multi-cycle strategy. However, some drawbacks of the individual processes have to be addressed: the low flow rates of the 1-cycle SANEX process combined with the low loading capacity of the solvent. Also, both processes used sulfur-containing complexing agents, thus being incompatible with the CHON principle. It is important to improve the mechanistic understanding of the chemical and physical reactions involved in the solvent extraction processes (thermodynamics and kinetics) and the diverse safety issues involved in the chemical processes under operational and malfunctional conditions. This is being done in close cooperation with European partners under the current FP7 EU project SACSESS (duration 2013-2015).

Acknowledgements

Financial support for this research was provided by the European Commission (projects ACSEPT – Contract No. FP7-CP-2007-211 267 and SACSESS – Contract No. FP7-Fission-2012-323-282) and the German Federal Ministry of Education and Research (Contract No. 02NUK012E and 02NUK020E).

References

- [1] OECD-NEA (2011), "Potential Benefits and Impacts of Advanced Nuclear Fuel Cycles with Actinide Partitioning and Transmutation", *OECD, Nuclear Energy Agency (NEA)*, NEA No. 6894.
- [2] K. L. Nash *et al.* (2006), "Actinide Separation Science and Technology", in *The Chemistry of Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R. *et al.*, Eds. Springer: Dordrecht, The Netherlands, pp. 2622-2798.
- [3] C. Madic *et al.* (2000), "New partitioning techniques for minor actinides", *European Commission*, Luxembourg, EUR 19149 EN.
- [4] C. Madic *et al.* (2004), "PARTNEW - New Solvent Extraction Processes for Minor Actinides - Final Report", *CEA-report 6066*,
- [5] C. Madic and N. Ouvrier (2008), "EUROPART: EUROpean research program for the PARTitioning of minor actinides from high active wastes arising from the reprocessing of spent nuclear fuels", *Radiochim. Acta*, 96 [4-5], pp. 183-185.
- [6] G. Modolo *et al.* (2012), "A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate", *Radiochim. Acta*, 100 [8-9], pp. 715-725.
- [7] S. Bourg *et al.* (2011), "ACSEPT - Partitioning technologies and actinide science: Towards pilot facilities in Europe", *Nucl. Eng. Des.*, 241 [9], pp. 3427-3435.
- [8] E. Aneheim *et al.* (2012), "Studies of a Solvent for GANEX Applications Containing CyMe₄-BTBP and DEHBA in Cyclohexanone", *Separ. Sci. Technol.*, 47 [5], pp. 663-669.
- [9] J. Brown *et al.* (2012), "Plutonium loading of prospective grouped actinide extraction (GANEX) solvent systems based on diglycolamide extractants", *Solvent Extr. Ion Exch.*, 30 [2], pp. 127-141.
- [10] K. Bell *et al.* (2012), "Progress Towards the Development of a New GANEX Process", *Proc. Chem.*, 7, pp. 392-397.
- [11] A. Geist *et al.* (2012), "Actinide(III)/lanthanide(III) Separation Via Selective Aqueous Complexation of Actinides(III) Using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-yl)-Pyridine in Nitric Acid", *Solvent Extr. Ion Exch.*, 30 [5], pp. 433-444.
- [12] C. Rostaing *et al.* (2012), "Development and Validation of the EXAm Separation Process for Single Am Recycling", *Proc. Chem.*, 7, pp. 367-373.
- [13] D. Warin, C. Poinssot and S. Bourg (2011), "Future Nuclear Fuel Cycles: Meeting Sustainability through Actinide Recycling", *Proc. of GLOBAL*, p. 478580 (Paper No.).
- [14] A. Wilden *et al.* (2012), "The Recovery of An(III) in an innovative-SANEX process using a TODGA-based solvent and selective stripping with a hydrophilic BTP", *Proc. Chem.*, 7, pp. 418-424.
- [15] A. Wilden *et al.* (2011), "Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe₄BTBP and TODGA as 1-cycle SANEX Solvent", *Solvent Extr. Ion Exch.*, 29 [2], pp. 190-212.
- [16] M. Nilsson and K. L. Nash (2007), "Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process", *Solvent Extr. Ion Exch.*, 25 [6], pp. 665-701.
- [17] C. Hill (2009), "Overview of Recent Advances in An(III)/Ln(III) Separation by Solvent Extraction", in *Ion Exchange and Solvent Extraction, A Series of Advances*, Moyer, B. A., Ed. CRC Taylor and Francis: 19, pp. 119-193.
- [18] X. Hérès *et al.* (2009), "Results of recent counter-current tests on An(III)/Ln(III) separation using TODGA extractant", *Proc. of GLOBAL*, pp. 1127-1132, paper 9384.

- [19] G. Modolo *et al.* (2008), "Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from a Simulated PUREX Raffinate, Part II: Centrifugal Contactor Runs", *Solvent Extr. Ion Exch.*, 26 [1], pp. 62-76.
- [20] D. Magnusson *et al.* (2009), "Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate Part III: Centrifugal Contactor Run using Genuine Fuel Solution", *Solvent Extr. Ion Exch.*, 27 [1], pp. 26-35.
- [21] D. Magnusson *et al.* (2011), "Computer Code Development for Flow-Sheet Design and Modeling with Verification Towards a Novel Partitioning Process", *Proc. of GLOBAL*, p. 355757 (Paper No.).
- [22] D. Magnusson *et al.* (2009), "Demonstration of a SANEX Process in Centrifugal Contactors using the CyMe₄-BTBP Molecule on a Genuine Fuel Solution", *Solvent Extr. Ion Exch.*, 27 [2], pp. 97-106.
- [23] D. Magnusson *et al.* (2013), "Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe₄-BTBP and TODGA as 1-cycle SANEX Solvent Part II: Flow-sheet Design for a Counter-Current Centrifugal Contactor Demonstration Process", *Solvent Extr. Ion Exch.*, 31 [1], pp. 1-11.
- [24] D. Magnusson and R. Malmbeck (2012), "Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors", *Solvent Extr. Ion Exch.*, 30 [2], pp. 115-126.
- [25] D. Magnusson *et al.* (2009), "Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors", *Radiochim. Acta*, 97 [3], pp. 155-159.
- [26] D. Magnusson *et al.* (2012), "Flow-sheet design for an innovative SANEX process using TODGA and SO₃-Ph-BTP", *Proc. Chem.*, 7, pp. 245-250.
- [27] A. Geist and G. Modolo (2009), "TODGA Process Development: an Improved Solvent Formulation", *Proc. of GLOBAL (The Nuclear Fuel Cycle: Sustainable Options & Industrial Perspectives)*, pp. 1022-1026, paper 9193.
- [28] M. Sypula *et al.* (2012), "Use of polyaminocarboxylic acids as hydrophilic masking agents for fission products in actinide partitioning processes", *Solvent Extr. Ion Exch.*, 30 [7], pp. 748-764.
- [29] A. Geist *et al.* (2006), "6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine, an effective extracting agent for the separation of americium(III) and curium(III) from the lanthanides", *Solvent Extr. Ion Exch.*, 24 [4], pp. 463-483.
- [30] P. J. Panak and A. Geist (2013), "Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands", *Chem. Rev.*, 113 [2], pp. 1199-1236.
- [31] G. Modolo *et al.* (2013), "Development and Demonstration of a new SANEX Partitioning Process for Selective Actinide(III)/Lanthanide(III) Separation using a mixture of CyMe₄BTBP and TODGA", *Radiochim. Acta*, 101 [3], pp. 155-162.
- [32] S. Trumm *et al.* (2011), "An Improved Hydrolytically-Stable Bis-Triazinyl-Pyridine (BTP) for Selective Actinide Extraction", *Solvent Extr. Ion Exch.*, 29 [2], pp. 213-229.
- [33] F. W. Lewis *et al.* (2011), "Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-triazine Ligand", *J. Am. Chem. Soc.*, 133 [33], pp. 13093-13102.