Spiked Laboratory-scale Continuous Counter-Current Centrifugal Contactor Demonstration of a Novel innovative-SANEX Process

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Abstract

In this paper the development and laboratory-scale demonstration of a novel “innovative-SANEX” process using annular centrifugal contactors is presented. In this strategy, the An(III) and Ln(III) are co-extracted from simulated PUREX raffinate, and the loaded solvent is subjected to several stripping steps. A solvent comprising the TODGA extractant with addition of 5 vol.-% 1-octanol showed very good extraction efficiency of Am(III) and Cm(III) together with the trivalent lanthanides (Ln(III)) from simulated PUREX raffinate solution without 3rd phase formation. The problem of co-extraction of Zr and Pd was overcome using CDTA (cyclohexanediaminetetraacetic acid) as masking agent.

The An(III) were selectively stripped using the hydrophilic complexing agent SO_3-Ph-BTP. For the subsequent stripping of the Ln(III), a citric acid based solution was used.

A 32-stage process flow-sheet was designed using computer-code calculations and tested in annular miniature centrifugal contactors in counter-current mode. The innovative SANEX process showed excellent performance for the recovery of An(III) from simulated HAR solution and separation from the fission and activation products. ≥99.8% An(III) were recovered with only low impurities (0.4% Ru, 0.3% Sr, 0.1% Ln(III)). The separation from the Ln(III) was excellent and the Ln(III) were efficiently stripped by the citrate-based stripping solution. The only major contaminant in the spent solvent was Ru, with 14.7% of the initial amount being found in the spent solvent. Solvent cleaning and recycling therefore has to be further investigated.

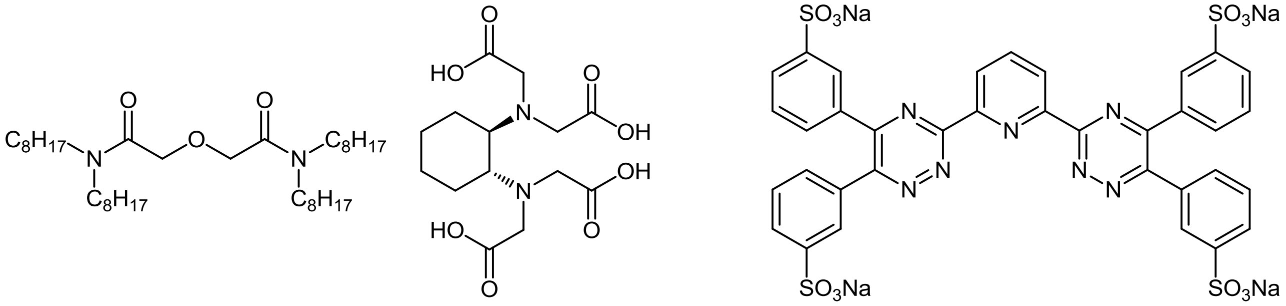
This successful spiked test demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle which is a great improvement over the former multi-cycle strategy. The results of this test are presented and discussed.

Introduction

For the advanced minor actinide (MA) partitioning following the PUREX process, several multi-cycle processes have been developed.[1] In the USA e.g. the TALSPEAK process[2] has been intensely investigated as part of the CTH process.[3] Recent research in Europe focused on the development of single-cycle processes, e.g. 1-cycle SANEX[4-6], EXAm[7]. The French CEA successfully demonstrated an An(III)/Ln(III) separation process based on a TODGA/TBP solvent with a selective An(III) stripping step using hydrophilic polyaminocarboxylic acid in a buffered solution.[8]

Single cycle processes are advantageous as they could make the advanced MA partitioning more economical and easier. However, the used extraction systems have to cope with a number of challenges, e.g. high nitric acid concentration, loading, selectivity for the desired trivalent actinides over fission and activation products, stability towards hydrolysis and radiolysis. Currently, no single molecule fulfils all the requirements and therefore, a sophisticated stepwise approach was chosen in this study.

The TODGA (*N*,*N*,*N'*,*N'*-tetraoctyldiglycolamide, Figure 1) extractant is known to co-extract An(III) and Ln(III) efficiently from highly concentrated nitric acid solutions.[9] The co-extraction of Zr and Pd was overcome using the polyaminocarboxylic acid CDTA (trans-1,2-diaminocyclo-hexane-*N*,*N*,*N'*,*N'*-tetraacetic acid, Figure 1) as masking agent.[10] Third phase formation was suppressed by addition of 5 vol-% 1-octanol.[11] For the selective recovery of the An(III) the hydrophilic complexing agent SO_3-Ph-BTP (Figure 1) was used.[12] Based on the selected extractants (TODGA), masking (CDTA) and selective stripping agents (SO_3-Ph-BTP), a novel innovative-SANEX process was developed and tested in a spiked counter-current demonstration test using annular centrifugal contactors. The results of this test are presented and discussed.



TODGA **CDTA** **SO_3-Ph-BTP**

Figure 1. Chemical structures of TODGA, CDTA and SO_3-Ph-BTP.

Composition of the Feed Solution

The composition of the synthetic PUREX raffinate used as the feed solution for the innovative-SANEX process is shown in Table 1. It was prepared by a specific strategy for the dissolution of the reagents, which is mainly based on the use of metal nitrate salts.[13-14] The initial HNO_3 concentration was 4.45 mol/L HNO_3. 0.05 mol/L CDTA was added as a masking agent for Zr and Pd to the innovative SANEX feed.

Table 1. Composition of the synthetic PUREX raffinate solution (HAR) used as feed solution for the demonstration of the innovative SANEX process.

Element	Concentration [mg/L or as shown]	Element	Concentration [mg/L]	Element	Concentration [mg/L]
^{241}Am	5 MBq/L	Ag	11	Pd	204
^{244}Cm	3 MBq/L	Al	2	Rb	59
^{152}Eu	9 MBq/L	Ba	259	Rh	72
Y	79	Cd	22	Ru	355
La	214	Cr	94	Sb	3
Ce	482	Cs	499	Se	35
Pr	189	Cu	19	Sn	0.1
Nd	860	Fe	1900	Sr	161
Sm	144	Mo	658	Te	116
Eu	29	Na	1600	Zr	382
Gd	41	Ni	45		
HNO_3	4.45 mol/L				
CDTA	0.05 mol/L				

Flow-sheet design

The main goals of the flow-sheet design was to achieve a high recovery yield of actinides (>99.9%) and to obtain decontamination factors for fission products (FP) that were as high as possible. The constraints taken into account for the calculations were the number of stages available (16 +16). Important parameters to be optimized were the total number and distribution of contactors between the extraction, scrubbing and stripping sections, concentrations (acidity, complexing agents, etc.) and flow rates. The flow-sheets were optimized using batch data, single-stage centrifugal contactor experiments and data from previous TODGA processes.[13, 15-16] The kinetics of the system is a very important parameter for the flow-sheet design with centrifugal contactors due to the short residence time in the contactors.[17] Calculations were carried out using the SX Process code, described in ref.[18-20], which is designed for centrifugal contactors with an emphasis on a simple model for the system's kinetics. Details of the flow-sheet design for this process are described in ref.[21] and the final flow-sheet is shown in Figure 2.

The innovative SANEX process was designed using an organic phase comprising 0.2 mol/L TODGA in TPH + 5 vol.-% 1-octanol and an aqueous phase containing 18 mmol/L SO_3-Ph-BTP in 0.35 mol/L HNO_3 for the An(III) selective stripping. This process consists of 4 main steps:

Step 1: Co-extraction of An(III) and Ln(III): 4 stages.

Step 2: Scrubbing of co-extracted Mo, Sr and HNO_3 using two scrubbing solutions: 8 stages of Scrub 1 (0.05 mol/L CDTA + 0.2 mol/L oxalic acid in 3 mol/L HNO_3) and 4 stages of Scrub 2 (0.5 mol/L HNO_3).

Step 3: 6 stages for the selective back-extraction of An(III) using the selective aqueous complexing agent SO_3-Ph-BTP at appropriate acidity (0.35 mol/L HNO_3) and additional 6 stages for Ln(III) re-extraction.

Step 4: Stripping of lanthanides and residual elements remaining in the solvent, using a citric-acid-buffered solution at pH3: 4 stages.

Due to the availability of only 16 contactors in the laboratory, the test had to be split into two parts and performed on consecutive days. The loaded solvent leaving the Scrub 2 section of the contactor battery was collected, stored overnight in a closed bottle, and fed into the cleaned and newly prepared contactor battery as shown in Figure 2.

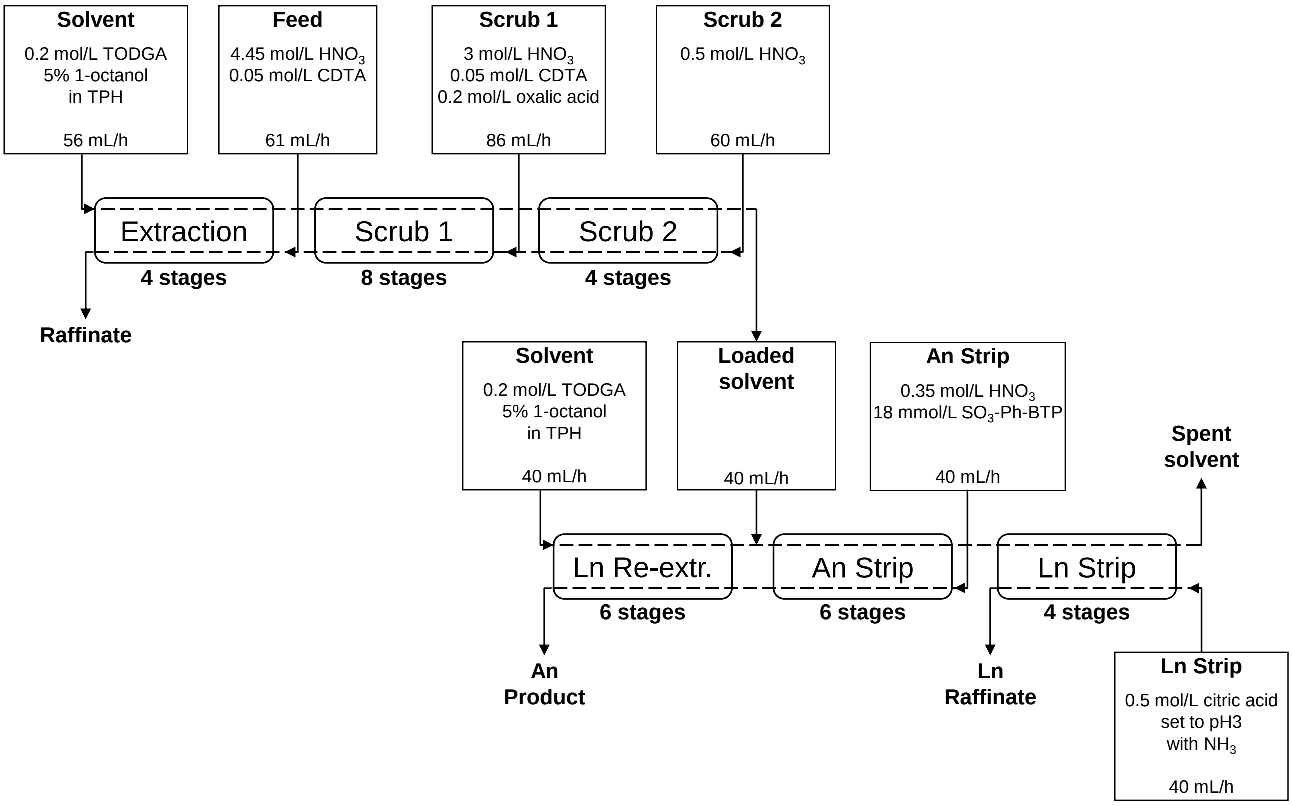


Figure 2. Flow-sheet of the SO_3-Ph-BTP innovative SANEX demonstration process.

Results and Discussion

As described above, the demonstration test had to be performed in two parts on consecutive days. The ^{241}Am and ^{152}Eu profile of the first part, the extraction and scrubbing sections, is shown in Figure 3, while the Sr and Ru profiles are shown in Figure 4. An(III), Y(III) and Ln(III) were well extracted (>99.9%) and very high feed/raffinate decontamination factors were achieved (>750 for An(III), Table 2). Four stages were sufficient to reach the high feed/raffinate decontamination. The trivalent actinides and lanthanides stayed in the organic phase during the two scrubbing sections with high distribution ratios. The distribution ratios decreased slightly in the last 4 stages, due to the lower nitric acid concentration in those stages, needed for Sr scrubbing. The addition of 0.05 mol/L CDTA to the feed efficiently limited the co-extraction of Zr and Pd. The lower acidity Scrub 2 solution proved to be very efficient for scrubbing Sr, as distribution ratios of 0.21 were observed and only 0.3% of the initial amount of Sr was found in the collected organic solvent (stage 16). Figure 4 shows the Sr and Ru concentration profiles. Sr was extracted very well and passed the Scrub 1 section. Only in the Scrub 2 section back-extraction was observed. This in turn lead to an accumulation of Sr in the Extraction and Scrub 1 sections of the test, observable by the high steady-state concentrations in stages 1-12 compared to the initial feed concentration. However, steady state was reached for Sr (constant effluent concentrations at the aqueous and organic outlets) and the maximum concentration of Sr in the solvent accounted for only ~10% loading of TODGA (assuming a 1:2 Sr:TODGA complex [22]). 16% of the initial Ru amount was co-extracted; the behavior of Ru was very similar to that observed in earlier tests using TODGA-based solvents.

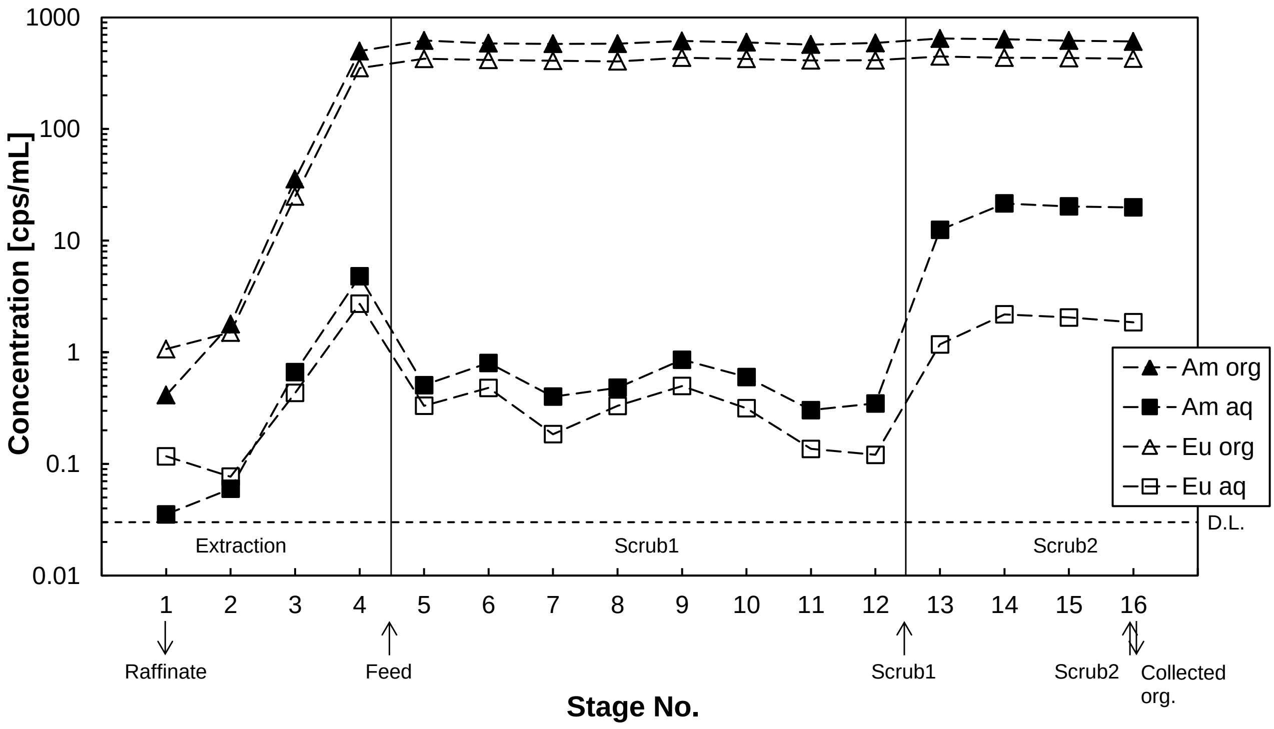


Figure 3. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the 1st part of the innovative SANEX test.

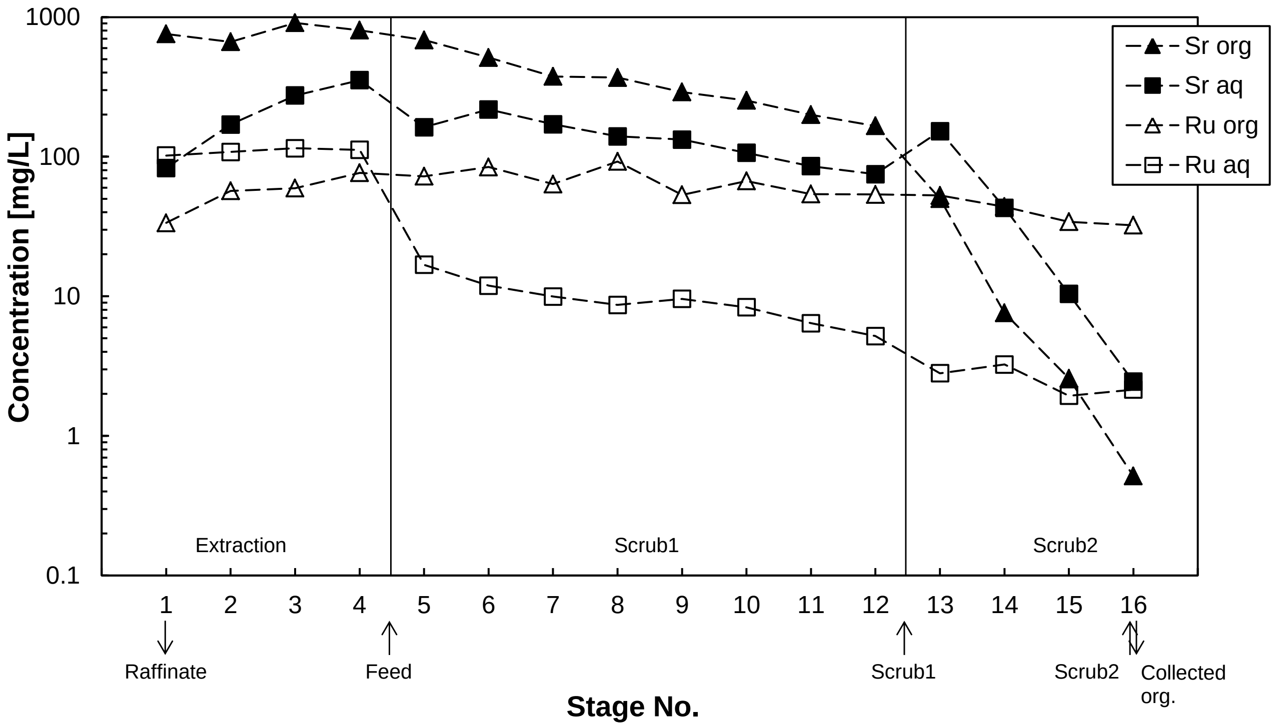


Figure 4. Experimental aqueous and organic concentration profiles of Sr and Ru during the 1st part of the innovative SANEX test.

On the second day of the demonstration test, the selective back-extraction of An(III) with SO_3-Ph-BTP was conducted. Figure 5 shows the ^{241}Am and ^{152}Eu profiles and Figure 6 shows the Sr and Ru profiles. Selective back-extraction of An(III) with SO_3-Ph-BTP was very efficient with distribution ratios ≤0.06. The An(III) were efficiently stripped within six stages and >99.8% Am(III) and Cm(III) were recovered in the An product fraction. Good separation from the Ln(III) was achieved in the Ln Re-extraction section, the Am(III) + Cm(III) product was fairly clean and only contaminated with 0.3% Sr, 0.4% Ru and <0.1% Ln(III). The Ln(III) were very efficiently stripped in the last four stages using a citric acid based stripping solution. Only four stages were needed for nearly quantitative Ln(III) stripping. The spent solvent after stripping contained <0.1% of Am(III), Cm(III), and Eu(III). The only major contamination of the spent solvent was Ru. Figure 6 shows that Ru was not stripped by SO_3-Ph-BTP or the citric-acid based stripping solution and 14.7% Ru were found in the spent solvent. A similar behavior was already described for other demonstration tests using the TODGA extractant.[13, 15]

The hydrodynamic behavior of the solvent was excellent during the whole spiked test and no phase entrainment or 3rd phase formation was observed.

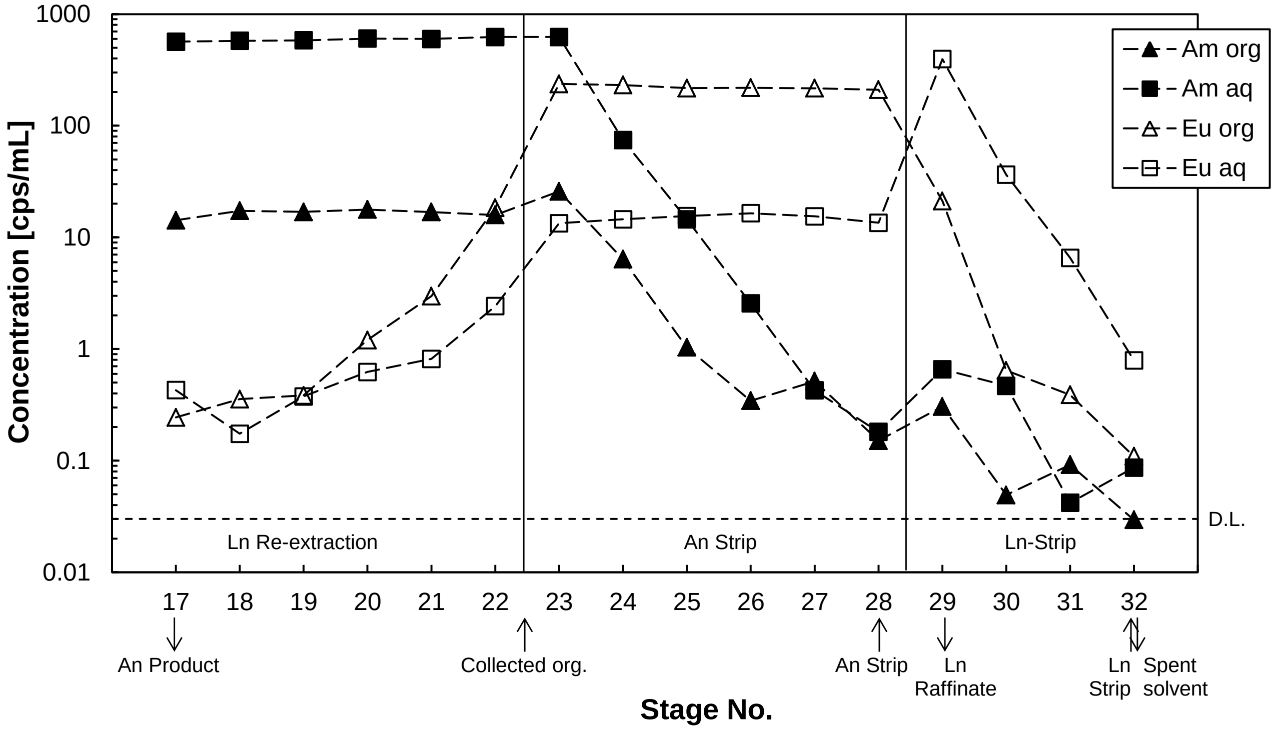


Figure 5. Experimental aqueous and organic concentration profiles of ^{241}Am and ^{152}Eu during the 2nd part of the innovative SANEX test.

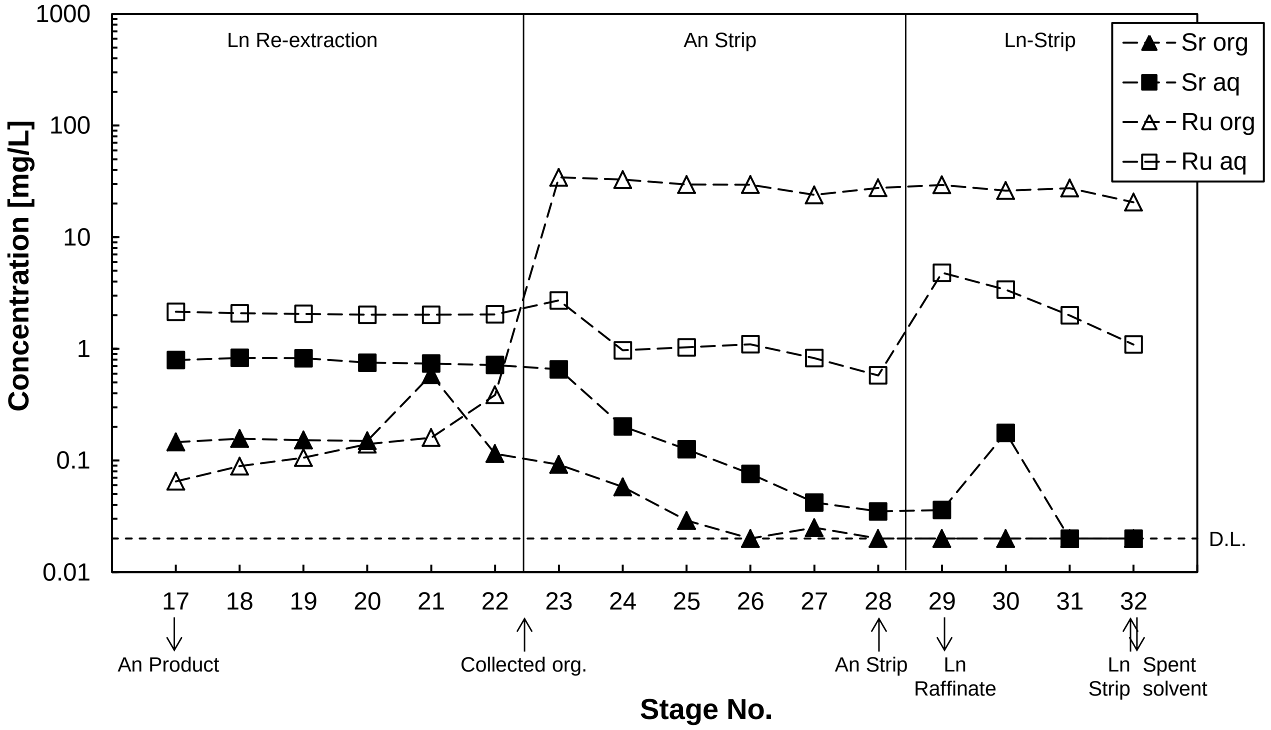


Figure 6. Experimental aqueous and organic concentration profiles of Sr and Ru during the 2nd part of the innovative SANEX test.

Table 2 shows the mass balance, recovery and process decontamination factors (feed/raffinate) obtained in the innovative-SANEX test.

Table 2. Mass balance, recovery and process decontamination factors obtained in the innovative-SANEX test.

Element	% in raffinate	% in loaded solvent	% in An(III) product	% in Ln(III) product	% in spent solvent	$DF_{feed/raffinate}$
^{241}Am	<0.1	99.9	99.9	0.1	<0.1	2.6E+3
^{244}Cm	0.1	99.9	99.8	0.1	0.1	750
^{152}Eu	0.1	99.9	0.1	99.8	0.1	1.1E+3
La	<0.1	99.9	0.1	99.5	0.4	2.3E+4
Ce	<0.1	99.9	D.L.	99.7	0.3	5.7E+5
Pr	<0.1	99.9	D.L.	99.7	0.3	2.2E+5
Nd	<0.1	99.9	D.L.	99.8	0.2	3.9E+4
Sm	<0.1	99.9	D.L.	99.9	0.1	3.4E+3
Eu	0.3	99.7	D.L.	99.7	0.1	380
Gd	<0.1	99.9	D.L.	99.9	0.1	4.9E+4
Y	<0.1	99.9	D.L.	99.9	D.L.	4.7E+4
Ru	84.0	16.0	0.4	0.9	14.7	1.2
Pd	97.2	2.8	<0.1	2.8	<0.1	1.0
Zr	99.9	0.1	0.1	<0.1	<0.1	1.0
Mo	99.9	0.1	0.1	<0.1	<0.1	1.0
Sr	99.7	0.3	0.3	<0.1	D.L.	1.0
Ag	52.1	D.L.	D.L.	D.L.	D.L.	1.0
Rh, Rb, Ba, Cs, Te, Cd, Sn, Sb, Cu, Ni, Cr, Fe, Na	99.9	D.L.	D.L.	D.L.	D.L.	1.0

D.L. = below detection limit
Se and Al could not be determined by ICP-MS.

Conclusions

The presented innovative-SANEX process showed excellent performance for the recovery of An(III) from simulated HAR solution using a TODGA-based solvent and An(III) selective stripping using SO_3-Ph-BTP. It demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle. The use of SO_3-Ph-BTP is an improvement over the formerly use of buffered polyaminocarboxylic acid solutions, as precise pH control and salting out agents are no longer needed.

However, some drawbacks of the process have to be addressed. The process uses a sulphur-containing complexing agent, thus being incompatible with the CHON principle. Recycling of the An(III)-selective stripping agent SO_3-Ph-BTP would be desirable for reduction of cost and waste minimization, a topic currently being studied.[23] Recycling of the TODGA-based solvent must also be addressed, especially cleaning from co-extracted Ru and other minor metal impurities, but also cleaning from radiolysis degradation products.

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 maloperational conditions, which is currently being studied in the European collaborative research project SACSESS.

Acknowledgements

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References

1. Hill, C. Overview of Recent Advances in An(III)/Ln(III) Separation by Solvent Extraction. Chap. 3 in Ion Exchange and Solvent Extraction, A Series of Advances, Vol. 19, Moyer, B.A., CRC Taylor and Francis: pp 119-193, **2009**.
2. Weaver, B.; Kappelmann, F.A. TALSPEAK: A new Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacetic Organophosphate or Phosphonate; ORNL-3559; Oak Ridge National Laboratory; Oak Ridge; 1964.
3. Nilsson, M.; Nash, K.L. Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process. Solvent Extr. Ion Exch. **2007**, *25* (6), 665-701.
4. Wilden, A.; Modolo, G.; Schreinemachers, C.; Sadowski, F.; Lange, S.; Sypula, M.; Magnusson, D.; Geist, A.; Lewis, F.W.; Harwood, L.M.; Hudson, M.J. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of $CyMe_4BTBP$ and TODGA as 1-cycle SANEX Solvent Part III: Demonstration of a Laboratory-scale Counter-Current Centrifugal Contactor Process. Solvent Extr. Ion Exch. **2013**, *31* (5), 519-537.
5. Magnusson, D.; Geist, A.; Wilden, A.; Modolo, G. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of $CyMe_4$-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. **2013**, *31* (1), 1-11.
6. Wilden, A.; Schreinemachers, C.; Sypula, M.; Modolo, G. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of $CyMe_4BTBP$ and TODGA as 1-cycle SANEX Solvent. Solvent Extr. Ion Exch. **2011**, *29* (2), 190-212.
7. Bollesteros, M.-J.; Calor, J.-N.; Costenoble, S.; Montuir, M.; Pacary, V.; Sorel, C.; Burdet, F.; Espinoux, D.; Hérès, X.; Eysseric, C. Implementation of Americium Separation from a PUREX Raffinate. Proc. Chem. **2012**, *7*, 178-183.
8. Warin, D.; Poinssot, C.; Bourg, S. Future Nuclear Fuel Cycles: Meeting Sustainability through Actinide Recycling, Proceedings of GLOBAL 2011, Makuhari, Japan, 11.-16.12.2011, p 478580 (Paper No.).
9. Ansari, S.A.; Pathak, P.; Mohapatra, P.K.; Manchanda, V.K. Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning. Chem. Rev. **2012**, *112* (3), 1751-1772.
10. Sypula, M.; Wilden, A.; Schreinemachers, C.; Malmbeck, R.; Geist, A.; Taylor, R.; Modolo, G. Use of polyaminocarboxylic acids as hydrophilic masking agents for fission products in actinide partitioning processes. Solvent Extr. Ion Exch. **2012**, *30* (7), 748-764.
11. Geist, A.; Modolo, G. TODGA Process Development: an Improved Solvent Formulation, Proceedings of GLOBAL (The Nuclear Fuel Cycle: Sustainable Options & Industrial Perspectives) 2009, Paris, 6-11 September, pp 1022-1026, paper 9193.

12. Geist, A.; Müllich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T. Actinide(III)/lanthanide(III) Separation Via Selective Aqueous Complexation of Actinides(III) Using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-yl)-Pyridine in Nitric Acid. Solvent Extr. Ion Exch. **2012**, *30* (5), 433-444.
13. Modolo, G.; Asp, H.; Vijgen, H.; Malmbeck, R.; Magnusson, D.; Sorel, C. Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from a Simulated PUREX Raffinate, Part II: Centrifugal Contactor Runs. Solvent Extr. Ion Exch. **2008**, *26* (1), 62-76.
14. Heits Zusammensetzung und Herstellung von HAW/HAWC-Simulaten gemäß den Planungsgrundlagen der DWK und den Erfahrungen der WAK; Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen mbH; Karlsruhe; 1982.
15. Magnusson, D.; Christiansen, B.; Glatz, J.-P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate Part III: Centrifugal Contactor Run using Genuine Fuel Solution. Solvent Extr. Ion Exch. **2009**, *27* (1), 26-35.
16. Magnusson, D.; Geist, A.; Wilden, A.; Modolo, G.; Malmbeck, R. Computer Code Development for Flow-Sheet Design and Modeling with Verification Towards a Novel Partitioning Process, Proceedings of GLOBAL 2011, Makuhari, Japan, 11-16 December, p 355757 (Paper No.).
17. Magnusson, D.; Christiansen, B.; Glatz, J.-P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors. Radiochim. Acta **2009**, *97* (3), 155-159.
18. Magnusson, D.; Malmbeck, R. Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors. Solvent Extr. Ion Exch. **2012**, *30* (2), 115-126.
19. Magnusson, D.; Geist, A.; Malmbeck, R. SX process-A code for solvent extraction processes in centrifugal contactors simulation. Chem. Eng. Sci. **2013**, *99*, 292-297.
20. Magnusson, D.; Geist, A.; Malmbeck, R.; Müllich, U. Study of the Mass Transfer Behavior in a Centrifugal Contactor and Verification of the Solvent Extraction Model for the SX Process Program. Solvent Extr. Ion Exch. **2013**, *31* (6), 578-589.
21. Magnusson, D.; Geist, A.; Malmbeck, R.; Modolo, G.; Wilden, A. Flow-sheet design for an innovative SANEX process using TODGA and SO_3-Ph-BTP. Proc. Chem. **2012**, *7*, 245-250.
22. Sasaki, Y.; Tsubata, Y.; Kitatsuji, Y.; Sugo, Y.; Shirasu, N.; Morita, Y.; Kimura, T. Extraction Behavior of Metal Ions by TODGA, DOODA, MIDOA, and NTAamide Extractants from HNO_3 to n-Dodecane. Solvent Extr. Ion Exch. **2013**, *31* (4), 401-415.
23. Munzel, D.; Galán, H.; Núnez, A.; Müllich, U.; Cobos, J.; Geist, A. i-SANEX process development studies: stability and recyclability of SO_3-Ph-BTP, Proceedings of Sustainable Nuclear Energy Conference 2014, Manchester, UK, 09.-11.04.2014.