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The SACSESS Hydrometallurgy Domain — an Overview

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Abstract

The EURATOM FP7 project SACSESS (Safety of Actinide Separation Processes) is in continuity of a long line of preceding EURATOM projects. SACSESS is organised along four domains, one of them related to the development of hydrometallurgical (i.e. solvent extraction based) actinide separations processes. Within this domain, the most promising processes developed in previous projects are further developed, improving their technology readiness level (TRL) towards the point at which safe industrial implementation will be achievable.

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1. Introduction

The potential benefits of recycling plutonium and minor actinides as nuclear fuel — rather than direct disposal of spent fuel without actinide recycle — are discussed and studied in the context of sustainable nuclear energy production.^{1,2} The recycling of actinides requires their prior separation from the used nuclear fuel, i.e. from fission products. Solvent extraction is a suitable separation method.³ While the separation of plutonium by the PUREX process is well established, separating minor actinides has not been performed on an industrial scale. Solvent extraction processes for separating minor actinides (mainly americium and curium) have been developed in Europe in a continuous series of EURATOM research programmes, initiated in the early 1990s by the late Charles Madic and the late Mike Hudson. In the course of these projects a plethora of new molecules for extracting actinide ions were synthesised and tested. The most suitable of them, together with selected molecules developed by scientists from outside these projects, were used for lab scale process development and testing. Many process flow-sheets were developed and tested on the lab scale. Several were selected as reference flow-sheets, i.e. versions of the so-called r-SANEX,^{4,5} i-SANEX,⁶ 1c-SANEX,⁷ EURO-GANEX^{8,9} and CHALMEX^{10,11,12} processes. However, many aspects relevant to a safe implementation of such processes have never or only marginally been addressed. Consequently, a focus was needed on filling the identified knowledge gaps. This is the overall aim of the latest EURATOM project, SACSESS (Safety of Actinide Separation Processes)

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that ran from March 2013 to June 2016. In this way, SACSESS promotes a longer term ambition of raising the technology readiness level (TRL) of the hydrometallurgical processes selected.

Several baseline molecules — hydrophobic extracting agents and hydrophilic complexing agents — used in the above flow-sheets were selected and are studied regarding their behaviour under irradiation, their effect on downstream processes and waste management and the effect of degradation products on process performance. Alternative molecules were identified, that offered potential improvements in performance. Furthermore a multi-scale modelling approach is followed, ranging from the molecular scale via equilibrium and kinetics modelling to flow-sheet calculations.

Addressing a specific gap in options for safe actinide recycling, processes are developed extracting only americium directly from PUREX or COEX™ raffinate solutions but rejecting curium. Such processes have not been studied in earlier EURATOM projects.

Finally, a formal cooperation between the US Department of Energy (DOE) and SACSESS was agreed upon. This cooperation includes joint workshops and mutual access to internationally important facilities such as an irradiation loop and centrifugal contactor equipment.

This paper is an overview of the SACSESS hydrometallurgy domain. For more details please refer to further papers found in the proceedings of the 5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles, published in *Procedia Chemistry*.

2. The molecules studied

The hydrophobic extracting agents and hydrophilic complexing agents used in the reference flow-sheets are shown in Figure 1.

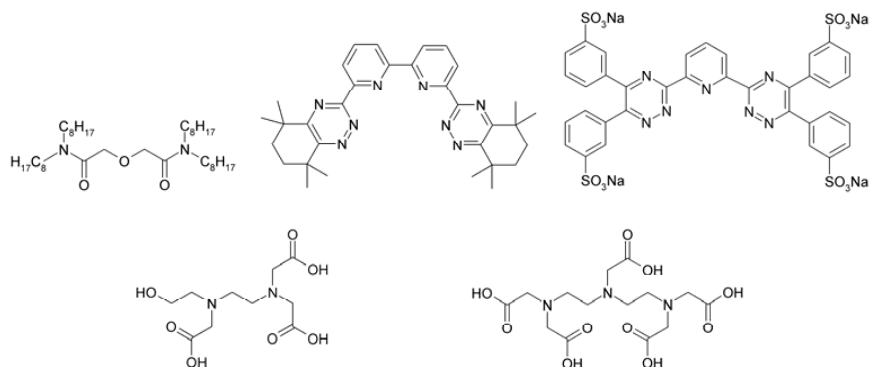


Fig. 1. SACSESS reference compounds: TODGA, CyMe₄-BTBP, SO₃-Ph-BTP (top, from left), HEDTA, DTPA (bottom, from left).

N,N,N',N'-tetra-*n*-octyl diglycolamide (TODGA) is used in i-SANEX,⁶ EURO-GANEX^{8,9} and Am-only extraction processes to co-extract actinides and lanthanides from high-acidity raffinate solutions, separating them from the non-lanthanide fission products. TODGA is furthermore added to r-SANEX⁵ and 1c-SANEX⁷ solvents to accelerate the rather slow extraction kinetics of CyMe₄-BTBP.¹³ As a possible alternative to TODGA, Me-TODGA (Figure 2) is studied. Being a weaker extracting agent, the unwanted co-extraction of strontium is less pronounced than with TODGA.¹⁴

6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) is the extracting agent used in r-SANEX,^{4,5} 1c-SANEX⁷ and CHALMEX^{10,11,12} processes. It extracts actinides selectively over lanthanides and many other fission products. Bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine (CA-BTP)¹⁵ and 2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-1,2,4-triazin-3-yl)-1,10-phenanthroline (CyMe₄-BTPhen)¹⁶ (Figure 2) are alternatives to CyMe₄-BTBP, having faster extraction kinetics. However, issues with the scale-up of the syntheses have so far kept these compounds from superseding CyMe₄-BTBP.

N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA) (Figure 1) are used to strip actinides selectively over lanthanides from an organic phase containing both actinides and lanthanides. This TALSPEAK-like chemistry is applied in processes such as the i-SANEX¹⁷ and GANEX¹⁸ processes developed at CEA.

2,6-bis(5,6-di(3-sulphophenyl)-1,2,4-triazin-3-yl)pyridine (SO₃-Ph-BTP,¹⁹ Figure 1) was developed to overcome some of the drawbacks of HEDTA and DTPA, such as the narrow pH window they are effective in. It is used for actinide stripping in an i-SANEX process⁶ and in the EURO-GANEX process.^{8,9} 2,6-bis(1-(3-hydroxypropyl)-1H-1,2,3-triazol-4-yl)pyridine (PyTri-diol, Figure 2) can be used for such processes as well. Having the advantage of being a CHON compound, it avoids the secondary waste generation caused by the sulphur content of SO₃-Ph-BTP.

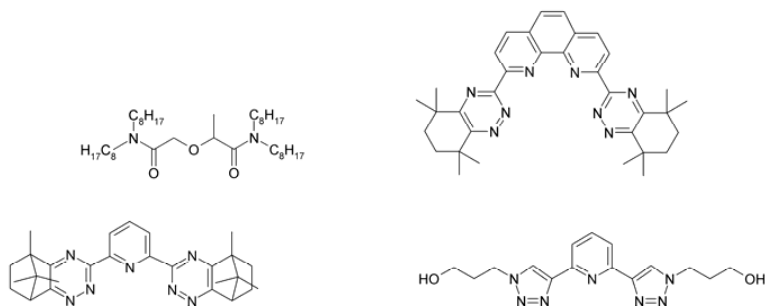


Fig. 2. SACSESS alternatives to the reference molecules: Me-TODGA, CyMe₄-BTPhen, (top, from left), CA-BTP, PyTri-diol (bottom, from left).

3. Safety-related properties

In earlier European research projects each process developed was more or less treated as a closed unit; the interactions between processes were not adequately studied. Thus, SACSESS puts a focus on topics related to safe process implementation: radiolytic degradation, identification and impact of degradation products, downstream effects of process chemicals and loading issues.

The behaviour upon static gamma irradiation of TODGA,²⁰ Me-TODGA,²¹ CyMe₄-BTBP and CyMe₄-BTPhen extracting agents as well as of some diluents used to prepare organic phases²² was studied in detail. Also, aqueous solutions containing SO₃-Ph-BTP or PyTri-diol were irradiated.

The main TODGA degradation products were identified and synthesised as pure components. These products' extraction behaviour was studied to assess whether their build-up would impair the extractive properties of TODGA solvents.

Irradiation of CyMe₄-BTBP and CyMe₄-BTPhen diluted in 1-octanol forms a primary degradation product which was identified as an octanol adduct. This explains why CyMe₄-BTBP and CyMe₄-BTPhen solvents keep their extractive properties even if the CyMe₄-BTBP or CyMe₄-BTPhen concentration decreases upon irradiation — the compounds are not destroyed but form an adduct with similar properties.²³

Static irradiation of SO₃-Ph-BTP solutions showed the molecule to be significantly more sensitive towards radiolytic degradation than are e.g. TODGA or CyMe₄-BTBP.²⁴ However, a dynamic irradiation test in the irradiation loop setup at Idaho National Laboratory did not result in a deterioration of its properties.²⁵

Hydrogen generation rates (G-values) have also been determined from nitric acid and TODGA / kerosene phases under alpha irradiation (from plutonium and americium ions) and compared to gamma irradiation. This is an important safety-related issue in the design of any future industrial scale process.

Studies within SACSESS have also started the key task of integrating the novel separation processes with the other parts of the overall reprocessing and recycling plant. Specifically, the effects of the aqueous phase complexing agents such as DTPA and HEDTA on the downstream product finishing process is studied. Assuming the oxalate co-precipitation process as the baseline finishing process,²⁶ initial studies have considered the effects of the complexing agents on residual metal ion solubility post-oxalate precipitation. Methods of decomposing the complexants have been tested, either before oxalate precipitation or in the oxalate mother liquor before acid recycling (examples of this work are found in other papers at the *ATALANTE 2016* conference).

4. Multi-scale modelling

Reliable modelling tools are indispensable for designing and optimising separations processes and for understanding the chemical systems these processes are based on. Within SACSESS, a multi-scale modelling approach is adopted. Starting on the molecular scale, quantum chemistry is used for predicting the radiolytic degradation and the selectivity²⁷ of extracting agents. On the macroscopic scale, flow-sheet models are used to design lab-scale process demonstration tests and to perform sensitivity studies to probe the flow-sheet response to various maloperation scenarios. These models contain sub-models for describing the equilibria involved (e.g. extraction of nitric acid²⁸ and of metal ions) and the kinetics of the chemical systems used. Within the SACSESS project, a focus was placed on modelling the i-SANEX process and examples for this work are found in other papers presented at the *ATALANTE 2016* conference.

5. Am-only extraction processes

Curium does not significantly contribute to long term heat load. However, it complicates fuel fabrication because of its high neutron dose rate and short term heat load. Hence, processes for separating americium from curium have been developed in the

past.^{29,30} These processes were intended to be placed downstream of SANEX processes, meaning that curium would be carried through the complete sequence of separation cycles.

Processes have been developed in SACSESS which extract only americium from PUREX or COEX™ raffinate, routing curium together with the fission products to the high level waste. This constitutes a significant simplification, requiring less solvent extraction cycles to produce an americium-only product.

Building on experience gained from the EXAm process developed at CEA,^{31,32} several chemical systems have been studied in SACSESS which show promise for americium-only extraction processes. The bottleneck is the similar behaviour of americium and curium, being present in solution as trivalent cations. Since extracting agents useful for such processes (e.g. TODGA) have a rather low separation factor for Am(III) over Cm(III) (typically ≈ 1.6), they are combined with water soluble complexing agents having the reverse selectivity. This yields separation factors of 2.5–3, significantly reducing the number of stages required for sufficient separation.

Several Am-only extraction systems are studied in SACSESS. They use a solvent containing TODGA to co-extract Am(III), Cm(III) and Ln(III). A water soluble ligand is used to preferentially strip Am(III) from the loaded solvent while Cm(III) and Ln(III) remain in the solvent: TPAEN, SO₃-Ph-BTBP³³ or SO₃-Ph-BTPhen³⁴ (Figure 3). The TPAEN system is currently being developed towards a hot test. A spiked process test is planned with the SO₃-Ph-BTBP system.

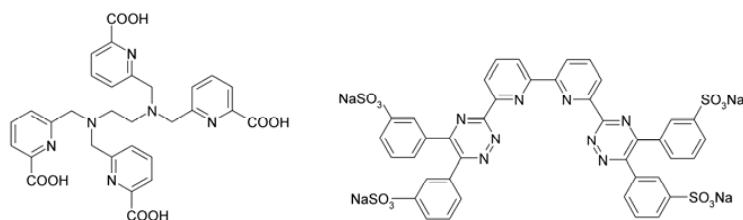


Fig. 3. Water soluble stripping agents proposed for use in Am-only extraction systems: TPAEN and SO₃-Ph-BTBP.

6. DOE-SACSESS collaboration

A technical exchange and cooperation arrangement between the US Department of Energy (DOE) and SACSESS was agreed upon. This is the first time such a co-operation has been developed under the framework of the series of EURATOM actinide separations projects and specifically now brings together the integrated European actinide separations community and the US Sigma Team for Minor Actinides Separations. Within this cooperation several topics are covered:

- Joint experiments on radiolytic stability
- Americium chemistry
- Kinetics
- Modelling
- Training and education

As part of the joint experimental work, an irradiation campaign using the TODGA/SO₃-Ph-BTP i-SANEX system was performed in the irradiation loop setup at Idaho National Laboratory. Currently, preparations are performed for running a test in the centrifugal contactor setup in Jülich using a flow-sheet developed by US scientists.

A joint workshop on americium chemistry and separations was held which was followed by a second workshop on kinetics. Furthermore, the First SACSESS International Workshop, held in Warsaw in April 2015, was well attended by US scientists who presented their recent work in a number of talks. The same is the case for the Second SACSESS International Workshop which is part of this very conference, *ATALANTE 2016*.

7. Conclusions

SACSESS within its hydrometallurgy domain addresses important aspects related to the safe implementation of solvent extraction processes for actinide separations. These results, combined with results from global safety analyses performed within another domain of the project, are essential for underpinning and eventually raising the technology readiness levels (TRL) of the most promising processes towards the level at which they can be considered ready for industrial scale operations.

Acknowledgements

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