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SACSESS
Safety of actinide separation processes

Final Report

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Table of contents

Final publishable summary report

1 Executive summary

Within ACSEPT, several aqueous partitioning processes were selected and developed up to scientific feasibility, through hot-tests. These processes involved new extracting or complexing organic molecules and new diluents. To be developed further, these processes require now a comprehensive study of the multiform safety issues that any chemical process requires under operation conditions or maloperation. This implies a better understanding of the chemical systems involved and the need to enhance the future process operation at the industrial level. SACSESS addresses these issues. These are (i) TODGA based systems (co-extracting An(III) and Ln(III) in i-SANEX or GANEX processes); (ii) CyMe4-BTBP based systems (r-SANEX, 1c-SANEX and CHALMEX systems selectively extracting An(III) either directly from PUREX raffinate or from the An(III) + Ln(III) product solution coming from a TODGA process); (iii) hydro-BTP based systems (i-SANEX systems selectively stripping An(III) from a loaded TODGA phase using water soluble BTP); (iv) systems based on “TALSPEAK”-chemistry (i-SANEX systems selectively stripping An(III) from a loaded TODGA phase using DTPA or HEDTA). For each chemical system, parameters involved in safety case analysis have to be studied, such as radiolytic solvent stability, solvent clean-up, management of the secondary wastes, physico-chemical solvent stability, loading capacity, and kinetics. The behaviour of the extractants, complexants, diluents all together (solvent stability) must be studied in process conditions, but also out of these operation ranges (mal-operation), in order to identify the weak points and find solutions to assess the safety of the processes. The work is organised by chemical systems selected for each tested process options, including, when accurate, the alternative system. Furthermore, a list of transversal key issues has been established. For each system, this allows us to define the studies needed to be able to optimise the processes and assess their safety. On the second period, the radiolytic stability of the most relevant systems was studied, hydrogen generation due to irradiation was quantified, aqueous phase ligand recycling and destruction was addressed. In addition, loading, losses and phase stability were studied in several systems. Furthermore, several safety related aspects of aqueous phase ligands were studied. Finally, the kinetics of several systems was studied using a variety of experimental techniques.
In the field of process operation, the simulation of these systems is developed from the chemistry to the process, allowing a better and safer management of the plant in the longer term. This includes multiscale modelling, radiolysis modelling and process modelling. In addition, new online monitoring techniques are under studies. On the second period, the work on mass transfer and flow-sheet models for key systems was continued as well as radiolysis modelling, on-line monitoring and An(III) activity coefficients. Regarding the topic of EURO-GANEX maloperations, experimental data were implemented into flow-sheet codes, a malop flow-sheet was designed and a malop trial was performed.
In parallel, an alternative process to those already developed is studied, allowing the partitioning of americium alone, reducing the hazards related to the handling of curium in fuel for enhanced safety. On the second period, the TODGA/TPAEN system was selected for process development. Unfortunately, precipitations encountered during the spiked process trials prevented running a hot process demonstration.

In pyrochemistry, SACSESS focuses on the recovery of MA from of metallic fuels and inert matrix transmutation targets. Results, experiences and knowledge gained in the previous ACSEPT program will be used to modify and optimise the studied molten salt separation processes on a safety basis.
To optimise the work and develop this safety approach at a larger scale, this work is associated to a Russian research project supported by ROSATOM and dealing with some common issues (PYROSMANI). Within ACSEPT and former European projects, two processes were identified and further developed at the lab scale. However, at this stage, some safety issues have still to be addressed. The first ones are those related to the use of molten salts and liquid metals at high temperature. Data are still lacking in the literature to have a relevant understanding of the systems. The physico-chemical behaviour that impacts the chemical safety (solubility, volatility, influence of oxygen ingress, heat capacity, viscosity, etc) both in chloride and in fluoride are under study. The experimental program addresses specifically the gaps in knowledge for the selected chemical systems. On the second period, the molecular dynamic and thermodynamic modelling showed the structure and speciation of U and rare earth species in molten chloride and fluoride salts. The viscosity of LiCl-KCl and LiF-AlF3 molten salts in dependency on the dissolved rare earth elements speciation was evaluated. The UV-vis spectroscopy probes for on-line concentration determinations in LiCl-KCl melt were developed and the usability of the method assessed. The robust Pt and W microelectrodes were fabricated and the method was proved capable of quantitative measurement in molten chloride salt, including fundamental characterisation and monitoring and possibility of quantitative multiple species measurement.

The electroreduction of cermet fuel was proven feasible, however using only inactive material, and conditions of the process were optimised. The electrochemical behaviour of molybdenum as the matrix of the cermet fuel in molten chlorides was evaluated including the E-pO2- diagrams and its influence on the electrorefining process was assessed. The experimental results were complemented with thermodynamic modelling. MgO behaviour in fluoride melts was evaluated and the impact of Mg presence in the melt on the reductive extraction process was assessed. Feasibility of this process was successfully demonstrated by reprocessing of a FUTURIX cercer pellet containing 200mg of Pu and 200mg of Am. A strong impact of Mo on the reductive extraction process was shown, but the process was also demonstrated feasible as the dissolved Mo can be removed from the melt before the extraction.
Concerning waste conditioning, the modelling was developed to assess the energetics of Cs, Na, Li and K occlusion and adsorption into zeolites and SrCl2 ion-exchange experiments were completed on a selection of the optimal zeolites. The parameters for fabricating the glass-bonded sodalite wasteform for spent salt were determined. Characterization of the SAP-based matrices containing Rb, Ba, La and Ce chlorides was done, leading to experimental comparative analysis of the leaching behaviour of the different salts.

With the above studies, being driven by safety considerations, a specific domain is dedicated to global safety and integration whereby safety case studies is performed on each process concept to identify the weak points in order to give feedback and reorient the experimental program. Integration studies will gather all the results to deliver optimized process flowsheets.
With the help of TSOs and with feedback from safety analyses, specific methodologies were developed during the first period and have been applied to these processes in order to identify safety issues and then to optimise these processes through specific workshops. On the second period, all work streams were continuation of work undertaken during the previous period. This occurred with minimal changes in the strategy and achieved work in line with the declared deliverables. The headline outputs from this period of work were the D3.1.3 Safety report which is the umbrella document from work package 1 and the Roadmap Actinides separation processes 2015" ISBN 9782919313099 which was presented at the Atalante Conference 2016 prior the final meeting of SACSESS and very much appreciated by the audience of the conference.

Our training and education programme aims to share the knowledge among communities and generations in order to militate against the decline of students, teachers and research experts in the nuclear domain and maintain nuclear expertise at the fore-front of Europe to prepare for the dynamic knowledge-based society. This programme is implemented in close connection with other European initiatives (such as CINCH), and addresses the safety issues of nuclear energy in chemical treatments. The second school co-organised with ASGARD was run on the 4th to the 8th May 2015 (M25). The subject was plutonium laboratory management and was hosted by Chalmers, who provided all the school materials, practical sessions and staff. Lectures included among others plutonium analysis and detection and radiation protection. Students took part in three practical sessions, using plutonium, in Chalmers laboratories. The school was attended by 11 students, from Lancaster University, Forschungszentrum Jülich GmbH, University of Leeds, CTU, Politecnico di Milano and Nuclear Research and Consultancy Group

2 Project context and objectives

Nuclear power plays a key role in limiting the EU's emissions of greenhouse gases, and makes an important contribution to improving the European Union's independence, security and diversity of energy supply. However, its social acceptance is inextricably linked to enhanced safety management and to a safe management of long-lived radioactive waste contributing to resource efficiency and cost-effectiveness of this energy and ensuring a robust and socially acceptable system of protection of man and the environment against the effects of ionising radiation.
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.

Within ACSEPT, several aqueous partitioning processes were selected and developed up to scientific feasibility, through hot-tests. These processes involved new extracting or complexing organic molecules and new diluents. To be developed further, these processes have required a comprehensive study of the multiform safety issues, under operation conditions or maloperation.

Table: ACSEPT reference systems to be studied in SACSESS; status of knowledge.

Reference compound →	**TODGA**	**CyMe$_4$-BTBP**	**Hydro-BTP**	**HEDTA DTPA**
Alternative →	TWE21	CA-BTP	Pytritetraol	
Chemical issues				
radiolytic/hydrolytic stability of the system	done	done	TBD*	n/a**
identification of degradation products	done	TBD	TBD*	n/a**
impact of deg.pro. on extraction/separation	TBD	TBD	TBD*	n/a**
clean-up of solvent or An strip phase	TBD	TBD	TBD*	n/a**
Downstream effects	TBD	TBD	TBD	?
Process issues				
loading (and impact on performance)	partly done	partly done	TBD	?
physico-chemical stability (3rd phase, precipitation)	partly done	TBD	TBD	?
transfer kinetics (and impact on performance)	partly done	done	TBD	?
losses to second phase	partly done	TBD	TBD	?

Note that "done" or "partly done" refers only to the reference system as studied in ACSEPT. Modifications to the system (e.g. different diluent, alternative extracting or complexing agent) may require performing these studies on the modified system.

done = studies already performed in ACSEPT or elsewhere (however not for the alternative system)
TBD = to be done
n/a = does not apply
**if hydro-BTP is to be recycled*
***complexing agent is not recycled, hence damage is expected to be negligible*
? = check data availability

This implies a better understanding of the chemical systems involved and the need to enhance the future process operation at the industrial level. SACSESS will address these issues. These are (i) TODGA based systems (co-extracting An(III) and Ln(III) in i-SANEX or GANEX processes); (ii) CyMe$_4$-BTBP based systems (r-SANEX, 1c-SANEX and CHALMEX systems selectively extracting An(III) either directly from PUREX raffinate or from the An(III) + Ln(III) product solution coming from a TODGA process); (iii) hydro-BTP based systems (i-SANEX systems selectively stripping An(III) from a loaded TODGA phase using water soluble BTP); (iv) systems based on "TALSPEAK"-chemistry (i-SANEX systems selectively stripping An(III) from a loaded TODGA phase using DTPA or HEDTA).
For each chemical system, parameters involved in safety case analysis must be studied, such as radiolytic solvent stability, solvent clean-up, management of the secondary wastes, physico-chemical solvent stability, loading capacity, and kinetics. The behaviour of the extractants, complexants, diluents all together (solvent stability) are also key information that need to be validated in process conditions, but also out of these operation ranges (mal-operation), in order to identify the weak points and find solutions to assess the safety of the processes. Furthermore, a list of transversal key issues has been established. For each system, this will allow us to define the studies needed to be able to optimise the processes and assess their safety. The table above summarizes the chemical systems and the parameters.

In the field of process operation, the simulation of these systems must be developed from the chemistry to the process, allowing a better and safer management of the plant in the longer term. This includes multiscale modelling, radiolysis modelling and process modelling. In addition, new online monitoring techniques are required, allowing a fine tuning of the plant operation parameters.

In parallel, an alternative process to those already developed should be developped, allowing the partitioning of americium alone, reducing the hazards related to the handling of curium in fuel for enhanced safety. As far as possible, the most promising systems already identified must be adapted to meet the requirements of such a process and optimised. Solubility issues, kinetics, loading capacities are important data to assess the safety of this new process.
All the new generated data will be integrated thanks to flowsheeting and system studies to allow a feedback to the R&D programme and an assessment of the global safety of the designed processes.

In pyrochemistry, SACSESS focuses on the recovery of MA from of metallic fuels and inert matrix transmutation targets. Results, experiences and knowledge gained in the previous ACSEPT program are a strong basis that will be exploited to modify and optimise the studied molten salt separation processes on a safety basis.
To optimise the work and develop this safety approach at a larger scale, this work is associated to a Russian research project supported by ROSATAM and dealing with some common issues. Within ACSEPT and former European projects, two processes were identified and further developed at the lab scale. Thanks to this work, today, the electrorefining process on aluminium can be considered as an alternative to the IFR concept process (based on U electrorefining on inert cathode and transuranics recovery on liquid cadmium cathode) for the treatment of metallic fuels. The liquid-liquid reductive extraction process in molten fluoride/liquid aluminium is more specifically dedicated to the treatment of refractory oxide fuels. In addition, oxide reduction electrochemical processes could allow the treatment of oxide fuels by electrorefining. Specific salt treatment for recycling and waste conditioning were also proposed
However, at this stage, some safety issues have to be addressed. The first ones are those related to the use of molten salts and liquid metals at high temperature. Data are still lacking in the literature to have a relevant understanding of the systems. The physico-chemical behaviour that impacts the chemical safety (solubility, volatility, influence of oxygen ingress, heat capacity, viscosity, etc) both in chloride and in fluoride is stioll unknown. The experimental program addresses specifically the gaps in knowledge for the selected chemical systems. Online monitoring development is also of a primary importance for a future industrial implementation both for safety and safeguards issues.
In addition, for each selected process and each step, parameters that can impact the safety must be identified and studied. This includes risks of accumulation of an element in liquid or solid phase, of precipitation, of formation of volatile species… Molten salt modelling must also be developed, first to help to calculate physico-chemical parameters and reduce the number of necessary complex experiments and second, to develop the modelling of pyrochemical processes in the longer term.
As in the aqueous separation domain, all the new generated data will be integrated to allow a feedback to the R&D programme and an assessment of the global safety of the designed processes.
The safety issues related to process development are also be addressed. On the basis of the two processes already developed in ACSEPT, the key steps will be further studied taking into account the specificity of the fuels to be reprocessed and the impact of specific parameters on safety will be studied in order to optimise these processes. For example, the behaviour of inert matrices (MgO, Mo) in the chemical separation steps is not well known. The impact of these matrices on process performances and safety will be studied at the head-end steps (e;g; oxide reduction to metal) and in the reference process cores, both in chloride and fluoride media.
The conditioning of the used molten salts (chloride and fluoride) and/or or other process chemicals (metals…) into waste streams suitable for a safe storage/repository will also be considered, including the impact of matrix material.

With all the above studies, being driven by safety considerations, a specific domain will be dedicated to global safety and integration whereby safety case studies will be performed on each process concept to identify the weak points in order to give feedback and reorient the experimental program. Integration studies will gather all the results to deliver optimized process flowsheets.
With the help of TSOs and with feedback from safety analyses, specific methodologies will be developed and applied to these processes in order to identify safety issues and then to optimise these processes. In addition, all the results will be integrated to optimise the flowsheets, to perform system studies and will ensure the link with other projects and initiatives to ensure the relevance of the SACSESS research program.

Knowledge management will also be carefully considered. A great deal of knowledge and data have been generated during past and current research projects. Yet no tool exists currently to allow an optimal use if this knowledge. In the first instance the cheminformatics database will focus primarily on molecules used within the ACSEPT programme with a view to being expanded thereafter. Similarly, many relevant internal reports, journal papers, conference proceedings, and other text documents are contained in various locations and a searchable web based repository is proposed to provide users with a route to search easily for relevant documentation. Such repositories will provide an invaluable tool for the nuclear stakeholder community to quickly determine past work, avoid replication and thereby improve efficiency.
A training and education programme will be carried out which aims to share the knowledge among communities and generations in order to militate against the decline of students, teachers and research experts in the nuclear domain and maintain nuclear expertise at the fore-front of Europe to prepare for the dynamic knowledge-based society. This programme will be implemented in close connection with other European initiatives (such as CINCH), and will address the safety issues of nuclear energy in chemical treatments. In the continuation of the successful initiatives applied in ACSEPT, student exchanges, support to student participation to international conferences or summer/winter schools, invitation of international experts to specific SACSESS training sessions will be continued.

These challenging objectives are be addressed by a multidisciplinary consortium composed of European universities, nuclear research bodies, public authorities and industrial stakeholders. This consortium will generate fundamental safety improvements on the future design of an Advanced Processing Unit and bring a significant help to Japan in order to manage Fukushima corium in the best conditions in the future. SACSESS will thus be an essential contribution to the demonstration, in the longer term, of the potential benefits of actinide partitioning to the global safety of the long-lived waste management and will give to a safe management of corium.

3 Main S&T results/foregrounds

For several decades, studies have been carried out in Europe to develop a reliable management of nuclear waste. An alternative to the direct underground disposal of spent fuel is the partitioning of actinides including the minor actinides and their transmutation. This strategy would allow a significant reduction of the radiotoxicity and the heat load of the ultimate waste and therefore an enhance safety of their management. However, such a development will only be achievable if the separation processes requested to implement this strategy are themselves demonstrated as safe for both the public at large, those living around the plants and the workers in the plants.

Two technologies have been studied so far to achieve actinide separation:

- Aqueous separation processes that benefit from more than 60 years of research and development and a long-lasting proven experience at the industrial level,
- Pyrochemical processes, first studied in the 50-60s for the treatment of spent fuel from Molten Salt Reactors and Breeder Reactors and - more recently - with a renewed interest at the end of the 80s, for specific applications, but without reaching industrial development level.
-

SACSESS further developed the separation processes selected within former European projects both with aqueous and pyro separation by focusing on the assessment and the improvement of their safety including maloperation.

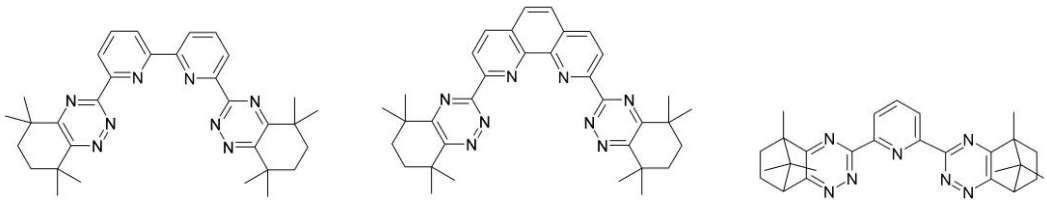
1.1 Main S&T results/foregrounds of Domain 1: Hydrometallurgy

The SACSESS Hydrometallurgy Domain addressed the safety of operation of hydrometallurgical separations processes for actinides. This was achieved by investigating relevant aspects such as the stability of process chemicals, the impact of degradation products, radiolytic hydrogen generation (see **WP 11**), loading and solubility issues, transfer kinetics (see **WP 12**) among others. Models for calculating distribution ratios were improved or established and implemented into flow-sheet codes, micro electrodes for on-line monitoring were developed, see **WP 13.**

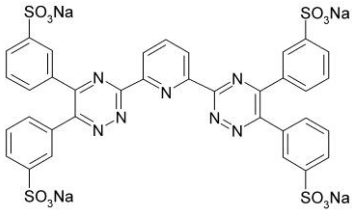
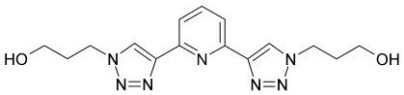
Building on the results from previous projects (ACSEPT, EUROPART and earlier projects), the portfolio was restricted to several reference extracting and complexing agents (including back-up solutions) to be applied for the reference European processes, r-/i-/1c-SANEX and EURO-GANEX. One novel process route not studied so far in European projects, the direct extraction of only Am(III) from PUREX or COEX raffinate, was also studied and developed, see **WP 14.**

The reference extracting and complexing agents, TODGA, $CyMe_4$-BTBP, SO_3-Ph-BTP were considered the benchmark. From the back-up compounds, TWE-21, $CyMe_4$-BTPhen, CA-BTP and PyTri-Diol (see the schemes below), only PyTri-Diol proved to be a viable alternative. The other compounds did not turn out to surpass the reference compounds. The more widely used compounds, DTPA, HEDTA and CDTA, were also studied.

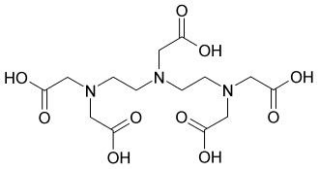
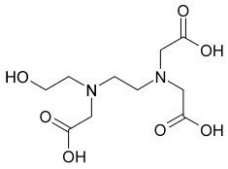
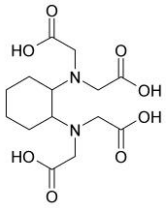
Non-specific An/Ln extracting agents, TODGA and TWE-21.



Selective An extracting agents, $CyMe_4$-BTBP, $CyMe_4$-BTPhern and CA-BTP.

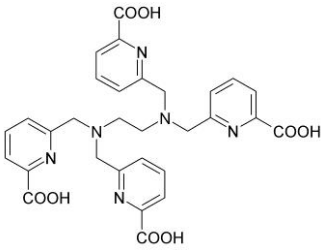
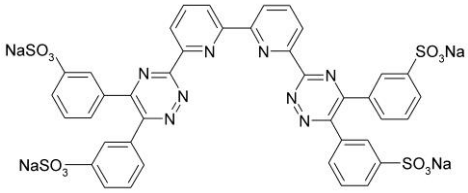



Selective An stripping agents, SO_3-Ph-BTP and PyTri-Diol.

Aqueous phase ligands, DTPA, HEDTA and CDTA.

A further topic related to the safety of the fuel cycle was addressed, namely the handling of curium. While curium does not significantly contribute to long term radiotoxicity and heat load its *short term* behaviour poses problems during fuel fabrication. A solution would be routing curium to the high level waste rather than recycling it in the fuel cycle. This requires separating Cm(III) from Am(III), preferably in an upstream process extracting only Am(III) from a PUREX or COEX raffinate, routing curium with the fission products. Two compounds for selectively stripping only Am(III) were considered for developing an Am-only process, EURO-EXAm. These are TPAEN and SO_3-Ph-BTBP (see structures below). The former was finally selected for process development and demonstration, see **WP 14.**

Am(III) selective stripping agents, TPAEN and SO_3-Ph-BTBP.

20 deliverables related to Domain 1 were prepared and submitted, compiling the scientific progress achieved in the Hydrometallurgy domain of SACSESS.
A highlight within Domain 1 is the establishment of a **formal collaboration between the US Department of Energy (DOE) and SACSESS.** Three joint workshops were organised and two joint experiments were performed within this collaboration. Workshops on americium separation chemistry, on kinetics and on radiation chemistry were held. An experiment on the irradiation of the SO_3-Ph-BTP/TODGA i-SANEX system developed in ACSEPT was performed at Idaho National Laboratory's irradiation loop; a spiked counter-current flow-sheet test utilising the Advanced TALSPEAK system developed by US scientists was performed at JUELICH. This collaboration has been a true success; we hope to be able to extend it into the future.

1.1.1 Main S&T results/foregrounds of WP 11: Safety of chemical systems

1.1.1.1 Introduction

WP 11 focused on the safety of the chemical systems, non-specific An/Ln extracting agents, selective An extracting agents, selective An stripping agents and aqueous phase ligands. The systems' chemical and radiolytic stability was studied and degradation products were identified. The impact of degradation products on distribution ratios, loading and phase behaviour was studied. Furthermore, the radioloytic hydrogen generation due to irradiation of several solvents and diluents was quantified. Another topic was the decomposition of ligands which could interfere with downstream processes. Finally, a maloperation scenario flow-sheet was performed.

1.1.1.2 Non-specific An/Ln extracting agents

The selected non-specific An/Ln extracting agents in this project are TODGA and TWE-21 which are proposed for use in the i-SANEX, GANEX and EXAm processes. Among the key features studied are: extraction enthalpy, hydrogen gas evolution and radiolytic degradation products.
Studies of hydrogen evolution due to alpha and gamma radiolysis of TODGA solutions in *n*-dodecane were undertaken, showing that the hydrogen yield does not significantly depend on TODGA or organic phase HNO_3 concentration or on the presence of a small 1-octanol volume fraction. However, hydrogen yield was lower than that from *n*-dodecane without TODGA.
Degradation products of both TODGA and TWE-21 were identified, synthesised and studied regarding complexing and extracting properties towards metal ions as a function of nitric acid concentration. Two TODGA degradation products showed to have significant extraction properties towards actinide and lanthanide ions. Some degradation products extract other fission products, potentially reducing decontamination factors. Amine degradation products may cause solubility issues. It is recommended that these degradation products be removed during solvent clean-up.
A microcalorimetry extraction procedure was developed in order to facilitate accurate determination of thermodynamic entities during an extraction process. The extraction enthalpy was measured for both TODGA and TWE-21 together with neodymium in a nitrate solution by the above mentioned method, showing a similar behaviour for the two ligands. The extraction process is in both cases enthalpically driven and the enthalpy value is lower for TWE-21 than for TODGA.

1.1.1.3 Selective An extracting agents

The selective An extracting agents studied in WP 11 are $CyMe_4$-BTBP and $CyMe_4$-BTPhen which are proposed for r-SANEX, 1c-SANEX, CHALMEX and EXAm processes. Predominately irradiation studies were performed to investigate the different extracting agents' behaviour.
Gamma irradiation studies of $CyMe_4$-BTBP and $CyMe_4$-BTPhen dissolved in 1-octanol were performed both in the presence and in the absence of an aqueous phase containing nitric acid. While in the absence of nitric acid Am(III) and Eu(III) extraction drastically deteriorated, no ($CyMe_4$-BTBP) or only a small ($CyMe_4$-BTPhen) effect was detected. This is despite the fact that the extracting agents concentration was reduced to ≈ 50 % ($CyMe_4$-BTBP) or ≈ 10 % ($CyMe_4$-BTPhen) after 300 kGy. A tentative explanation for this behaviour is the formation of extracting agent-diluent adducts having extraction properties similar to those of the original extracting agents.
Several studies with $CyMe_4$-BTBP and $CyMe_4$-BTPhen dissolved in various cyclohexanone based diluents were performed. The major degradation products actually are adducts formed by reactions between $CyMe_4$-BTBP or $CyMe_4$-BTPhen and reactive intermediates from diluent degradation.
Phenyltrifluorometyl sulfone (FS-13) was investigated together with $CyMe_4$-BTBP as well as $CyMe_4$-BTBP and TBP. Promising results were found for both hydrolytic and radiolytic stability. Preliminary electrochemical studies on its redox stability showed FS-13 to have a large solvent window against $Ag/AgNO_3$.
Decomposition of $CyMe_4$-BTPhen was generated using electron beam irradiation, showing that the reaction of $CyMe_4$-BTPhen with solvated electrons and $H\cdot$ is two possible paths of ligand degradation. Second order rate constant were determined for the reactions as well as the rate constant of the $CyMe_4$-BTPhen reaction with ketyl radicals.
Finally, it was demonstrated that the hydrogen generation from irradiation of 1-octanol was slightly lower than from irradiation of kerosene.

1.1.1.4 Selective An stripping agents

Work on the selective actinide stripping agents focused on SO_3-Ph-BTP and PyTri-Diol that have applications in i-SANEX and GANEX processes. The research aimed to identify degradation and the impact of degradation products and safety related issues such as radiolytic generation of gases and stainless steel corrosion.
Radiation degradation experiments of SO_3-Ph-BTP in the aqueous phase showed that ≈ 90% of the molecule are degraded following gamma irradiation with 250 kGy in closed vials, despite its very good chemical stability. In contrast, SO_3-Ph-BTP did not show signs of degradation following gamma irradiation with 175 kGy in presence of the organic phase and of oxygen, i. e. under conditions more similar to those encountered in a process. The latter experiments were performed in an irradiation loop setup at Idaho National Laboratory in the framework of a DOE-SACSESS collaboration.
Several samples of PyTri-Diol solutions were irradiated to a total absorbed doses or either 100 kGy or 200 kGy. The stability is sufficient for allowing further work towards a process development using PyTri-Diol as an actinide stripping agent.
Electrochemical corrosion experiments on 304L and 316L steels in the presence of SO_3-Ph-BTP revealed that SO_3-Ph-BTP inhibits secondary steel passivation to the same degree as AHA, driving trans-passive dissolution. Trans-passive dissolution of SS304L and SS316L steels is enhanced using both AHA and SO_3-Ph-BTP

together, compared to experiments in the presence of AHA or SO_3-Ph-BTP. The surface roughness increased significantly and the surface started showing early signs of pitting corrosion.

1.1.1.5 Aqueous phase ligands

The aqueous phase ligands studied in this project are different stripping or masking agents such as HEDTA, DTPA, CDTA, glycolic acid, citric acid and oxalic acid. These have applications in i-SANEX, GANEX and EXAm processes.
Decomposition studies in nitric acid under refluxing conditions showed that oxalic acid was completely decomposed in 12 mol/L HNO_3 at 115 °C after 5 h. HEDTA and DTPA were quickly destroyed. However, acetic and formic acid which are degradation products are quite stable and could accumulate under evaporator conditions. The same is true for glycolic and citric acid. Additional treatment with H_2O_2 may be required to reduce remaining TOC.
Residual Nd(III) solubility after oxalate precipitation in the presence of DTPA and acetic acid (key degradation product) was studied. While acetic acid appeared to have a negligible effect on oxalate precipitation, DTPA tended to reduce the solubility of neodymium in the oxalate mother liquor.

1.1.1.6 Maloperation scenario flow-sheeting

A trial was successfully completed to assess the impact of a scrub acid maloperation upon plutonium recycle and accumulation in the EURO-GANEX flow-sheet. This was identified as a potentially serious maloperation during a process safety review of the EURO-GANEX flow-sheet due to potential criticality issues.
A significant reduction in the scrub acid feed concentration did not result in the backwashing and recycle of plutonium in the extract-scrub contactors. A constant plutonium loading of the solvent was maintained under both normal and maloperation conditions. The formation of hydrolysed plutonium species or colloidal plutonium was observed under the low acid conditions of the maloperation. However, the species produced at low acidity were retained in the solvent phase and did not lead to the misrouting or precipitation of plutonium. These results demonstrate the EURO-GANEX flow-sheet is robust to the recycle or misrouting of plutonium for maloperations involving significant deviations of the scrub acidity.
The results also show that the behaviour of plutonium during a low acid maloperation in the EURO-GANEX process is quite different to similar maloperations in a conventional PUREX solvent (TBP/OK), where plutonium is recycled and accumulates across the extract-scrub section.
Although routing of plutonium was not affected under the conditions of this maloperation, the reduction in the scrub acidity led to significant backwashing and recycle of americium. Analysis of the solvent product shows that under these conditions approximately 85 % of the americium present in the active feed was being recycled.

1.1.1.7 Conclusion

Work performed in WP 11 (in combination with results from other WP) helped establishing TODGA and $CyMe_4$-BTBP as reference extracting agents for Am(III)-Ln(III) co-extracting or separation, respectively. By better understanding their behaviour under irradiation, the safety level of related processes could be improved. Studying further aspects such as radiolytic hydrogen generation, ligand decomposition and stainless steel corrosion also contributed. The i-SANEX system irradiation campaign performed at Idaho National Laboratory within the DOE-SACSESS collaboration agreement deserves being mentioned as a highlight.

1.1.2 Main S&T results/foregrounds of WP 12: Performance optimisation of chemical systems

1.1.2.1 Introduction

WP 12 adopted the same structure to WP 11 focusing on non-selective (Task 1) and selective (Task 2) extracting agents for actinide ions as well as selective stripping agents (Task 3) and aqueous phase ligands (Task 4). Based on an assessment of the state of the art knowledge at the end of the FP7 ACSEPT project, critical knowledge gaps were identified and these formed the basis of the process optimisation studies in WP 12. A priority was given to knowledge gaps that affected process safety (links to WP 11) as well as efficiency and waste minimisation. Deliverable reports were compiled with contributions from all partners involved, describing new and comprehensive research results across six key topics; the results of these studies are summarised below.

1.1.2.2 State of the art concerning TODGA & TWE21 molecule based systems

TODGA is the reference non-selective actinide extractant used in r-/i-SANEX and EURO-GANEX processes that were developed in ACSEPT. “TWE-21” is a diglycolamide (DGA) molecule variation developed by European partners that is complementary to alternatives being proposed internationally (Japan, USA, India). Work in SACSESS was aimed at making a decision on whether to replace TODGA with TWE-21 as the reference

molecule for these processes. Distribution data for actinides, lanthanides and major fission products were obtained together with speciation studies using advanced spectroscopic techniques such as TRLFS and EXAFS. Radiolytic and hydrolytic stabilities were compared and degradation products identified. At the end of the project, it was concluded that TWE-21 had insufficient advantages to merit replacing TODGA as the reference molecule, noting the greater technological maturity that is gained by use of the established TODGA extractant in the solvent extraction processes. Nevertheless, much deeper understanding of how variations to the DGA backbone affect the chemistry of actinide extraction has been obtained through these studies and this opens up new possibilities to target specific properties through rational synthesis of DGA ligands. A state of the art comprehensive literature review on the applications of DGA ligands in actinide separation processes was consequently submitted to the journal *Solvent Extraction and Ion Exchange* in 2016.

1.1.2.3 Survey of possible maloperation events and their effects

A major goal of SACSESS was to start European studies of the effects of potential maloperation or process upsets on the reference separation processes. This is a new area of research compared to previous framework projects and of vital importance in underpinning safety assessments and demonstrating process safety improvements over current reprocessing technologies. WP 12 worked in conjunction with WP 11 and WP3.1 to meet these objectives. A Safety Assessment Methodology was developed and applied to the EURO-GANEX process flow-sheet in WP 31. Specifically, in WP 12, the output of the expert assessment from Domain 3 was further analysed and critical maloperation scenarios identified. A specific maloperation was then selected for experimental testing under WP 12. The maloperation selected in WP 12 was the reduction of the scrub acidity in the extract-scrub section of the EURO-GANEX flow-sheet. By analogy with known PUREX behaviour, it was considered that this could lead to cycles of extraction and backwashing of plutonium within the contactor and hence the accumulation of plutonium leading to potentially hazardous conditions (radiation, criticality). The report recommended that an experimental test in centrifugal contactors at realistic conditions of plutonium (10 g/L) be carried out as well as some underpinning chemistry and modelling to evaluate the wider potential implications of the full or partial loss of scrub acid.

1.1.2.4 Identification of losses of extracting gents and diluents and their effects in the different processes

Losses of one phase into the other phase either by limited solubility or phase entrainment are key parameters that affect the efficiency of separations by solvent extraction. This can also have safety concerns, e.g. red oil formation. It is, therefore, important to quantify these losses for the reference molecules and their degradation products in the reference processes. Irradiated EURO-GANEX solvent showed no detectable transfer of organic components to the aqueous phase although some insoluble drops and waxy deposits (mixtures of amines) were obtained with doses up to 1000 kGy. Studies of SO_3-Ph-BTP suggested some formation of mixed Am(III) or Eu(III) TODGA complexes are possible. Extraction of PyTri-alcohols into i-SANEX solvent was found to be < 4 %.

1.1.2.5 Description of loading issues in the different processes and identification of possible solutions

Solvent loading data are needed to predict the onset of third phase or precipitation reactions; both effects can have serious consequences on process safety and operability and the extracting gents used in the reference processes are quite susceptible to these effects. Loading data were generated for Nd(III) in TODGA, TWE-21 and D^3DODGA (N,N-didodecyl-N',N'-dioctyl-DGA) based solvents. For the CHALMEX process, no precipitation of plutonium was observed with 10 mmol/L $CyMe_4$BTBP and 30 % TBP either in FS-13 or cyclohexanone diluents even at 40 g/L Pu initial aqueous phase concentration. For the EURO-GANEX process, loading issues were considered in some depth in the FP7 ACSEPT project. Under SACSESS, the effects of loading with solvent degraded by gamma radiation were examined and it was shown that lanthanide extraction was maintained at 1000 kGy dose. The role of key degradation products in accumulating actinides and lanthanides was also investigated with some acidic derivatives potentially causing solubility problems.

1.1.2.6 Kinetics of extraction and stripping

Fundamental data on mass transfer kinetics are important in the development of predictive process models of solvent extraction flow-sheets; this is particularly important in predicting how flow-sheets will respond under maloperation scenarios. These data do not exist for the SANEX and GANEX processes. In WP 12 substantial efforts were made to address this knowledge gap using complementary techniques: moving drop (CEA); microfluidics (CTU); rotating diffusion cell, RDC (ULANC) and rotating membrane cell, RMC (CNRS-PECSA). However, the first three methods all required significant development efforts to get them working; the RMC had been developed in the FP7 ACSEPT project. Therefore, the i-SANEX solvent system was chosen as a reference system in order to compare results obtained from the different methods. Moving drop, RMC and RDC methods

were used to measure Eu, Am and Ce extraction rate constants and ULANC developed a new mathematical treatment for the RDC. Additionally, CNRS-PECSA used the RMC to investigate extraction and stripping kinetics with $CyMe_4$BTBP; SO_3-Ph-BTP; HEDTA and DTPA. A comparative scale of these reactions from slow to fast kinetics was thus established. An addendum to the initial report was made later that compared and contrasted the different methods, indicating their complementarity and highlighting the benefits of a multi-technique approach to kinetics. CTU collaborated with Argonne National Laboratory in the development of microfluidics and ULANC are continuing their RDC studies under the UK research council funded project “PACIFIC”.

1.1.2.7 Effects of hold back ligands on the safety of the waste management from the processes

This report addressed three main studies on the use of aqueous phase ligands in the reference processes that were made under WP 12. Firstly, the use of polycarboxylate ligands in the TALSPEAK-like minor actinide separation processes that selectively strip actinides in buffered high pH solutions (versions of SANEX and EXAm processes developed in Europe) leads to these ligands being transferred to the downstream conversion process. The baseline conversion process is oxalate precipitation and calcination and it is possible that these ligands or their degradation products could interfere with this conversion process either causing unacceptable losses of actinides to the oxalate mother liquor (OML) or affecting the product quality of the resulting mixed oxide. It was shown that the presence of DTPA surprisingly reduced the residual concentration of Nd(III) ions (analogue for Am(III)) in the OML and this was probably due to a formation of a mixed Nd complex containing DTPA, or a degradation product of DTPA, with oxalate. No effects of acetic acid, an expected generic degradation product from these types of ligands, on Nd solubility were found. Secondly, methods of decomposing DTPA and acetic acid, either before or after oxalate precipitation, were investigated. Proof of principle experiments showed that mediated electrochemical oxidation (using Ag(II) ions as mediators) was a very promising technology for ligand decomposition with both DTPA and acetic acid being decomposed to near background levels in ≈ 4 hours (based on total carbon analysis).
Finally, methods were developed for recycling the SO_3-Ph-BTP ligand, the reference stripping agent in i-SANEX and EURO-GANEX processes. Conditions for recovering americium from the SO_3-Ph-BTP molecule as well as recycling the SO_3-Ph-BTP into a low acidity nitric acid solution – using trioctylamine in 1-octanol – were defined.

1.1.2.8 Conclusion

WP 12 made important steps forward in underpinning the reference European separation processes, particularly with regards to optimisation of safe and efficient flow-sheets. Based on the state of the art knowledge, TODGA and $CyMe_4$BTP are confirmed as the optimum choice for non-selective and selective ligands whilst PyTri-Diol was shown to be a promising CHON replacement for SO_3-Ph-BTP. Important structural, kinetic, radiolysis and loading data were accumulated for the reference molecules and their degradation products. Chemistry of solvent, acid and ligand recycling and aqueous phase ligand decomposition by mediated electrochemical methods was addressed for the first time.

1.1.3 Main S&T results/foregrounds of WP 13: Safety of process operation

1.1.3.1 Introduction

Safely and fully assessing a complex system such as a liquid/liquid extraction separation process requires a reliable modelling of the different steps of this process. WP 13 aimed at developing reliable models based both on a multi-scale modelling approach development and on the acquisition of trustworthy experimental data using appropriate analyses and online monitoring.

1.1.3.2 Molecular studies

Molecular studies were performed on extracting agents aggregation (and micelle stability vs. amount of water in the aggregate). The diamide ligand DMDOHEMA was chosen as a model extractant because its aggregation in aliphatic diluents is well described in the scientific literature. Two axes were explored so far: the Umbrella Sampling for water association and dissociation pathways in aggregates containing 4 or 3 DMDOHEMA and the calculation of extraction equilibrium constants. The composition of malonamide reverse aggregate in n-heptane was investigated by molecular dynamics simulations. Then Umbrella Sampling simulations, allowed to calculate free energy of aggregation as a function of the number of water molecules in aggregates containing 4 DMDOHEMA molecules, one $La(NO_3)_3$ salts and 1 to 5 water molecules. Aggregates composed of 3 or 4 water molecules have the highest stability in *n*-heptane. A correlation of aggregation free energy profiles with corresponding water molecules was established and the corresponding aggregates equilibrium constant K_0 of extraction have been calculated.

1.1.3.3 Actinide(III) activity coefficients modelling

The complexation of Cm(III) with NO_3^- in nitric acid was studied using Time Resolved Laser induced Fluorescence Spectroscopy. Conditional stability constants of the stepwise formation of the $Cm(NO_3)_n^{3-n}$ complexes were derived from titration experiments, and were transformed to thermodynamic stability constants by fitting of ion interaction coefficients into the SIT (Specific Ion Interaction Theory) model.

1.1.3.4 Radiolysis modelling

Diglycolamides are promising and already widely tested extracting agents for An(III) and Ln(III) co-extraction from High Level Liquid Waste. For the involved process development it is necessary to demonstrate hydrolytic and radiolytic stability of the organic ligands. After several experimental stability studies, theoretical studies using quantum chemistry have been started. For all the involved organic ligands, the optimal geometric structure was found and the electronic structure was calculated. Several descriptors based on the electron density were calculated to analyse the expectations suggested by the experimental work. Here the radical Fukui function appeared to be a good indicator showing clearly the probability and site selectivity of possible radical attack. The maxima identified the hydrogen atoms of TODGA as the most susceptible to the release caused by an approaching radical. Such maxima are not present in the case of methylated of di-methylated TODGA, where the initiation of a radical degradation process is less probable, in good agreement with the experimentally demonstrated enhanced stability of the methylated ligands.
Using the same approach, the $CyMe_4$-BTBP organic extractant and its prevailing degradation products created after irradiation in the 1-octanol solution were also studied. The UV-Visible absorption spectra of the original compound and the proposed 1-octanol adduct were calculated and compared to the experimentally observed data.
These calculations conducted to meet the experimental findings and to support and investigate the stability changes of molecules of interest for the separation processes developed in the project.

1.1.3.5 Equilibrium, mass transfer and flow-sheet modelling

A lot of work was accomplished for the development of equilibrium models related to (i) the extraction of HNO_3 and Am(III) in TODGA / 1-octanol mixtures and (ii) the i-SANEX process using the same organic phase together with SO_3-Ph-BTP for selectively stripping Am(III) and Cm(III) from the loaded TODGA solvent.
For the equilibrium model development of the extraction in TODGA / 1-octanol mixtures, first, models of nitric extraction into 1-octanol / diluent mixtures or TODGA / diluent mixtures were developed separately to accurately predict solvent phase acidity for wide range of nitric acid concentrations. Then, the models described above were combined to provide a preliminary model of acid extraction into TODGA / 1-octanol / diluent mixtures, assuming no synergistic or antagonistic effects arising from the use of two extracting agents in conjunction. Systematic differences between the predictions from this model and experimental data suggest that these effects do in fact occur with an antagonistic effect below 1.5 mol/L HNO_3 and a synergistic effect at higher acidity. A second model of nitric acid extraction into TODGA / 1-octanol / diluent mixtures was therefore developed, with the addition of mixed complexes (n HNO_3.TODGA.Octanol for n = 0, 2, 3). Finally, a model for Am(III) extraction was developed that accurately predicts distribution ratios for Am(III). In parallel, the equilibrium model for the calculation of Am(III) and HNO_3 extraction from HNO_3 into an TODGA + SO_3-Ph-BTP based i-SANEX process was developed. The possible formation of mixed extractable M(III)/TODGA/SO_3-Ph-BTP complexes was taken into account in the new model, leading to a better agreement between calculated and experimental values for Am(III) and Eu(III) extraction.
Based on these equilibrium models, mass transfer and flow-sheet models were subsequently established for Am(III) and Ln(III) cations in i-SANEX system including temperature variation influence. The extract-scrub section of the i-SANEX flow-sheet tested at JUELICH was simulated to validate the model, and sensitivity studies were then carried out to test the extract-scrub flow-sheet against some representative maloperation scenarios.
A meeting was held at NNL Chadwick House with NNL, KIT, and ULANC to discuss i-SANEX kinetics and modelling.

1.1.3.6 Online monitoring

Researches in the field of online monitoring focused on the setup and test of microelectrodes working in high nitric acid concentration. Platinum micro-disc electrodes were designed and fabricated using established micro-fabrication processes on silicon substrates. They were then tested in nitric acid solutions in a range of relevant nitric acid concentrations with or without exemplary redox species. Very high repeatability and essentially 100 % yield were achieved, with electrochemical measurement demonstrated as being possible over several days. Quantitative analysis showed very good agreement with literature values and previous preliminary work, confirming the suitability for extracting physical parameters characteristic of the nitric acid system for both

monitoring and analysis. The detection limits were demonstrated as being from tens of milimolar to micromolar concentrations. Equivalent performance was achieved in both standard electrochemical set-up using external counter and reference electrodes, as well as a dip-in-probe sensor with an integrated on-chip counter/pseudo-reference electrode. A three electrode dip-in-sensor system was also developed, and a small volume configuration was also designed and tested, which opens up the prospect of small volume active studies. When combined with previous measurements, which highlighted their insensitivity to forced convection and their ability to distinguish closely separated redox species, these results confirm the applicability of these systems to electrochemical on-line monitoring and analysis hydrochemical and reprocessing.

1.1.3.7 Conclusion

Substantial progress was made in WP 13 related to equilibrium, mass transfer and flow-sheet modelling, radiolysis modelling and on-line monitoring. These are aspects important to a safe implementation of hydrometallurgical separation processes for actinides. The TODGA equilibrium and flow-sheet models were used for performing the calculations related to the malop flow-sheet trial, linking them to WP 11, WP 12 and WP31.

1.1.4 Main S&T results/foregrounds of WP 14: Safety of MA handling in the cycle

1.1.4.1 Introduction

WP 14 aims at developing a hydrometallurgical process to separate only trivalent americium from the PUREX high active raffinate. This improves the safety of the fuel cycle by avoiding the presence of curium in the fuel fabrication. The most promising systems for Am(III)/Cm(III) separation already identified in the previous European projects (EUROPART, ACSEPT) were taken into consideration to meet the requirements of an Am(III) only separation process. The optimisation studies included the determination of thermodynamic and kinetic data to design the extraction as well as scrubbing and stripping stages of a flow-sheet. The most efficient system for directly extracting Am(III) from a PUREX raffinate was implemented in a continuous counter-current. The results of these studies were compiled in three deliverable reports and are summarised below.

1.1.4.2 Optimisation of chemical systems

Two main approaches were studied for the development of an Am(III) only extraction process: The first is based on the selective extraction of Am(III), leaving Cm(III) and most Ln(III) in the raffinate of the process. The 1-cycle SANEX process developed at Jülich was considered as a basis. $CyMe_4$-BTPhen was proposed as lipophilic ligand for selective Am(III) extraction, while TEDGA (as in the EXAm) was used for complexing Cm(III) in the feed solution. At an acidity range of 0.5–1 mol/L HNO_3 suitable distribution ratios ($D_{Am} > 1$ and $D_{Cm} < 1$) and rather high Am(III)/Cm(III) separation factors of 3.5 are obtained.
The second approach is based on the co-extraction of An(III) and Ln(III) from a PUREX raffinate in an organic phase containing TODGA as extractant, followed by selective stripping of Am(III) with Cm(III) and Ln(III) remining in the solvent (similar to the innovative-SANEX process developed during the ACSEPT project). Three ligands for selective Am(III) stripping were studied: TPAEN developed and tested at CEA Marcoule, SO_3-Ph-BTBPhen developed at UREAD and tested at Jülich and SO_3-Ph-BTBP developed and tested at KIT.
Very promising results were achieved for all systems. However, within SACSESS the focus was set on the TODGA-TPAEN chemical system.
Laboratories involved in the optimisation of the process were CEA, Jülich, KIT, UNIPR and NNL. A solvent containing 0.2 mol/L TODGA + 5 % 1-octanol is used to co-An(III) and Ln(III) from 3–4 mol/L HNO_3 solutions. Am(III) is stripped selectively from Cm(III) and Ln(III) into an aqueous phase containing TPAEN at pH ≈ 1. The An(III) + Ln(III) co-extraction step had already been developed by Jülich, ITU and KIT teams for the i-SANEX process.
A huge amount of batch experimental data were acquired to understand the effects of the following parameters on distribution ratios and separation factors: concentrations of TPAEN and lanthanide cations, acidity and nitrate concentration, kinetics and temperature. Finally a thermodynamic model for TODGA extraction and TPAEN complexation was developed for the calculation of flow-sheets, to be tested in centrifugal contactors, see below.

1.1.4.3 Flow-sheet development

Experiments were carried out to study and identify the main phenomena that occurred between Actinides and lanthanides cations, TODGA, TPAEN, acidity and temperature. Based on these data, a model was developed to simulate the behaviour of actinides and lanthanides under TODGA extraction and TPAEN complexation (stoichiometry of complexes, extraction and complexation constants). The flow-sheet was designed with the well-known PAREX code. A series of single stage contactor trials have been completed to investigate the effect of key parameters (temperature, residence time and acidity) on Am(III) stripping efficiency and separation from

the light lanthanides in the Euro-EXAm process. The results show that stripping of Am with TPAEN is highly dependent upon the residence time in centrifugal contactors. Consequently, low flow rates (longer residence times) are required to ensure effective stripping of Am and improve the separation factor between Am and the light lanthanides. Finally a flow-sheet was designed for a spiked test at Jülich that took into account kinetics effect.

1.1.4.4 Continuous counter-current test

Two spiked tests were run in the JUELICH laboratories using a 16-stages centrifugal contactor battery of Chinese type 1 cm contactors installed in a fume hood. The flow-sheet was designed to be run in 16 stages and it was therefore decided to only test the Am(III) stripping part. As the TPAEN stripping is based on the i-SANEX test demonstrated in JUELICH, the loaded solvent would correspond to the solvent after the extraction/scrubbing part of the i-SANEX test. The same high active raffinate solution as used in the i-SANEX test was used and subsequently it was contacted in a batch modus with TODGA solvent. During the batch extraction and scrubbing steps most of the fission and corrosion products were separated. Only An(III), Ln(III) and some Ru were present in the loaded solvent, which was used finally for the demonstration tests.
The first spiked flow-sheet test failed in separating Am(III) from Cm(III) and the light lanthanides. Steady state was reached for Am(III), Cm(III) and heavier Ln(III) but not for light Ln(III). Due to precipitation of TPAEN the pH increased slightly and the concentration of TPAEN was lower than intended. The increased pH led to lower distribution ratios and therefore to a failure of the test.
A second spiked flow-sheet test was run, again in the JUELICH centrifugal contactor battery. Based on the results of the first test, the flow-sheet was changed: The Ln(III) re-extraction section was extended and the Am(III) strip section was reduced. The flow-rates were changed and the composition of the TPAEN solution was also changed: The pH was decreased to pH 0.9 and the $NaNO_3$ concentration was increased to 0.5 mol/L. No hydrodynamic problems occurred during 11 hours. However no Am(III) was detected in the aqueous product fraction. Therefore, the test was stopped ahead of schedule and the contactors were opened. A precipitation was discovered in some of the centrifugal contactors, mainly those near the aqueous inlet. Presumably TPAEN precipitated, causing high distribution ratios of Am(III), explaining why it was mainly routed to the organic outlet. The analyses of aqueous and organic concentration profiles revealed that Am(III), Cm(III) and Ln(III) were routed to the organic outlet.

1.1.4.5 Conclusion

Several teams (CEA, KIT, JUELICH, UNIPR, NNL) were involved to study the TPAEN system, which was chosen for the development of the new EURO-EXAm process to be tested in centrifugal contactors at Jülich (spiked test) and finally at ITU (hot test). In spite of the promising results obtained in the development work of the TPAEN system, spiked centrifugal contactor tests failed to verify a functioning flow-sheet. The reasons are precipitation of TPAEN in the preparation of the first test causing a problem of pH during that test and insufficient solubility of TPAEN in the presence of nitrates during the second test.
The stability of TPAEN solutions vs. precipitation has to be studied in more detail as the precipitation was different in glass ware batch shaking experiments than in the centrifugal contactors and the operational limits have to be determined. This issue must be addressed before continuation of the process development for this system.
In any case, failed spiked tests are show stoppers for the continuation of a hot demonstration test. The decision was taken not proceed with the hot EURO-EXAm process.

1.2 Main S&T results/foregrounds of Domain 2: Pyrometallurgy

Domain 2 was devoted to study safety aspects of the pyrochemical separation processes for recovery of actinides from various types of fuels, namely oxide, metallic and refractory cer-cer and cer-met fuels. The first work package evaluated the physico-chemical behaviour of actinides and fission products that impacts the chemical safety, e.g., solubility, volatility, influence of oxygen ingress and viscosity, both in chloride and in fluoride melts. In addition, tools for online monitoring of pyrochemical separation processes were developed, namely the electrochemical and spectroscopic techniques. Within the second work package, safety related aspects of the separation processes for treatment of metallic fuels were studied. The selectivity and efficiency of the electrorefining process for homogeneous recovery of all actinides using reactive solid aluminium cathode was demonstrated in a lab-scale using irradiated metallic fuel. The third work package focused on assessment of safety factors related to refractory cermet and cercer fuels treatment. The reductive extraction process was successfully demonstrated by reprocessing of a cercer pellet containing 200mg of Pu and 200mg of Am. The fourth work package investigated the conditioning of the used chloride and fluoride molten salts. A model was developed for the ion-exchange of LiCl-KCl using zeolites and a range of the selected zeolites was tested

experimentally. The parameters for fabricating the glass-bonded sodalite wasteform for spent salt were determined. Characterization of the SAP-based matrices was done as well as the experimental analysis of the leaching behaviour of the different salts, while the normalised releases of Cs and Sr from the SAP wasteform by leaching tests were confirmed as being very low.

1.2.1 Main S&T results/foregrounds of WP 21: Safety aspects of pyrochemical systems

WP2.1 focussed on understanding the physico-chemical behaviour of high temperature molten salt systems in order to assess safety of pyrochemical reprocessing. Parameters that impact the chemical safety such actinide and lanthanide halide solubility and volatility, influence of oxygen ingress, heat capacity, viscosity, was studied in both chloride (LiCl-KCl eutectic) and in fluoride systems (LiF-AlF_3). As the acquisition of experimental data on actinide systems and especially on irradiated fuel systems is difficult, modelling will be an important tool to assess and determine boundary operating conditions of the selected molten salt systems. In parallel, on-line monitoring of molten salt systems will be developed as an essential tool to process control and operational safety which is of a primary importance for a future industrial implementation both for safety and safeguards considerations. Consequently, there were two main tasks for WP2.1:

- Task 2.1.1 Basic data acquisition of physico-chemical properties of actinide containing molten salt systems, and
- Task 2.1.2 Molten salt system on-line monitoring

Within the first task, data acquisition was conducted both computationally and experimentally. Particular properties of interest included actinide and lanthanide speciation (oxidation state and coordination environment), solubility, viscosity and activity coefficients under variable conditions such as concentration and temperature. The impact of oxygen ingress on metal speciation and solubility in molten salts was also explored. The second task aimed to explore the feasibility of techniques for on-line monitoring a molten salt process in order to ascertain the presence and concentration of key species and identify possible maloperations. The techniques explored in this work were microelectrodes and UV-visible-nIR spectrophotometric probes.

Task 2.1.1 Basic data acquisition of physico-chemical properties of actinide containing molten salt systems:

Molecular dynamics (MD) simulations was performed of chloride (i.e. LiCl-KCl eutectic) and fluoride molten salt systems containing relevant actinide and lanthanide cations that are likely to be encountered in spent nuclear fuel. The impact of temperature and actinide/lanthanide concentration in these melts has been studied. These MD simulations have led to the calculation of chemical and physical parameters such as viscosity, activity coefficients, coordination environment of metal ions and phase diagrams (e.g. Fig. 1). These calculations have generally shown good agreement with what little relevant experimental information is indeed available, indicating the simulation process for these systems is valid.

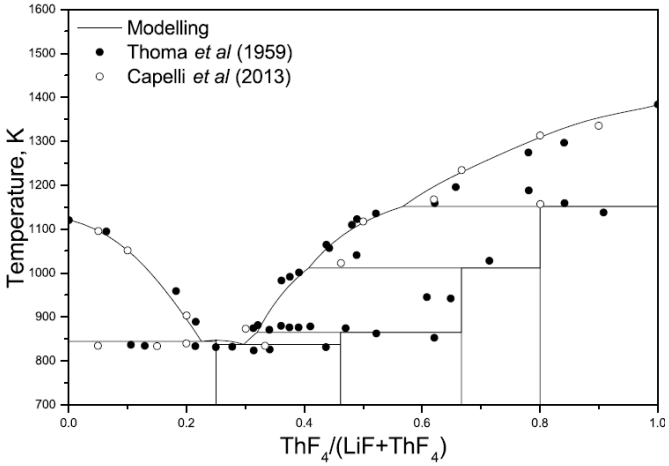


Figure 1 : LiF-ThF_4 phase diagram

Task 2.1.2 Molten salt system on-line monitoring :

The design and fabrication of microelectrodes has been developed throughout the term of this project resulting in significant improvements in the operation of these electrodes within the highly corrosive environment of a molten chloride salt, to the extent that these devices could be effectively deployed as on-line monitoring devices for a molten salt process for recycling spent fuel. Visual inspection indicates improved electrode robustness with lifetimes generally of at least four hours operation (Fig. 2). The analysis of electrochemical data obtained from

these improved microelectrode devices were in close agreement with previous data and also literature values, establishing the analytical capability of these devices. It is considered likely, with the application of modern design approaches, this microelectrode technology could be readily developed for deployment as a single dip probe device.

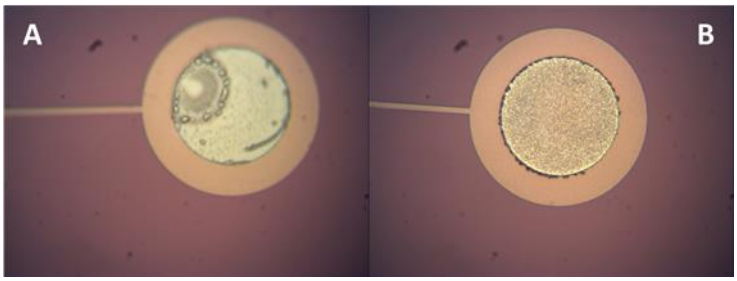


Figure 2: Photographs of electrodes removed from the melt after electrochemical cycling for up to 4 hours

UV-visible-nIR spectroscopic probes were studied for use as on-line monitoring devices in conditions likely to be encountered in a molten salt electrorefiner system. The dominant constituents, which are not spectroscopically silent, in the salt are most likely uranium (4-7 wt %), plutonium (~ 1 %) and a selection of the early lanthanides (up to 2 wt%). Given the dominant soluble uranium oxidation state in the melt is likely to be U(III) and the Pu(III) oxidation state was found to stabilise in chloride melts, superposition of the spectra of U(III), Pu(III) and Nd(III) at process-like concentrations shows that U(III) dominates the spectral profile even in the nIR region (Figure 3). Therefore as a technique for on-line concentration determinations, UV-vis-nIR spectroscopy could be deployed to ascertain U(III) concentrations in the melt but other elements are unlikely to be resolved. The impact of the alkali and alkali earth fission product elements on the spectral profile of U(III) and other actinides is likely to be minimal given the lack of any changes in the spectral profile of Ln(III) with increasing Cs and Sr concentrations in LiCl-KCl eutectic. Concerns on the impact of blackbody radiation can be readily addressed at least for relatively low melting point chloride melts like LiCl-KCl eutectic. However, if operating at very high temperatures of ~ 1000 °C blackbody radiation may prove to be too problematic to overcome for the effective use of UV-visible spectroscopy as an analytical tool. UV-vis-niR spectroscopy could also be used to check for oxygen ingress maloperations in molten salt processes which typically result in precipitation occurring. The major challenge in the deployment of UV-vis-nIR spectroscopy as an *in-situ* probe for molten salts processes is materials performance. General corrosion concerns clearly need to be addressed and in this work the use of quartz as a window material can prove to be problematic for collecting quantifiable data due to phase transitions that occur at high temperatures.

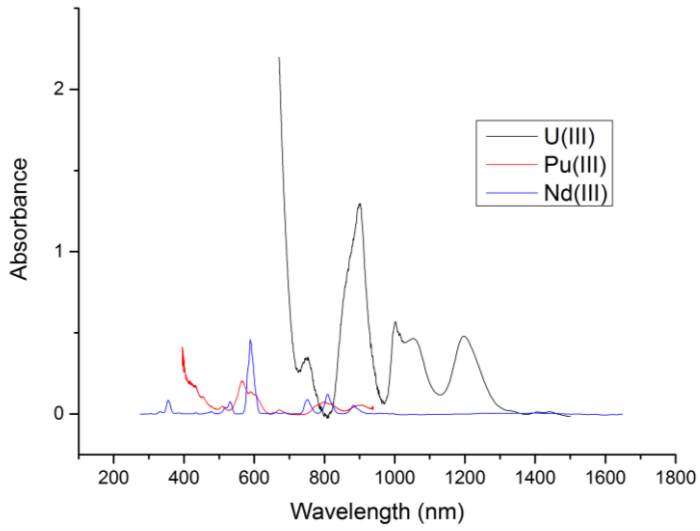


Figure 3: Superposition of the spectra of U(III) 6wt %, Pu(III) 1.2wt%, and Nd(III) 1wt% in LiCl-KCl eutectic at 450 °C using a 1 mm pathlength cell

1.2.2 Main S&T results/foregrounds of WP 22: Safety related to metallic fuel treatment

WP2.2 aimed at investigating safety aspects related to the treatment of metallic fuel by electrorefining. The electrorefining has been developed up to the scientific feasibility within the previous framework programs (PYROREP, EUROPART, and ACSEPT) and the core process developed is now well understood and has been demonstrated using non-irradiated material onto Al. Within the framework of SACSESS program investigations focussed on the performance of the solid Al cathode in presence of the complete fission spectrum using irradiated metallic fuel materials and removal of An from the salt after the electrorefining process is carried out by the so called exhaustive electrolysis process.

Thus WP2.2 was divided into two tasks:

Task 2.2.1 Salt clean-up by exhaustive electrolysis – performance of the process:

The exhaustive electrolysis process was investigated with the initial aim to explore boundary conditions for the performance of the process. The experiments were carried out to optimize and maximise the recovery using first inactive lanthanides. The final goal was to demonstrate then the process with mixtures of lanthanides and actinides. The involved partners in the task were: CEA, ITU and CNRS-LGC. The so called exhaustive electrolysis is planned to recover a maximum amount of actinides remaining in the salt bath after the electrorefining step and at the later stage possibly also to purify the salt from all electrochemically removable fission products. During the exhaustive electrolysis, chlorine gas is produced at the anode.

It was initially agreed between the different partners that one of the most important point would be to improve the knowledge on the behaviour of Cl_2 in the melt, since Cl_2 interaction with the cathode material may be one of the most critical point regarding the feasibility of the electrolysis. The, first experiments on the feasibility of the electrochemical process were carried out on the recovery of lanthanides from LiCl-KCl salts. A constant current was used between a graphite anode and tungsten or aluminum cathodes. Problems of adherence of the deposit onto inert W electrodes were observed as suspected. Results on cerium recovery onto aluminium cathodes were found promising since more than 90% of the cerium initially present in the salt could be collected on the aluminium cathode. The initial concentration of Ce^{3+} ions (0.4 wt%) could be lowered after the exhaustive electrolysis step down to roughly 0.05 w%. These results pointed out that the exhaustive electrolysis can be an efficient process to clean spent electrorefining salts.

The best set-up could also be assessed investigating different experimental conditions, particularly different Cl_2 producing anode designs. The optimal set-up consists of an open-end tube for the anode and large surface area for the cathode.

A thermodynamic study was performed in order to evaluate the Pu/Ce separation for the exhaustive electrolysis step. Special attention was paid on the formal potential determination. From these formal potential, the theoretical final concentration of Pu in the salt after the exhaustive electrolysis step was assessed, taking into account the different E'° for a cut-off potential. In the same time, the experimental program in active glovebox started using a melt containing both $CeCl_3$ and $PuCl_3$ but this experiment could not be achieved since important contamination in oxygen and moisture in the reactor led to precipitation of Pu in the salt. Nevertheless the theoretical approach has shown that Pu/Ce separation is possible using the exhaustive electrolysis.

Furthermore, the experimental data coming from prior investigations (concentrations of An and Ln, thermodynamic data, electrochemical potentials…) on the exhaustive electrolysis in molten chlorides were analysed: the goal is to model the system under diffusion control and not activation. Although the modelling of the electrolysis could not be reached, a methodology was proposed in order to achieve the calculations.

Some important key issues still need to be investigated in the future. Especially, the first task would be to assess a good model of the salt composition at the end of the electrorefining step. This model should define if the electrolysis has to be selective or not regarding the An recovery and it should also define the final specification of cathodes deposit during this cleaning step (as well as the final composition of the salt sent to final disposal). At last, an upgraded version of the dedicated electrolyser should be manufactured and tested in active conditions prior a final validation in hot cell, using a salt coming from electrorefining step, e.g. electrorefining of METAPHIX fuel for example.

Task 2.2.2 Process demonstration on genuine fuel materials:

The performance of the Al cathode was demonstrated in electrorefining experiments using genuine irradiated metallic alloy fuel materials. Arrangement of experimental plan, preparation and evaluation of results from electrorefining experiments using irradiated METAPHIX-1 fuel alloy and solid aluminium cathodes were carried out in collaboration between JRC-ITU and CRIEPI.

A series of electrorefining of irradiated METAPHIX-1 fuel was carried out in a hot cell under controlled Ar atmosphere. A tantalum basket loaded with approximately 3 g of the fuel was used as anode for all runs. The fuel had composition 66U-18Pu-10Zr-2MA-2RE before irradiation. Aluminium plates and rods were used as cathodes. Both anode and cathode potentials were measured using reference electrode based on U^{3+}/U couple. 130 g of LiCl-KCl salt was used. Altogether, 7 runs using 5 Al plate cathodes and 2 rod cathodes were carried out. All experiments were galvanostatic using different constant current densities. Each run was stopped after reaching the uranium metal deposition potential in order to evaluate the thickness of An-Al alloy layer on the electrode surface at given current density. Salt and deposit samples were regularly taken to determine the separation factors and current efficiencies from elemental analysis by ICP-MS.

The experiments were stopped after reaching the U metal deposition potential and only An-Alx alloys were formed without deposition of An metals. A uniform, dense and well adhered metallic-shiny deposit was obtained. As expected, at lower current density the slower deposition rate allowed formation of thicker An-Al alloy surface layer before deposition of U metal than at high current density. The process of An-Al alloy formation was determined by the intermetallic diffusion of An and Al through the increasing alloy layer, which is formed with different rates according to the applied current density. The dependency of the thickness of the An-Al alloy layer in dependency on the current density was found linear. The current densities were determined from the initial and in addition also from the final surfaces of the electrodes.

Concerning experiments carried out using Al rod cathodes, the experiments were stopped after reaching the uranium metal deposition potential and when the anode potential got too close to the Zr dissolution potential (0.3 V vs. quasi U reference). Uniform alloy layers were formed but not homogeneous.

Further four potentiostatic runs were carried out using Al plate cathodes with the main aim to complete the evaluation of the diffusion coefficient of An in solid Al. The deposits were also used for evaluation of the separation factors of actinides and lanthanides during a potentiostatic process. The obtained results were in a very good agreement with the value determined from the galvanostatic runs. Therefore, the previous evaluation was confirmed. Under the same assumptions as used for the previous calculations which correspond to uniform $AnAl_3$ alloy, the diffusion coefficient of An in Al was estimated to be $1.85 \cdot 10^{-7}$ $cm^2 s^{-1}$.

During all runs of the irradiated METAPHIX-1 electrorefining, salt and deposit samples were taken for analysis and molar ratio of Al to An (sum of U, Pu, Np, Am and Cm) were calculated. Most of the deposits were composed of $An-Al_3$ alloys, but the molar ratio changed from 3 to 4 with decrease of the specific charge.

1.2.3 Main S&T results/foregrounds of WP 23: Safety related to refractory oxide fuel treatment CERCER, CERMET

The direct oxide solubilisation (DOS) process application on MgO based CERCER and Mo based CERMET transmutation targets reprocessing was investigated. These type of fuels consist of a mixture of minor actinides (MA) oxides embedded in an inert (oxide MgO or metallic Mo) matrix. Since the DOS process was developed for reprocessing of oxide type fuels a prior oxidation of Mo into oxide form step must be considered for reprocessing of CERMET. Points to be assessed consist in the reductive extraction behaviour of Mg or Mo in metallic Al and the impact of Mg and Mo on the efficiency of An reductive extraction. The present work aimed at demonstrating the feasibility, or not, to reprocess CERCER and CERMET material using the liquid-liquid pyrochemical extraction process. It aimed also to highlight the key issues that must be optimised to perform such process.

This WP was divided into 3 tasks: one concerns the CERMET conversion into metal in chloride and fluoride salts as a head-end step to further retreat it. Then, the 2nd one is about the Mo species electrochemical properties in chlorides and their impact on the electrorefining process. This experimental study was completed by thermodynamic modelling. In the last task, the impact of Mg and Mo species (oxides and fluorides) from CERCET and CERMET on the liquid-liquid extraction process in molten fluorides was investigated, in terms of extraction efficiency, solubility limits, fusion temperatures and speciation.

In the 1st task, electroreduction of CERMET (CeO_2-Mo and UO_2-Mo) pellets was investigated.

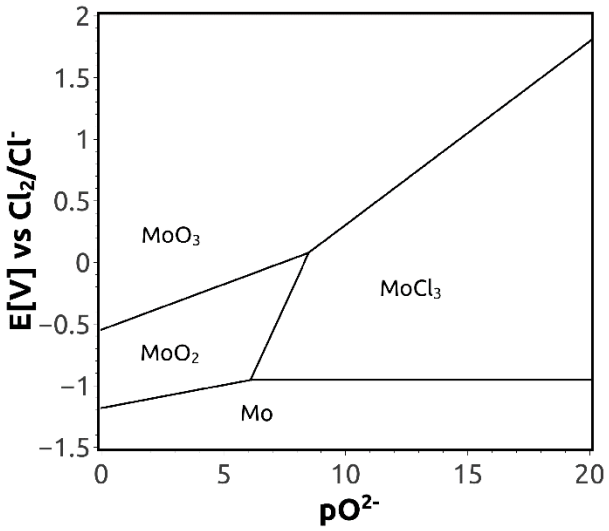
During electrolyses on CeO_2, the potential of the pellet reduction was around the Li^+/Li potential. This showed the difficulty of reducing CeO_2, which is close to the solvent reduction potential. The reaction mechanism thus might be both the direct electroreduction and a chemical reaction of CeO_2 with Li, formed by the decomposition of the solvent. From the results of electroreduction tests, several conclusions can be drawn:

- A high porosity with a minimum of 15 vol.%
- Small pieces, below 1 mm thick are recommended
- A current density between 6-60 mA/cm² has no effect on the reduction yield if the pellet size is small (1 mm thickness is recommended)

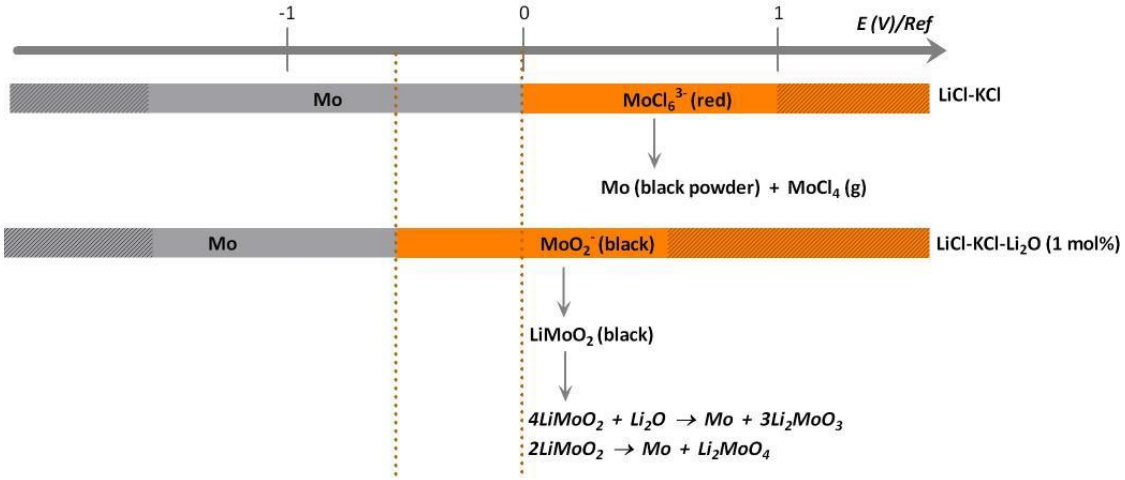
• The amount of oxide phase has no impact on the reaction for identical porosities with a foreseeable limit when the oxide phase is no longer present as aggregates in the matrix.

Thanks to these conclusions, a CeO_2-Mo was fully reduced into Ce-Mo, demonstrating the possibility to convert oxide into metal. Tests were also performed with a UO_2-Mo pellet but due to experimental problems (constant break of the salt container), the results are not available.

The 2nd task was about the electrochemical study of Mo species was performed in chloride salts. A part was related to the modelling of Mo E-pO^{2-} diagram, which is divided into the regions of stability of the pure metal, metal oxide and metal oxychloride. A thorough review of the available literature data has been done to acquire experimental and theoretical information on molybdenum in LiCl-KCl and LiF-AlF_3 (determination of stable or unstable species, thermodynamic data). The information on excess Gibbs energy for binary systems together with the information on thermophysical properties of pure compounds was used to study complex systems and the result is presented below in LiCl-KCl at 750K:



Electrochemical measurements on molybdenum electrode in LiCl-KCl and LiCl-KCl-Li_2O molten salts at 500°C have been realized. In the two salts, metallic Mo is oxidized into Mo(III). The analysis of the electrochemical results show that chemical reaction with disproportionation of Mo(III) occurs in the salt in presence of oxide ions to produce Mo at higher oxidation states. In anhydrous LiCl-KCl molten salt, metallic Mo is oxidized to Mo(III) which disproportionates to Mo and $MoCl_4$(g). $MoCl_5$ is not stable in the chloride molten salt containing oxide ions or not. The complex Mo electrochemical system can be resumed as:



A very good agreement between the thermodynamic modelling and the experimental results was found. However, regarding the CERMET treatment, the full back-recovery of Mo is not possible, meaning that its direct reprocessing can't be envisaged.

In the 3rd task, the impact of Mg and Mo species (oxides and fluorides) from CERCER and CERMET on the liquid-liquid extraction process in molten fluorides was investigated, in terms of actinides extraction efficiency, solubility limits, fusion temperatures and speciation. By high temperature NMR, additions of MgO in LiF-AlF_3 lead to spectra composed of signals corresponding to a mixture of solid and liquid phases. The ^{17}O chemical shift value in solid was measured and an oxygen transfer from Mg to Al was evidenced. The XRD patterns obtained on solidified mixtures after cooling at room temperature confirm the transformation of MgO according to the chemical equilibrium $2AlF_3 + 3MgO = Al_2O_3 + 3MgF_2$.

Thermodynamic calculations were performed to investigate the following reaction, showing a spontaneous reaction between AlF_3 and MgO. Magnesium compounds accumulation in the LiF-AlF_3 solvent has also been studied by MgF_2 additions at 900°C but no electrochemical change was observed: magnesium ions reduction can't be observed in LiF-AlF_3. To conclude, MgF_2 presence won't influence the liquid-liquid extraction step as MgF_2 is inert with both AlF_3 and Al. However, its influence of the bath melting point has to be taken into account. This experiment was initially planned but DSC measurements couldn't be done on such mixtures.

The DOS process was finally tested on a $Pu_{0.5}Am_{0.5}O_2$-MgO CERCER pellet, containing 200 mg of Pu and 200 mg of Am embedded inside 325 mg of MgO. After predissolution step, the salt was recovered with the dissolved actinides. After the liquid/liquid contact, almost all the actinides were reduced and transferred into the metallic phase, e.g. 97% of Am and 99% of Pu. At the same time the quantification indicated that less than 5% of the initial Nd amount and almost no Mg (below detection limit) were found in the metallic phase. These results clearly demonstrate the feasibility of the reprocessing of a CERCER pellet using the DOS process.

The CERMET composed of Mo and An, was investigated to know the behaviour of Mo species during the separation process. Electrochemical studies in LiF-AlF_3 eutectic mixtures (85-15 mol% and 65-35 mol%) at 820°C were performed and Mo oxides was added. Unfortunately, due a co-reduction between aluminum ions and molybdenum ions, the reduction mechanism of molybdenum oxide couldn't be found and Al-Mo alloys are formed. The possibility of a pure metallic Mo recovery is then impossible. Moreover, in the liquid-liquid extraction process, the LiF-AlF_3 salt is in contact with Al, where molybdate ions will be reduced into the liquid pool. It should thus solidify as the melting temperatures of Al-Mo mixtures are higher than 1000K. Moreover, only a small quantity of An would be transferred in the metallic pool and An would thus remained in the salt.

Mo impact on An extraction efficiency was checked experimentally. It has been observed that U in the metallic phase decreased from 98% (when no Mo is introduced in the crucible) to 44% for a Mo/U ratio equal to 4. Thus, the decrease of extraction efficiency is possibly due to a direct competition between Mo and U reduction by Al. However, thanks to the chemical properties of Mo, an adapted head end step could be proposed in order to remove efficiently more than 99% of Mo. Such removal of Mo should turn possible the application of the pyrochemical process for treatment of CERMET material.

1.2.4 Main S&T results/foregrounds of WP 24: Safety of pyrochemical process waste

In Task 2.4.1, NNL developed a Molecular Dynamics (MD) salt-zeolite model to assess the energetics of Cs, Na, Li and K occlusion and adsorption. Born-Huggins-Mayer potentials for interactions within a (Li,K)Cl molten salt were implemented with LTA and MOR zeolite frameworks. However, the main findings of the work completed in this programme were:

- In LTA and MOR, insertion of K is always more energetically favourable than Cs
- Also, Cs insertion in MOR is energetically more unfavourable than in LTA;
- However, insertion of K and Na species is also more unfavourable in MOR;
- Hence, a slight increase in Cs adsorption might be seen for MOR compared to LTA.

Following improvements to the experimental set-up, which were validated against similar results obtained in previous projects, a series of ion-exchange trials (see Figure 1) were completed on a selection of the zeolites identified in the MD modelling.

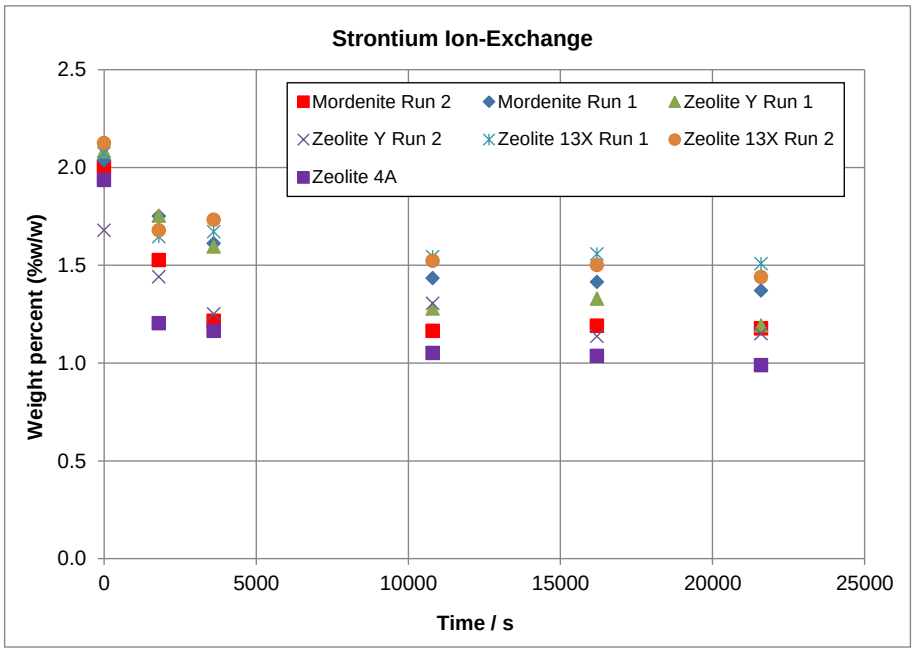


Figure 1 : Summary of $SrCl_2$ ion-exchange experiments using different zeolites

None of the alternative zeolites tested (FAU or MOR frameworks) gave an improvement in the ion-exchange of strontium in LKE compared to the baseline zeolite-4A (LTA). However, significant question marks in the results remain due to experimental discrepancies caused by the use of fine powders *vs* beads, poor mass balance and high moisture levels in the experimental apparatus.

Overall, the combined results of both modelling and experimental studies indicated that there is unlikely to be a significant improvement in the ion-exchange affinity of aluminosilicate zeolites for Cs and Sr in LKE by modifying the framework structure. Hence, future studies should focus on alternative management options. The salt model should be continued to be developed in terms of general salt properties in order to support this activity, as well as other pyrochemical processing operations.

Also in task 2.4.1, CRIEPI conducted a parameter survey to determine the optimised heating temperature and weight loading for the pressure-less consolidation (PC) of the glass-bonded sodalite (GBS) wasteform for spent (L, K)Cl salt to investigate their influences on properties of the fabricated product. The modified heating conditions are shown in Table 1.

Table 1 Modified heating condition for the glass-bonded sodalite (GBS) wasteform

	Modified condition	Reference condition
(1) Maximum temperature	820°C	915°C
(2) Duration in heating at the maximum temperature	5 hours	
(3) Glass ratio of material	25 wt%	
(4) Load value of weight	200 g/cm^2	70 g/cm^2

Powders and coupons of the GBS wasteforms made using the modified heating condition were leach tested in de-ionised water at 70ºC. After leaching, the pH and concentrations of various elements were measured, along with SEM/EPMA analysis of the surface and sections of the coupons. The pHs ranged from ~8.1 to 8.7 after 90 days, with the normalised release rates of relevant elements shown in Figure 2. No dependence on the fabrication conditions was observed, and the values in Figure 2 do not exceed the standard value for typical nuclear waste glass, i.e. 10^{-3} g/m^2/day Si release. For the SEM/EPMA analysis of the coupons, it was shown that the distribution of elements on the surface of the samples was almost uniform and no degradation was recognized.

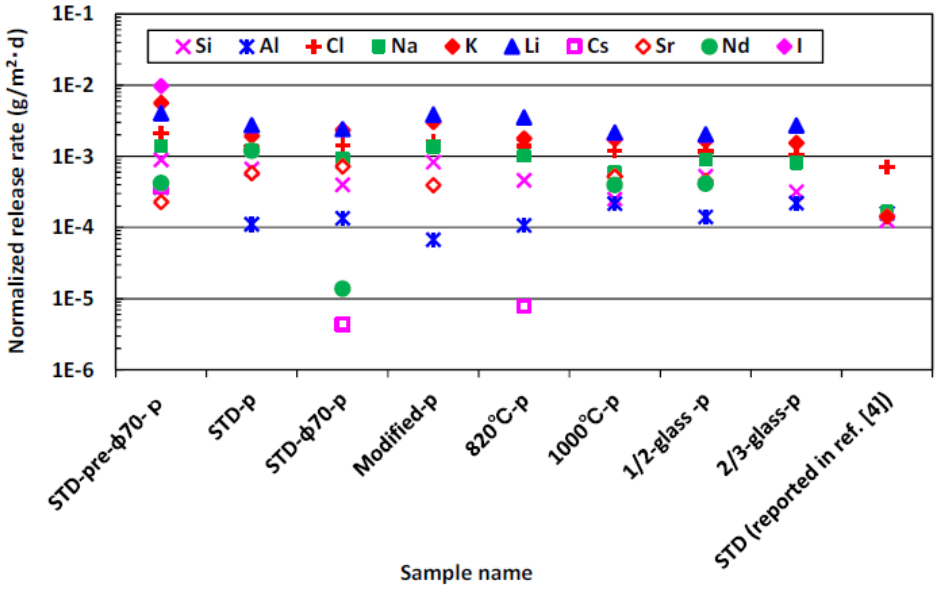


Figure 2 : Normalised release rate of elements from fabricated waste forms

Also in Task 2.4.1, according to the current knowledge on spent salt treatment using zeolite-A, CRIEPI's flowsheet of a pyro-reprocessing plant was revised. Considering the pre-treatment of zeolite before use, the absorption isotherm of cesium by zeolite-A in molten salt, adhering spent salt on zeolite granules after column operation, and the apparent density of the ceramic waste form, the annual amount of the exhausted salt waste volume was re-evaluated, i.e. about 8.2 kg of REs and 3.2 kg of other FPs are absorbed in the zeolite per day. 176 kg of zeolite is used to immobilize them and 69 kg of glass is also mixed. This yields an annual amount of sodalite waste of ~58 tonnes, or 36 m^3 assuming a density of ~1.6 g/cm^3.

In Task 2.4.2, the optimum conditions for fabricating a SiO_2-Al_2O_3-P_2O_5 (SAP)-based wasteform (as developed by KAERI) for immobilizing (Li, K)Cl salt containing various metal cations acting as surrogates for fission products (Rb, Cs, Sr, Ba, La, Ce and Nd) were determined by ENEA. Based on X-ray diffraction, the best SAP:salt ratio was found to be 2:1 heated at 950°C for 30 hours. However, the leach rates from these SAP-(Li, K)Cl wasteforms, as determined by PoliMi, was found to be too high. Hence, SAP-based samples were blended with two types of glass powder, i.e. borosilicate glass (BG) and a commercial glass frit (GF), and heated at 1150°C for 4 hours. From the leach tests results shown in

Figure **3**, the GF bonding agent was found to perform the best. Moreover, the leaching behaviour of Salts.SAP.GF samples was compared to that of analogous sodalite-based wasteforms studied within the ACSEPT project. According to the results obtained by PoliMi, the release rate for the elements confined in the SAP matrix is in general lower than that obtained with the sodalite matrix.

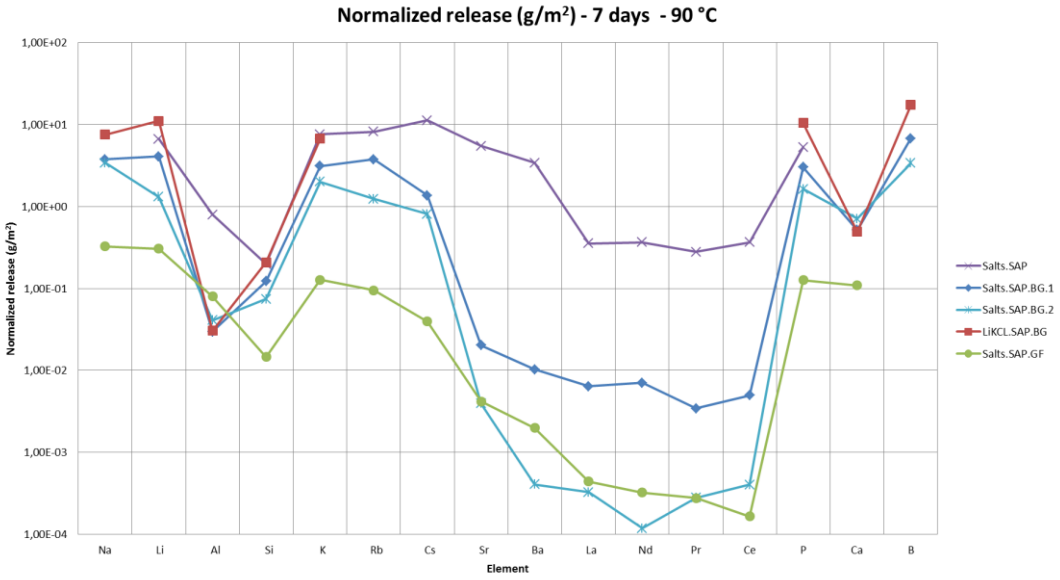


Figure 3 : Normalized release of SAP-based samples, not blended and blended with borosilicate glass (BG) and glass frit (GF), leached at 90°C for 7 days

1.3 Main S&T results/foregrounds of Domain 3: Global safety and Integration

Domain 3 has cross cutting objectives that are pertinent to both the pyromettalurgy and aqueous separation activities undertaken within SACSESS. Fundamental understanding and process development are the building blocks from which an industrial process can be formed and this is the focus of domains 1 and 2; but the eventual goal of these activities is to create an industrial process which deploys this research. Industrialisation and engineering disciplines need to evidence the ability to safely operate a chemical process, at scale and also to understand that's its safety is maintained even in the event of maloperations. Additionally to build technical maturity and technical readiness level (TRL's) for a process defining the activities that have been undertaken and that will be required in roadmapping exercises are important tools in industrialisation. It is these activities that are undertaken in this domain. The headline outputs from this period of work were the D3.1.3 Safety report which is the umbrella document from work package 1 and the Roadmap Actinides separation processes 2015" ISBN 9782919313099 which was presented at the Atalante Conference 2016 prior the final meeting of SACSESS and very much appreciated by the audience of the conference.

1.3.1 Main S&T results/foregrounds of WP 31: Global Safety

The global safety work package focused on undertaking safety assessment of flowsheets developed in Domains 1 and 2. The maturity of the technology within the project is lower than industrial approaches such as HAZOP are initiated at, as they primarily consider the engineering solutions to safety and operability of plant. This work adopted the principals of existing processes and produced a methodology which assesses the scientific flowsheet. The purpose of the activity is not to develop the engineering design but to develop an understanding of how the work in the domains is progressing the state of the art towards a safe system, highlight the areas of risk and inform future research requirements where information deficits exist.

Assessment of a reference pyrochemical flowsheet and a Euro-Ganex flowsheet were undertaken using the methodology produced, encompassing both normal operational considerations and potential mal-operations of the flowsheets. In addition independent assessment of chemical and criticality hazards was undertaken.

The key output document was D3.1.3 SACSESS Completed - Safety Review Summary Report. The output from this report has been used as a key document in shaping a proposed successor program to SACSESS. The output recommendations and potential chemical combination tables for breakthrough during mal-operations summarise the key findings.

No.	Recommendation	Priority
1	In order to understand the implications of temperature fluctuations in the system it is necessary to know the explosive and flammable properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA. Therefore further work is required to determine the lower flammability limits of TODGA, DEHiBA, DMDOHEMA, BTP & AHA.	High
4	For each of the possible inventory permutations detailed in Table 2 and Table 3 in Appendix 1 (normal operations and mal-operations), the behaviour in the storage tanks needs to be understood with relation to the following safety-critical aspects: - Radiolysis - Hydrolysis - Degradation products - Chemical reactions - Chronic precipitation	High
5	For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DEHiBA (Stream 4) for reuse (stream 2). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.	High
6	For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DMDOHEMA / TODGA solvents (Stream 15) for reuse (Stream 14). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.	High
7	In order to understand the potential toxic and corrosive consequences associated with using nitric acid in conjunction with various other compounds it is necessary to quantitatively understand the potential for NO_x generation. Therefore further work is required to determine the location and worst-case rate of evolution of NO_x gases throughout the EURO-GANEX process.	High
8	Determine the range of concentration ratios at which the chemical processes will work efficiently to define the operating envelope.	High
10	Experimental and thermodynamic modelling work should be conducted to define the operating temperature range at which the defined separation factors are valid for each stage of the process (during normal operating conditions and fault conditions), and for the process as a whole.	High
12	Determine the location and worst-case rate of evolution of hydrogen from the EURO-GANEX process to allow process venting requirements to be defined to prevent a possible explosive atmosphere.	High
13	The formation of an interfacial crud through complex interactions in the PUREX system is known. Investigate the possibility of interfacial crud formation in a GANEX system, the conditions under which it could form and the resulting effects.	High
15	Investigate the possibility of Pu deposition in mal-operations temperature and concentrations in the TRU extract and scrub stages.	High
2	For industrialisation of this process it will be necessary to understand the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that the conventional and handling hazards can be suitably managed. Therefore further work is required to determine the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that they can be categorised in line with European Regulation No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regs).	Low
3	The PUREX process has known issues associated with the production of hydrazoic acid, which is handled by Solvent Wash processes. Investigate whether similar issues are likely to be present within the EURO-GANEX system, and methods of treatment if they are.	Low
9	Define suitable CFA for each product and waste from the EURO-GANEX process to allow for process parameters (e.g. concentrations and flowrates to be defined).	Low
11	Determine the heat generation of product streams to then determine the engineering requirements of storage tanks and subsequent process plant.	Low
14	Investigate the possibility of solids deposition due to insolubility in the EURO-GANEX process.	Low

Summary Table of High Priority Recommendations for Euro-Ganex development

		Species						
		U	*FP*	*An*	*Ln*	*DEHiBA*	*DEHiBA Degradation Products*	*HNO_3*
Tank	*U Product*	✓	×	×	×	×	×	✓
	CDTA Mixing	×	✓	✓	✓	×	×	✓
	FP	×	✓	×	×	×	×	✓
	An/Ln Buffer	×	×	✓	✓	×	×	×
	Ln Product	×	×	×	✓	×	×	✓
	An Product	×	×	✓	×	×	×	×

		Species				
		Hydrazine/ Hydrazoic Acid	*CDTA*	*DMODOHEMA/ TODGA*	*DMODOHEMA/TODGA Degradation Products*	*HNO_3/ AHA/BTP*
Tank	*U Product*	×	×	×	×	×
	CDTA Mixing	✓	✓	×	×	×
	FP	✓	✓	×	×	×
	An/Ln Buffer	×	×	✓	✓	×
	Ln Product	×	×	×	×	×
	An Product	×	×	×	×	✓

Table 2 - Possible species combinations in the EURO-GANEX process tanks during normal operations (ticks indicate the possible presence of the chemical)

		Species						
		U	*FP*	*An*	*Ln*	*DEHiBA*	*DEHiBA Degradation Products*	*HNO_3*
Tank	*U Product*	✓	✓	✓	✓	✓	✓	✓
	CDTA Mixing	✓	✓	✓	✓	✓	✓	✓
	FP	✓	✓	✓	✓	✓	✓	✓
	An/Ln Buffer	✓	✓	✓	✓	✓	✓	✓
	Ln Product	✓	✓	✓	✓	✓	✓	✓
	An Product	✓	✓	✓	✓	✓	✓	✓

		Species				
		Hydrazine/ Hydrazoic Acid	*CDTA*	*DMODOHEMA/ TODGA*	*DMODOHEMA/TODGA Degradation Products*	*HNO_3/ AHA/BTP*
Tank	*U Product*	✓	×	×	×	×
	CDTA Mixing[1]	✓	✓	✓	✓	×
	FP	✓	✓	✓	✓	×

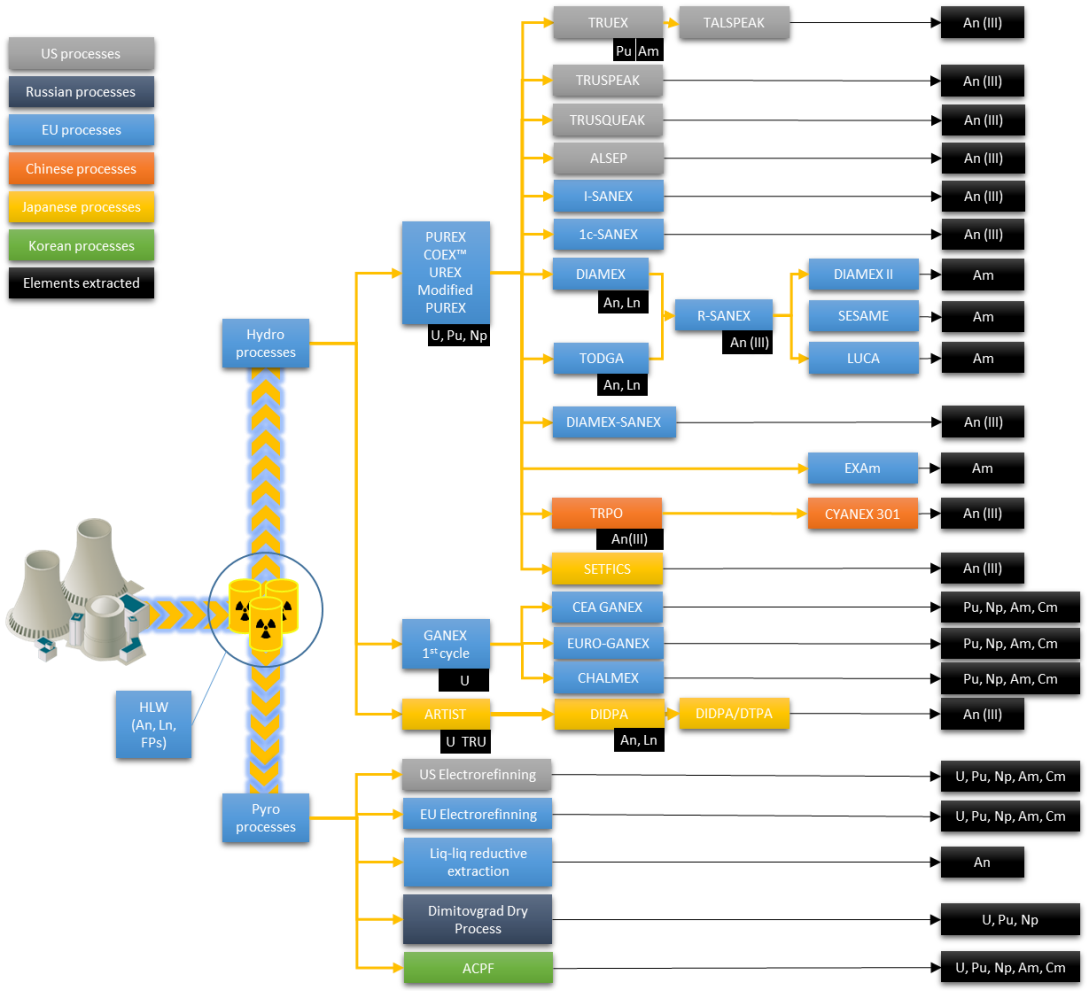
[1] It is assumed that the chemicals from the subsequent stage may be present in the buffer/mixing tank, however it is not carried to the previous stage, e.g. DMDOHEMA/TODGA may be present in the CDTA mixing tank, but will not carry through to the GANEX 1st Cycle.

	An/Ln Buffer1	✓	✓	✓	✓	✓
	Ln Product	✓	✓	✓	✓	✓
	An Product	✓	✓	✓	✓	✓

Table 3 – Possible species combinations in the EURO-GANEX process tanks during mal-operations (ticks indicate the possible presence of the chemical)

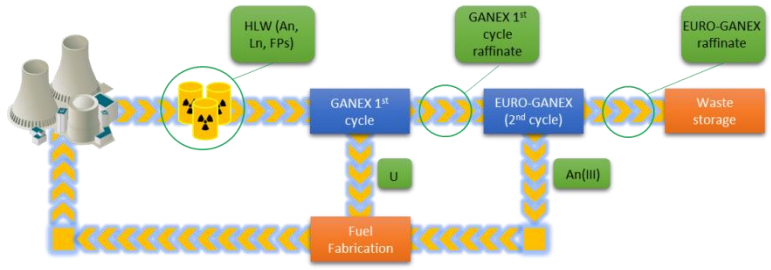
1.3.2 Main S&T results/foregrounds of WP 32: Integration

The most promising processes from task 32.1 have been collected in this report and are presented in Figure 4. The scheme aims at presenting the different processes, the country/region of creation, the type (hydro or pyro) and the flow of the processes and the products obtained with each of them.

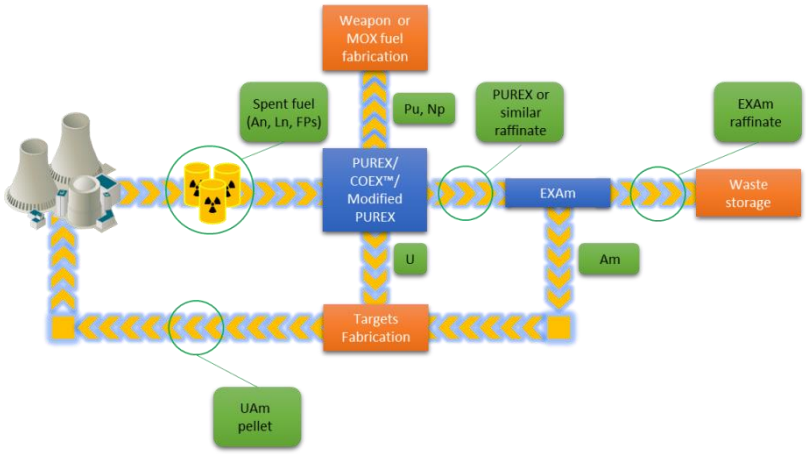


The processes selected from the mapping in task 32.2 were analysed and the R&D needed for further development identified. A summary is provided below.

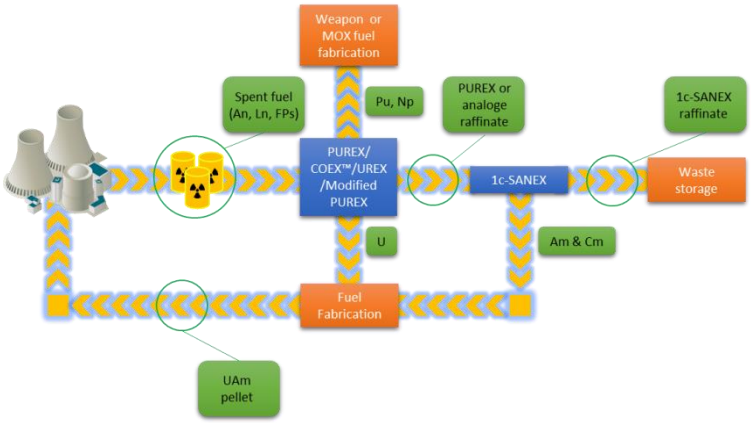
- The Euroganex process: The EURO-GANEX is an evolution of the CEA-GANEX. This process was developed in the framework of the FP7 ACSEPT (2008-2012) and further developed in the framework of FP7 SACSESS (2013-2016). Despite the CEA, the process have been developed by JULICH (Germany), KIT (Germany) and is currently under testing at UNISTRA (France), CIEMAT (Spain) and NNL (UK).



- The ExAm Process: The EXAm process is a solvent-extraction process developed in France in the framework of the Waste Management Act from 2006. The process has been studied at Atalante facilities by the “Commissariat à l’énergie atomique et aux énergies alternatives” (CEA). The EXAm process aims at recovering americium alone contained in the PUREX raffinate. The process has been developed in order to reuse the Am with uranium to produce UAmO2 pellets. The main stakeholders involved in the EXAm process development are the CEA Marcoule (chemistry and process development), and the CEA Saclay (analytical purpose).

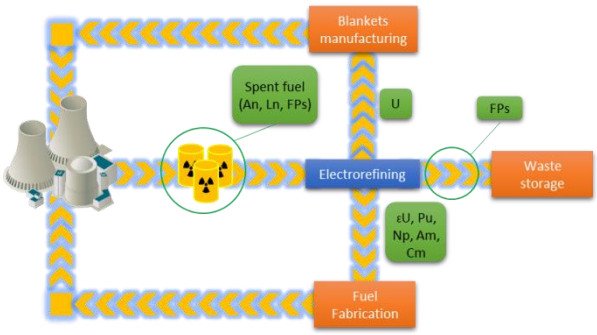


- The 1c-SANEX process: The 1c-SANEX process (one cycle selective actinide extraction), is a solvent-extraction process developed in the framework of the European ACSEPT project This process has been studied at JÜLICH (Germany) and is currently under study at CTU (Czech Republic), IIC, (Czech Republic), UNISTRA (France), KIT (Germany), POLIMI (Italy), at UNIPR (Italy), ICHTJ (Poland), and ULANC (UK). It aims to extract selectively the minor actinides (Am and Cm) directly from a PUREX raffinate, avoiding the DIAMEX step.



- The electrorefinning process: This process is the result of researches conducted in the framework of the following European project: FP5 PYROREP, FP6 EUROPART and FP7 ACSEPT. The electrorefining process builds on the process proposed by the Argonne National Laboratory to reprocess oxide fuel. The flowsheet was simplified for use with metal fuel, for which a prior reduction step is not necessary. This process is currently under study at ITU (Germany), CEA (France), CNRS

(France), ENEA (Italy), POLIMI (Italy), PSI (Switzerland), NNL (UK), UNIMAN (UK), and CRIEPI (Japan).



1.4 Main S&T results/foregrounds of Domain 4: Dissemination, Knowledge Management, Training and Education

Domain 4 contains 3 work packages:

- WP41: Dissemination and Communication, led by LGI
- WP42: Knowledge Management, led by NNL
- WP43: Training and Education, led by Univleeds

1.4.1 Main S&T results/foregrounds of WP 41: Dissemination and Communication

The following tasks were completed under this work package.

1. Task 4.1.1 Project presentation (LGI, CEA)

2. Task 4.1.2 Communication action plan (LGI, CEA)
- Communication action plan was produced and distributed to the PCC for use on the project.

3. Task 4.1.3 Open website (LGI, CEA)

A website was created with:

- a news & events section;
- a homepage with the last info on the project, editor update;
- a “work with us” section and job offers update;
- Information on SACSESS International Workshops;
- Information on the publication of the SACSESS book;

4. Task 4.1.4 External interaction (LGI, CEA)
- The publication of deliverable D32.1 was at OCDE.

5. Task 4.1.5 Organisation of an international workshop (LGI, CEA)
- Two international workshops (Warsaw, April 22-24 2015 and ATALANTE 2016, June 5-10 2016) were run. The ATALANTE 2016 event included the launch of the SACSESS Book and a book of abstracts for the conference. These Workshop was the corner stone of our programme for the dissemination and education. Indeed, in addition to the high visibility given to the work performed in SACSESS, the floor was widely given to the young generation, both for the oral talks and the chairmanship (in Warsaw) or co-chairmanship (at ATALANTE 2016) of the sessions. Therefore, our young researchers appeared closely in interaction with many recognized international experts with whom they could exchange all along the workshop.

1.4.2 Main S&T results/foregrounds of WP 42: Knowledge Management

The plan in Work Package 4.2 was to create a chemoinformatics database and a document database. After discussions with SACSESS partners it was decided to make both of these two components available via one interface for ease of access.

Consultations with SACSESS partners took place in Year 1 to ensure that the database fields captured everything deemed of use by the community that would ultimately be using the database. An initial version of the database was then developed in-house by NNL Software Enginneer's and this was presented at the SACSESS meeting in March 2014 for comment. A few improvements were suggested & these were made during the subsequent period of work. This included extending the scope of the project to also include a section for the results from the pyro work. The improved version of the database was then made available for users to test out & feedback received. After a final round of small modifications the database was completed & ready to roll out at the end of 2014.

It has taken a while to sort out & finalise the hosting of the database online as there were questions that needed addressing relating to the location of the database online & related security & access issues. Following the SACSESS meeting in April 2015 it was decided that, for the sustainability of the SACSESS results, and to ensure SACSESS partners have time to input their data after completion of research, that hosting of the database online would be pre-paid and extend for 2 years post the end of SACSESS (i.e. March 2016-March 2018). After this date, the database is frozen & the data collected onto CD & distributed to SACSESS partners.

The backend database is MSSQL Server and it has asp.net MVC application + Lucene index's built on top. The database allows users (once logged in) to add information and search the input information from others across 3 categories : documents, pyro, chemcials.

The database is now online and available to sacsess partners at https://database.sacsess.eu to enter and search for data. A number of moderators have had accounts created across the SACSESS partners that have the ability to perform roles such as invite new users.

1.4.3 Main S&T results/foregrounds of WP 43: Training and Education

1. WP43.1 Status of the first winter school (NNL, Univleeds, UMAN)

The first school was run on April 7/8th 2014 (M13). The subject was uranium laboratory management and is being hosted by NNL at their Preston Laboratory. Contributions from UNIVLEEDS and UNIMAN provide a university perspective, but the majority of the course was delivered by NNL personnel. A summary of the syllabus is as follows:

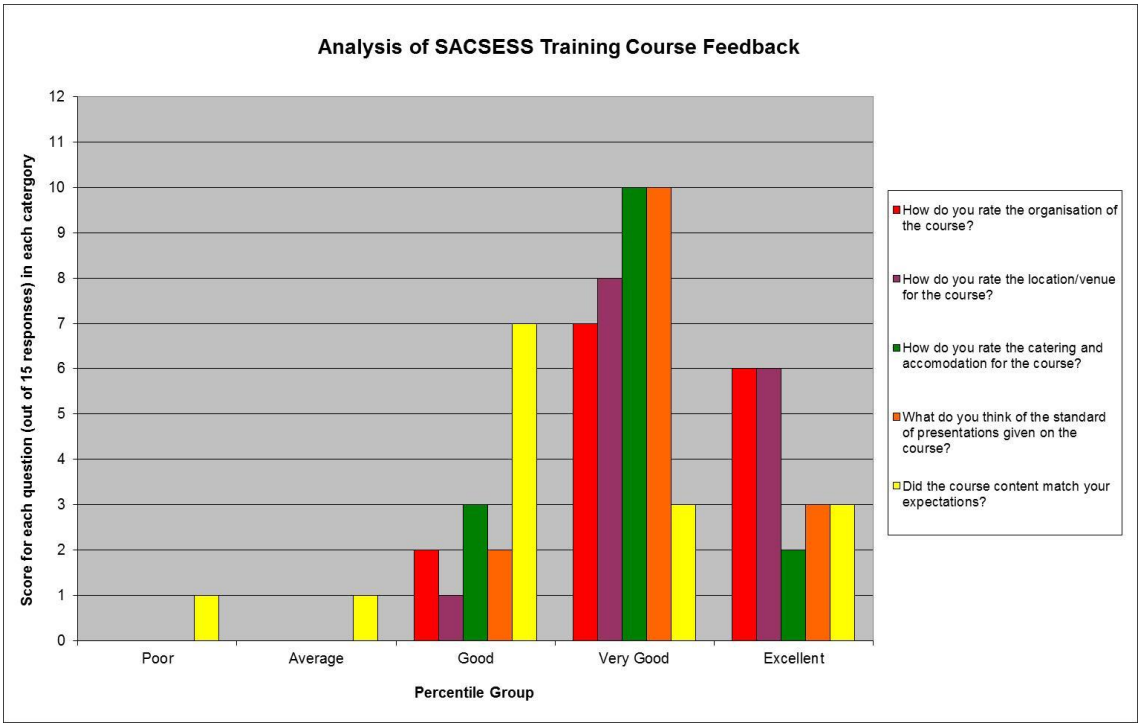
	Taught Courses	Resource
1	Basics of ionizing radiation	NNL
2	Classification of working areas	NNL
3	Dosimetry	NNL
4	Monitoring & contamination management	NNL
5	Managing criticality	NNL
6	Chemotoxic hazards of Uranium	NNL
7	Waste management issues and routes for dealing with effluents	NNL
8	Transport of materials containing U	INS
9	UK university perspective - working with U in an unsupervised laboratory	UNIVLEEDS
10	UK university perspective - working with U in a supervised laboratory	UMAN

The course could have accommodated up to 20 students and 15 students attended, from the following institutions:

3 – University of Leeds
2 – University of Manchester
1 – CEA, France
1 - Forschungszentrum Jülich GmbH, Germany
2 – Chalmers, Sweden
3 – Lancaster University
1 – University of Edinburgh
1 - Institute of Nuclear Chemistry and Technology, Poland
1 - CIEMAT, Spain

Feedback from the course attendees indicated that it had been a good event to attend, with comments generally indicating that instructions on handling materials had been useful. A comment point raised is that future schools need to take account of is that attendees wanted more on the chemistry and behaviour of the materials in question.

An overall view of the school is given in the following figure.



2. WP43.2 Status of the second winter school (Univleeds, Chalmers)

The second school was run on the 4th to the 8th May 2015 (M25). The subject was plutonium laboratory management and was hosted by Chalmers, who provided all the school materials, practical sessions and staff.

Lectures included, an introduction to plutonium, Plutonium analysis and detection and radiation protection

Students took part in three practical sessions, using plutonium, in Chalmers laboratories:

- Plutonium oxidation and extraction
- Separation of plutonium and americium
- Uranium oxide fuel production by the sol gel method

The school was attended by 11 students, from the following institutions:

1.	Dominic Laventine	Lancaster University
2.	Elizabeth Howett	Lancaster University
3.	Suzanne Buckmaster	Lancaster University
4.	Holger Schmidt	Forschungszentrum Jülich GmbH
5.	James Goode	University of Leeds
6.	Jess Shiels	University of Leeds
7.	Charlotte Parrington	University of Leeds
8.	Pavel Bartl	CTU
9.	Iveta Pelikanova	CTU
10.	Annalisa Ossola	Politecnico di Milano
11.	Jessica Bruin	Nuclear Research and Consultancy Group

Feedback from the school attendees indicated that it had been a good event to attend, with comments indicating that the opportunity to work with plutonium, in laboratory conditions, had been great. The students also indicated that all the staff at Chalmers had been very welcoming, knowledgeable and helpful.

3. WP43.3 Status of the third winter school (Univleeds)

A third "Winter" school was planned for the 27th to 29th June 2016, hosted by the University of Leeds.

The subject of the workshop was to be experimental design, analysis and optimisation. The workshop was to include a mix of lectures, laboratory exercises and modelling and be of particular use to researchers involved in experimental programmes linked to process development. A summary of the programme was:

- Day 1 – Introductory lectures and background, laboratory planning and then start of laboratory exercises.
- Day 2 – completion of laboratory exercises and data analysis
- Day 3 –laboratory and modelling exercise to link to processing and multiphase mass transfer.

The workshop had been developed from a series of similar exercises run by the University of Leeds for Astra Zeneca to optimise research on new pharmaceutical compounds.

Unfortunately, due to a low number of registrations (2) the PCC decided to cancel the school

4. WP43.4 Status on student exchange (Univleeds)

SACSESS created 30 travel grants, worth €1000 (including indirect costs). These were offered to Post Graduate and Graduate researchers/students to support travel to training and education events. A maximum of 2 grants per partner, per event, were offered and were awarded by the SACSESS PCC after a selection process.

Only training and education events that were sponsored or supported by SASCESS were eligible. The first eligible event was the SACSESS International Workshop in Warsaw 22-24 April. Afterwards applications were accepted on an ad-hoc basis.

In total, eleven grants were awarded, for a total of €11600.

Details of the grants are:

Researcher Name	Organisation	SACSESS contact	Purpose	Amount awarded
Nadya Rauff-Nisthar	Lancaster University, UK	Colin Boxall	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Lukasz Steczek	Institute of Nuclear Chemistry and Technology, Poland	Jerzy Narbutt	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Ana Núñez	CIEMAT, Spain	Hitos. Galán	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Peter Kaufholz	Forschungszentrum Jülich GmbH, Germany	Giuseppe Modolo	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Holger Schmidt	Forschungszentrum Jülich GmbH, Germany	Giuseppe Modolo	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Gregory Horne	University of Manchester, UK	Simon Pimblott	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
James Westwood	University of Reading, UK	Laurence Harwood	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Andy Smith	University of Reading, UK	Laurence Harwood	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Johal Sukhraaj	Lancaster University, UK	Colin Boxall	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Ossola Annalisa	Politecnico di Milano	Mario Mariani	SACSESS International Workshop in Warsaw, April 2015	€ 1,000
Tomas Koubsky	Czech Technical University,Prague	Jan John	Radical Behavior workshop at the Idaho National Laboratory	€ 1,600
			TOTAL =	**€ 11,600**

4 Potential impact

The Fukushima Dai-ichi accident in March 2011 has reopened the debate about the practicability and safety of nuclear energy use. The extraordinary meeting of the European Energy Council held in Brussels on 21st March 2011 pointed out that it is absolutely necessary for the EU to understand how safe its nuclear plants actually are. In fact, an assessment, a so-called “stress test”, was proposed in order to ascertain how resistant plants are to both natural disasters, for example earthquakes or floods, and to man-made problems such as technical error and a loss of power in the reactors, as well as a terrorist attack of a technical nature. Such a series of assessments would help to increase protection, but would not completely eliminate the risk of an incident comparable to that which occurred 25 years ago in Chernobyl, for example.

Nevertheless, nuclear power is and remains a resource which that is capable of guaranteeing a higher quantity of energy at an acceptable expense, but at the same time involves inevitable risk. Human error and natural disaster are variables which must always be considered; as the well-documented events at Fukushima and Chernobyl have shown, the consequences can be dramatic. Then there is the eternal problem of how to dispose of nuclear waste. Here also safety is a key issue, not only for the final disposal repository design but also all along the process that leads to the fabrication of this ultimate waste form, including the safety of the separation processes when implemented through a fuel cycle strategy.

Presently, the European nuclear consortium leads to the annual production of 1800-2000 t/y of spent fuel, containing approximately 20 t of Plutonium, 2,8 t of minor actinides (MA, namely Np, Am, Cm) and 2,5 t of long-lived fission products (LLFPs). These MA and LLFPs stocks need to be managed in an appropriate way. The spent fuel reprocessing followed by the geological disposal or the direct geological disposal are today the envisaged solutions depending on national fuel cycle options and waste management policies. Required time scale for the geological disposal exceeds our accumulated technological knowledge and this raises problems of public acceptance. P&T has been pointed out in numerous studies and more recently in the frame of the Generation IV initiative as the strategy that can relax the constraints on the geological disposal, and reduce the monitoring period to technological and manageable time scales, whatever in the case a nuclear industry development or a phase-out of nuclear. If scientific and technical solutions are now available, their safety has to be assessed to allow their development at a higher scale.

The nuclear community also has to demonstrate that it is possible to manage safely a post-accidental situation, allowing the safe decommissioning and dismantling of the damaged facilities with the production of waste that can be safely managed in the longer term. By working in close connection with Japan, Europe has an important role to play and will definitely benefit from this new knowledge.

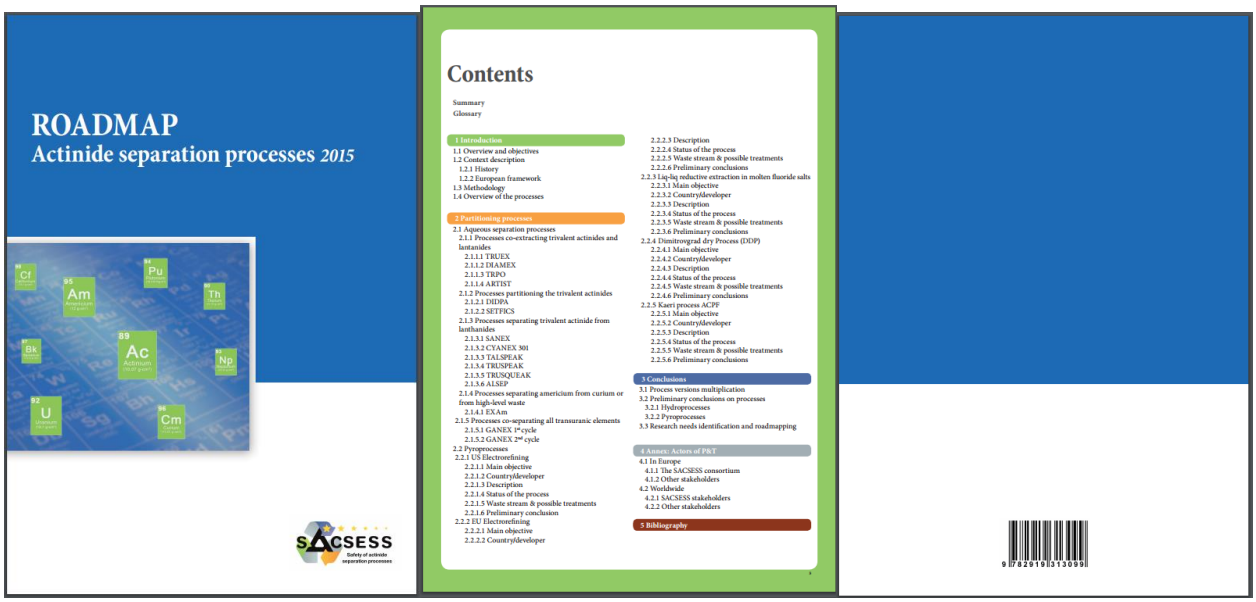
SACSESS has contributed to address these key issues at a high level and helps Europe to hold a top level position in this domain.

Moreover, beyond sharing national experience, it is essential for Europe actively to participate in longer term international efforts to prepare the future in order to perpetuate competences in the field of actinide sciences, chemical separation and fuel fabrication processes in order to be able to ensure the safety of the chemical processes developed.

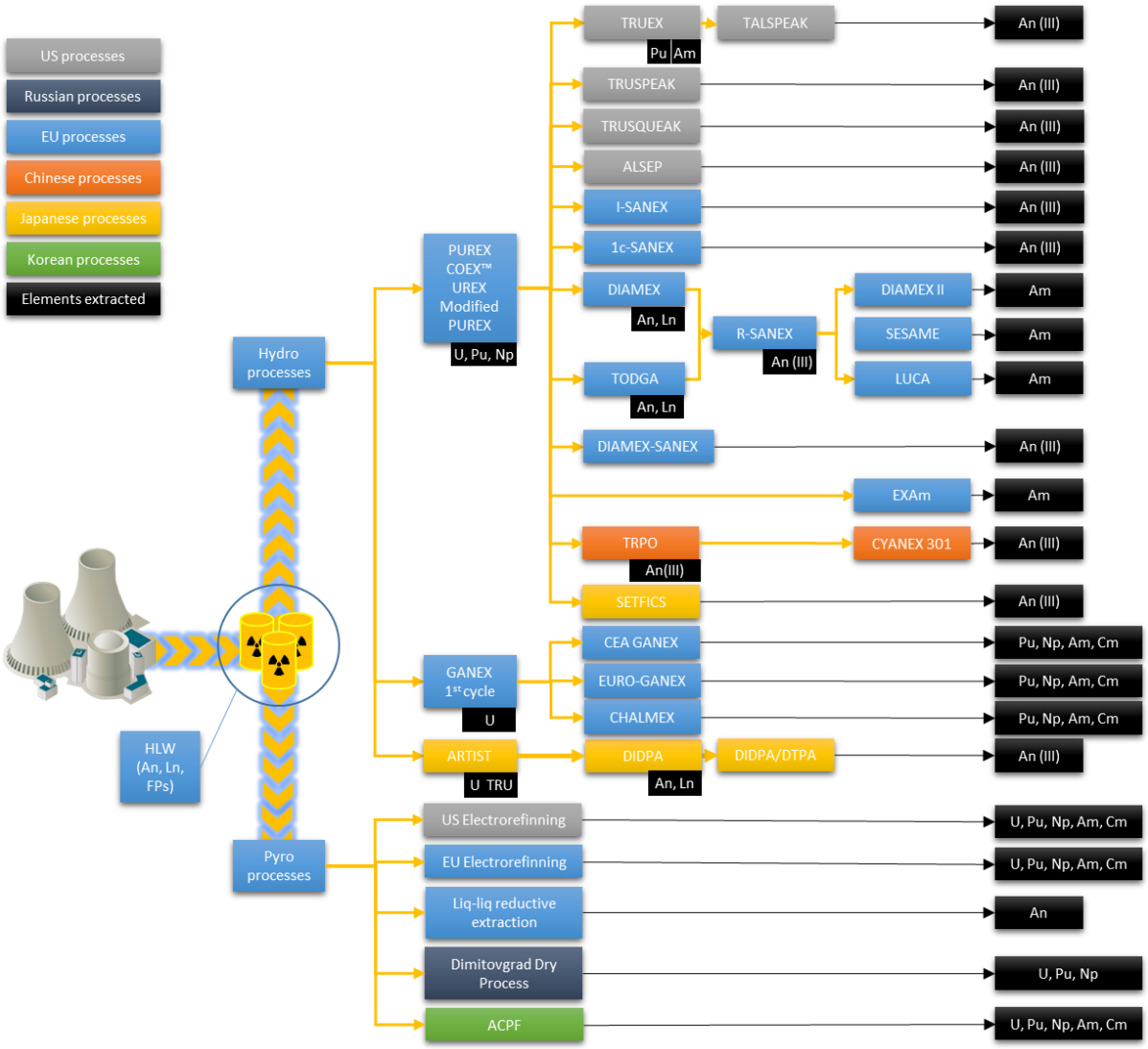
5 Project communication tools

The address of the project public website, if applicable as well as relevant contact details.

www.sacsess.eu



Roadmap Actinides separation processes 2015" ISBN 9782919313099 which was presented and distributed at the Atalante Conference 2016



Furthermore, project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc…), as well as the list of all beneficiaries with the corresponding contact names can be submitted without any restriction.