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# ACSEPT

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## ACTINIDE RECYCLING BY SEPARATION AND TRANSMUTATION

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# FINAL PROJECT REPORT Part I: Publishable Summary & Part II: Use & Dissemination of Foreground

Collaborative Project

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# PROJECT FINAL REPORT

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## EXECUTIVE SUMMARY

All along the last four and half years, the FP7 EURATOM Collaborative Project ACSEPT (Actinide recycling by SEParation and Transmutation) has coordinated the European Research on aqueous and pyro-actinide chemical separation processes. A clear structuration of the work and an enthusiastic collaboration between partners have allowed significant progress in actinide separation process development.

In the field of aqueous reprocessing, hot-test demonstrations have been carried out based on chemical systems developed in former European Projects (NEWPART, PARTNEW, EUROPART) or directly in ACSEPT. Process flowsheets are now available for the regular SANEX, the innovative SANEX, the 1-cycle SANEX and the GANEX concepts (some of them being more elaborate alternatives to reference existing processes) paving the way for further optimisation. This progress was made possible thanks to a well driven organic synthesis work. It allowed the testing of more than 150 new molecules and the selection of about 5 of them for further process development. In addition, specific issues related to advanced fuel cycles involving materials with high Pu loading or minor actinides were addressed such as MOX dissolution or co-conversion into solid forms suitable for fuel fabrication.

In the field of pyrochemical process development, two reference cores of process were selected within EUROPART (the electrorefining on solid aluminium cathode in molten chloride and the liquid-liquid reductive extraction in molten fluoride/liquid aluminium). In ACSEPT, the work has been continued with a focus on key process steps such as the exhaustive electrolysis allowing a quantitative recovery of the transuranics after the electrorefining or the actinide back extraction from an aluminium alloy, crucial step for the two reference processes. In addition, a specific effort has been allocated to the head-end step (oxide pre-reduction, thermal treatment), the salt recycling (chloride salt purification by precipitation, fluoride salt purification by distillation) and the specific salt waste conditioning.

This experimental work has been extended to cross cutting studies, such as system studies, scale up studies, corrosion studies and online process monitoring developments for molten salts. The MARIOS irradiation performed in FP7 FAIRFUELS was also designed in ACSEPT to allow a better schedule of this long run experiment. A report was also issued on the reprocessibility of advanced CERCER and CERMET fuels, leading to an experimental program now implemented within the FP7 ASGARD project.

In parallel, one of the major successes of ACSEPT has also been its investment in people with the funding of two post-doctoral positions and of a dozen of student exchanges between partners allowing these students to broaden their field of competences and to increase collaboration between partners. Specific workshops and seminars were also organised to allow a better exchange between partners. Two international workshops (the first one in Lisbon in 2010 and the second one as a specific one day session of ATALANTE 2012 international Conference) gave the consortium the opportunity to present widely the work performed in ACSEPT.

## Acronyms

AE: Alikaline Earth

AM: Alkali Metals

ASTM: American Society for Testing and Materials

BET: Brunauer–Emmett–Teller theory allowing the measurement of the specific surface area of a material

BTBP: Bis-Triazinyl Bipyridine

BTP: Bis-Triazinyl Pirydine

DIAMEX: (DIAMide EXtraction) process

EDS: Energy Dispersive Spectroscopy

FP: Fission Products

FR: Fast Reactor

FTIR: Fourier Transform InfraRed Spectroscopy

GANEX: Grouped ActiNide Extraction

MA: Minor Actinides

MOx: Mixed Oxide fuel

NMR: Nuclear Magnetic Resonance

PUREX: Plutonium and Uranium Refining by Extraction

SANEX: Selective ActiNide Extraction

SEM: Scanning Electron Microscopy

TODGA: Tetra-Octyl DiGlicolAmide

TRU: Trans Uranium elements

UOx: Uranium oxide fuel

XRD: X Ray Diffraction spectroscopy

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# PART I: FINAL PUBLISHABLE SUMMARY REPORT

## I PARTNERS AND SCIENTISTS INVOLVED IN ACSEPT

The ACSEPT consortium gathers groups of national and international reputation in the field of partitioning and transmutation. It includes national as well as European nuclear research laboratories, universities and national fundamental research laboratories, and nuclear industrial companies. These complementarities bring the guarantee that innovative and exploratory researches are suitably integrated through process development activity in the view to future large-scale demonstrations. The consortium provides well balanced activities and a consistent continuum from research up to industry. All the proposed partners have a long standing experience and renowned skills in the field of actinide science, chemical separation processes either by hydrometallurgy or pyrochemistry, and in the field of fuel fabrication processes. While some partners have been focused on specific topics of research in the field of actinide partitioning, some key partners (CEA, FZJ, KIT-INE, JRC-ITU, NNL) have shown proven capabilities of science and engineering integration towards large scale or industrial units design. To make the best exploitation of achievements generated within ACSEPT, potential end-users partners (ALCAN, AREVA, EDF, NRI, CINC) are participating to the consortium. The partners have been carefully selected for their skills, their previous experience relevant to the scientific and technical fields that are addressed within ACSEPT, their strong motivation to work in the direction expected by the project as well as their capability to commit themselves towards the ambitious objectives of the project.

In the field of hydrometallurgy, strong efforts have been provided on the design, synthesis and screening of new extracting/complexing molecules which call for appropriate resources in use-inspired basic studies. This activity was the engine of the project since it provided the new extracting systems that were further developed into process. Numerous partners from universities or national fundamental research laboratories (CHALMERS, UREAD, UNISTRA, ULG, TWENTE, CSIC, CUNI, ICIQ, UNIPR, POLIMI, CNRS, CTU, ICHTJ, ITN...) gathered their resources in this field which has been one of the most challenging activity of ACSEPT (in previous Framework Programmes no molecule that meets all the process criteria has been found so far for either selective or group actinide separation). As part of this activity can be undertaken by modelling or running simple analytical tests in laboratories equipped with gloveboxes, on the opposite, the development of the processes was assured by nuclear research bodies that dispose of nuclear research facilities with either a set of gloveboxes or hot cells for handling nuclear materials, and the capacity to integrate and run integral tests (CEA, CIEMAT, ENEA, FZJ, KIT-INE, JRC-ITU, NNL). Among the latter ones, only CEA and JRC-ITU have committed to offer their hot cells as a resource for ACSEPT hot tests. NNL enhanced their activity by carrying out alpha tests. FZJ was able to performe important spiked tests for the qualification of the concepts.

Pyrometallurgy shows promising assets as an alternative option and for the longer term for the group actinide recycling. However there is still much work and significant progress to be achieved beyond the current state of the art. In particular the recent interest addressed to fluoride media show the wide diversity of process options. If major efforts have been provided by the past in acquiring basic data, efforts shall be given now on exploring, developing, testing and finally assessing different process options. CEA, CIEMAT, CNRS, JRC-ITU, NNL, NRI, POLIMI, CRIEPI, ANSTO,... have jointly gathered their efforts to study all the envisaged separation process options (electrorefining, electrochemistry, either in chloride or fluoride salts, reductive extraction in fluoride salts,...) as well as ancillary processes such as head-ends treatments, salt decontamination, fission products confinement,... There is also a strong need to progress in technologies, materials, on-line monitoring so as to implement these developments at a larger scale, yet still laboratory scale. The expertise of ALCAN in the field of pyrochemistry with a long standing experience in technologies has been a strong insight for ACSEPT as it brought support to technology developments already undertaken by EDF, ENEA, NNL and in a less extent by CEA and JRC-ITU. Some basic research supported these developments with innovative inputs from CNRS, UEDIN. CRIEPI is a Japanese company performing research for Japanese utilities which has a long standing collaboration with JRC-ITU and this company was accepted within the project as some of the proposals have been jointly funded by JRC-ITU and CRIEPI. At last ANSTO, already working for IP EUROPART, will also bring some work on alternative processes for actinide separation, salt decontamination or FP confinement. These two non EU partners were not funded by ACSEPT. As pyrochemistry remains a rather limited field of activity, international collaboration have been emphasized to optimize the work with strong links with ISTC projects and KAERI. Specific exchange

meetings were organized yearly.

All the technical results were integrated by developers or integrators so that early feedback towards R&D were assured (CEA, FZJ, KIT-INE, JRC-ITU, NNL, POLIMI) ; this integration has been undertaken under the auspices of industrial partners.

More than 90 people were regularly involved in the research activities. Under the coordination of Stéphane Bourg and with the help of the Scientific Secretary, Noël Ouvrier – CEA, the Project Coordination Committee drove the project thanks to the contribution of top level senior scientists acknowledged as experts in their field (Clément Hill – CEA, Andreas Geist – KIT, Concha Caravaca – CIEMAT, Chris Rhodes – NNL, Danny Fox – NNL, Robin Taylor – NNL, Philippe Guilbaud – CEA, Christian Ekberg – CHALMERS, Gisueppe Modolo – FZJ, Laurent Cassayre – CNRS, Rikard Malmbeck – ITU, Mike Harrison – NNL, Giorgio de Angelis – ENEA, Amparo Espartero – CIEMAT, Sylvie Bouvet – ALCAN, Frodo Klaassen – NRG). It is noticeable that about 40 students (from under graduate to post-doc) deeply contributed to the project. 12 of them were involved in the student exchange program and two of them received a post-doctoral grant.

## II DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

Consistently with potentially viable recycling strategies, ACSEPT provided a structured R&D framework with the ambitious objective to develop chemical separation processes compatible with fuel fabrication techniques, in view of their future demonstration at the pilot level.

For several decades, many European countries have chosen the strategy of closed fuel cycle, currently involving (i) the reprocessing of spent nuclear fuels to recover uranium and plutonium (both fissile materials that can be recycled) and (ii) the vitrification of long lived radionuclides (the final waste being expected to be disposed of in deep geological repositories). Nevertheless, the sustainability of an advanced fuel cycle relies on the possibility to maximise the energy use of nuclear spent fuel and to provide improved waste forms for long-term storage: the removal of minor actinides (*i.e.*: Np, Am, Cm, Cf) with U and Pu from the waste and their recycling in fast neutron reactors, will significantly reduce the radio-toxic inventory. Therefore, the separation of all significant Trans-Uranium (TRU) elements and their incineration in fast neutron reactors or Advanced Driven Systems is a key feature of advanced fuel cycles. However, new reprocessing technologies (spent fuel dissolution, actinide separation and fuel refabrication) are required to address the challenges, which cannot be met by current generation of chemical plants. Two strategies are proposed for the recycling of the actinides issuing from the various forms of future nuclear fuels (oxides, carbides and nitrides or metallic fuels): (i) their homogeneous recycling in mixed fuels (via a prior group separation of the actinides: GANEX concept) and (ii) their heterogeneous recycling in targets or core blankets (via their selective separation from fission products).

Two major technologies have been explored so far to meet these challenges:

- Aqueous separation processes that benefit from more than 60 years of research and development and a long-lasting proven experience at the industrial level, and
- 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 the industrial development level.

Considering technically mature aqueous separation processes, ACSEPT worked at optimizing and selecting:

- The most promising processes dedicated to actinide partitioning via two different routes : the first route is the one cycle direct selective extraction of minor actinides (Am, Cm) from a PUREX raffinate or the alternative two cycle process with direct selective extraction from a first cycle DIAMEX raffinate. This work was built on the acquired knowledge from the SANEX studies based on nitrogen heterocycle ligands (BTPs) undertaken within IP EUROPART; a second route is the selective stripping of minor actinides in one or two cycle processes and based on selective aqueous complexation of actinides. This selective stripping was explored as a new concept in ACSEPT,
- The processes featuring a group separation of actinides such as GANEX after a first U separation. The efforts were concentrated on the challenging development of processes for group actinide separation (Np, Pu, Am, Cm,...) rather than on the separation of uranium that represents less difficulties. The group separation process concepts were directly derived from those studied for the one or two cycle selective extraction or stripping of minor actinides, but with higher challenging scientific issues that are due mainly to the presence of plutonium and to a lesser extent due to neptunium in the feed solution.

These three routes were studied in parallel. For each of them, the aim was to achieve the following successive milestones: the design and synthesis of promising molecules, the selection of the most promising extractant system, the elaboration of flowsheets for further experimental implementation, cold and/or 'spiked' tests of these flowsheets and finally hot test demonstration at the lab-scale.

To sustain these developments, an exploratory research was carried out at an appropriate level for the design of new molecules, this topic being considered as the driving force of the project to further develop aqueous separation processes. Strong efforts were consequently brought to this field so as to stimulate new ideas, new molecules. The visible outcome of these studies was the production of sets of promising molecules to be further studied for process implementation.

Concerning pyrochemical separation processes, ACSEPT contributed to develop them beyond the current state-of-the-art, as an alternative option, for a longer term.



In PYROREP and EUROPART projects carried out in FP5 and FP6 respectively, two reference routes were identified and proposed by the European community: the electrorefining of actinides onto solid aluminium cathode in molten chloride salts and the liquid-liquid reductive extraction in molten fluoride salts/liquid aluminium. In ACSEPT, the studies were focused on the enhancement of these two cores of process by working on critical ancillary steps such as the exhaustive electrolysis or the actinide recovery from aluminium, a common step for the two processes. In parallel, studies on an electrochemical core process in molten fluoride media were continued as an alternative.

R&D efforts were also brought to key scientific and technical points compulsory for building a whole separation process such as head-end steps that make the interface with fuels and/or targets, salt treatment in view of its recycling that minimize the final volume of waste and the development of specific matrices for waste conditioning that make the processes sustainable.

In addition dedicated pyrochemical technological issues such as material corrosion, on-line monitoring were explored.

All this work was carried out consistently with previous system assessments while still keeping an eye open on innovative routes. The studies helped to assess the most promising processes or process options and finally to propose relevant viable flowsheets and technology elements for future integral tests and demonstration at the lab-scale.

In order to foster and strengthen the links between partitioning and transmutation with a view to consolidate future actinide recycling strategies, ACSEPT carried out studies to pave the way towards more integration between Partitioning and Transmutation. First the design of the MARIOS experiment which was implemented within FP7 FAIRFUELS was realized in ACSEPT to optimize the timing of FAIRFUELS. ACSEPT investigated also fuels and targets dissolution, conversion of separated elements to solid precursors prior to fuel fabrication. This conceptual review led to the implementation of an experimental program which is now part of the FP7 ASGARD project. These actions contributed to reinforce the consistency of the research in the field of P&T.

Experimental results were integrated by carrying out engineering and systems studies on aqueous and dry (pyro) processes to prepare for future demonstration at a pilot level. However ACSEPT did not intend to deliver a picture of what could be a preliminary design of a future demonstrator, which would require a more technico-economical approach, out of its scope. The philosophy of process studies is rather to integrate the technical results generated within the technical domains so as to provide an early feedback on R&D, taking into account scale-up criteria. This guarantees the sound basis for the future design of a demonstrator.

A training and education programme was carried out which aimed at:

- Sharing the knowledge among communities and generations,
- Fighting against the decline of students, teachers, nuclear research experts and
- Maintaining the nuclear expertise at the fore-front of Europe to prepare for the dynamic knowledge-based society.

### III DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

#### III.1 Domain 1 – Hydrometallurgy

Domain 1 addresses the hydrometallurgical separation (i.e. applying chemical liquid-liquid extraction) of actinides from irradiated nuclear fuels of the metal oxide (UO<sub>x</sub> or MO<sub>x</sub>) type. First, **the fuel is dissolved** in hot nitric acid, the so-called head-end step. Next, the **actinides are separated** from fission products and from corrosion products via several consecutive extraction processes. Finally, the product solution(s) containing the actinides are **converted into solid actinide products** from which new fuels or targets can be fabricated.

The first separation process, the commercially implemented PUREX process, separates U and Pu, leaving behind the so-called high active raffinate (HAR), which is currently vitrified. The PUREX process can be modified to co-separate Np. The separation of the remaining actinides, Am and Cm, from the HAR had been studied in previous projects, making use of the DIAMEX and the *r*-SANEX processes. Aim of the ACSEPT process was to simplify this process scheme by merging the DIAMEX and SANEX processes into one process. Two routes were studied:

1. The **1c-SANEX** process: Am(III) and Cm(III) are directly extracted from the HAR, without implementing a DIAMEX process;
2. The **i-SANEX** process: Am(III), Cm(III) and lanthanides(III) are co-extracted in a DIAMEX-like process; Am(III) and Cm(III) are selectively stripped from the loaded organic phase with selective water-soluble complexing agents, leaving the lanthanides(III) in the organic phase from which they are stripped separately.

Another route followed in the ACSEPT project was the development of **GANEX** (Grouped Actinide Extraction) processes. Aim is developing processes co-managing all transurium elements (TRU = Np, Pu, Am, Cm), avoiding pure Pu products. A GANEX process is advantageous regarding non-proliferation issues and is well suited for the homogeneous recycling of actinides.

##### III.1.1 Head-End Steps

###### III.1.1.1 Introduction

The Head End steps of a spent fuel recycling plant, specifically the dissolution chemistry of advanced fuels, has not been considered in previous projects. A substantial effort was made in ACSEPT to assess the dissolution of different fuel types. Both conceptual studies and experimental work were performed.

###### III.1.1.2 Fuels and outline flowsheets

A review considering historic, current and potential future practices for the treatment options for metal, oxide, carbide, nitride and composite reactor fuels to produce a dissolver product that is compatible with a solvent extraction process was completed. This review highlighted the specific difficulties introduced by each fuel type; examples are listed below:

- Oxide and carbide fuel types can produce dissolver residues that contain significant undissolved plutonium residues.
- Carbide fuel dissolution liquor contains organic compounds that must be destroyed to provide feed liquor compatible with a solvent extraction processes.
- Carbide and nitride (<sup>14</sup>N) fuels produce large quantities of <sup>14</sup>C, requiring increased abatement efficiencies to minimise environmental impact.
- Nitride (<sup>15</sup>N) fuels may require <sup>15</sup>N recovery on economic grounds; however, direct dissolution causes isotopic mixing during dissolution with <sup>14</sup>N nitric acid.
- Metal alloy and composite materials often contain large quantities of an alloying element that increases waste volumes or necessitates their recovery.

These fuel specific issues, together with other process specifications, such as continued reduction in environmental discharges from reprocessing operations, may drive head-end process chemistry to include other steps in addition to direct dissolution. Two example processes are high-temperature pre-treatment and enhanced dissolution technologies. High-temperature pre-treatment offers the potential to allow the evolution of <sup>3</sup>H, <sup>14</sup>C, <sup>129</sup>I and noble gases (<sup>85</sup>Kr, <sup>133</sup>Xe) for abatement. A process step prior to dissolution is the only

viable option to abate some radionuclides, such as  $^3\text{H}$ , before they are isotopically mixed or greatly diluted. Other benefits could be the conversion of carbide fuel to oxide, to minimise the amount of organics formed during dissolution, or the oxidation of nitride fuel, allowing the recovery of  $^{15}\text{N}$  for reuse. Enhanced dissolution techniques show potential towards the dissolution of plutonium-rich residues or the destruction of organics from carbide dissolutions. An example process is mediated electrochemical oxidation (MEO), which uses an electrochemically generated reagent that acts as a catalyst with a high standard electropotential, such as  $\text{Ce}^{4+}$ ,  $\text{Co}^{3+}$  or  $\text{Ag}^{2+}$ , to dissolve or destroy. The application of high-temperature pre-treatment or enhanced dissolution technologies do, however, have the disadvantage of making head-end more complicated and thus costly. Also both process steps have the potential to evolve highly radiotoxic elements, such as  $^{106}\text{Ru}$ , into the off-gas system, which would require very high abatement efficiencies (capture and neutralization of the evolved gas into liquid traps).

These issues were further considered in order to outline flowsheets for advanced dissolution processes. The most significant conclusion from this work is that some overall ‘process specifications’ or ‘process criteria’ for the advanced reprocessing plant need to be defined to guide future R&D, probably across a number of future fuel cycle options (scenarios) to account for the inherent uncertainties in such an exercise. This specification will allow the thorough assessment of the available technologies and access where information or technology gaps exist as well allowing conceptual flowsheets to be proposed. This in turn will allow research and development to be appropriately focused such that progress can be made towards the development and design of a pilot plant for the assessment of future fuel reprocessing.

### III.1.1.3 Practical oxide dissolution studies

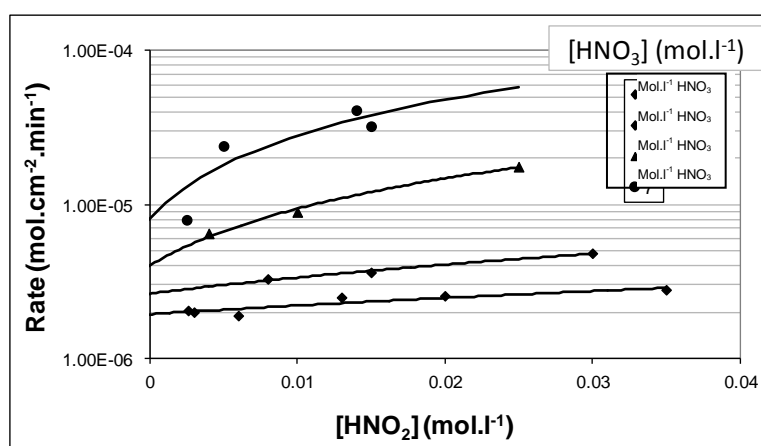
Uranium dioxide ( $\text{UO}_x$ ) and mixed uranium plutonium oxide ( $\text{MO}_x$ ) are the most common reactor fuels. Their aqueous reprocessing (including dissolution) will remain of primary importance into the future. One of the more significant factors in the context of fuel dissolution is the rate of dissolution. Although there has been a great deal of work published about the dissolution of uranium oxide in nitric acid, much less has been published discussing the dissolution of  $\text{MO}_x$ .

The dissolution of uranium dioxide in nitric acid is known to occur through an autocatalytic mechanism. This mechanism is considered to be nitrate initiated, and catalysed by nitrous acid, which is a reduction product of nitrate. Based on this information the dissolution rate is affected by nitric acid and nitrous acid concentrations, and as nitrous acid can decompose to nitrogen oxides, other factors such as gas purging, agitation and temperature. As part of this project experiments with uranium dioxide powders have been carried out that supported this mechanism.

The dissolution of  $\text{MO}_x$  has a further complication; that is as  $\text{MO}_x$  is manufactured by the mechanical blending of uranium and plutonium oxides,  $\text{MO}_x$  is actually a range of uranium and plutonium contents. Significantly this material contains small particles (typically pre-irradiation  $< 0.5\%$ ) plutonium-rich oxide grains. As plutonium dioxide does not dissolve readily in nitric acid, these are left after dissolution as plutonium-rich residues. To consider this further two areas of work have been undertaken:

1. Investigations into nitric acid dissolution chemistry for  $\text{MO}_x$  with variable plutonium contents
2. Investigations into the potential of the recovery of undissolved plutonium-rich residues from dissolver sludges that contain insoluble fission products (IFPs), using  $\text{Ag}^{2+}$  MEO.

Batch dissolution experiments using ca. 5 % Pu  $\text{MO}_x$  powders and pellets were undertaken to investigate the role of nitrous acid in the dissolution in nitric acid. Experiments with high surface area  $\text{MO}_x$  powders largely at low temperature have confirmed the significant role nitrous acid plays, **Error! Reference source not found.** The results of these experiments have been used to derive a dissolution kinetic rate expression. Experiments with low surface area  $\text{MO}_x$  pellets were carried out at higher temperatures and high nitric acid concentrations also highlight the significant role nitrous acid plays. The results from these experiments confirm the relevance of conventional nitric acid chemistry for bulk phase  $\text{MO}_x$ . However, thermodynamic calculations show that the ‘nitrous acid’ reaction pathway is energetically unfavourable at higher plutonium contents, corresponding to a published step-change in the solubility of  $\text{MO}_x$  fuel.



**Figure 1: Linear dissolution rate constant for 4.7 % Pu MOx powder, effect of nitric acid and nitrous acid.**

To help consider the viability of the recovery of plutonium-rich residues from dissolver sludges, a 100 mL bulk electrolysis dissolver cell has been designed, constructed and tested. Inactive experiments using linear staircase voltammetry and bulk electrolysis experiments allowed the dissolution cell to be characterized and current limits determined under various conditions. The bulk electrolysis experiments have been modelled and provide a quantitative description of the experimental results. The model allows for the decomposition of water by  $\text{Ag}^{2+}$  and shows the generation, steady state and decomposition (after the current is turned off) of  $\text{Ag}^{2+}$ . After cell characterisation plutonium dioxide powder dissolution experiments were undertaken. These experiments included in-line determination of  $\text{Ag}^{2+}$  and dissolved plutonium concentrations, which have previously only been published by at-line analysis. Comparison of the  $\text{Ag}^{2+}$  and dissolved plutonium results highlighted some interesting features in the chemical kinetics. These experiments provide a sound platform to consider the detrimental effect of the insoluble fission products upon plutonium-rich residue dissolution and to assess the viability of the process for dissolution of advanced fuels.

### III.1.1.4 Conclusions

One of the key steps in any further work programmes considering reprocessing options for future fuels is to develop a 'process specification'. Existing technologies can then be assessed against the specification and technology gaps can be highlighted. Then R&D can be targeted towards these areas. This is particularly important in the area of head end which takes the spent fuels and provides the feed solution to the primary separation plant.

Experimental and mechanistic studies have advanced the knowledge of dissolution chemistry of (unirradiated) bulk-phase MOx and the associated plutonium-rich regions. Also, these and future planned developments in the dissolution of plutonium dioxide with  $\text{Ag}^{2+}$  will allow further assessment of dissolution in the presence of insoluble fission products which are also present in dissolver sludge.

## III.1.2 Ligand Design and Assessment

### III.1.2.1 Introduction

The relevant processes under development in ACSEPT for which new ligand syntheses have been performed are: the 1-cycle SANEX (**1c-SANEX**), the innovative SANEX (**i-SANEX**) and the **GANEX** processes.

**1c-SANEX** aims at simplifying the regular SANEX (*r*-SANEX) that has already been demonstrated with spiked and hot continuous lab-scale tests. The 1c-SANEX co-extracts Am(III) and Cm(III) from a PUREX raffinate solution (i.e., containing Am(III) + Cm(III) + fission products + corrosion products in 3-4 mol/L  $\text{HNO}_3$ ), skipping the DIAMEX process. This requires new ligands highly selective for Am(III) and Cm(III) over the lanthanides(III), fission and corrosion products. Alternatively, masking agents must be found to prevent the co-extraction of some of these elements.

**i-SANEX** aims at co-extracting actinides(III) and lanthanides(III) from the PUREX raffinate, followed by a selective back-extraction An(III) and a final back-extraction of Ln(III). Although this process has already been demonstrated, it can be improved by using new aqueous complexing agents able to perform the back extraction of An(III) at high nitric acid concentration (i.e. without buffering and salting out reagents).

**GANEX** aims at co-separating TRU, after bulk uranium has been removed in a first cycle, from approximately 4 mol/L HNO<sub>3</sub> aqueous solution. In order to be more efficient than the GANEX process that has been developed and tested in CEA/Marcoule, two major improvements could be: (i) finding an extracting agent able to extract directly *only* the actinides from the 1<sup>st</sup> cycle raffinate, and (ii) finding aqueous complexing agents selective for actinides *and* working at high acidity.

### III.1.2.2 Synthesis and screening

During the project, more than 120 new molecules have been synthesized and tested for their potential ability to be used in one of these separation processes. Two third of these molecules are lipophilic extractants intended for the selective extraction of actinides. One third are hydrophilic molecules intended as selective complexing agents either for actinides or for fission and corrosion products.

In order to manage synthesis and assessment and to evaluate the newly synthesised compounds two databases were created: a first one with the compounds synthesised and distributed within ACSEPT, and a second one with the corresponding screening test results. These databases have constantly been updated and published on the ACSEPT website (and were therefore available to the project community throughout the project duration). To prevent synthesis of compounds out of the scope or of compounds already tested elsewhere, the synthesis of new molecules had to be validated by the Project Coordination Committee (PCC): the groups planning the synthesis had to request permission from the PCC before starting the synthesis. Based on the experience from previous European projects it was decided to focus on four organic molecules families: (i) nitrogen heterocyclic compounds, (ii) mixed nitrogen/oxygen-donor compounds, (iii) amide compounds and (iv) sulfur-donor compounds.

Two protocols for testing the lipophilic extractants and the aqueous complexing agents have been established to be followed by the groups involved in this task.

Despite the large number of molecules synthesized and tested, only few have passed the screening tests, i.e. have shown to be more efficient than known molecules for the 1c-SANEX, *i*-SANEX, or GANEX processes.

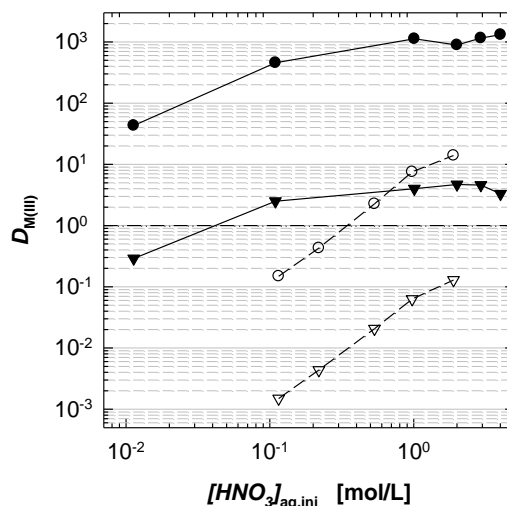
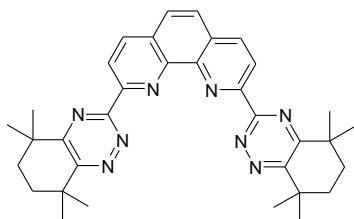
Several new molecules synthesized in the first year and a half of the project are suitable for an *r*-SANEX process. Since however the *r*-SANEX process has been studied and demonstrated earlier, these molecules are out of the scope of ACSEPT. Some new compounds were not soluble enough in the diluents or aqueous phases of interest for ACSEPT (e.g. PyOct-Ac, T8-phen-diketone and COONa)<sub>2</sub>-BTBP). Other molecules had reasonable selectivity for Am(III) over Eu(III) but with too low distribution ratios (e.g. PyTri, PicAc, EsPyTri, PyAcet-Ac, T8-PHEN-CAM, T8-PHEN-TAM, T8-THP-CAM, T8-THP-TAM, T8-phen-diESTER, T8-THP-C/TAM, TWE-23, TWE-27, TWE-28, TWE-29, TWE-33, and TWE-34). Furthermore, some molecules showed good extraction or complexation of Am(III), but without the required selectivity over Eu(III) (e.g. DMDCATHP, UAM-123, UAM-124, TWE-21, TWE-22, TWE-24, TWE-35 and TWE-36). Finally, some new molecules were able to separate Am(III) from Eu(III) without being more efficient than known compounds like the ones developed in the EUROPART project, (e.g. BTTP molecules compared to BTP or BTBP; <sup>1</sup>BuCyMe<sub>4</sub>-BTBP and MeCyMe<sub>4</sub>-BTBP compared to CyMe<sub>4</sub>-BTBP).

However, some of the compounds synthesized and tested during the ACSEPT project had promising properties regarding a possible application in 1c-SANEX, *i*-SANEX and GANEX processes. The most important results are presented below.

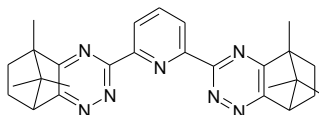
#### III.1.2.2.1 Lipophilic extracting agents

Among the **lipophilic compounds** able to separate Am(III) from Eu(III) in the organic phase, **CyMe<sub>4</sub>-BTPhen** (Figure 2 left) is one of the more promising new molecules. It actually extracts Am(III) with a very good selectivity over Eu(III) (see Figure 2 right) and with extraction kinetics faster than the current reference molecule, CyMe<sub>4</sub>-BTBP. Unfortunately, distribution ratios are very high, which may cause problems in the back extraction part of the process.

**CA-BTP** (Figure 3) has also been demonstrated to be an extracting agent selective for actinides(III), eliminating certain drawbacks of CyMe<sub>4</sub>-BTBP such as low solubility or slow kinetics. Unfortunately CA-BTP is not suitable for 1c-SANEX or GANEX applications due to the formation of a precipitate at the acidity required for the above processes. It may nevertheless be of interest for *r*-SANEX applications since this process works at a lower acidity.



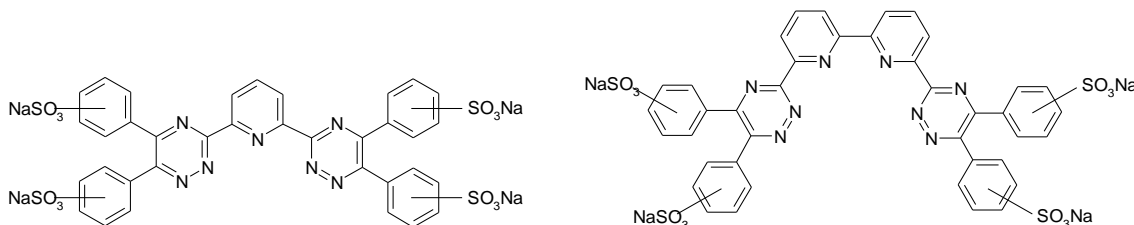
**Figure 2:** Am(III) and Eu(III) extraction into CyMe<sub>4</sub>-BTPhen (filled symbols) or CyMe<sub>4</sub>-BTBP solution (open symbols), distribution ratios ( $D_{Am(III)}$ , circles;  $D_{Eu(III)}$ , triangles) as a function of nitric acid concentration. Organic phase, 10 mmol/L CyMe<sub>4</sub>-BTPhen in 1-octanol or 10 mmol/L CyMe<sub>4</sub>-BTBP + 0.25 mol/L DMDOHEMA in 1-octanol. Aqueous phase, <sup>241</sup>Am(III) + <sup>152</sup>Eu(III) in HNO<sub>3</sub>.



**Figure 3:** CA-BTP.

### III.1.2.2.2 Water soluble complexing agents

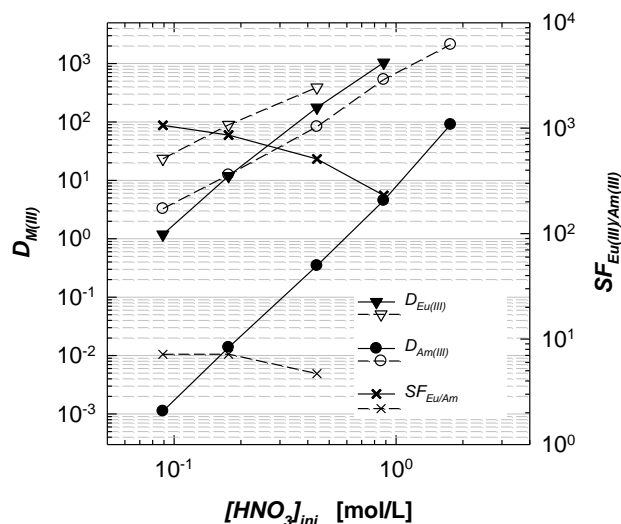
Regarding the **hydrophilic complexing agents**, 3 new molecules have shown remarkable properties: PyTri-Tetraol, SO<sub>3</sub>-Ph-BTP and SO<sub>3</sub>-Ph-BTBP. These ligands do in fact complex Am(III) selectively over Eu(III) in a nitric acid aqueous phase ( $[HNO_3] > 1$  mol/L). They may therefore be used in an *i*-SANEX or GANEX process in order to separate actinides(III) from the lanthanides(III).



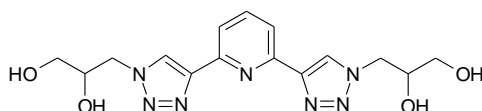
**Figure 4:** SO<sub>3</sub>-Ph-BTP (left) and SO<sub>3</sub>-Ph-BTBP (right).

**SO<sub>3</sub>-Ph-BTP** and **SO<sub>3</sub>-Ph-BTBP** are able to complex Am(III) with a very good selectivity over Eu(III). They can perform this separation up to 2 mol/L HNO<sub>3</sub>, meaning that they can be used without salting out and buffering agents in both the *i*-SANEX and GANEX processes. As shown in Figure 5, addition of 9 mmol/L SO<sub>3</sub>-Ph-BTP to the aqueous phase significantly suppresses Am(III) extraction into a TODGA solvent, whereas it has only small influence on Eu(III) extraction. For 0.1 mol/L <  $[HNO_3]$  < 0.6 mol/L,  $D_{Am(III)} < 1$  and  $D_{Eu(III)} > 1$ . The separation factor  $SF_{Eu/Am}$  is in the range of 250–1000 (as compared to  $SF_{Eu/Am} \approx 7$  without SO<sub>3</sub>-Ph-BTP, being the selectivity of TODGA). Similar results were achieved with SO<sub>3</sub>-Ph-BTBP.

**PyTri-Tetraol** is an effective and selective complexing agent for Am(III) vs. Eu(III). It is able not only to perform this separation in the range of pH = 1–3 ( $SF_{Eu/Am} = 80$ –110,  $D_{Am} < 1$  in combination with a TODGA organic phase), but is also efficient at higher acidities ( $[HNO_3] = 0.5$ –1 mol/L). PyTri-Tetraol is therefore a promising complexing agent for implementation in the *i*-SANEX process. While PyTri-Tetraol is less selective than SO<sub>3</sub>-Ph-BT(B)P, it does not contain sulphur, which is an advantage with respect to the generation of secondary waste.



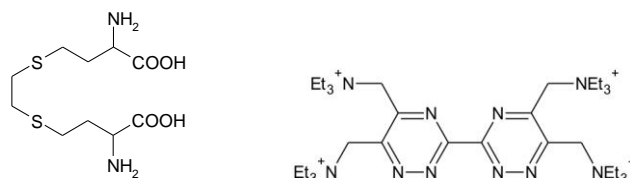
**Figure 5. Effect of SO<sub>3</sub>-Ph-BTP on the extraction of Am(III) and Eu(III) into TODGA.**  
Organic phase, 0.2 mol/L TODGA + 5 % vol. 1-octanol in TPH. Aqueous phase, <sup>241</sup>Am(III) + <sup>152</sup>Eu(III) in HNO<sub>3</sub>, with (filled symbols, solid lines) or without (open symbols, dashed lines) 9 mmol/L SO<sub>3</sub>-Ph-BTP.  
(*D*: distribution ratio on the left scale; *SF*: separation factor on the right scale)



**Figure 6: PyTri-Tetraol.**

### III.1.2.2.3 Masking agents

Finally, some **fission product masking agents** were synthesised and tested. Some of them showed encouraging properties. In the 1c-SANEX or the CHALMEX (Chalmers GANEX) processes, two masking agents gave good results, complexing some fission and corrosion products which would otherwise be extracted by CyMe<sub>4</sub>-BTBP: (i) BIMET is able to complex palladium, molybdenum and zirconium cations without any effect on the extraction of Am(III) or Eu(III); and (ii) (CH<sub>2</sub>-N-Et<sub>3</sub>X)<sub>2</sub>-BT that was demonstrated to be a good masking agent for nickel, palladium and silver.



**Figure 7: BIMET (left) and (CH<sub>2</sub>-N-Et<sub>3</sub>X)<sub>2</sub>-BT (right).**

### III.1.2.3 Structural studies

Additionally structural and speciation studies have been performed on some of the new compounds. Most of these studies have focused on the nitrogen heterocyclic compounds (BTP, BTBP and BTPhen families) in order to assess their behaviour on a molecular scale, which is not exhaustively understood so far.

Even if only a small amount of the newly synthesized and tested molecules are emphasised here it should not be forgotten that the work that has been done in this task has generated a huge amount of data that improve the knowledge and the understanding regarding (i) the strategies to develop new molecules for liquid/liquid extraction processes and (ii) the complexation and extraction of the actinide and lanthanide cations.

### III.1.2.4 Conclusions

Approximately 25 scientific papers have been published in international journals, 4 patents have been registered and more than 40 presentations have been given during the project period. This data shall be considered as a goldmine for the future researches in this field.

The results highlight the difficulty to develop new molecules for challenging liquid/liquid extraction

processes, and aiming at separating elements with similar chemical properties. In fact, (i) the idea at the origin of the synthesis of CyMe<sub>4</sub>-BTPPhen (i.e. to improve extraction, selectivity and kinetics by fixing the rotation around the central C-C bond between the two pyridinyl groups) has been successfully addressed, and (ii) CA-BTP has better extraction properties than most of the previous nitrogen heterocyclic compounds.

Nevertheless, a weakness in only one of the upgraded criteria (the extraction efficiency which is too high for CyMe<sub>4</sub>-BTPPhen, or the trend to form precipitates for CA-BTP) may prohibit the use of these molecules in a liquid/liquid extraction process. The synthesis, the assessment and the structural characterisations that have been performed around these new ligands have however allowed us to increase the knowledge in this domain. Furthermore, CyMe<sub>4</sub>-BTPPhen has also displayed very interesting results regarding its Am(III)/Cm(III) selectivity which might be appropriate for future processes aiming at extracting Am(III) alone (i.e. without Cm(III)).

### III.1.3 Process Development

#### III.1.3.1 Introduction

Several of the molecules synthesized and screened have passed the criteria for being further studied towards process development. This requires determining relevant equilibrium and kinetic data, investigating stability, calculating flowsheets and, finally, performing counter-current process tests.

#### III.1.3.2 Optimisation studies

Optimisation studies were performed using new or known molecules in order to collect the data necessary for designing a separation process. The most advanced optimisation studies were directed towards the development of 1c-SANEX, *i*-SANEX and GANEX processes.

##### III.1.3.2.1 1c-SANEX system

A system for the direct extraction of Am(III) and Cm(III) from a PUREX raffinate was developed based on a solvent consisting of 15 mmol/L CyMe<sub>4</sub>-BTBP + 5 mmol/L TODGA in kerosene/1-octanol (40:60 vol.). Oxalic acid and L-cysteine were used to suppress the co-extraction of some fission products such as Zr, Mo and Pd. Distribution ratios for Am(III), Cm(III), fission and corrosion products under extraction, scrubbing and stripping conditions were determined. Additionally, kinetic measurements in a single-stage centrifugal contactor were performed. A promising 1c-SANEX system was developed which has already been tested successfully (see III.1.3.4.1).

##### III.1.3.2.2 *i*-SANEX system

Two *i*-SANEX systems were developed, based on the co-extraction of Am(III), Cm(III) and Ln(III) from PUREX HAR into a solution of 0.2 mol/L TODGA + 5 % 1-octanol in kerosene. The co-extraction of Zr, Mo and Pd can be suppressed by any masking agent used in DIAMEX processes (HEDTA, oxalic acid, CDTA). One *i*-SANEX system uses PyTri-Tetraol and the other one uses SO<sub>3</sub>-Ph-BTP as stripping agents for Am(III) and Cm(III). In both cases HNO<sub>3</sub> of appropriate concentration is used to keep Ln(III) in the organic phase.

The **PyTri-Tetraol** system shows good separation between Am(III) and Eu(III) (see III.1.2.2.2) and stripping of Am(III) from a loaded organic phase is fast. A drawback of this system is the low separation factor between Am(III) and the light Ln(III) ( $SF_{La(III),Ce(III)/Am(III)} < 2$ ).

The **SO<sub>3</sub>-Ph-BTP** system has very good selectivity for Am(III) and Cm(III) over all Ln(III). With an aqueous phase consisting of 18 mmol/L SO<sub>3</sub>-Ph-BTP in HNO<sub>3</sub>, Am(III) and Cm(III) are stripped (i.e.  $D_{Am(III),Cm(III)} < 1$ ) while Ln(III) stay in the organic phase (i.e.  $D_{Ln(III)} > 1$ ) for 0.2–0.8 mol/L HNO<sub>3</sub>. The minimum separation factor is  $SF_{La(III)/Am(III),Cm(III)} \approx 50$ . Stripping kinetics is fast.

##### III.1.3.2.3 GANEX systems

Two systems for the GANEX 2<sup>nd</sup> cycle were developed, the CHALMEX system and the EURO-GANEX system. The latter system was selected for the hot GANEX tests to be performed in ACSEPT.

The **CHALMEX** system was developed for the direct co-extraction of TRU from the 1<sup>st</sup> cycle raffinate, similar to the 1c-SANEX process. The CHALMEX solvent is a solution of 10 mmol/L CyMe<sub>4</sub>-BTBP + 30 % vol. TBP (or DEHBA) in cyclohexanone. Compared to 1-octanol, a cyclohexanone diluent makes for better solubility of CyMe<sub>4</sub>-BTBP and for faster extraction kinetics. The combination of CyMe<sub>4</sub>-BTBP and TBP (or



DEHBA) allows the extraction of the TRU without redox control; extractable fission products can be masked or scrubbed using suitable masking products or scrubbing solutions. The system has good radiolytic and chemical stability (see III.1.3.3.1). Unfortunately, the density difference between the aqueous and the loaded organic phase proved to be too low for an implementation in centrifugal contactors unless high concentrations of nitrate salt were added to the aqueous phase.

The **EURO-GANEX** system co-extracts TRU + Ln from the 1<sup>st</sup> cycle raffinate, followed by selective TRU stripping, similar to the *i*-SANEX process. Following extensive solvent screening, a solvent consisting of 0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in kerosene was developed which can handle high Pu(IV) loading (e.g. approx. 30 g/L at 4 mol/L HNO<sub>3</sub>). A substitute for oxalic acid (used as a Zr masking agent in DIAMEX processes but not useful in the presence of Pu(IV)) had to be found: CDTA (1,2-cyclohexanediaminetetraacetic acid) efficiently suppresses the extraction of Zr and also masks Pd which would otherwise be co-extracted. In the selective TRU strip section actinides are back-extracted into an aqueous solution containing SO<sub>3</sub>-Ph-BTP + AHA (acetohydroxamic acid) in appropriate concentrations (depending on the amount of Pu(IV) to be stripped). Lanthanides are kept in the organic phase by a sufficiently high nitric acid concentration (approx. 0.5 mol/L); no salting out or buffering agents are required. The challenge with this system is to keep Np in an extractable state, i.e., Np(IV) or Np(VI).

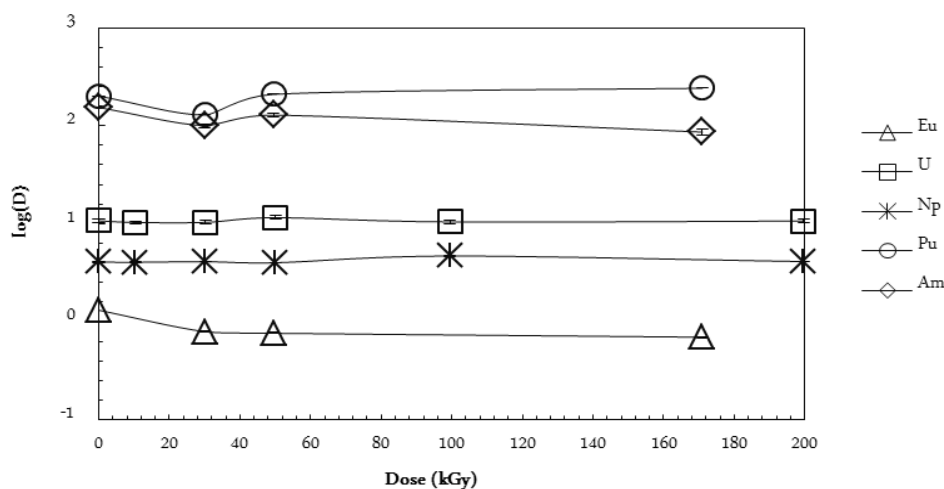
### III.1.3.3 Assessment of ligand stability

The radiolytic and chemical stability of extracting molecules as well as diluents is essential for the development of actinide separation processes. Several molecules suitable for process development were studied with respect to their stability versus radiation and nitric acid. Since these molecules have sufficient stability when in contact with nitric acid the major part of the work performed has been on the radiolytic stability.

In previous projects some studies had been performed on if and how irradiation affects extraction efficiency. While this approach was further followed in ACSEPT, a new focus was set on understanding radiolysis by identifying and quantifying the degradation products. Some degradation products were synthesized and their extraction behaviour was studied. This knowledge could, in a future perspective, help to get a better understanding to design molecules with increased stability.

#### III.1.3.3.1 BTBPs

Although **C5-BTBP** is known to rapidly degrade in contact with nitric acid and upon irradiation, it was used as a model compound to study degradation pathways. A number of degradation products were identified in irradiated solvents containing C5-BTBP in different diluents. These products are formed by oxidative attack of the pentyl moieties of the C5-BTBP molecule. The presence of these degradation products varies with time, absorbed dose and diluent used.



**Figure 8: Gamma irradiation of 0.01 M CyMe<sub>4</sub>-BTBP + 30% TBP in cyclohexanone in contact with 4 M HNO<sub>3</sub>.** Dose rate approximately 0.9 kGy/h for <sup>235</sup>U and <sup>237</sup>Np; approximately 18 kGy/h for <sup>152</sup>Eu, <sup>238</sup>Pu and <sup>241</sup>Am extraction (lines added to guide the eye).

The radiolytic stability of **CyMe<sub>4</sub>-BTBP** was studied by gamma and alpha irradiation. Gamma irradiation with doses of several 100 kGy caused severe degradation of CyMe<sub>4</sub>-BTBP in different diluents not contacted

with nitric acid. However, extraction properties remained practically unaffected when solutions of CyMe<sub>4</sub>-BTBP in contact with nitric acid were irradiated to approximately 200 kGy, see Figure 8.

A comparison of alpha and gamma irradiation of CyMe<sub>4</sub>-BTBP (in presence of HNO<sub>3</sub>) showed slightly less degradation by alpha irradiation ( $7.9 \cdot 10^{-4}$  kGy<sup>-1</sup>) than by gamma irradiation ( $1.1 \cdot 10^{-3}$  kGy<sup>-1</sup>). Investigating radiolytic stability using gamma radiation is therefore (at least in this system) conservative.

#### III.1.3.3.2 TODGA

An exhaustive characterisation of degraded TODGA solutions through a qualitative and quantitative was developed and performed (identification of all the possible degradation fragments and determination of the amount of each of them). The influence of integrated dose, dose rate, polarity of the diluents, pre-treatment (particularly the influence of nitric acid), the structure, and the metal coordination were studied.

TODGA solutions irradiated in contact with nitric acid showed good radiolytic stability; a moderate decrease in Am(III) and Eu(III) distribution ratios was observed. As with BTBPs, a protective effect of nitric acid was observed. Different degradation products were identified in solutions degraded by nitric acid only and in solutions degraded by nitric acid and radiolysis. While degradation by nitric acid is mainly caused by cleavage of the amide group, radiolysis produced additional degradation products from cleavage of the ether bond and from abstraction of octyl moieties. Additionally, TODGA solutions loaded with metal ions showed less degradation.

#### III.1.3.3.3 Conclusions

The radiolysis studies have made significant progress in ACSEPT compared to previous projects. Some lessons learnt are:

1. In order to be relevant with respect to a process, irradiation should be performed in presence on the aqueous phase.
2. Gamma radiolysis is conservative and can thus be used instead of alpha radiolysis.

The identification and synthesis of degradation products have facilitated the possibility not only to construct a more optimized and safer process but also open ways of finding molecules with improved stability.

#### III.1.3.4 Process demonstration

One of the main goals of ASCSEPT was demonstrating novel process options such as 1c-SANEX, *i*-SANEX and GANEX processes. Applying some of the chemical systems developed, several process tests were successfully performed using lab-scale counter-current contactor setups.

Computer codes were used to calculate flow-sheets for lab-scale demonstration tests of 1c-SANEX, *i*-SANEX and GANEX processes to be performed in counter-current centrifugal contactor setups. These calculations are based on equilibrium and kinetic data collected in the optimisation studies.

##### III.1.3.4.1 1c-SANEX

A spiked 1c-SANEX test was performed using the system developed in ACSEPT (see III.1.3.2.1). A flow-sheet was calculated (see Figure 9) and the test was performed using a spiked synthetic PUREX raffinate as feed solution. The co-extraction of Zr and Mo was prevented using oxalic acid. Co-extracted Pd was selectively stripped using an L-cysteine scrubbing solution. The recovery yield in the product solution was 99.8% for Am(III) and 99.4% for Cm(III). Except for Y(III) (8.8 % of the initial amount), the product solution contained only low concentrations of Pd (0.8 % of the initial amount) and Ln(III) (< 1 % of the initial amount). Experimental and calculated concentration profiles were in good agreement. For further optimization of the flowsheet, an additional scrubbing has to be added for the specific management of yttrium.

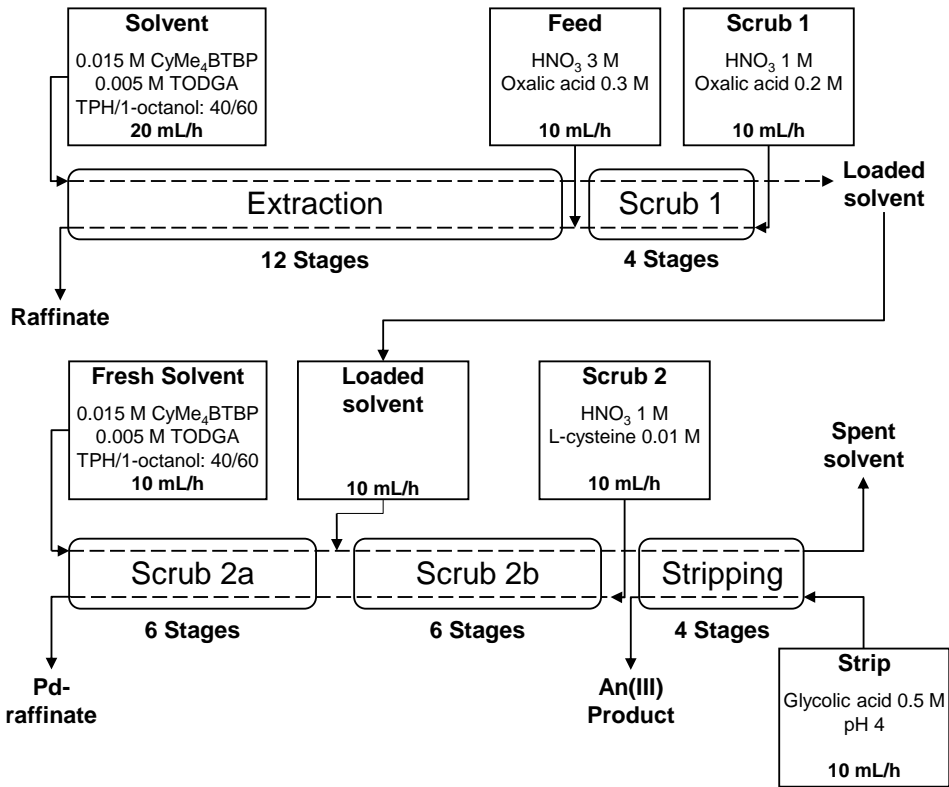


Figure 9: 1-cycle SANEX process flow-sheet.

### III.1.3.4.2 *i*-SANEX

A hot *i*-SANEX process demonstration was carried out using a system based on the co-extraction of Am(III), Cm(III) and Ln(III) into a TODGA + TBP solvent followed by selective stripping of Am(III) and Cm(III) using a buffered DTPA solution (see Figure 10 for the flow-sheet).

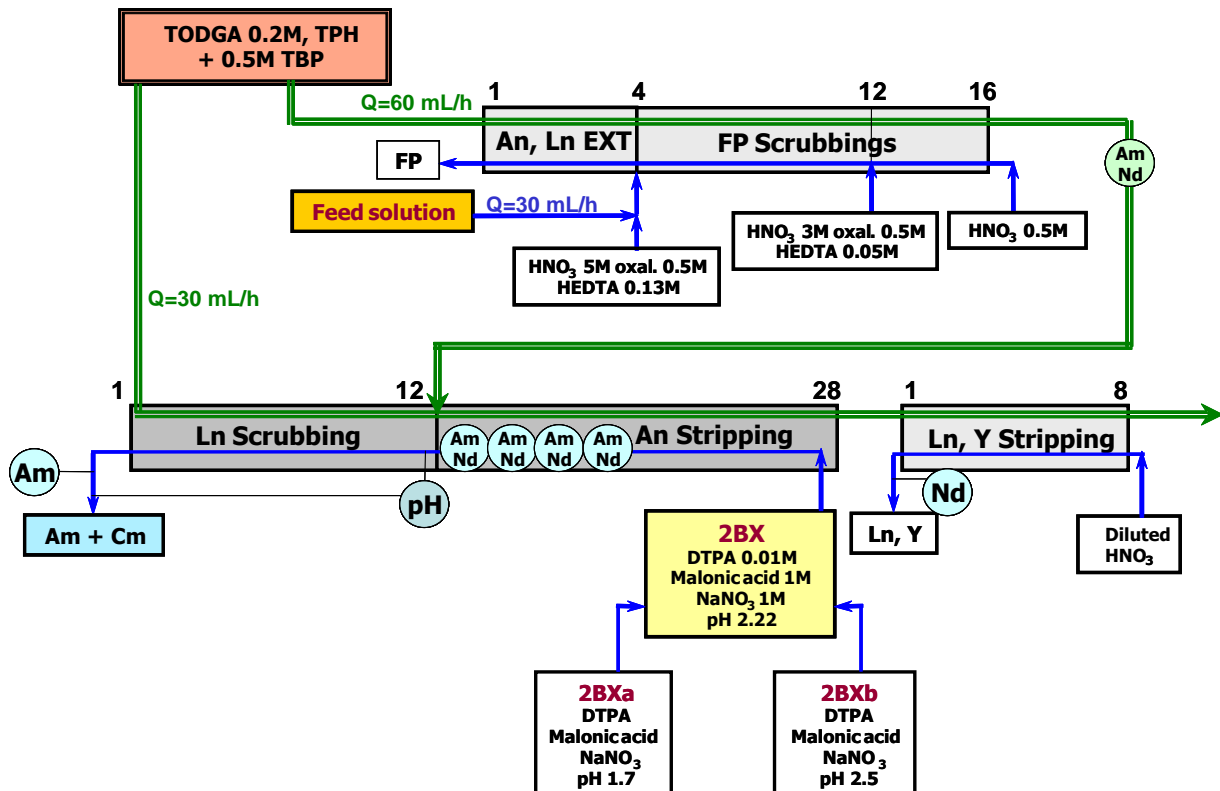


Figure 10: Optimized process flowsheet for the *i*-SANEX hot test.

Feed solution was a genuine raffinate from a PUREX hot test performed earlier. The test performed successfully. The recovery yield was > 99.8% for Am(III) and 99.9% for Cm(III). Moreover, the Ln(III) decontamination was excellent (less than 2% by weight of Ln(III) versus An(III) in the final product). Calculated concentration profiles were in good agreement with experimental results.

### III.1.3.4.3 GANEX

Based on the EURO-GANEX system (see III.1.3.2.3) a flow-sheet was developed and optimised. Several process tests were run using spiked surrogate feed solutions containing Pu in nominal concentration (10 g/L), giving feedback to the flow-sheet calculations towards a final flow-sheet for the hot test.

Before the hot EURO-GANEX process test a GANEX 1<sup>st</sup> cycle process had to be run to prepare the genuine feed solution (Figure 11). 117 g fast reactor fuel was dissolved in 6 mol/L HNO<sub>3</sub>. U was extracted from this solution in a GANEX 1<sup>st</sup> cycle process, leaving a raffinate solution containing 10 mg/L U, 18.3 g/L Pu and 240 mg/L Am. This solution was adjusted to 10 g/L Pu and 5.9 mol/L HNO<sub>3</sub> and used as feed solution in the hot EURO-GANEX test.

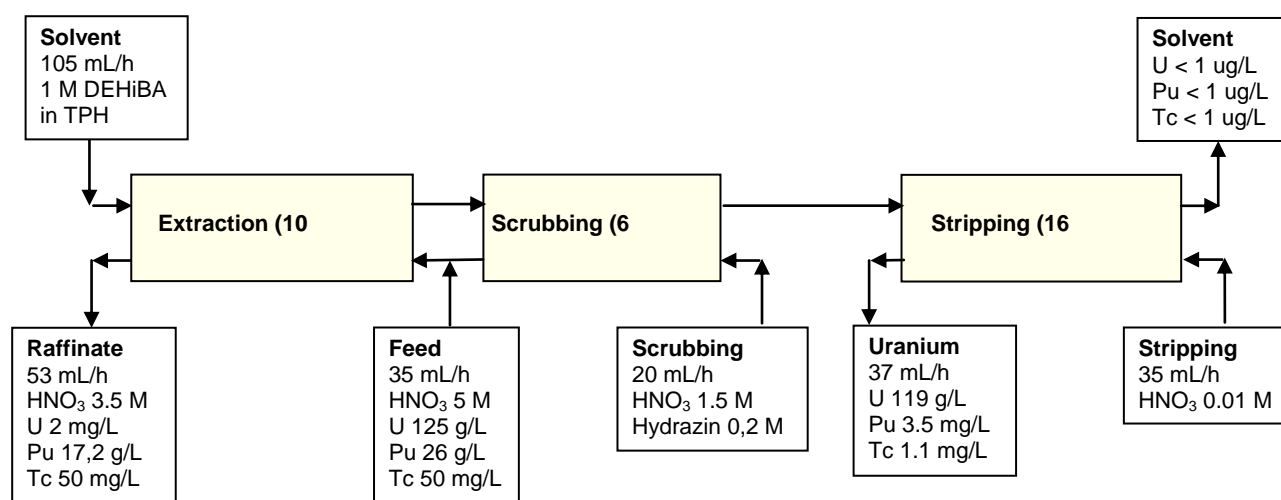


Figure 11. 1<sup>st</sup> cycle GANEX flowsheet with calculated efficiencies developed by CEA for the ITU tests.

The hot EURO-GANEX test (see Figure 12) was run on two consecutive days (day 1, extraction/scrubbing; day 2, stripping). The extraction/scrubbing experiment was run for 6 hours to build up steady state conditions and continued for another 10 hours for collection of loaded organic phase at steady state. Recoveries are shown in Figure 13. Using 12 extraction stages a near to complete separation of An was achieved. In particular, losses of Np, to the raffinate were minimal (less than 0.1 %).

The flow-sheet used for the back-extraction of actinides and lanthanides is shown in Figure 14. Selective backextraction of actinides was achieved by a mixture of water soluble BTP in combination with AHA, at an acidity of 0.5 M in 6 stages. 6 stages are used for re-extraction of lanthanides backextracted with the actinides. Finally 4 stages are used for backextraction of lanthanides using 0.01 M HNO<sub>3</sub>.

The process has been highly successful. An almost complete recovery (99.9%) of Pu, Np and Am has been achieved. The selectivity is also excellent with less than 0.1 % of the lanthanides in the actinide product. The lanthanides have also been efficiently backextracted into the Ln product (recovery > 99.9 %), together with less than 0.1 % of the actinides. The level of An and Ln impurities in the used solvent is also less than 0.1 %. Impurity levels can be managed to even lower levels if more stages are added.

With these experiments the GANEX process, i.e. global recovery of all actinides, has been successfully demonstrated using a Pu rich fast reactor fuel. This was one of the main objectives of the ACSEPT program.

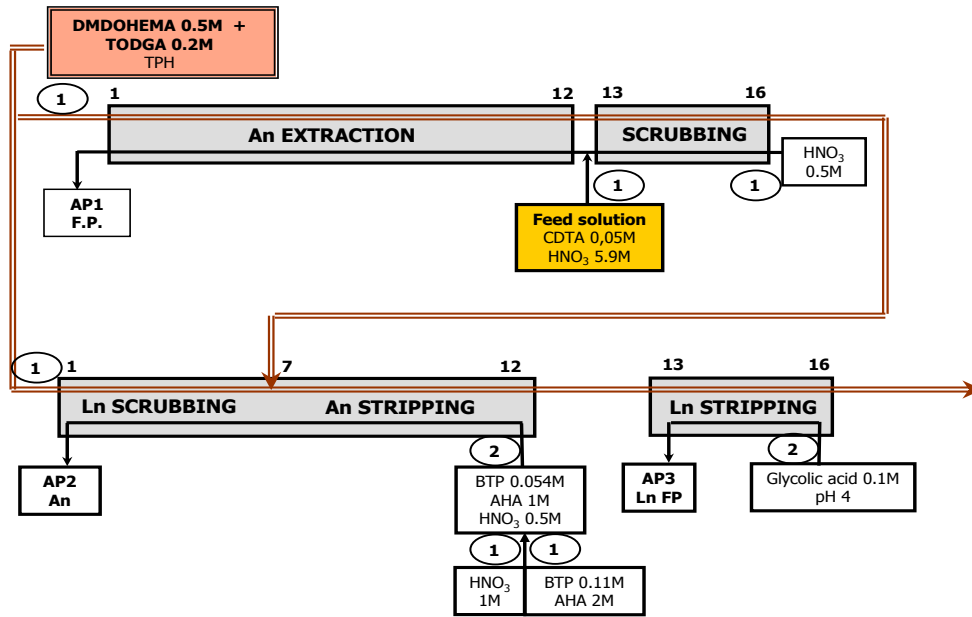


Figure 12. EURO-GANEX flow-sheet for the hot test.

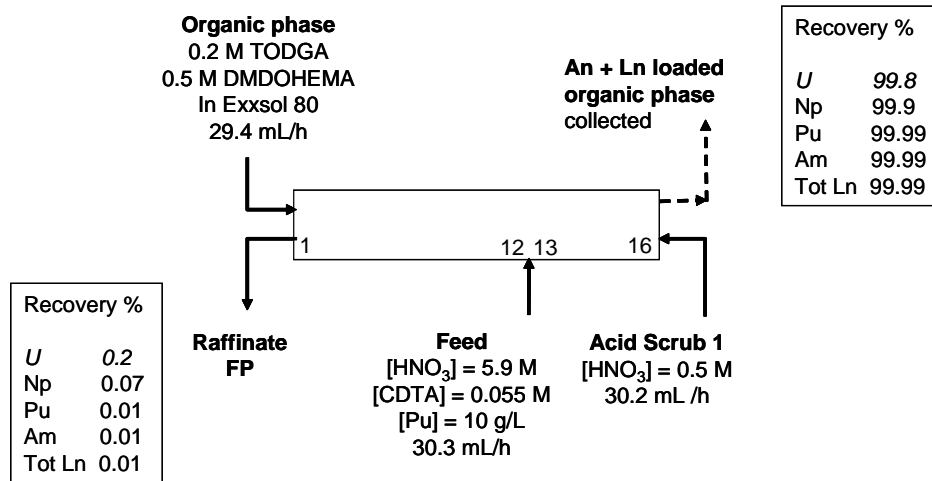


Figure 13. 2<sup>nd</sup> cycle GANEX flow sheet – An extraction and scrubbing

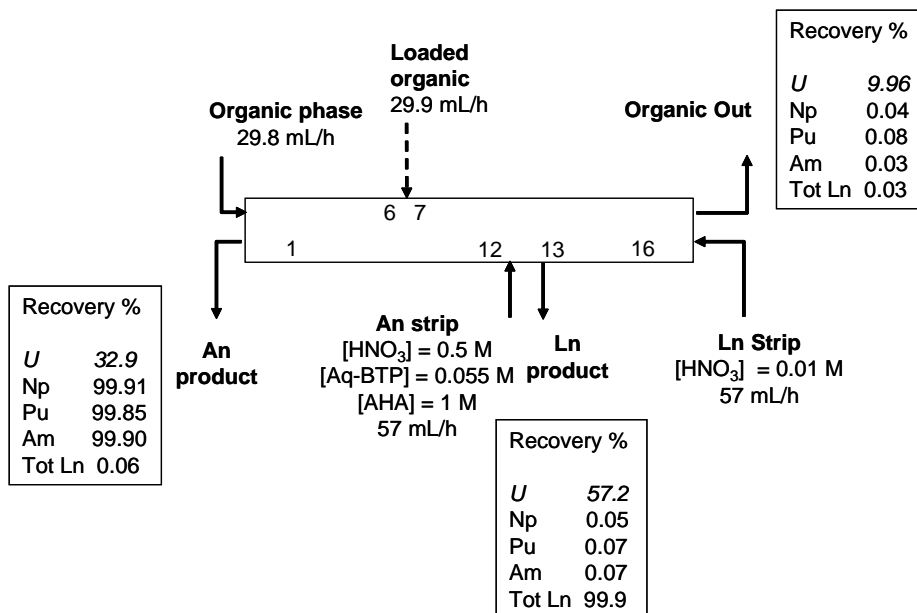


Figure 14. 2<sup>nd</sup> cycle GANEX flow sheet – An stripping

### III.1.3.5 Conclusions

Based on new molecules synthesized and screened in ACSEPT, several new systems were developed and optimised: a 1c-SANEX system and two *i*-SANEX systems for the separation of Am and Cm from PUREX raffinate and two GANEX systems for the co-separation of all TRU. CyMe4-BTBP and TODGA, two molecules of crucial importance to these processes, were investigated with respect to their stability versus radiation in contact with HNO<sub>3</sub>. Finally, several flow-sheets were developed and a spiked 1c-SANEX test, a hot *i*-SANEX test, several Pu-active GANEX tests and a hot GANEX test were successfully performed.

## III.1.4 Actinide co-conversion

### III.1.4.1 Introduction

In the various concepts for future nuclear systems, co-management of two or more actinides (and possibly an “inert” element) has often been put forward recently. It improves and simplifies the nuclear fuel cycle for many reasons, particularly when dealing with minor actinides, noticeably at the back-end of the spent fuel treatment and at the front-end of the fabrication of a new fuel.

Then, actinide co-conversion processes can play an important role by closing the actinide co-partitioning steps and producing in the same time mixed actinide solid compounds used as starting materials for the fabrication of new objects. Different co-conversion concepts are today conceivable, based on co-precipitation operations, sol-gel transition, matrix infiltration, thermal co-denitration or other related techniques.

For the development of innovative fuel cycles such as those conceived in GenIV reactors, uranium based material was taken as the reference fuel matrix material within the ACSEPT project, whereas in EUROPART inert matrix material (zirconium based) was investigated.

At CEA and FZJ the internal gelation route in continuation of the EUROPART project was studied. Synthesis of ascorbate- hydroxyl- uranyl sols directly from uranium trioxide and ascorbate- nitrate hydroxyl-uranyl sols from uranyl nitrate and ammonium poliuranates (ADU) has been elaborated at ICTHJ using the Complex Sol-Gel Process (CSGP). Among the innovative methods for such co-conversion of mixed actinides solutions, the method based on the application of the so called “solid extractants” (SEXs) was studied at CTU in Prague.

### III.1.4.2 Co-conversion by internal gelation

The internal gelation is a well-known method to produce microspheres suitable as sphere-pac fuel or as precursors for fuel pellet fabrication. In common with all such processes, concentrated metal nitrate feed solutions are prepared, cooled, and mixed with cold concentrated solutions of HMTA and urea to form a broth that can be dispensed as droplets. In this context the research at FZJ was focused onto the following topics: the preparation of Acid Deficient Uranyl Nitrate solution (ADUN), the determination of the gelation point by viscosity method, studies on the radiolytic stability of the organic compounds involved in the sol-gel process, the calculation of the hydrolysis of Nd<sup>3+</sup>, Pu<sup>3+</sup> and Am<sup>3+</sup> in uranyl nitrate solution, the fabrication of U/Nd microspheres by internal gelation, and the improvement of the thermal treatment of the microspheres in order to optimize the integrity.

Microspheres containing 90% U and 10% Nd (as minor actinide surrogate) have been successfully fabricated. It was found that crack-free microspheres can be generally obtained from a saturated uranyl nitrate precursor solution, if the organic compounds are added in solid form instead of dissolving them prior to addition. However, the use of ADUN is beneficiary, since the uranium concentration and pH increases in precursor solution and therefore less HMTA is needed for gelation. The effect of HMTA on sinterability and crystallinity was demonstrated by SEM and XRD studies after thermal treatment. The less HMTA was needed for gelation the better the sinterability and crystallinity and finally the integrity of the microspheres was observed. Concerning the optimisation of thermal treatment it was found that a reduction to UO<sub>2</sub> in the calcination step mainly improves the stability of the microspheres during calcination and sintering because it prevents an intermediate oxidation of the microspheres from UO<sub>3</sub> to U<sub>3</sub>O<sub>8</sub>.

Subsequently to the internal gelation of uranium and mixtures of U and Nd, experiments related to U/Pu and U/Am gelation were carried out at CEA, within the Atalante facility. In cooperation with CEA, Marcoule internal gelation of Pu<sup>3+</sup> (5 – 45 mol%) and Am<sup>3+</sup> (10 mol%) microspheres was successful. From ultra-violet-visible spectrophotometry (UV-Vis) measurements, the oxidation states of Pu and U in the precursor solution was found to be +III and +VI, respectively. No significant changes in UV-Vis spectra of Am containing gels before and after drying were evident. After a calcination at 600 °C a solid solution of (U/Pu)O<sub>2</sub> and (U/Am)O<sub>2</sub>

was observed in XRD measurements.

#### ***III.1.4.3 Co-conversion by external gelation***

The external gelation processes are the widest used processes in the sol-gel production of nuclear fuels. Research and production of advanced ceramic materials by classic sol-gel methods have been carried out in the Sol-Gel Laboratory of ICTHJ for more than thirty years. During these years, modifications of classic sol-gel method were compiled. One of them is the Complex Sol-Gel Process (CSGP) studied within ACSEPT.

This process consists of a preparation of starting metal(s) salts solution, an addition of very strong complexing agents (ascorbic acid) with strong reducing power, the formation of a complex sol solution, a partial hydrolysis of sols by an addition of ammonia accompanied with controlled increasing viscosity, then a gelation by evaporation of water accompanied by a partial evolution of volatile components and finally a non-destructive thermal treatment in conditions required for preparation of final materials with desired properties. Three ways of preparation of uranyl sols by the Complex Sol-Gel Process (GSGP) were studied at ICTHJ:

- I. Synthesis of ascorbate- hydroxyl- uranyl gels from  $\text{UO}_3$ ,
- II. Synthesis of ascorbate- nitrate- hydroxyl- uranyl gels from uranyl nitrate,
- III. Synthesis of ascorbate- nitrate- hydroxyl- uranyl gels from ammonium poliuranates (ADU).

Irregularly shaped powders and microspheres were obtained from these sols. The gels obtained were thermally treated and then reduced to  $\text{UO}_2$ . The CSGP process can be used to synthesize  $\text{UO}_2$  doped with Nd (as minor actinide surrogate), as irregularly shaped powders or spherical particles. Neodymium oxide was homogeneously distributed in the  $\text{UO}_2$  phase, and does not form any separate phase.

#### ***III.1.4.4 Co-conversion of actinides using solid extractants***

Solid extractants are composite materials containing a liquid extracting agent (or its solution in an organic diluent) supported on a suitable carrier (supporting material or binder). Nowadays, these materials are mostly used for separation and concentration of ions by extraction chromatography. Several such solid extractants, using polyacrylonitrile (PAN) as a support, were developed at CTU in Prague and studied in the EUROPART project for the separation of minor actinides from the radioactive waste issuing reprocessing of the spent nuclear fuel.

The results of the studies carried out in ACSEPT demonstrated that U, Eu, Ce, and Th solutions may be converted to the respective mixed metal oxides by means of solid extractants containing fully combustible extraction agents. Mixed oxides of the type U/Eu, U/Ce, Ce/Eu, and U/Th were prepared. The oxides produced are clean and they contain 0.2–0.4 % (wt/wt) of graphite.

The products of the conversion are microcrystalline and easy to handle, e.g. by pressing. All the oxides produced were characterised by XRD analysis. It was verified that all cases, after uranium reduction, fluorite type cubic crystal lattice is produced and that minor metal is distributed in the crystals as a solid solution.

Application of DMBTDMA (DMDOHEMA), TODGA, and Aliquat 336 extraction agents or their mixtures was tested; however, any extraction agents meeting the CHON principle may be used. This flexibility enables a broad variability of the conditions for the conversion. Infiltration method using porous beads of neat polyacrylonitrile (B-PAN) was tested in addition to the solid extractant method. The advantage of the infiltration method is that this method may be used also for direct infiltration of organic solutions of extraction agents containing extracted actinides.

#### ***III.1.4.5 Conclusions***

From the results that have been obtained from FZJ, CEA, ICTHJ and CTU and the cooperation of all groups it can be concluded that the internal gelation, the GSGP as well as the solid extractant based co-conversion route are suitable methods to fabricate  $\text{UO}_2$  microspheres containing trivalent actinides (or at least surrogates in some cases, up to now) for the heterogeneous recycling of MA in Gen IV reactors. The highlight of this working package was the successful fabrication and characterization of U/Pu and U/Am microspheres.

## **III.2 Domain 2 – Pyrometallurgy**

In pyrometallurgy, the objectives of the ACSEPT were to develop pyrochemical separation processes beyond the current state of the art, as an alternative option for the longer term. The work was centered on the two reference cores of process identified during EUROPART, and aimed at the validation of the scientific feasibility of each technological brick, at laboratory scale. Indeed, studies were not limited to the recovery of actinides, but also focused on the head-end steps, on the salt purification and recycling and on the waste conditioning, the ultimate goal being to propose a reprocessing scheme allowing actinide fluxes suitable for fuel refabrication.

Among the initially identified key issues, the recovery of actinides from both actinide-aluminum alloys and used salt has been demonstrated at laboratory scale with innovative methods, which strengthen the two reference processes. Some methods have been validated with experiments involving transuranic elements (use of irradiated MOX fuel for thermal treatment studies and reductive extraction in liquid cadmium; assessment of minor actinides behavior during the reductive extraction and the back extraction on/from liquid aluminum; exhaustive electrolysis of chloride salts containing U-Pu-Np), while some others have been established with uranium only (electroreduction of  $\text{UO}_2$  in fluoride solvents, back extraction of U from U-Al alloys by chlorination, U electrodeposition in molten fluoride salts). As developed in the following sections, many other steps have been addressed with inactive materials.

The work also led to the development of new experimental devices, like an inductive vaporization device coupled to ICP-MS analysis, an in-situ HF gas generation set-up, a glove box equipped with an HF line for fluoride processes studies, a liquid metal drooping system, an electrolyser for maximizing the actinide recovery in used salts.

Finally, several studies were devoted to more fundamental research that improves the basic knowledge of high temperature molten salts chemistry (molecular dynamics simulation, NMR studies of fluoride salts, thermochemical data acquisition).

The main results of the program are presented in the following sections.

### **III.2.1 Head-End Steps**

The head-end steps cover all operations taking place ahead of the core of process, i.e. mainly the decladding, the thermal treatment and the conversion of the fuel into a form suitable for its dissolution in the molten salt solvent. Apart from conversion of oxide fuels by chlorination in the view of dissolution in chloride salts, head-end steps were not a priority in the frame of the previous projects PYROREP and EUROPART. Within ACSEPT, the work focused on the thermal treatment of the fuel, and on its conversion into metal or fluorides.

#### **III.2.1.1 Thermal treatment**

Along with the recent developments in the head-end of reprocessing technology, a novel technique of thermal treatment for actinide recovery from irradiated fuel has been proposed and successfully tested at PSI. The method is aimed to separate the short-lived and neutron absorbing Fission Products (FPs) from irradiated fuel into the gas phase when thermal release is promoted by means of inductive heating under controlled redox conditions. The device for Inductive Vaporization (InVap) was designed using the computer aided engineering (CAE) approach. Coupling of the InVap to the inductively coupled plasma mass spectrometer (ICP-MS) allows online tracing of the FPs released. After the operational parameter optimization, the InVap was shown to give good reproducible signals at the highest operational temperature of 2300°C. Annealing tests with non-active material as well as with irradiated oxide fuel with different burnups were performed to demonstrate the capabilities of the InVap concept. Post-annealing gamma spectrometry examination showed that almost no detectable activity was left in the samples.

In parallel theoretical calculations of the FP speciation (thermodynamic modeling) and kinetics of the FP release from the fuel was performed using Gibbs Energy Minimization Selector (GEMS) and Module of Fission Product Release (MFPR), respectively. The mentioned theoretical approaches help to evaluate experimental results and to get better insight into the irradiated fuel chemistry and FP behavior under elevated temperature conditions, which is of high concern for reprocessing technology.

The release of most of the heat-inducing FPs from the samples was proven to be possible while U and TRU remain in the sample holder of the InVap device. This fulfills one of the main requirements of the future reprocessing technology of the closed fuel cycle. Moreover, by applying a definite annealing regime in combination with reducing or oxidizing gas mixtures, it is possible to promote the selective removal of FPs,



whose chemical state and properties are different as a function of the redox conditions.

Annealing of non-irradiated carbide has been investigated with use of thermal gravimetric analysis (TGA) under different redox conditions. The most efficient treatment was shown to proceed under CO<sub>2</sub> atmosphere. The final product of incineration (UO<sub>2</sub>) possesses the best dissolution properties, whereas the reaction is less exothermic than the oxidation under ambient air oxygen concentration. Such a treatment is compatible with the InVap design and can be performed prior the partitioning of FPs by annealing treatment.

### ***III.2.1.2 Fuel conversion into fluoride and metal***

Two ways of fuel conversion have been studied within ACSEPT. The first, developed at CEA, aimed at converting oxide fuel into fluorides. The other, studied both at CIEMAT and CNRS-LGC, was focused on the reduction of the fuel into metal.

At CEA, the feasibility of hydrofluorination with an "in situ" HF gas generation set-up was assessed. Some elements on thermodynamics and kinetics of hydrofluorination reaction were learnt thanks to this study. The reliability of the hydrofluorination set-up through a chemical reaction involving "in situ" HF gas generation was demonstrated. This set-up could be implemented in a hot cell.

The work evidenced an important issue concerning the hydrofluorination route: zirconium conversion is, at the best, only partial. This is not a serious problem in the case of a high activity experiment with objectives limited to studying some steps of the process. On the other hand, obtaining an incomplete zirconium fluorination could be an issue for the process flowsheet, so the consequences of this point will have to be more closely investigated in the future.

At CIEMAT and CNRS-LGC, the so-called direct reduction process, consisting in an electroreduction of solid oxides into metal in a molten salt solvent, was studied. This route is the reference process for the conversion of spent fuel in USA, Japan and Korea, but there was no expertise within the European community before the start of the ACSEPT programme.

The complete reduction of the oxides tested in chloride media (CIEMAT) was not achieved. In the case of TiO<sub>2</sub> only a partial reduction of TiO<sub>2</sub> into Ti oxides of lower valence and calcium titanates were obtained; these compounds are formed in the early stages of the reduction as it is published in the literature. In the case of UO<sub>2</sub>, only traces of metallic U were detected in a couple of samples. The under-potential deposition of the solvent cations was observed, indicating thus that chemical reduction is also produced. The problems encountered with the anode performance show that in this media the oxide content, in Li<sub>2</sub>O or CaO, is an important parameter to take into account as well as a good separation of the anode compartment.

The low temperature used in the experiments performed at CIEMAT was not appropriate for this type of process. The diffusion of oxide ions in solid phase as well as the oxide solubility in the molten salt are processes favoured at higher temperature than those used. Moreover, the low conductivity of the oxide material tested and its low porosity was an additional difficulty for the progress of the reduction reaction. Due to internal problems, no work on SIMFUEL material has been performed.

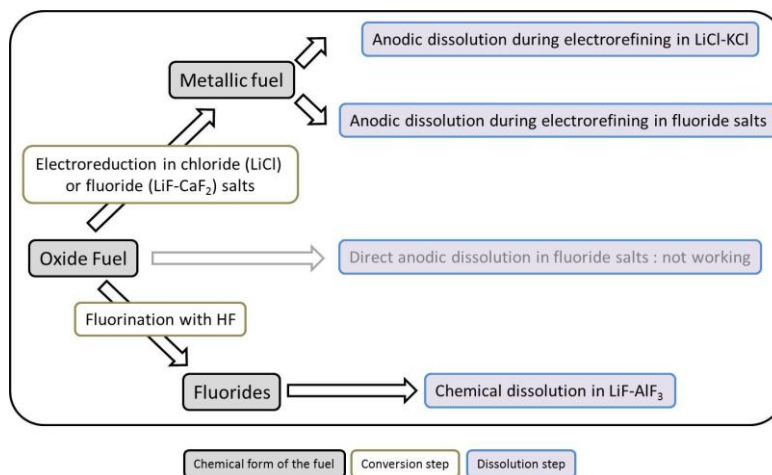
At CNRS-LGC, for the first time, fluoride salts have been tested instead of the usual chloride molten salts (CaCl<sub>2</sub> or LiCl) in order to evaluate their potentialities as electrolytes for the direct electrochemical reduction. An oxygen-evolving gold electrode was used as an anode, for which an absence of corrosion has been observed. This could help to solve the recurrent problem of the anode material faced in chloride medium (the options being to use a consumable carbon anode which produces CO<sub>2</sub>, but also carbides at the cathode, or a Pt anode which is subject to a noticeable corrosion). A complete conversion into metal for Fe<sub>3</sub>O<sub>4</sub>, SnO<sub>2</sub>, and TiO<sub>2</sub> was achieved at 750-850°C. UO<sub>2</sub> samples were also fully reduced, which demonstrates the feasibility of using the electrochemical direct reduction as a head-end step in the pyro-treatment process. Moreover, the first results on MOX direct reduction obtained are promising (performed at ITU).

With these lab-scale experiments, the results regarding the cathodic reaction obtained in fluoride salts are of comparable quality with those published by many workers in chloride salts, with the advantage of using an inert gold anode. However, a drawback is that the frozen salt trapped in the metallic matrix is difficult to remove at the end of the reduction reaction, since the fluorides are not water-soluble.

### ***III.2.1.3 Fuel dissolution***

The way of dissolving the fuel into the molten salt solvent is strongly depending on both the chemical form of the fuel and on the subsequent core of process. A **summary of the options** is presented in Figure 12.

The fuel conversion into fluorides using hydrofluorination aims at a chemical dissolution in the LiF-AlF<sub>3</sub> solvent, for further liquid-liquid extraction of actinides in an aluminium pool. The fuel conversion into metal aims at an anodic dissolution during an electrorefining process. On top of these routes, an exploratory study aiming at the direct anodic dissolution of oxide fuel into a fluoride salt mixture was performed at CNRS-LGC. The expected reaction, based on past studies on the dissolution of SnO<sub>2</sub> in fluoride melts, was finally not successful in the case of UO<sub>2</sub>: the anodic dissolution of oxide fuel into soluble U(IV)/U(III) species in molten fluoride salts was proven to be inefficient.



**Figure 12: Summary of the options concerning the conversion/dissolution of the fuel during head-end steps**

The work concerning the head-end steps has thus provided additional knowledge on the pyrochemical process of spent fuel. In the case of a core of process based on electrorefining, the direct reduction of the fuel into metal is confirmed as the main option, and fluoride-based solvents may solve drawbacks of the reference process involving chloride solvents. In the case of liquid-liquid reduction in molten fluoride salts, the fuel conversion could be realized by the way of hydrofluorination, but it requires more work about the conversion of zirconium oxide.

### III.2.2 Process Development

The main objective of this activity has been defined as the development of the processes involved in pyrochemical separation of actinides, according to the reference technologies selected within the last projects: liquid-liquid reductive extraction and electrorefining of actinides onto solid aluminium cathodes. In order to cover the fields (Electrochemical processes in molten chloride medium, Electrochemical processes in fluoride medium, Processes based on reductive extraction and Methods for the recovery of An from Al), the following topics have been studied:

- Evaluation of the electrochemical processes (electrorefining, exhaustive electrolysis) in chlorides (ITU),
- Definition and lab-scale demonstration of a process for recovery of An from An-Al alloys (ITU, CEA),
- Validation of efficiency of reductive extraction in molten chlorides (CRIEPI, ITU),
- Evaluation of the electrochemical processes in molten fluorides (ITU, CNRS-LGC, NRI, ANSTO, CEA),
- Alternative electrochemical process in fluorides using liquid metal dropping electrode (CEA).

#### III.2.2.1 An recovery by electrorefining including the exhaustive electrolysis in chloride medium

A high efficiency of the electrorefining process, an excellent recovery of An over Ln, a high capacity of solid Al to take-up An was already demonstrated. Studies of electrochemical properties of the An-Al alloys formed during the process have been launched. In the present project, the electrochemical behaviour of Np, Pu and Am in molten LiCl-KCl was investigated on reactive solid Al electrodes at temperatures 400 - 550°C. The composition and structure of the An-Al alloys were investigated by XRD and SEM-EDX.

All studied actinides have shown very similar characteristics on Al and the formation of An-Al alloys was detected at potentials more positive than reductions of An to the pure metals (under-potential deposition effect). The observed deposition potentials  $E(M^{3+}/M^0-Al)$  at 450°C are -2.25V, -2.38V, -2.43V and -2.48V vs. Cl<sup>-</sup>/Cl<sub>2</sub> reference for M = U, Np, Pu and Am, respectively. The structures of the deposits were evaluated. While granular deposits with relatively high porosity were obtained in case of U, dense deposits with only

small cracks filled with salt have been observed for the Np and Pu. The alloys were composed mainly of  $\text{AnAl}_3$  (major for U, Np and Am) and  $\text{AnAl}_4$  (major for Pu) compounds. In addition, Zr electro-chemical behaviour during the electrorefining process of An-Zr based fuel was studied in order to evaluate the portion of recovered An without dissolution of Zr from the fuel in dependency on the current density. The results indicate possibility to dissolve majority of An (97%) without massive dissolution of Zr at the current density of  $15 \text{ mA/cm}^2$ . Almost complete An content, 99.1%, was dissolved with only 3 % of co-dissolved Zr. 81.2% of An was dissolved with no co-dissolution of Zr. Only low Zr content was detected in the deposits and its quality was not influenced.

The exhaustive electrolysis technique has been studied to evaluate feasibility of the process for purification of the salt from electrorefining. A dedicated experimental set-up was designed, manufactured and tested successfully during the project. The main parts are chlorine gas producing inert anodes and a quartz electrolyser with an Inconel gas tightened lid enabling precise manipulation with the electrodes. A series of galvanostatic electrolyses aimed to the selective recovery of An were carried out in molten LiCl-KCl electrolytes, followed by an experiment focused on a complete recovery of all An with certain portion of Ln in a multistage electrolysis. First experiments were carried out with melts containing only  $\text{UCl}_3$  and a mixture of  $\text{UCl}_3\text{-NdCl}_3$  at a mass ratio of approximately 1:1. Almost all U was recovered; the final concentrations in the melts were 0.1 and 0.14 wt%, respectively. Relatively high current efficiencies ( $>90\%$ ) were achieved, but low normalised average current densities had to be applied,  $-2.5$  and  $-1.3 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{wt}\%(\text{U})^{-1}$ , respectively, to keep selectivity. In the final experiment, Pu and Np were completely recovered from an electrolyte containing 3 times higher concentration of Nd than the initial content of the An. Concentration of An was decreased from 2.1 down to 0.7 wt% during selective part of the experiment, when the current density was above  $-2.0 \text{ mA}\cdot\text{cm}^{-2}$ . Then co-deposition of actinides and Nd was carried out up to recovery of all actinides with average current density  $> -4.0 \text{ mA}\cdot\text{cm}^{-2}$ .

### ***III.2.2.2 Evaluation of the electrochemical processes in molten fluorides***

In order to develop a novel separation process based on electrochemical methods in fluoride melts, the knowledge of fluoride systems has to be expanded. Dedicated experimental set-ups were designed and manufactured, electrochemical behavior of uranium and selected relevant elements in  $\text{LiF-CaF}_2$  and  $\text{LiF-NaF-KF}$  melts was studied and recovery of uranium by electrolysis using pulsed current technique in molten fluorides using reactive Ni cathode was investigated. Negative influence of oxygen contamination was experienced and preliminary tests of oxygen catching ability of  $\text{ZrF}_4$  were performed. Possibilities of a liquid Bi cathode in molten fluorides were evaluated and the relevant anodic reaction was investigated and defined as nitrogen evolution.

The new equipment for electrochemical experiments in molten fluoride media and synthesis of actinide fluorides has been designed, constructed and installed in the laboratory in ITU: Argon glove-box connected to a HF gas line, a high temperature Inconel electrolyser resistant against HF gas and a high temperature fluorination reactor. A new high temperature electrolyser for work with  $\text{LiF-CaF}_2$  melts was designed, manufactured and successfully set to operation in NRI. A special apparatus for measurement of interfacial tension of liquid metal in molten fluorides has been prepared in CEA.

The electrochemical behaviour of U(III) was studied in molten  $\text{LiF-CaF}_2$  at 1083 K on inert W and reactive Ni electrodes. Electrorefining of uranium plate in a melt containing Gd(III) ions was performed and selective reduction of U(0) on Ni electrode was achieved. Mechanism of uranium nucleation during the electrolysis on inert electrode was described by CNRS-LGC using cyclic voltammetry, square wave voltammetry and chronoamperometry techniques. The study has shown that the uranium germs on an inert substrate are formed instantaneously, their growth is three dimensional and limited by the diffusion of U(III) ions.

Electrolytic experiments in  $\text{LiF-NaF-KF-UF}_4$ ,  $\text{LiF-NaF-UF}_4$  and  $\text{LiF-CaF}_2\text{-UF}_4$  systems on Ni working electrode were carried out initially using potentiostatic technique. To improve the uranium recovery yield, pulse-current electrolytic experiments were carried out on Mo and Ni electrodes. The results from pulse-current technique have shown significant differences from these obtained by potentiostatic electrolysis. Black compact deposits with regular areas of metallic shine were obtained on all electrodes. Electrolysis by pulsed current was evaluated as a promising method although the quantitative analysis is complicated due to the significant melt presence in the deposit.

### ***III.2.2.3 Alternative electrochemical process in fluorides using liquid metal dropping electrode***

The work focused on the assessment of the performance of an An-Ln electrolytic separation process in molten fluorides *versus* chlorides in terms of An recovery yield and separation efficiency. It was decided that the experiments would be performed using a liquid metal cathode. The validation experiments were carried out in molten chlorides with the aim of future adaption of the method for the fluoride salts.

An electrode was developed for production of reproducible and polarisable Bi drops in molten salts, allowing the use of an important volume of the liquid metal. An optimal configuration and injection method was developed. A specific furnace made of transparent envelopes was designed and manufactured to provide visualization of the Bi drop in LiCl-KCl eutectic at 450°C. The experiments have shown promising results in terms of mechanical and thermal resistance of the electrode. An experiment on the electrochemical behaviour of Nd onto liquid Bi electrode was successfully carried out, including potentiostatic electrolysis of Nd. The observations are in good agreement with the theory.

The next step will consist in transposing the electrode to the fluoride media, where no visualization of the drop is possible. An investigation of the interfacial tension between LiF-CaF<sub>2</sub> and liquid Bi at 810°C will be necessary to set correctly the experimental parameters. An experiment is planned in LiF-CaF<sub>2</sub> using a suitable element with well-known electrochemical behaviour to verify application of the method in molten fluoride salts.

### ***III.2.2.4 Reductive extraction of TRUs from chlorinated products from real HLLW***

As the basic distribution data necessary to estimate the separation behaviour were already achieved in the past, tests with irradiated fuels were necessary to validate the efficiency of the process. A demonstration experiment of actinide recovery using material obtained by chlorination of denitrated real high level liquid waste (HLLW) was carried out. The experiment has consisted of preparation of the initial material and its reductive extraction using a Li-Cd alloy as a reduction agent and liquid Cd as an extractant. Raffinate from PUREX reprocessing of MOX fuel irradiated in a PWR has been used as the initial material. To increase Pu and Np content, solutions containing these An were added to the raffinate. About 520g of the HLLW was prepared containing 8400µg/g of uranium, 600µg/g of TRUs, and 2000µg/g of FPs including 870µg/g of rare-earth FPs. The raffinate was denitrated at 90-120°C, dried in a stainless steel crucible at 100-140°C and calcined at around 500°C in a closed reactor. Afterwards, the denitration product was introduced in a graphite crucible together with LiCl-KCl eutectic salt and chlorinated by pure chlorine gas at 650°C. Part of the chlorination product was loaded in a MgO crucible together with pure Cd metal. The reductive extraction was carried out at 500°C using step by step addition of Cd-Li alloy containing 0.685wt.% of Li. The reduced An were extracted into the liquid Cd pool at the bottom of the crucible.

It has been shown that almost 100% of all transuranic elements (TRU) including americium and curium contained in the initial HLLW was recovered in the liquid cadmium phase. The separation of these actinide elements from rare-earth fission products (FPs) is in a good agreement with the previous data obtained using unirradiated TRUs and FP surrogates. Hence, the reductive extraction was successfully demonstrated.

### ***III.2.2.5 Definition and lab-scale demonstration of a recovery process of An from An-Al alloys***

A chlorination route was investigated in ITU to recover An from the An-Al alloys formed during the electrochemical separation processes. The chlorination route consists in three steps: (i) Vacuum distillation for removal of the salt adhered on the electrode, (ii) chlorination of the An-Al alloys by Cl<sub>2</sub>(g) or HCl(g) and (iii) sublimation of the formed AlCl<sub>3</sub>. A thermochemical study was performed and showed a thermodynamic feasibility of all three steps. On the basis of the calculated conditions, experiments using pure UAl<sub>3</sub> alloy were carried out to evaluate and optimise the chlorination step using both proposed chlorination agents. The work was focused mainly on the determination of the optimal working temperature, providing complete chlorination of the alloy without formation of volatile UCl<sub>5</sub> and UCl<sub>6</sub>. A very efficient chlorination (up to 99.8% conversion) with no volatilisation of U was achieved by Cl<sub>2</sub>(g) already at 150°C. A major part of AlCl<sub>3</sub> (between 85% and 94%) was removed already during the chlorination. The chlorination by HCl(g) enabled higher reaction temperatures, which indicated higher process rates. A complete conversion of UAl<sub>3</sub> to non-volatile chlorides was achieved at 300 and 350°C during 20 h, while 99.6% was chlorinated during 4 h at 350°C. During the experiment using U-Pu-Al alloy prepared by electrorefining, somewhat lower efficiency of chlorination step was achieved, but still minimum 97% of the alloy was chlorinated with no An losses by volatilisation.

An actinide oxidative back-extraction process was developed in CEA for recovery of An from the Al matrix obtained by a reductive extraction process using liquid Al as extractant in molten fluoride media. Bibliographic and the thermodynamic studies have shown the advantage of using chloride media for the process and the experimental conditions were predicted (salt composition, working temperature 700°C). The first experiments led to the optimization of both the experimental set-up and the experimental conditions. CaCl<sub>2</sub>-LiCl (70-30 mol%) salt was selected and a ratio AlCl<sub>3</sub>/An = 6–7 was determined as optimal for the back-extraction process. The last step of the experimental study has demonstrated the feasibility of the An back-extraction. The recovery of Pu and Am was quantitative in a single stage, whilst U is the most difficult actinide to be back-extracted and cannot be fully recovered in a single step. The An/Ln selectivity is of first importance during the extraction step. The study has demonstrated that the liquid-liquid oxidative back-extraction is a very simple and fast process and it is perfectly adapted to the pyroprocessing developed by the CEA.

### III.2.3 Salt treatment for recycling

The pyrochemical treatment of spent nuclear fuel must aim to minimise the amount of waste created in order to demonstrate industrial and economic feasibility. Therefore, it will be advantageous to recycle the salt used in the main pyrochemical processes as much as possible. Furthermore, the separation of fission products from the salt will not only minimise the final highly active (HA) waste volume, but will also remove the large water-soluble component that could potentially cause significant issues for disposal.

#### III.2.3.1 Exploratory studies of distillation in fluoride salts

At CEA, **distillation was considered for the decontamination of the LiF-AlF<sub>3</sub> salt** used in the pyrochemical liquid-liquid extraction process for the treatment of spent carbide or oxide fuel. In order to facilitate the adjustment of the LiF-AlF<sub>3</sub> composition to that required in the main process, it was also investigated whether it is possible to recover several fractions during the distillation, one being enriched in AlF<sub>3</sub>, which would then be removed.

After some thermodynamic calculations to check the feasibility of the distillation and determine experimental parameters, a modelling of the distillation was performed. This showed it should be possible to recover at least two fractions. Subsequently, laboratory scale studies of the distillation of pure or contaminated LiF/AlF<sub>3</sub> salt were carried out that demonstrated the feasibility and the efficiency of the decontamination process.

The first important observation was the substantial reduction of the volume of FP-containing waste as 95% of the solvent salt can be recovered and recycled. However, although it was possible to obtain a phase enriched in aluminium compared to the initial solvent, its composition does not meet the requirements to fully optimise the flowsheet. For the successful implementation of fluoride salt distillation for clean-up and recycle, further work is required on development of the technology and apparatus to give better temperature control.

#### III.2.3.2 Evaluation of the processes for chloride salt decontamination

There are a number of options that have been proposed for the removal of fission products from the used salt arising from a chloride-based pyrochemical spent fuel treatment process. These techniques include the following, with the ones investigated in ACSEPT indicated in **bold**:

- **Zeolite ion-exchange - NNL**
- **Aqueous dissolution and ion-exchange process - ANSTO**
- Precipitation using carbonates or phosphates
- **Precipitation using gaseous reagents, e.g. water vapour – CNRS-LECIME**
- **Electrolysis - CIEMAT**
- Chemical reduction using lithium
- Zone refining or fractional crystallization

The following conclusions can be made from the work carried out during the ACSEPT project:

- Zeolite ion-exchange was confirmed as the only demonstrated process for removing all of the fission products simultaneously, although the efficiency for the AMs (Cs/Rb) was particularly poor. A number of practical aspects of the zeolite-salt interaction were studied, including the implementation

in column geometry, the effect of temperature and relative quantities, and competition effects.

- Although the work was discontinued, the initial results from a study of the various operations required for a closed hybrid aqueous loop were promising.
- The selective electrolytic extraction of AM and AE using a liquid lead cathode is not feasible without co-reduction of Li and K. The major elements recovered were Ba, Sr and Li.
- Precipitation of the lanthanide FPs is feasible using a wet argon sparging process. This process does not increase the overall salt volume and yields  $\text{LnOCl}$  or  $\text{Ln}_2\text{O}_3$ .

In terms of comparing the various potential decontamination techniques listed above, a full evaluation was not possible with the data available. However, a quantitative assessment was carried out, see Table 1.

**Table 1: Summary of chloride salt decontamination processes with an indication of their effectiveness**

Salt Decontamination Process	Lanthanides (La, Ce, Nd, Pr)	Alkaline Earths (Sr, Ba)	Alkali Metals (Cs, Rb)
<i>Ion-exchange (zeolites)</i>	FE	PE	SE
<i>Hybrid aqueous closed loop</i>	AE	AE	AE
<i>Precipitation (carbonates/phosphates)</i>	PE	SE	Inn
<i>Precipitation (oxygen sparging)</i>	FE	Inn	Inn
<i>Precipitation (wet argon sparging)</i>	AE	Inn	Inn
<i>Electrolysis</i>	FE	Inn	Inn
<i>Li-Reduction</i>	FE	Inn	Inn
<i>Melt crystallisation</i>	AE	PE	PE

FE	Fully effective, demonstrated at lab-scale (>90% efficient)
PE	Partially effective, demonstrated at lab-scale (10-90% efficient)
SE	Slightly effective, demonstrated at lab-scale (<10% efficient)
Inn	Ineffective, demonstrated at lab-scale (0% efficient)
AE	Assumed effective, but not fully demonstrated

### III.2.3.3 Status on the exploratory studies on FP behaviour in chloride and fluoride salts

The aim of this programme was to study the speciation and transport properties of fission products in molten salts for nuclear applications using NMR at CNRS-CEMHTI and molecular dynamics (MD) at UPMC.

The information given by the evolution of the NMR chemical shifts of the different elements present in a melt provides a unique description of the local structure around these elements. Using specific airtight crucibles associated with a  $\text{CO}_2$  laser heating device for NMR experiments up to  $1500^\circ\text{C}$ , it is now possible to study *in situ* molten fluorides mixtures and to describe the ionic species formed in the melts depending on the composition and the temperature. Different systems were investigated in order to better identify the influence of CsF in a fluoride melt containing rare earth and oxides:  $\text{LaF}_3\text{-AF}$  (A=Li, Na, K, Rb and Cs),  $\text{LaF}_3\text{-LiF-CsF}$ ,  $\text{LaF}_3\text{-LiF-CaF}_2$ ,  $\text{LaF}_3\text{-LiF-CaO}$ ,  $\text{LaF}_3\text{-LiF-La}_2\text{O}_3$ ,  $\text{LaF}_3\text{-LiF-CaO-CsF}$ . High temperature NMR experiments were performed to follow *in situ* the evolution of the NMR signals for the different observable nuclei such as  $^{19}\text{F}$ ,  $^{23}\text{Na}$ ,  $^{85}\text{Rb}$ ,  $^{133}\text{Cs}$  and  $^{139}\text{La}$ . In  $\text{LaF}_3\text{-AF-CsF}$  and  $\text{LaF}_3\text{-AF-CaF}_2$  systems, the coordination number of lanthanum cation ranges from 6 to 8 depending on the  $\text{LaF}_3$  concentration and on the nature of the solvent thus on the polarizability of the other cations. The addition of oxide (CaO) leads to the formation of lanthanum oxyfluoride species that precipitate as LaOF when CaO concentration is increased. The addition of CsF to  $\text{LaF}_3\text{-LiF-CaO}$  yields to a displacement of the proportion dissolved versus precipitated LaOF.

The effects of adding 3% of  $\text{BaF}_2$  in the molten  $\text{LiF-ThF}_4$  fluoride were investigated by MD simulation. Only a slight increase in the density and decrease in the heat capacity were observed, showing that such concentrations are not enough to change drastically the thermo-physics of the liquid salt. For molten chlorides, new interaction potentials for  $\text{RbCl}$ ,  $\text{CsCl}$  and  $\text{SrCl}_2$  have been parameterized. These can be used to study the effect of adding these fission products to the  $\text{LiCl-KCl}$  eutectic melt in future work.

## III.2.4 Waste Conditioning

### III.2.4.1 Assessment of sodalite as a matrix for conditioning chloride wastes

The general aim of the work, performed jointly between ENEA, Polimi and CEA, was the evaluation of

sodalite as a matrix suitable for containment of chloride salt wastes coming from pyroprocesses. To this end, two different methods have been used to synthesize sodalite, in order to condition the wastes: the former, starting from kaolinite through nepheline; the latter, directly from silica and sodium aluminate. The obtained products have been characterized by means of various tests and analyses - stereomicroscopy; scanning electron microscope, SEM-EDS; density; surface analysis, BET; thermogravimetric analysis; X-rays diffraction patterns; infrared spectra, FTIR - which revealed that the synthesis from kaolinite is by far the best method, provided that rigorous conditions are followed: in particular, the preparation of pellets of reagents under an argon atmosphere, followed by heating at 800°C in an oven for not less than 100 hours is a penalty to obtain a good product. The sodalite powder thus synthesized was then sintered by using a hot uniaxial pressing equipment. Sintering the powder by batch of about 1 – 2 g in a diameter matrix of 10 mm, at 900°C during 5 hours and under 25 MPa, permitted to obtain excellent densification ratios  $\geq 96\%$ . About 25 pellets were realized, to obtain about 45 g of sintered sodalite. One pellet was used to realize a dynamic leach test using a soxhlet device, at 100°C, to determine the initial dissolution rate. It can be estimated between 12 and 16 g/m<sup>2</sup>/d, which is a too high value for a high level waste conditioning matrix. The other pellets were crushed in the [63 – 125]µm granulometry and used for the leaching tests under static conditions, according to ASTM C1285-02 (reapproved 2008). To this end, twelve leaching tests have been performed for six contact times (1, 7, 15, 30, 90, 150 days) at room temperature (23 ± 2°C) and in an oven at 90° ± 2°C on sodalite powder (22 grams). Furthermore, SEM analysis puts into evidence an irregular surface and an underneath structure of the sample after 30 days of leaching, while a lot of small holes appear on the surface of the sample after 150 days.

Further experiments have been made in order to demonstrate the feasibility of sodalite synthesis through a pressureless consolidation process recently proposed by ANL in the USA. Experiments have been made at a laboratory scale, starting from a homogeneous powder of nepheline, chloride salts and glass. The mix was put into an alumina crucible and slightly pressed with another alumina crucible of a smaller diameter, inside which a stainless steel bar of about 280 g had been inserted. The entire assembly was introduced in a furnace inside an argon-atmosphere glove-box. The furnace temperature was then raised at 10°C/min to 500°C where it was held for about one hour, in order to allow any residual moisture to evaporate. The temperature was then raised to 925°C for 7 hours. The product obtained has then been characterized by means of density measurements, thermal analysis, SEM and stereomicroscopy observations, as well as XRD and FTIR. Both XRD and infrared spectra of the product correspond to the one of sodalite. Two different types of glass were used as blending agents: a commercially available glass frit, and a borosilicate glass, in order to evaluate their influence on the final properties, with a special attention to the leaching behaviour. Leach tests under static conditions, according to ASTM C1285-02 (reapproved 2008), have then been carried out on the powdered product. The results obtained at 1, 7, 15, 30, 90 and 150 days of leaching, reported as both graphs and tables, show a significant release of the elements, especially at 90°C. Furthermore, SEM analysis puts into evidence small holes on the surface of the samples due to a dissolution process. In spite of the fact that the sodalite mixed with borosilicate glass appears more compact and quite hard to break with respect to the sodalite mixed with glass frit product, a major porosity and the formation of the highly soluble alite cause higher release rates. A comparison of the results obtained with those from a similar test by Argonne National Laboratory concerning a ceramic waste form prepared with the addition of a glass frit show a comparable release of the matrix elements Al and Si. The influence of the glass composition on the properties of the final waste form, however, would require further research efforts. From these studies, it is now stated that sodalite is not a relevant matrix for the confinement of high level chlorinated salt waste

#### ***III.2.4.2 Studies on chlorapatite as a matrix for spent chloride salt confinement***

The potentialities of other oxychloride phases, like chloroapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ , and chlorospodiosite,  $\text{Ca}_2\text{PO}_4\text{Cl}$ , have been studied, especially in terms of **leaching behavior**.

To this aim, synthesis and sintering of such compounds were studied, in order to obtain pure and densified ceramics. Syntheses were performed under dry conditions, and the two phases were obtained pure after three calcinations at 850°C/12h for chloroapatite, and 750°/15h for spodiosite. The sintering step was realized by Hot Uniaxial Pressing. Densification ratios upper than 90% were obtained under 950°C / 30 MPa / 10 – 24h for chloroapatite, and 800 – 900°C / 25 – 30 MPa / 7 – 24h for chlorospodiosite. Nevertheless, a lot of optimizations should be brought and a microstructural study should be performed by SEM to examine the microstructure of bulk of the sample, especially in terms of porosity. Actually, the densification of oxychlorides phases proved very difficult, involving troubles to study their leaching behaviour. As the S/V ratio of chloroapatite powder evolved during the leaching test, accurate initial dissolution rates couldn't be calculated. In order to compare the two materials and to avoid surfaces artifacts, the alteration fraction

(Normalized Weight Loss x Sspec) versus time was deduced, and compared to the one of sodalite. This comparison allowed us to estimate that chloroapatite and chlorospodiosite seem to be more durable than sodalite. These preliminary results are very positive, because the leaching study on sodalite was concluded by the fact that this oxychloride was not durable enough for high level waste. However, in order to study more precisely the leaching behavior of these phases, it would be necessary to optimize the densification parameters, and to perform two more leaching tests, under dynamic conditions with pure water at 100°C on a monolithic sample, in order to estimate the initial dissolution rate  $r_0$  (soxhlet test) and also in static conditions on powder, in order to increase the S/V ratio, at 90°C, to estimate the residual leaching rate.

#### **III.2.4.3 Studies on metallic matrices for conditioning metallic fission products**

The electrochemical behaviour of copper-nickel alloys for conditioning metallic fission products has been studied in a synthetic groundwater. In aerated conditions, copper and copper alloys are covered by porous oxide/hydroxide layers which do not allow surface protection towards corrosion. Nevertheless, when nickel percentage increases into the copper matrix, corrosion resistance increases principally due to an improvement of film resistance. In aerated media, nickel and nickel alloys are passive. However, for nickel alloys passivation kinetic is reduced and samples are more sensitive to crevice and pits certainly related to discontinuities in the passive layer. In CO<sub>2</sub> saturated water, the difference between corrosion currents recorded on copper and nickel alloys are less marked. Copper and copper alloys have nearly the same behaviour than in aerated-only conditions. Nevertheless, with acidic environment the oxide layer is thinner (partial oxide dissolution) and this accelerates corrosion. Nickel and nickel alloys are more sensitive to this change of acidity. In fact, in such conditions, nickel is in a pre-passive domain which induces changes in the passive layer properties. The film could be less homogeneous and allow the diffusion of aggressive species towards the interface, therefore inducing an important increase of corrosion currents in comparison with those recorded in aerated conditions. Under this storage conditions, copper addition will be limited to 30 wt.%. Moreover, a localized corrosion could occur and disposal procedures have to prevent crevice or pitting corrosion. Given the weakness of the passive film induced by the presence of copper oxide within nickel oxide, the best compromise must be looked for, between the copper content in the volume of the material (for mechanical properties) and within the passive film for a greater corrosion resistance.

### **III.3 Domain 3 – Process**

The objectives of the ACSEPT program in the field of engineering were to develop the engineering requirements for the implementation of partitioning and transmutation into the nuclear fuel cycle. The work was centered on developments in both hydrometallurgy and pyrochemical separations, with the aim of seeking integration between these two technology groups within the project. The topics covered in this domain looked at system studies to further develop the understanding of processes beyond the fundamental science. The key issues identified were the requirement to agree with GenIV reactor programmes feed and product specifications required for integration of P&T with the fuel cycle. A broad operating envelope was provided to frame the ACSEPT project but requires convergence in future programmes towards a final goal.

The development of a pilot plant concept was a key output from the domain and provides a focus for future work to aim towards. It is clear from this report the depth of the science and engineering work still required to move P&T technologies into full scale implementation.

The work undertaken on science and engineering integration provided good insights into the challenges faced with scaling of the science to industrial levels. Development of microelectrodes and online LIBS techniques both show promise for monitoring of industrial plants though both have significant development issues left to overcome if they are to succeed. Scaling of TODGA manufacture yielded repeatable results of producing quality product at industrial scale and the work into scaling of centrifugal contactors has provided computer modeling that enables theoretical scale up of flowsheets using this technology (though more data is needed to validate this model fully). The corrosion studies on metals in the presence of molten salts provided important data for material selection for plant design for molten fluoride flowsheets.

Finally, the work on fuels and targets ensures compatibility between its own R&D results and the work performed in similar FP7 projects (such as FAIRFUELS), devoted to transmutation. The work on inert matrix fuels identified clear issues with respect to reprocessing techniques which have subsequently informed work packages instigated in other EU projects, namely ASGARD.



### III.3.1 Conceptual studies, safeguard, and early integration

#### III.3.1.1 System studies, flow sheet evaluation

The System Studies work package covered a range of work. The work undertaken by NNL had the initial aim of collating feedstock data in order to define a likely fuel type envelope for various separation processes and to obtain a notional map of the quantity and type of feedstock in terms of relevant isotopic content and other parameters. A theoretical calculation of various irradiated fuel parameters from basic data produced by the RED-IMPACT project ([ftp.cordis.europa.eu/pub/fp6-euratom/docs/red-impact-final-published-report\\_en.pdf](ftp.cordis.europa.eu/pub/fp6-euratom/docs/red-impact-final-published-report_en.pdf)) was produced. This has shown that most fuels in a 2004 survey of reactor burnup and initial enrichment from European stations are within this envelope. The envelope calculation produced several different irradiated fuel parameters in order to aid in the design of separation processes.

NNL undertook a study to determine the details of how various aspects of flow sheets, fuel cycle analysis and decision making would fit into the ACSEPT programme. The fuel cycles to be considered in ACSEPT were:

1. Base scenario: Single re-use MOX in PWRs
2. Fast reactor scenario: UOX to start FR fleet
3. ADS scenario: UOX moving to MOX with ADS to burn MA

Within these fuel cycles, there are several separation processes and this work has presented flowsheets for each of DIAMEX, TODGA-TBP, SANEX, GANEX and PYRO. This work presented some examples of fuel cycle analysis used to determine the impact of different reprocessing recovery factors, highlighting the necessity of achieving a very high efficiency in the separation processes applied. It is intended that multi-criteria analysis (MCA) will be used as a means of assessing and comparing the various fuel cycles.

With an increased application of nuclear technology for civil use there comes a potential increase in the risk of proliferation of nuclear materials unless various methods are in place to reduce the likelihood of such events. A key method is the application of international safeguards such as those set out by the IAEA. Various methodologies to assess the security of these fuel cycles were reviewed. The methodologies are based around the concept of non-proliferation of special nuclear materials processed through the fuel cycles.

For optimizing the pyroprocess, flowsheet of the chloride process to reprocess metal fuel and oxide fuel were developed by CRIEPI and evaluation of the material balance and quantitative analysis of waste were carried out for optimization of the system. The material balance and amount of HLW were evaluated for the reprocessing of spent metal fuel of 38ton-HM. In the present estimation, the recovery yields of U, Pu, Np are 99.8% and Am, Cm are 99.5% and, 144 HLW canisters are generated per year in case of using the zeolite with the composition of  $\text{Li}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$ .

CRIEPI also studied accountancy of nuclear materials where some correlations between fission gas composition and fuel burnup were investigated for a typical PWR-MOX fuel in order to examine the feasibility of a novel method for estimating the actinide composition in the spent fuel based on the plenum gas analysis. Calculations were made for burnup up to 16 at.% (e.g; 140-150 GWd/tU). An analytical evaluation with the ORIGEN- 2.2 code revealed that the burnup of PWR-MOX fuel can be estimated from the correlation curve of  $^{131}\text{Xe}/^{132}\text{Xe}$  with the uncertainties of  $\pm 0.5\text{at.}\%$  if the experimental error associated with the isotopic analysis is assumed to be  $\pm 3\%$ .

Burnup dependence of fission gas release was also investigated for fast reactor (FR) metal fuels. According to the previously reported data on fission gas release from the irradiated metal fuel, there is a strong correlation between plenum gas accumulation and fuel burnup higher than  $\sim 1\text{ at.}\%$ . Assuming the fission gas amount released from the fuel pins can be measured with an uncertainty of a few percent including measurement error, it is expected that the actinide composition in the fuel can be predicted with an accuracy of  $\pm \sim 1\%$ .

#### III.3.1.2 Industrial cross fertilisation

This task is dedicated to seminars from the pyrochemical industries to educate the nuclear community on the engineering constraints associated with pyrochemical separations to allow for their early consideration. During the ACSEPT project, seminars were organized by RT Alcan to share its experience:

- Sep 2008 – Prague – a one day seminar about non-nuclear industrial electrolytic processes in fused salts media (Na, F<sub>2</sub>, Al, Ti) and aluminum production (including chemistry in cryolite bath and effect on the process, cell dynamics, pot modeling)
- Sep 2009 – Bologna – Workshops dedicated to solve together technical issues (How to add HF to purify a

- fluoride bath when HF gas can't be use? Why NiF<sub>2</sub> is spontaneously reduced in a LiF-NaF bath? ).
- Sep 2010 – Petten – The use of “Flux Expert” software (an open software) for modelling processes: Current line distribution (up to ternary distribution), possibly coupled with thermal effect.
- Sep 2011 – Goteborg – seminar about uranium recovery through electrowinning and the requisite laboratory scale cell design. At the end this seminar an Excel file to design a cell was made available.

### III.3.1.3 Tracking Evolution of the Pilot Plant Concept Design

The main objective of this task was to highlight the gaps and uncertainties on how and what a pilot plant could look like bearing in mind the scientific/technical results obtained in this project. This work was performed by NNL based on the data collated throughout the project from the Hydro domain. This report presented the state of the art and associated design to progress the work towards a concept plant and process design for the ACSEPT pilot plant which will undertake group actinide separation from GEN IV feed fuels and convert them into new feed fuels for return to the fuel cycle.

The GANEX flowsheet proposed by NNL has been selected by a steering group in ACSEPT for the final hot test of the flowsheet within the project. It is on the results of an active trial of this flowsheet that the development of a pilot plant concept has been based, assuming a design basis throughput of 4 THM/year, selected as a scaled throughput against existing reprocessing facilities

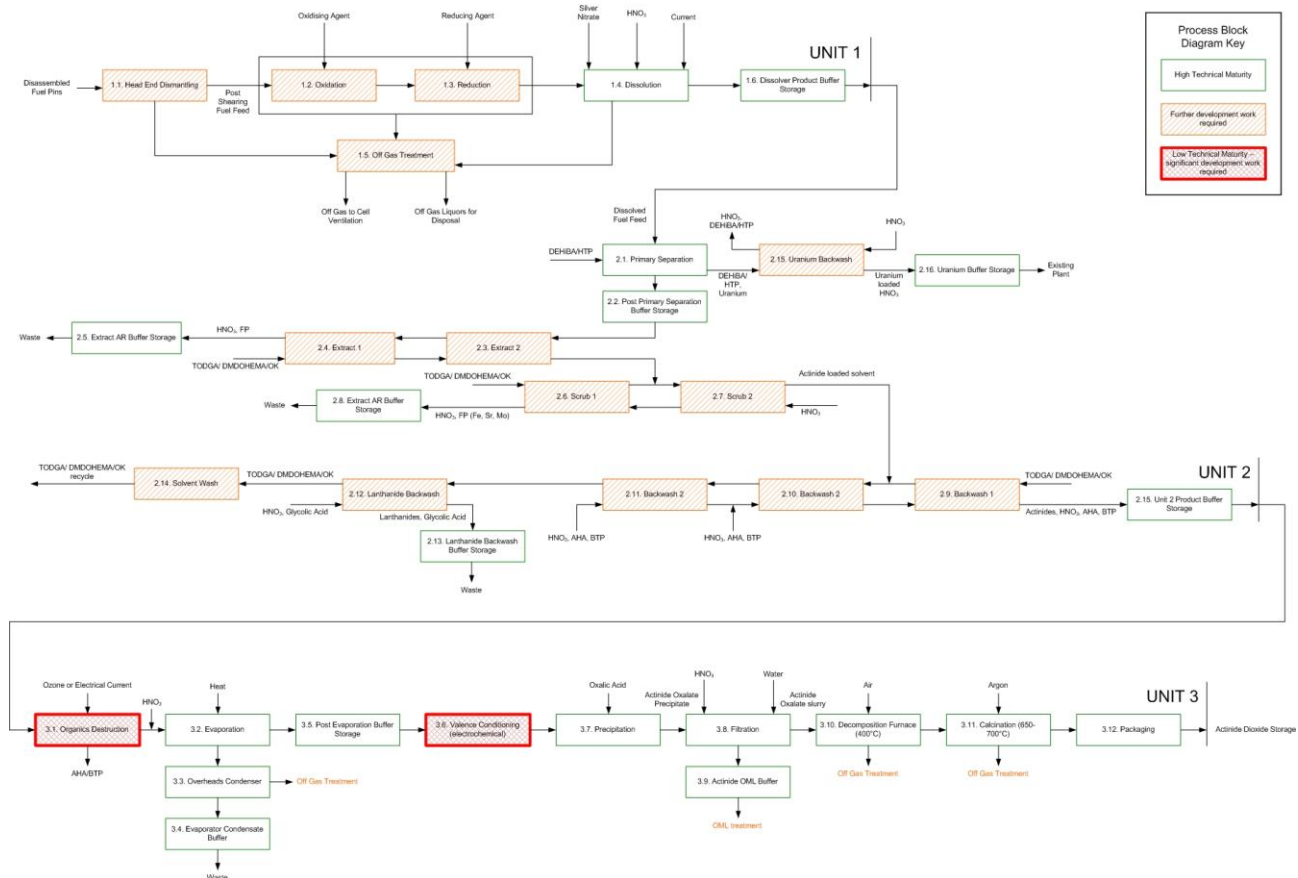


Figure 15. ACSEPT Pilot Plant Technology Readiness Process Block Diagram.

The processes to be considered in this concept pilot plant design will predominately be the variants to the standard fuel cycle that the facility will require. They have been determined to be three units:

- Head end pre-treatment (conditioning the fuel feed to be suitable for dissolution)
- Partitioning (separation of the key actinide species from uranium and fission products)
- Conversion of actinides to fuels (production of suitable feed materials for fuel fabrication)

Technical options for each of these units have been reviewed and, for the pilot plant, it has been proposed that voloxidation (oxidation and reduction of the fuel) is employed for the head end pre-treatment stage, solvent extraction using centrifugal contactors and the GANEX flowsheet be used for the partitioning stage, and a modified oxalate precipitation process be used to produce the final actinide product.

A process block diagram is presented Figure 15 to show the pilot plant operations with the readiness level, in addition to stream data from the scaled flowsheet upon which this plant design is based. Dimensions of key equipment items have been estimated from the available data and the expected operating conditions discussed. As an example, dimension of centrifugal contactors rotors and number of stages are given in Table 2 for each step of the separation flowsheet.

**Table 2: Centrifugal Contactor Estimated Rotor Diameters**

Process Stage	Estimated Rotor Diameter (cm)	Total number of contactor stages
Extraction (2.3, 2.4)	6.5	8
Split Acid Scrub (2.6)	5.8	8
Split Acid Scrub (2.7)	7.1	
Backwash 1 (2.9)	8.9	8
Backwash 2 (2.10)	9.9	8
Backwash 2 (2.11)	8.9	
Lanthanide Backwash (2.12)	9.9	12

### III.3.2 Science and Engineering Integration

The work was dedicated to a range of experimental studies which focus on science and engineering integration in three main directions: process operation and monitoring, corrosion issues and scale-up studies.

#### III.3.2.1 Process operation and online monitoring

Two different techniques were developed: the first one, the LIBS device (Laser Induced Breakdown Spectroscopy, also called Laser Ablation coupled with Optical Emission Spectrometry (LA-OES)) was developed by CEA teams; The second one was developed in the framework of a PhD thesis: UEDIN manufactured and characterized microelectrodes for in situ analysis in molten salts.

#### *LIBS device development*

CEA teams adapted the LIBS for working with molten salts by modifying the laser wavelength and designing a cell with a  $\text{CaF}_2$  window for the beam inlet and outlet. Then in a second part, a cerium calibration curve was obtained with different cerium concentrations in a molten  $\text{LiF-AlF}_3\text{-CeF}_3$  salt. The feasibility of a single-element (lanthanide or actinide) analysis is demonstrated. In addition, for multiple element analysis, it was theoretically verified for a given typical nuclear fuel composition, that at least one interference-free line could be identified for each species. The molten salt composition (for typical molten chloride and fluoride) was taken in account. The installation of a LIBS device in the Atalante facility at CEA Marcoule will allow the experiments to continue. However, failures, which occurred during this project, indicate a lack of robustness of this device to be used with molten salts.

#### *Microelectrodes development*

UEDIN manufactured and characterized microelectrodes to use them in molten salt ( $\text{LiCl-KCl}$  at  $450^\circ\text{C}$  was chosen for demonstration). The completion of characterisation of single and array microelectrodes enabled the fundamental response of these systems to be established and insight into their potential high temperature response to be gained. Characterisation in molten salt of the microsquare electrode systems then enabled several practical issues to be overcome, including consideration and mitigation of the effects of electromagnetic interference, corrosive attack and molten salt device wetting which resulted in contact corrosion. Finally, the response of these systems to the redox species  $\text{Sm(III)/Sm(II)}$  and  $\text{Ag(I)/Ag}$  in LKE molten salt, when benchmarked against macroelectrode response, was shown to be characteristic of the expected response of a microelectrode, with enhanced current densities, making them relatively insensitive to convection, with steady-state currents linearly dependent on electrode dimension. Such measurements as a function of temperature, have enabled diffusion coefficients, half-wave potentials and activation energies for diffusion to be extracted for e.g. the  $\text{Sm(III)/Sm(II)}$  couple. These results are very impressive and demonstrate the great potential of the developed microelectrode systems. However, the use of microelectrodes in molten salts requires further work to ensure that corrosion issues are solved with long duration.

The use of these microelectrodes in the 3M nitric acid solutions was also a success:  $\text{NO}_2^-/\text{NO}_3^-$  (in acid) and stripping/plating ( $\text{Ag(I)/Ag}$ ) redox species are both quantitatively and qualitatively measured. This

demonstrates that microelectrode system can be used in electroanalysis and on-line sensing and monitoring in hydrochemical reprocessing. Industrialization seems achievable even it requires some work.

### III.3.2.2 Scale-up studies

The scale-up of TODGA synthesis has been studied exploring different ways and methods (acid chlorides, mixed anhydrides, carbodiimide type coupling reagents, thermal conditions, microwave irradiation...) avoiding time and money consuming chromatographic purifications in order to minimize the price of the extractant. Some problems were detected for the extractant purification by distillation or liquid-liquid extraction, however the synthesis of macro amounts of TODGA has been accomplished using the commercially available diglycolyl chloride. Following this procedure allows obtaining pure TODGA, in high yields, without purification. Close to 300 g of TODGA were synthesized and delivered for process development studies to some partners such as NNL, UPMC, Chalmers, INE and PoliMi among others.

Experimental trials have been undertaken by University of Groningen (RUG) and CINC Solutions to explore the factors affecting interfacial area for mass transfer in annular centrifugal contactors. All trials used 30% TBP in Exxsol D80 diluent, at ambient temperature, with extraction of HNO<sub>3</sub> being studied at varying flowrates and phase ratios. Such an interfacial area is characterized by the droplet size distribution in the contactor. Trials at RUG used a 5cm contactor, fitted with a transparent window and measurement ports to facilitate measurement of droplet size in the annulus, whilst those at CINC used a 25cm contactor. Droplet size in the annulus was determined using a laser reflectance probe to measure chord length distribution which can be processed to give Sauter mean diameters for the droplets.

Results from the 5cm rig are best described if they are divided into operating regions above and below an organic/aqueous ratio of 2.5. Physically this division may correspond to solvent and aqueous continuous operating regimes. The results have been used in a model of the centrifugal contactor at NNL and the value of the dimensionless constant (K) in the Kolmogoroff expression for droplet size was estimated to be 0.28 for O/A ratios below 2.5 and 0.30 above 2.5. The results from the 25cm rig only showed one region of operation as they were conducted at higher organic phase/aqueous phase ratios and K was estimated to be 0.26. There was considerable scatter in the 5cm trial results, but the 25cm results are much more consistent. Scale-up of interfacial area from the 5cm to the 25cm annular centrifugal contactors is now possible using the model developed over the course of this work.

### III.3.2.3 Corrosion

Corrosion has long been recognised as a major industrial challenge especially in pyro processes with high temperatures and chloride or fluoride media which are highly aggressive media. Molten fluoride (LiF – NaF at 900°C) was chosen because of the working temperature range. Electrochemical techniques were used to study the corrosion processes and their kinetics.

This work was done within the frame work of the PhD thesis of Stéphanie Fabre at EDF R&D in cooperation with the Chemical Engineering Laboratory (LGC) at the University Paul Sabatier in Toulouse and the French atomic energy commission (CEA) at Saclay.

Firstly, pure metals (Ni, Cr, Fe and W) and binary alloys (mainly Ni-Cr alloys) were tested to develop the approach. The main results of this step are:

- Chromium, less electropositive than iron, corrodes more rapidly.
- The corrosion rate of the iron increases with temperature (activation energy was estimated to be 127 kJ.mol<sup>-1</sup>) and the corrosion is limited by corrosion product diffusion in the melt.
- The corrosion current densities vary with the composition of the fluoride mixture:  $i_{corr}$  (LiF-NaF) <  $i_{corr}$  (LiF-CaF<sub>2</sub>) <  $i_{corr}$  (LiF-AlF<sub>3</sub>) showing the importance of fluoroacidity, very probably due to complex formation by the various corrosion products.
- The presence of oxide in the medium accelerates iron corrosion up to a concentration of 2.5\*10<sup>-2</sup> mol.kg<sup>-1</sup> of Li<sub>2</sub>O added to the fluoride melts.
- For monophasic Ni-Cr alloys, oxidation gives rise to a reduction in the chromium content of a zone close to the surface, which is accompanied by the formation of pores.

The study of multi-element alloys drew attention to the difficulty of interpreting linear voltammograms with respect to the influence of the various elements composing the alloys. Nonetheless, the use of more conventional corrosion study methods such as measurement of mass loss, SEM imaging of test specimens and EDX analysis yielded complementary information on the process of material attack and the role of the nature

of the metals added to the nickel base. It is proposed that alloy oxidation involves two competing processes: the first controlled by medium chemistry, i.e. the reaction at the interface, and the second controlled by chromium diffusion within the alloy. Addition of tungsten or molybdenum to the binary Ni-Cr alloy slows down the diffusion of chromium toward the molten salt-material interface.

Lastly, comparison of the microstructures, de-chromed depths and quantities of current crossing the materials in the immersion tests and macro-electrolytes enabled the following finding: for the alloys tested, there is a relationship between the quantity of current, which corresponds to the quantity of chromium oxidized, and the depth de-chromed. By measuring the corrosion current density of an alloy, it is thus possible to estimate the de-chromed depth of the material for a given immersion duration on the basis of an imposed potential electrolysis for which the quantity of current is known. In the case of binary Ni-Cr alloys, monophasic solid solutions, the microstructure of the material following electrolysis was shown to be that obtained in the immersion test. In the context of this study, the proposal could not be extended to more complex materials for which the degradation mechanism has yet to be identified.

### III.3.3 Fuels and Targets

Work package 3.3 on Fuels and Targets was set up specifically to address potential missing links between the R&D on partitioning on the one hand and on transmutation on the other hand. In this way ACSEPT was able to ensure compatibility between its own R&D results and the work performed in similar FP7 projects (such as FAIRFUELS), devoted to transmutation. Two main tasks were set up:

1. Feasibility study of the MARIOS irradiation on minor actinide transmutation,
2. Comparison of the reprocessing capabilities and waste management of various minor actinide bearing matrices.

#### III.3.3.1 Feasibility of MARIOS fabrication and irradiation for MA transmutation

The Minor Actinide Bearing UO<sub>2</sub> Blanket (MABB) is a promising recycling option to be used in Sodium-cooled Fast Reactors (SFR). This concept realises Minor Actinide (MA) recycling in the radial blankets in the outer core regions of the SFR. Heterogeneous recycling on a UO<sub>2</sub> matrix has the advantage of providing flexible breeding gains and making fuel reprocessing possible in a standard fuel assembly flux, while limiting the proliferation risk of the blankets. This task was set up to define a first irradiation experiment MARIOS to evaluate the behaviour of americium-containing fuel under well-defined, controlled conditions.

The MARIOS has addressed in particular the temperature-dependent He-release and swelling behaviour of (Am,U)O<sub>2-x</sub> fuel pellets. On the basis of an analysis of the target characteristics and a bibliographical study on the behaviour of helium in a UO<sub>2</sub> matrix, the following targets have been set for MARIOS:

- Chemical composition Am<sub>0.15</sub>U<sub>0.85</sub>O<sub>1.94</sub> (with 100% Am-241),
- Pellets with increased open porosity (density 82.5% versus theoretical density-TD) to be compared with standard density pellets (92.5% TD),
- Ideally, fuel pellet temperatures ranging from 600°C to 1400°C in order to cover the expected regimes of He release,
- Fuel pellet temperatures being well-defined and stable over the course of the irradiation,
- He production at End of Irradiation to be  $\sim 10^{21}$  atoms/cm<sup>3</sup>.

Within ACSEPT, the irradiation parameters of MARIOS have been worked out and a preliminary design has been built for the experiment, based on irradiation temperatures of 1000°C and 1200°C and estimated He production after of  $7 \cdot 10^{20}$  atoms/cm<sup>3</sup>. This preliminary design has been detailed in FP7 project FAIRFUELS, with the MARIOS irradiation taking place in the High Flux Reactor Petten from March 2011 to May 2012.

#### III.3.3.2 Comparing reprocessing options for various MA-bearing matrices

An important objective of ACSEPT is to gain a comprehensive knowledge of the reprocessibility of actinide bearing inert matrix targets designed for transmutation involving multi-recycling. The work in this task was devoted to an initial system study to assess and then rank the most important matrices in terms of reprocessing capabilities and waste management. The matrices concerned are the MgO-based CERCER and the Mo-metal based CERMET. These matrices are compared with UO<sub>2</sub> as matrix. The study was focused on the process aspects of the target reprocessing. Other aspects, such as criticality, radiation protection, nuclear measurement, were not examined in this limited, initial survey.

The outcome of this task shows that, in terms of reprocessing feasibility and waste management:

- The UO<sub>2</sub>-MA-bearing targets can be reprocessed without any difficulty with the production of a regular fission product glass waste (R7T7 glass).
- The MgO-MA-bearing targets can be reprocessed without any difficulty, but the waste production is highly impacted: the assessment of waste production in the case of separate reprocessing leads, compared to UO<sub>2</sub>, to 10 times more containers with AVM glass, and to 75 times more containers with R7T7 glass. The reprocessing in dilution with available UOX spent fuel to be reprocessed reduces the waste production and leads to twice as many containers as the UO<sub>2</sub> target reprocessing with R7T7 glass.
- The Mo-MA-bearing targets cannot be reprocessed by a separate reprocessing or in dilution with other fuels. The waste production is highly impacted by the production of a specific conditioning of Mo.

From these conclusions, the ranking for reprocessing and waste management of minor actinide bearing matrices is from the best to the worst: 1. UO<sub>2</sub>-matrix > 2. MgO-matrix >> 3. Mo-matrix.

On the basis of this initial study, it has become clear that the use of inert matrices (MgO or Mo) would require a new approach with respect to reprocessing, compared to current industrial practice. More dedicated studies to address this issue have been taken up within the FP7 project ASGARD.

### III.4 Conclusion

Concerning dissolution studies, experimental and mechanistic studies have advanced the knowledge of dissolution chemistry of (unirradiated) bulk-phase MO<sub>x</sub> and the associated plutonium-rich regions. Also, these and future planned developments in the dissolution of plutonium dioxide with Ag<sup>2+</sup> will allow further assessment of dissolution in the presence of insoluble fission products which are also present in dissolver sludge.

In the field of aqueous reprocessing, hot-test demonstrations were carried out based on chemical systems developed in former European projects (NEWPART, PARTNEW, EUROPART) or directly in ACSEPT. Process flowsheets are now available for the regular SANEX, the innovative SANEX, the 1-cycle SANEX and the GANEX concepts (some of them being more elaborate alternatives to reference existing processes) paving the way for further optimisation. This progress was made possible thanks to a well driven organic synthesis work. It allowed the testing of more than 150 new molecules and the selection of about 5 of them for further process development. In addition, specific issues related to advanced fuel cycles involving materials with high Pu loading or minor actinides were addressed such as MOX dissolution or co-conversion into solid forms suitable for fuel fabrication.

In the field of pyrochemical process development, two reference cores of process were selected within EUROPART (the electrorefining on solid aluminium cathode in molten chloride and the liquid-liquid reductive extraction in molten fluoride/liquid aluminium). In ACSEPT, the work was continued with a focus on key process steps such as the exhaustive electrolysis allowing a quantitative recovery of the transuranics after the electrorefining or the actinide back extraction from an aluminium alloy, crucial step for the two reference processes. In addition, a specific effort has been allocated to the head-end step (oxide pre-reduction, thermal treatment), the salt recycling (chloride salt purification by precipitation, fluoride salt purification by distillation) and the specific salt waste conditioning. After almost ten years of research on sodalite, it is now stated that this material is not relevant for the confinement of spent chlorinated salt waste. Chloroapatite is an alternative. Nickel-copper alloys have been selected for metallic fission product waste.

This experimental work was extended to cross cutting studies, such as system studies, scale up studies, corrosion studies and online process monitoring developments for molten salts. The MARIOS irradiation performed in FP7 FAIRFUELS was also designed in ACSEPT to allow a better schedule of this long run experiment. A report was also issued on the reprocessibility of advanced CERCER and CERMET fuels, leading to an experimental program now implemented within the FP7 ASGARD project.

## IV POTENTIAL IMPACT, MAIN DISSEMINATION ACTIVITIES AND EXPLOITATION OF RESULTS

### IV.1 Potential impact

The work performed in ACSEPT, combined with the results obtained within EUROPART and former projects allowed us to propose a set of relevant flowsheets in hydrometallurgy to recover minor actinides from spent fuel, whatever the fuel reprocessing scenarii. These flowsheets are now scientifically assessed. According to the type of fuel, the reactor generation and the level of existing industrial developments, the potential industrial users can implement either DIAMEX – SANEX, Innovative SANEX, 1-cycle SANEX or GANEX. In pyrometallurgy, alternative processes to the electrorefining on liquid cadmium are now proposed, increasing the potentialities of such media.

Therefore, now, advanced closed fuel cycles including the recycling of actinides, even the minor actinides, could be proposed to governments, European utilities as well as technology providers. This strategy of technically feasible recycling of actinides produces positive arguments in the sense that:

- European decision makers and more globally public opinion could be convinced that some sound technical solutions for a better management of the nuclear wastes now exist.
- One of the identified major difficulties for nuclear energy public acceptance, i.e. to guarantee the non-dissemination of hazardous radionuclides within the bio-sphere in the far future, is on the way to be solved, thus paving the way towards sustainability.

In the next step, these processes will be optimized, taking into account safety issues related to the combination of chemical and radiochemical risks.

### IV.2 Dissemination activities

#### IV.2.1 Conferences

**On the first period**, two oral talks were given by the coordinator on the organization and objectives of ACSEPT at ATALANTE 2008 (France) and 10<sup>th</sup> IEMPT (Japan). A poster was also presented at the SNE-TP general assembly. The pyro activities of ACSEPT were presented at IPRC Conference (Korea). In addition, numerous scientific communications were done on ACSEPT research, with main participation at ATALANTE 2008 (10), ISEC'08 (USA) (4), 10<sup>th</sup> IEMPT (7), MS8 (Japan) (3), 235<sup>th</sup> ACS Meeting (USA) (1), NRC7 (Hungary) (1) & 2<sup>nd</sup> INCC (Mexico) (2).

**On the second period**, three oral talks were given on the organization and objectives of ACSEPT at FISA 2009 (Czech Republic), 238<sup>th</sup> ACS Meeting (USA) and GLOBAL 2009 (France). The pyro activities of ACSEPT were presented by a poster at FISA 2009 and orally by the coordinator in an IAEA Consultancy Meeting in pyrochemistry (Korea). In addition, numerous scientific communications were done on ACSEPT research, with main participation at GLOBAL 2009 (France) (12), ACTINIDES 2009 (USA) (5), 238<sup>th</sup> ACS Meeting (3) & ICCAP'09 (1).

**On the third period**, general presentations of ACSEPT were given at 239<sup>th</sup> ACS Meeting (USA), ENC 2010 (Spain), 11<sup>th</sup> IEMPT (USA), IPRC 2010 (Russia). The coordinator was invited by IAEA to contribute to a Consultancy Meeting in pyrochemistry (Austria) and ACSEPT will then contribute to an IAEA technical document in Pyro. Numerous oral communications and posters were presented on ACSEPT research, with main participation at 239<sup>th</sup> ACS Meeting (7), Plutonium Futures 2010 (USA) (1), NuMat 2010 (Germany) (5), IPRC 2010 (1), 11<sup>th</sup> IEMPT (6). The 1<sup>st</sup> ACSEPT International Workshop was organised in Lisbon, Portugal, from March 29<sup>th</sup> to April 2<sup>nd</sup> in collaboration with ITN. It gathered around 120 people. This meeting was dedicated to the “young generation”. 22 orals were given by ACSEPT students or young scientists. They were also in charge of the chairmanship of the sessions. Contributions from US, Japan, India, Russia enlarged the audience of the meeting (22 presentations).

**On the fourth period**, general presentations of ACSEPT were given at GLOBAL 2011 (Japan), NFCC'2012 (UK), ATALANTE 2012 (France) & 12<sup>th</sup> IEMPT (Czech Rep.). The pyro activities of ACSEPT were presented at IPRC 2012 (USA). A lot of oral & poster presentations were presented on ACSEPT results, being at the end of the project, with main participation at ISEC 2011 (Chile) (10), MS9 (Norway) (2), GLOBAL 2011 (2), NFCC'2012 (6), Plutonium Futures (UK) (2), IPRC 2012 (2), 12<sup>th</sup> IEMPT (4), and a huge

participation at ATALANTE 2012 (20 oral presentations & 13 posters), hosting the 2<sup>nd</sup> ACSEPT International Workshop for a better visibility.

## IV.2.2 Journals

Numerous publications (98) were submitted and accepted in 28 different peer reviewed journals all along the project.

The journals involved are: Journal of American Chemical Society (2011 Impact factor: 9.907) (1), Chemistry Communication (6.169) (1), Inorganic Chemistry (4.601) (3), Dalton Transactions (3.838) (5), Electrochimica Acta (3.832) (2), Organic & Biomolecular Chemistry (3.696) (1), Physical Chemistry Chemical Physics (3.573) (2), European Journal of Organic Chemistry (3.329) (2), European Journal of Inorganic Chemistry (3.049) (1), Synlett (2.710) (1), New Journal of Chemistry (2.605) (3), Journal of the Electrochemical Society (2.590) (1), Supramolecular Chemistry (2.145) (1), Polyhedron (2.057) (1), Journal of Nuclear Materials (2.052) (7), Hydrometallurgy (2.027) (1), Solvent Extraction and Ion Exchange (2.024) (20), Journal of Chemical and Engineering data (1.693) (1), Radiochimica Acta (1.575) (8), Journal of Radioanalytical and Nuclear Chemistry (1.520) (5), Radiation Physics and Chemistry (1.227) (1), Separation Science & Technology (1.088) (1), Progress in Nuclear Energy (0.849) (1), Nuclear Engineering and Design (0.765) (1), IOP Conference Series: Materials Science and Engineering (N/A) (2), ECS Transactions (N/A) (1), Energy Procedia (N/A) (2), Procedia Chemistry (N/A) (22).

The average impact factor<sup>1</sup> calculated on publications in Journals for which it is known (71 publications) is 2.50

## IV.3 Training and Education

Training and education is one of the more important aspects of a research project within the nuclear sector. Today not only the reactors are ageing but also the personnel. After the accidents in Three Mile Island 1979, Chernobyl 1986 and now Fukushima, the nuclear area has not been considered highly interesting for young scientists. Thus the normal replenishment by younger scientists have not occurred as it should. Therefore a strong effort now has to be put on training and education of the young ones in the field while the more experienced are still active. In ACSEPT an ambitious plan has been launched not only to increase the knowledge of our own younger scientists and students but also to spread the knowledge about our activities to a larger community around the world. By having these plans the training and education domain has been resting on 3 main pillars in order to maximize the value for money but also to have a long lasting effect.

### IV.3.1 Funding fellowships for mobility and transnational collaboration

For many young scientist the research is in the worst case closely linked to the own department and possibly at some points to present work at some conferences. In some cases it is better and collaboration exists with other universities and possibly also in other countries. Since the EU framework programme projects by nature involve several Member States, the students have the possibility not only to meet researchers from other labs but also to perform relevant work at other labs than their own. In ACSEPT we have taken this a step further and opened the possibility for PhD student or young scientists to apply for funding from the DM4 budget to facilitate transnational access to other relevant labs within ACSEPT. The period of this stay was not fixed but ranged typically from a couple of weeks to three months. Naturally the work had to be relevant to the ACSEPT community and each proposal was thus reviewed by the PCC before any decision was taken. In total 11 such inter laboratory visits were performed. The majority (7 out of 11) of these mobility grants were awarded to female scientists. These small projects are listed in Table 3.

**Table 3: Student Exchange granted by ACSEPT**

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<sup>1</sup> The impact factor (IF) of an academic journal is a measure reflecting the average number of citations to recent articles published in the journal. It is frequently used as a proxy for the relative importance of a journal within its field, with journals with higher impact factors deemed to be more important than those with lower ones. The impact factor was devised by Eugene Garfield, the founder of the Institute for Scientific Information. Impact factors are calculated yearly for those journals that are indexed in the Journal Citation Reports.



Students	From	To	Project
Irena Spendlikova and Petr Distler	CTU	CEA	Study of DTPA and malonic acid extraction system for Ln(III)/An(III) separation
Ana Núñez	CIEMAT	ICIQ	Radiolytic degradation of TODGA: Quantification of the degradation compounds
Hitos Galán	CIEMAT	ULG	NMR analysis of the complexation of lanthanide and actinide ions by TODGA
Elin Löfström-Engdahl	CHALMERS	KIT	Thermodynamic data for CyMe <sub>4</sub> -BTBP and curium/europium complexes
Henrik Daniels	FZJ	CEA	Investigation of the gelation of U(VI)-Pu(III) and U(VI)-Am(III) solutions
Michal Sypula	FZJ	UDS	Zr complexation by CDTA and EDT
Emma Aneheim	CHALMERS	FZJ	Centrifugal contactor tests of the Chalmers GANEX system
Marcin Brykala	ICHTJ	FZJ	Reduction and sintering of uranium gels, also doped by a lanthanide, prepared by CSGP to dioxides. Analysis of obtained products
Agnieszka Sulich	ICHTJ	CHALMERS	Irradiations studies of relevant SANEX systems
Barbara Zielinska	ICHTJ	CHALMERS	Prevention of unvented extraction in the Chalmers GANEX

### IV.3.2 Dissemination of Knowledge / Training

Table 4 : List of invited lecturers of the first International ACSEPT Workshop

First Name	Name	Institute	Country	Title of the contribution
Vasily	Babain	Radium Khlopin Inst	Russia	Fluorinated Diluents for HLW Processing – Technological point of view
Uddharan	Basak	IAEA	Austria	IAEA Activities on Assessment of Partitioning Processes for Transmutation of Actinides
Victor	Ignatiev	Kurchatov Institute	Russia	Critical issues of nuclear energy systems employing molten salt fluorides: from ISTC #1606 to #3749 (1 <sup>st</sup> year of project activity) and MARS/ EVOL co-operation.
Mikhael	Kormilitsin	RIAR	Russia	Strategies and national programs of closed fuel cycles - Russian Expert Vision
Bruce	Mincher	INL	USA	Irradiation Effects on Metal Oxidation States
Krishnamurthy	Nagarajan	IGCAR	India	Pyroprocess Research Activities at IGCAR, India
Ken	Nash	WSU	USA	Investigations of The Fundamental Chemistry of the TALSPEAK Process
Gerald	Ouzounian	ANDRA	France	Radioactive Waste Management, IGD-TP
Alena	Paulenova	Oregon state University	USA	Redox Chemistry of Neptunium in Solutions of Nitric Acid
Manuel	Pouchon	PSI	Switzerland	Conversion processes: Internal Gelation and the Sphere-pac concept
Kenji	Takeshita	Tokyo Institute of Technology	Japan	Extraction Separation of Trivalent Minor Actinides and Lanthanides by Hexadentate Nitrogen-donor Extractant, TPEN, and its Analogs
Terry	Todd	INL-DOE	USA	The U.S. Fuel Cycle Research and Development Program: Separations Research and Development
Janne	Wallenius	KTH	Sweden	Transmutation
Dominique	Warin	CEA	France	Minor Actinide Partitioning
Peter	Wikberg	SKB	Sweden	Present status of the Swedish nuclear waste management programme

In a large project like ACSEPT, it is expected that a significant wealth of information and scientific results are

produced. This information will need to be disseminated not only within the project but also to the surrounding world. For this purpose two international ACSEPT workshops were organized. The first one was held in connection with the Second Annual ACSEPT meeting in Lisbon, Portugal. In order to obtain maximum benefit for both the ACSEPT partners but also the surrounding scientific community several well-known scientists from different countries contributed, see Table 4.

In addition to the invited speakers there were also many attendees from all over the world making up the total number of participants to more than 130 persons. Another interesting event at this conference was that the selection of the presentations as well as the chairmanship was done by our younger staff. This was very well received and performed.

The second ACSEPT workshop was held together with the ATALANTE 2012 conference. In this conference 20 oral presentations and 12 poster presentations from the ACSEPT community were given. Considering the very large number of participants to the ATALANTE conference (400), the impact and spreading of the ACSEPT results were very high.

**Table 5 : Addressed topics and the contributors of the ACSEPT training sessions**

Meeting	Contributors	Topic
1 <sup>st</sup> half-year meeting, Prague	Hubert Boussier; Sylvie Delpech, Pierre Taxil, Pierre Chamelot	The pyrometallurgy explained to the ACSEPT Community
	Jan Olov Liljenzin	Introduction to solvent extraction
1 <sup>st</sup> annual meeting, Madrid	Hansoo Lee (KAERI)	The Korean Strategy in Nuclear Fuel Cycle
	Alexander Bychkov (RIAR)	Partitioning of fissile and radiotoxic materials from SNF. RIAR activities at present and prospects
	Frodo Klaassen	Fairfuels Project Presentation
	13 presentations from ISTC, KAERI and ACSEPT dedicated to students and young scientists	ISTC-KAERI-ACSEPT Training session in pyrochemistry
2 <sup>nd</sup> half-year meeting, Bologna	Melissa Denecke, Marie-Christine Charbonnel, Olivier Pauvert	Basic investigations
	Andrzej Deptula, Joe Somers, Dominique Warin	From actinide solution to fuel
	Bruce Mincher (INL), Steve Mezyk California State Univ), Laurence Berthon	Radiolysis
2 <sup>nd</sup> annual meeting, Lisbon		ACSEPT International Workshop
3 <sup>rd</sup> half-year meeting, Petten	W. Oziminski, D. Guillaumont, B. Shimmelpfennig, C. Simon, E. Sanchez (Univ Sevilla, Spain), P. Guilbaud, G. Wipff	Computational Chemistry Day
3 <sup>rd</sup> annual meeting, Manchester	13 presentations from ISTC, KAERI and ACSEPT dedicated to students and young scientists	ISTC-KAERI-ACSEPT Exchange Meeting
4 <sup>th</sup> half-year meeting, Uddevalla	Jim Willit (ANL, USA)	Pyrochemistry in the US
	Lize Stassen (NECSA, South Africa)	Overview of NECSA activities in nuclear chemistry
	Francis Livens (Univ Manchester, UK)	MBase Project
	Xavier Hérès	The chemistry of Np, Pu in nitric medium and industrial separations
4 <sup>th</sup> annual meeting, Karlsruhe	A. Geist, R. Taylor, G. Modolo, R. Malmbeck, X. Hérès	GANEX Meeting
Final meeting	S. Bourg	SACSESS, the follow-up of ACSEPT

The ACSEPT project covers many disciplines and not all of them are closely related but nevertheless highly important for the outcome of the project. Unfortunately, especially for the younger collaborators the basic knowledge to understand all the aspects of the different subjects can be very difficult. In order to remedy this

situation, special lectures were given or training sessions were organized at each ACSEPT meeting. The addressed topics and the contributors are given in Table 5. In addition, focused workshops were organized during the half-year meetings to address very specific issues linked to the objectives of the project, both in hydro- and in pyro-metallurgy.

Another important aspect of dissemination of knowledge is the possibility to present the work performed at international conferences and meetings outside the ACSEPT community. In many cases and for some laboratories (especially universities) the costs to attend a particular conference can be difficult to handle. In addition, in ACSEPT the younger scientists are strongly encouraged to be present in the bi-annual meetings in order to benefit maximally from the project. Such participation naturally increases the costs for each lab to participate to the meetings which may not be covered in the granted budget. As a response to this need it was decided that it should be possible for students and young scientists to apply for funding for conference attendance including travels and hotel costs. Each person applying should preferably have an accepted oral or poster presentation. The viability of each proposal was validated by the PCC. Some of the awarded grants are shown in Table 6:

**Table 6 : ACSEPT Travel grants for attending International Conferences**

Student	Conference	Contrib.	Title
Kamil Vavřinec Mares (CTU)	ATALANTE 2012	Poster	Mares, K. V.; John, J.; Šebesta, F.; Vlk, M.; Svobodova, T.: <i>Decontamination of Spent DIAMEX Solvents Containing Contaminants Difficult to Strip</i>
Petr Distler (CTU)	ATALANTE 2012	Oral	Distler, P.; John, J.; Štastná, K.; Lewis, F. W.; Harwood, L. M.; Hudson, M. J.: <i>Kinetic effects in the Am/Eu separation with BTBP-ligands.</i>
Tomas Koubsky (CTU)	ATALANTE 2012	Poster	Koubsky, T.; Kalvoda, L.: <i>Ab-initio Simulations of Chemical Stability Indicators of UAM-069 and its Radiation Degradation Products.</i>
Emma Aneheim (CHALMERS)	ATALANTE 2012	Oral	Aneheim, E., Bauhn, L., Ekberg, C., Foreman, M., Löfström-Engdahl, E.: <i>Extraction experiments after radiolysis of a proposed GANEX solvent - the effect of time.</i>
Elin Löfström-Engdahl (CHALMERS)	ISEC 2011	Oral	Löfström-Engdahl, E.; Aneheim, E.; Ekberg, C.; Mabile, N.; Skarnemark, G. <i>Solvent effects on the extraction rate in proposed GANEX processes</i>
Emma Aneheim (CHALMERS)	ISEC 2011	Oral	Aneheim, E., Ekberg, C., Mabile, N.: <i>Exchange of TBP for a monoamide extraction ligand in a GANEX Solvent - advantages and disadvantages.</i>
Emma Aneheim (CHALMERS)	ISEC 2011	Poster	Aneheim, E., Ekberg, C., Foreman, M. R. S., Löfström-Engdahl, E., <i>Palladium chemistry in the advanced reprocessing of spent nuclear fuel</i>
Marcin Brykala (ICHTJ)	NFCC 2012	Oral	<i>"Synthesis of Uranium Dioxide Microspheres by Water and Nitrate Extraction from Uranyl-Ascorbate Sols"</i>

In addition to the attendance to these conferences, the possibilities to attend the internal ACSEPT training sessions were also given. In order to facilitate attendance participation, costs were covered by ACSEPT after review by the PCC. The attendees for the pyrochemical training session as well as the hydrochemical training sessions are listed in Table 7.

The dissemination of the ACSEPT results was therefore highly successful. Not only the actual results were communicated to the broader scientific community but also younger scientists were given the possibility to take an active part in the organization of scientific sessions both from the preparation and well as chairing the sessions. In addition, thanks to the travel funding allocated in ACSEPT, more young scientists could participate in the half yearly meetings as well as present ACSEPT results at important international conferences.

**Table 7: List of granted students attending the hydro and pyro training sessions**

<b>Hydro training session</b>	<b>Pyro training session</b>
Irena Spendlikova (CTU)	Bertha Camafort (ICIQ)
Anna Fermvik (CHALMERS)	Stéphanie Fabre (EDF)
Emma Aneheim (CHALMERS)	Anne Huguet (CEA)
Ana Nunez (CIEMAT)	Sebastien Jaskierowicz (CNRS)
Hitos Galan (CIEMAT)	Olivier Lemoine (CNRS)
Charlotte Brady (UEDIN)	Olivier Pauvert (CNRS)
	Sami Tazi (CNRS)
	Geoffrey Vidick (ULG)

### IV.3.3 Communication / fostering visibility

Through the participation of the coordinator and researchers to international events (conferences, expert groups, summer schools, trainings...), the work performed within ACSEPT was widely disseminated in Europe, but also at the international level. ACSEPT, as itself, as well as the high quality of the work done is internationally acknowledged and is considered as a reference in terms of collaborative project. ACSEPT is very often cited by key representatives of international research bodies from US, Japan, Russia...

When a research is performed in Google with "ACSEPT" as a keyword, 17 results out of 20 are directly related to the project, from 12 different websites.

When the keywords are "actinide separation", ACSEPT is listed two times in the first 10 results (7<sup>th</sup> and 10<sup>th</sup>), amongst them, the ACSEPT Homepage (10<sup>th</sup>).

When the keywords are "actinide recycling", ACSEPT is listed two times in the first 10 results (2<sup>nd</sup> and 5<sup>th</sup>), amongst them, the ACSEPT Homepage (2<sup>nd</sup>).

When the keywords are "actinide FP7", ACSEPT is listed five times in the first 10 results, amongst them, the ACSEPT Homepage (5<sup>th</sup>).

This demonstrates clearly the high visibility of the project in its domain.

## IV.4 Exploitation of results

Within ACSEPT, in aqueous reprocessing, four hot-tests were carried out. At the time the project ended, it can be stated that three of them present performances along a development at a higher scale, if there would be an industrial need. The results on the fourth one were not available yet.

In pyroreprocessing, the two processes developed in ACSEPT remain valid options for the future. The electrorefining on aluminium cathode can be considered as an alternative to the IFR concept process involving liquid cadmium. Separation performances are higher, handling of Al is easier, toxicity and volatility is much lower, availability is much higher. Only the actinide recovery phase is more complex but still achievable, as demonstrated in ACSEPT. The liquid-liquid reductive extraction is an efficient process to treat very refractory spent oxide fuel or targets. Decontamination factors and recovery yields are very good. A development of these two processes at a higher scale is still needed to definitely assess their performances.

In the future, the researches will focus on the consolidation phase (safety approach, secondary waste management...).

## PART II: USE & DISSEMINATION OF FOREGROUND

### I SECTION A (PUBLIC): LIST OF ALL SCIENTIFIC (PEER REVIEWED) PUBLICATIONS & ALL DISSEMINATION ACTIVITIES

#### I.1 Scientific (Peer Reviewed) Publications

##### I.1.1 Journal of American Chemical Society (2011 Impact factor: 9.907)

- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.-H. Vu, J.-P. Simonin, "Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-Triazine Ligand", *J. Am. Chem. Soc.*, 2011, **133** (33), 13093–13102, published in issue on August 24, 2011, published on the web on July 19, 2011 - DOI: 10.1021/ja203378m - Paper highlighted in Chemistry World (see: <http://www.rsc.org/chemistryworld/News/2011/August/09081101.asp>).

##### I.1.2 Chemistry Communication (2011 Impact factor: 6.169)

- ✓ Reilly S. D., Gaunt A. J., Scott B. L., Modolo G., Iqbal M., Verboom W., Sarsfield M. J., "Plutonium(IV) complexation by diglycolamide ligands-coordination chemistry insight into TODGA-based actinide separations", *Chem. Commun.* **2012**, 48 (78), 9732-9734, published on the web on 23 Aug 2012 - DOI: 10.1039/C2CC34967A

##### I.1.3 Inorganic Chemistry (2011 Impact factor: 4.601)

- ✓ Véronique Hubscher-Bruder, Jaouad Haddaoui, Saliha Bouhroum, and Françoise Arnaud-Neu, "Recognition of Some Lanthanides, Actinides, and Transition- and Heavy-Metal Cations by N-Donor Ligands: Thermodynamic and Kinetic Aspects", *Inorg. Chem.* 2010, 49, 1363–1371, published in issue on 15 February 2010, published on the Web on 07 Jan 2010 - DOI: 10.1021/ic9010899
- ✓ M. Steppert, I. Císařová, Th. Fanghänel, A. Geist, P. Lindqvist-Reis, P. Panak, P. Štěpnička, S. Trumm, C. Walther, "Complexation of europium(III) by bis(dialkyltriazinyl)bipyridines in 1-octanol", *Inorg. Chem.* **2012**, 51 (1), 591–600, published in issue on January 02, 2012, published on the web on December 1, 2011 - DOI: 10.1021/ic202119x
- ✓ M. J. Hudson, L. M. Harwood, D. M. Laventine, F. W. Lewis, "Use of Soft Heterocyclic N-Donor Ligands to Separate Actinides and Lanthanides", *Inorg. Chem.*, **2012**, 51, published on the web on August 6, 2012 - DOI: 10.1021/ic3008848 (special forum issue "Inorganic Chemistry Related to Nuclear Energy").

##### I.1.4 Dalton Transactions (2011 Impact factor: 3.838)

- ✓ Anna Fermvik, Laurence Berthon, Christian Ekberg, Sofie Englund, Teodora Retegana and Nicole Zorz, "Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate" *Dalton Trans.*, 2009, 38, 6421–6430, published on the web on 3<sup>rd</sup> July 2009 - DOI: 10.1039/b907084b
- ✓ S. Trumm, G. Lieser, M.R.S. Foreman, P.J. Panak, A. Geist, Th. Fanghänel, "A TRLFS study on the complexation of Cm(III) and Eu(III) with 4-t-butyl-6,6'-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine in a water/2-propanol mixture", *Dalton Trans.* 2010, 39, 923–929 published on the web on 20<sup>th</sup> November 2009 - DOI: 10.1039/b919247f
- ✓ Lewis, F., Harwood, L. M., Hudson, M. J., Drew, M. G., Modolo, G., Sypula, M., Desreux, J. F., Bouslimani, N., Vidick, G., "Interaction of 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-1,2,4-benzotriazin-3-yl)-2,2':6',2''-terpyridine (CyMe<sub>4</sub>-BTTP) with some Trivalent Ions such as Lanthanide(III) Ions and Americium(III)", *Dalton Transactions*, 39, (2010), 5172-5182, published on the web on 23<sup>rd</sup> April 2010 - DOI: 10.1039/b924988e

- ✓ Frank W. Lewis, Laurence M. Harwood, Michael J. Hudson, Michael G. B. Drew, Michal Sypula, Giuseppe Modolo, Daniel Whittaker, Clint A. Sharrad, Vladimira Videva, Véronique Hubscher-Bruder and Françoise Arnaud-Neu, "Complexation of lanthanides, actinides and transition metal cations with a 6-(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine ligand: implications for actinide(III)/lanthanide(III) partitioning", *Dalton Trans.*, 2012, **41**, 9209-9219, published on the web on 18<sup>th</sup> May 2012 - DOI: 10.1039/c2dt30522d
- ✓ J. Narbutt, W. P. Oziminski, "Selectivity of bis-triazinyl bipyridine ligands for americium(III) in Am/Eu separation by solvent extraction. Part 1. Quantum mechanical study on the structures of BTBP complexes and on the energy of the separation", *Dalton Trans.*, 41(47) 14416-24, published on the web on 09<sup>th</sup> Oct. 2012 - DOI: 10.1039/c2dt31503c

### **I.1.5 Electrochimica Acta; (2011 Impact factor: 3.832)**

- ✓ M. Gibilaro, J. Pivato, L. Cassayre, L. Massot, P. Chamelot, P. Taxil, "Direct electroreduction of oxides in molten fluoride salts", *Electrochimica Acta* 56 (2011) 5410–5415, published in issue on 1 June 2011, published on the web on 24 March 2011 - DOI:10.1016/j.electacta.2011.02.109
- ✓ L. Massot, P. Chamelot, M. Gibilaro, L. Cassayre, P. Taxil, "Nitrogen evolution as anodic reaction in molten LiF–CaF<sub>2</sub>", *Electrochimica Acta* 56 (2011) 4949–4952, published in issue on 30 May 2011, published on the web on 7 April 2011 - DOI: 10.1016/j.electacta.2011.03.131

### **I.1.6 Organic & Biomolecular Chemistry (2011 Impact factor: 3.696)**

- ✓ N.I. Nikishkin, J. Huskens, J. Assenmacher, A. Wilden, G. Modolo and W. Verboom, "Palladium-catalyzed cross-coupling of various phosphorus pronucleophiles with chloropyrazines: synthesis of novel Am(III)-selective extractants", *Org. Biomol. Chem.* **2012**, *10*, 5443-5451, published on the web on 01 June 2012 - DOI: 10.1039/c2ob25787d

### **I.1.7 Physical Chemistry Chemical Physics (2011 Impact factor: 3.573)**

- ✓ G. Benay, R. Schurhammer and G. Wipff "BTP-based ligands and their complexes with Eu<sup>3+</sup> at "oil"/water interfaces: a molecular dynamics study", *Phys. Chem. Chem. Phys.*, 2010, *12*, 11089-11102, published on the web on 30 July 2010 - DOI: 10.1039/c000772b
- ✓ G. Benay, R. Schurhammer and G. Wipff, "Basicity, complexation ability and interfacial behavior of BTBPs: a simulation study", *Phys. Chem. Chem. Phys.* 2011, *13*, 2922–2934, published on the web on 16 Dec 2010 - DOI: 10.1039/c0cp01975e

### **I.1.8 European Journal of Organic Chemistry (2011 Impact factor: 3.329)**

- ✓ Hitos Galán, María Teresa Murillo, Rosa Sedano, Ana Núñez, Javier de Mendoza, Amparo González-Espartero, and Pilar Prados. "Hydrolysis and Radiation Stability of a m-Xylylene-bis-Diglycolamide (Bis-DGA). Synthesis and Quantitative Study of Degradation Products by HPLC-APCI", *Eur. J. Org. Chem.*, Vol. **2011** (20-21), 3959–3969, published in issue on July 2011, published on the web on 27 June 2011 - DOI: 10.1002/ejoc.201100443
- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, P. Distler, J. John, K. Stamberg, A. Núñez, H. Galán, A. G. Espartero, "Synthesis and Evaluation of Lipophilic BTBP Ligands for An/Ln Separations in Nuclear Waste Treatment: The Effect of Alkyl Substitution on Extraction Properties and Implications for Ligand Design", *Eur. J. Org. Chem.*, Vol. **2012** (8), 1509–1519, published in issue on March 2012, published on the web on 12 Jan 2012 - DOI: 10.1002/ejoc.201101576 - Paper Selected For Press Release

### **I.1.9 European Journal of Inorganic Chemistry (2011 Impact factor: 3.049)**

- ✓ S. Trumm, P.J. Panak, A. Geist, Th. Fanghänel, "A TRLFS study on the complexation of Cm(III) and Eu(III) with 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in water/methanol mixture", *Eur. J. Inorg. Chem.*, Vol. 2010 (19), 3022–3028, published in issue on July 2010, published on the web on 12 May 2010 - DOI: 10.1002/ejic.201000230

### **I.1.10 Synlett (2011 Impact factor: 2.710)**

- ✓ F. W. Lewis, M. J. Hudson, L. M. Harwood, "Development of Highly Selective Ligands for Separations of Actinides from Lanthanides in the Nuclear Fuel Cycle", *Synlett*, 22, **2011** (8), 2609–2632, published on the web on 25 October 2011 - DOI: 10.1055/s-0030-1289557

### **I.1.11 New Journal of Chemistry (2011 Impact factor: 2.605)**

- ✓ Benay, R. Schurhammer, J. Desaphy, G. Wipff, "Substituent effects on BTP's basicity and complexation properties with Ln<sup>III</sup> lanthanide ions", *New J. Chem.*, **2011**, 35, 184 – 189, published on the web on 11 Oct 2010, DOI: 10.1039/c0nj00527d
- ✓ M. Iqbal, J. Huskens, M. Sypula, G. Modolo and W. Verboom, "Synthesis and evaluation of novel water-soluble ligands for the complexation of metals during the partitioning of actinides", *New J. Chem.* **2011**, 35, 2591-2600, published on the web on 6 September 2011- DOI: 10.1039/c1nj20523d
- ✓ M. Iqbal, R.G. Struijk, J. Huskens, M. Sypula, A. Wilden, G. Modolo and W. Verboom, "Synthesis and evaluation of ligands with mixed amide and phosphonate, phosphin oxide, and phosphonothioate sites for An(III)/Ln(III) extraction", *New J. Chem.* **2012**, 36(10), 2048-2059, published on the web on 16 July 2012 - DOI: 10.1039/c2nj40330g

### **I.1.12 Journal of the Electrochemical Society (2011 Impact factor: 2.590)**

- ✓ C.P. Fabian, V. Luca, P. Chamelot, L. Massot, C. Caravaca, G.R.Lumpkin, "Experimental and simulation study of the electrode reaction mechanism of La<sup>3+</sup> in LiCl-KCl eutectic molten salt", *Journal of the Electrochemical Society*, 159 (4) F63-67 (2012), published in issue on January 30, 2012 - DOI: 10.1149/2.057204jes

### **I.1.13 Supramolecular Chemistry (2011 Impact factor: 2.145)**

- ✓ M. Iqbal, J. Huskens, W. Verboom, M. Sypula and G. Modolo, "Synthesis and Am/Eu extraction of novel TODGA derivatives", *Supramol. Chem.* **2010**, 22(11-12), 827-837, published in issue on 26 Aug 2010 - DOI: 10.1080/10610278.2010.506553

### **I.1.14 Polyhedron (2011 Impact factor: 2.057)**

- ✓ E. Aneheim, B. Grüner, C. Ekberg, M.R. Foreman, Z. Hájková, E. Löfström-Engdahl, M.G.B. Drew, M.J. Hudson, "Fission Product Interactions with Nitrogen Donor Ligands used for Spent Nuclear Fuel Treatment", *Polyhedron* (2012), 50 (1), published in issue on 13 February 2013, published on the web on 2 November 2012 Pages 154–163 - DOI: 10.1016/j.poly.2012.10.030

### **I.1.15 Journal of Nuclear Materials (2011 Impact factor: 2.052)**

- ✓ G. De Córdoba, A. Laplace, O. Conocar and J. Lacquement, "Determination of the activity coefficient of Am in liquid Al by electrochemical methods", *Journal of Nuclear Materials* 393 (2009) 459–464, published in issue on 15 September 2009 - DOI: 10.1016/j.jnucmat.2009.07.002
- ✓ P. Souček, R. Malmbeck, E. Mendes, C. Nourry, D. Sedmidubský, J.-P. Glatz., "Study of thermodynamic properties of Np-Al alloys in molten LiCl-KCl eutectic", *Journal of Nuclear Materials* 394 (2009), pp. 26-33, published in issue on 1 October 2009 - DOI: 10.1016/j.jnucmat.2009.08.003
- ✓ M. Gibilaro, L. Cassayre, O. Lemoine, L. Massot, O. Dugne, R. Malmbeck, P. Chamelot, "Direct electrochemical reduction of solid uranium oxide in molten fluoride salts", *Journal of Nuclear Materials* 414 (2011) 169–173, published in issue on 15 July 2011, published on the web on 24 February 2011 - DOI: 10.1016/j.jnucmat.2011.02.053
- ✓ L. Cassayre, P. Souček, E. Mendes, R. Malmbeck, C. Nourry, R. Eloirdi, J.-P. Glatz, "Recovery of actinides from actinide-aluminium alloys by chlorination: Part I", *Journal of Nuclear Materials* 414 (2011) 12–18, published in issue on 1 July 2011, published on the web on 30 April 2011 - DOI: 10.1016/j.jnucmat.2011.04.023
- ✓ E. Mendes, R. Malmbeck, C. Nourry, P. Souček, J.-P. Glatz, "On the electrochemical formation of Pu-Al alloys in molten LiCl-KCl", *Journal of Nuclear Materials* 420 (2012) 424–429, published in issue January 2012, published on the web on 12 October 2011 - DOI:10.1016/j.jnucmat.2011.09.017

- ✓ Anne-Laure Rollet, Emmanuel Veron, Catherine Bessada, "Fission products behavior in molten fluoride salts: Speciation of  $\text{La}^{3+}$  and  $\text{Cs}^+$  in melts containing oxide ions", *Journal of Nuclear Materials* 429 (2012) 40–47, published in issue October 2012, published on the web on 14 May 2012, published on the web on 12 October 2011 - DOI: 10.1016/j.jnucmat.2012.05.010
- ✓ C. Nourry, P. Souček, L. Massot, R. Malmbeck, P. Chamelot, J.-P. Glatz, "Electrochemistry of Uranium in molten  $\text{LiF-CaF}_2$ ", *Journal of Nuclear Materials* 430 (2012) 58–63, published in issue November 2012, published on the web on 4 July 2012 - DOI: 10.1016/j.jnucmat.2012.06.028

### **I.1.16 Hydrometallurgy (2011 Impact factor: 2.027)**

- ✓ Emma Aneheim, Christian Ekberg, Mark R. StJ. Foreman, "Aqueous Complexation of Palladium to Prevent Precipitation and Extraction in a Group Actinide Extraction System", *Hydrometallurgy* (115-116), pp. 71-76, 2012, published in issue March 2012, published on the web on 29 December 2011 - DOI: 10.1016/j.hydromet.2011.12.018

### **I.1.17 Solvent Extraction and Ion Exchange (2011 Impact factor: 2.024)**

- ✓ Teodora Retegan, Laurence Berthon, Christian Ekberg, Anna Fermvik, Gunnar Skarnemark, and Nicole Zorz, "Electrospray Ionization Mass Spectrometry Investigation of BTBP – Lanthanide(III) and Actinide(III) Complexes", *Solvent Extraction and Ion Exchange*, 27(5-6), 663-682 (2009), published in issue on 10 Nov 2009 – DOI: 10.1080/07366290903113991
- ✓ Murillo M. T., Espartero A. G., Sánchez-Quesada J., de Mendoza J., Prados P., "Synthesis of the Pre-Organized Bisdiglycolamides (BisDGA) and Assessment of their Extraction Properties for Actinides(III) and Lanthanides(III)", *Solvent Extraction and Ion Exchange*, 27(2), 107-131 (2009), published in issue on 25 Feb 2009, DOI:10.1080/07366290802672212
- ✓ D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, C. Sorel, "Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate, Part III: Centrifugal Contactor Run using Genuine Fuel Solution", *Solvent Extraction and Ion Exchange*, 27(2), 26–35 (2009), published in issue on 07 January 2009 - DOI: 10.1080/07366290802544726
- ✓ D. Magnusson, B. Christiansen, M.R.S. Foreman, A. Geist, J.-P.Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, C. Sorel, "Demonstration of a SANEX process in centrifugal contactors using the  $\text{CyMe}_4\text{-BTBP}$  molecule on a genuine fuel solution", *Solvent Extr. Ion Exch.*, 27(2), 97-106 (2009), published in issue on 25 Feb 2009 - DOI: 10.1080/07366290802672204
- ✓ A. Geist, "Extraction of nitric acid into alcohol-kerosene mixtures", *Solvent Extr. Ion Exch.*, 28 (5), 596–607 (2010), published in issue on 25 Aug 2010 - DOI:10.1080/07366299.2010.499286
- ✓ Mark J. Sarsfield, Howard E. Sims, Robin J. Taylor, "Modelling  $\text{Np(IV)}$  solvent extraction between 30 % tri-butyl phosphate and nitric acid in the presence of simple hydroxamic acids", *Solv. Extr. Ion Exch.*, 29 (1), 49-71 (2011), published in issue on 06 Feb 2011 - DOI: 10.1080/07366299.2011.539120
- ✓ A. Wilden, C. Schreinemachers, M. Sypula and G. Modolo, "Direct selective extraction of actinides (III) from PUREX raffinate using a mixture of  $\text{CyMe}_4\text{BTBP}$  and TODGA as 1- cycle SANEX solvent" *Solvent Extraction and Ion Exchange*, 29(2), 190-212 (2011), published in issue on 30 Mar 2011 - DOI: 10.1080/07366299.2011.539122
- ✓ S. Trumm, A. Geist, P.J. Panak, Th. Fanghänel, "An improved hydrolytically-stable bis-triazinylpyridine (BTP) for selective actinide extraction". *Solvent Extraction and Ion Exchange*, 29(2), 213-229 (2011), published in issue on 30 Mar 2011 - DOI: 10.1080/07366299.2011.539129
- ✓ L. M. Harwood, F. W. Lewis, M. J. Hudson, J. John, P. Distler, "The Separation of Americium(III) from Europium(III) by Two New 6,6'-Bistriazinyl-2,2'-bipyridines in Different Diluents", *Solvent Extraction and Ion Exchange*, 29(4), 551-576 (2011), published in issue on 18 Jul 2011 - DOI: 10.1080/10496475.2011.556989
- ✓ Aneheim E., Fermvik A., Ekberg C., Foreman M.R.S., "A TBP/BTBP-based GANEX Separation Process - Part 1: feasibility", *Solvent Extraction and Ion Exchange*, 28(4), 437-458 (2010), published in issue on 04 Jun 2010 - DOI: 10.1080/07366299.2010.480930
- ✓ E. Aneheim, C. Ekberg, A. Fermvik, M.R.S.J. Foreman, B. Grüner, Z. Hájková and M. Kvíčalová, "A TBP/BTBP-based GANEX separation Process, Part 2: Ageing, Hydrolytic & Radiolytic Stability", *Solvent Extraction and Ion exchange*, 29(2), 157-175 (2011), published in issue on 30 Mar 2011 -



DOI:10.1080/07366299.2011.539462

- ✓ Aneheim E., Ekberg C., Foreman M. R. StJ., "A TBP/BTBP-based GANEX Separation Process - Part 3: Fission Product Handling", accepted for publication in *Solvent Extraction and Ion Exchange*, vol. 31, 2013
- ✓ Sypula M., Wilden A., Schreinemachers C., Malmbeck R., Geist A., Taylor R., Modolo G., "Use of polyaminocarboxylic acids as hydrophilic masking agents for fission products in actinide partitioning processes", *Solvent Extr. Ion Exch.*, 30 (7), 748-764 (2012), published in issue on 14 Nov 2012, published on the web on 26 Jun 2012 - DOI: 10.1080/07366299.2012.700591
- ✓ Magnusson D., Geist A., Wilden A., Modolo G., "Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe<sub>4</sub>-BTBP and TODGA as 1-cycle SANEX Solvent Part II: Flow-sheet Design for a Counter-Current Centrifugal Contactor Demonstration Process", *Solvent Extr. Ion Exch.*, 30(7) (2012), published on the web on 26 Jun 2012, DOI: 10.1080/07366299.2012.700596
- ✓ D. Magnusson, R. Malmbeck, "Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors", *Solvent Extraction and Ion Exchange*, 30 (2), 115–126, 2012, published in issue on 29 Feb 2012 - DOI: 10.1080/07366299.2011.581085
- ✓ Geist A., Müllich U., Magnusson D., Kaden P., Modolo G., Wilden A., Zevaco T., "Actinide(III)/lanthanide(III) Separation via Selective Aqueous Complexation of Actinides(III) using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-Yl)-Pyridine in Nitric Acid", *Solvent Extr. Ion Exch.*, 30(5), 433-444 (2012), published in issue on 05 Oct 2012, published on the web on 23 Mar 2012 - DOI: 10.1080/07366299.2012.671111
- ✓ S. Trumm, A. Geist, P.J. Panak, Th. Fanghänel, "An improved hydrolytically-stable bis-triazinyl-pyridine (BTP) for selective actinide extraction", *Solvent Extr. Ion Exch.*, 2011, 29 (2), 213–229, published in issue on 30 Mar 2011 - DOI: 10.1080/07366299.2011.539129
- ✓ Jamie Brown, Fiona McLachlan, Mark Sarsfield, Robin Taylor, Giuseppe Modolo, Andreas Wilden, "Plutonium loading of prospective grouped actinide extraction (GANEX) solvent systems based on diglycolamide extractants", *Solv. Extr. Ion Exch.*, 30, 127-141 (2012), published in issue on 29 Feb 2012 - DOI: 10.1080/07366299.2011.609378
- ✓ M. J. Carrot, C. R. Gregson, R. J. Taylor, "Neptunium extraction and stability in the GANEX solvent: 0.2 M TODGA / 0.5 M DMDOHEMA / kerosene", *Solv. Extr. Ion Exch.*, 31(1) (2013), published on the web on 11 Oct 2012 - DOI: 10.1080/07366299.2012.735559
- ✓ L. M. Harwood, F. W. Lewis, M. J. Hudson, J. John, P. Distler, "The Separation of Americium(III) from Europium(III) by Two New 6,6'-Bistriazinyl-2,2'-bipyridines in Different Diluents", *Solvent Extr. Ion Exch.*, 29(4) 551–576 (2011), published in issue on 18 Jul 2011 - DOI: 10.1080/10496475.2011.556989

### **I.1.18 Journal of Chemical and Engineering data (2011 Impact factor: 1.693)**

- ✓ Christian Ekberg, Emma Aneheim, Anna Fermvik, Mark Foreman, Elin Ljöfström-Engdahl, Teodora Retegan, Irena Spendlikova, "Thermodynamics of Dissolution for BTBP-Class Ligands in Different Diluents and Its Reflection on Extraction", *Chem. Eng. Data*, 2010, 55(11), pp 5133–5137, published in issue on 11 November 2010, published on the web on 30 September 2010 - DOI: 10.1021/jc1005246

### **I.1.19 Radiochimica Acta (2011 Impact factor: 1.575)**

- ✓ Anna Fermvik, Christian Ekberg, Sofie Englund, M. R. S. J. Foreman, G. Modolo, Teodora Retegan, Gunnar Skarnemark, "Influence of dose rate on the radiolytic stability of a BTPB solvent for actinide(III)/lanthanide(III) separation", *Radiochim. Acta* 97(6), 319–324 (2009), published in issue and on the web on 1 June 2009 – DOI: 10.1524/ract.2009.1615
- ✓ D. Magnusson, B. Christiansen, R. Malmbeck, J.-P. Glatz, "Investigation of the radiolytic stability of a Cy-Me<sub>4</sub>BTBP based SANEX solvent", *Radiochimica Acta* 97(9) (2009), 497-502, published in issue and on the web on 1 August 2009 - DOI: 10.1524/ract.2009.1647
- ✓ Magnusson D., Christiansen B., Glatz J.-P., Malmbeck R., Modolo G., Serrano-Purroy D., Sorel C., "Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors", *Radiochimica Acta* 97(3) (2009) 155 – 159, published in issue and on the web 1 August 2009 - DOI:

10.1524/ract.2009.1587

- ✓ Fermvik A., Gruner B., Kvicalova M., Ekberg C., "Semi-quantitative and quantitative studies on the gamma radiolysis of C5-BTBP", *Radiochimica Acta* 99(2). 113-119 (2011), published in issue and on the web on 1 Feb 2011 - DOI: 10.1524/ract.2011.1800
- ✓ S. Trumm, G. Wipff, A. Geist, P. J. Panak, Th. Fanghänel, "Optimising BTP ligands by tuning their basicity", *Radiochim. Acta* 99(1), (2011) 13-16, published in issue and on the web on 1 January 2011 – DOI: 10.1524/ract.2011.1794
- ✓ Anna Fermvik, Emma Aneheim, Bohumir Gruner, Zuzana Hájková, Magdaléna Kvicalova, Christian Ekberg, "Radiolysis of C5-BTBP in cyclohexanone irradiated in the absence and presence of an aqueous phase", *Radiochim. Acta* 100(4), 273–282 (2012), published in issue Apr 2012 and on the web on 12 March 2012 – DOI: 10.1524/ract.2012.1908
- ✓ P. Distler, I. Spendlikova, J. John, L. M. Harwood, M. J. Hudson, F. W. Lewis, "Influence of diluent alkyl substitution on the extraction of Am(III) and Eu(III) by a 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligand dissolved in alkylated cyclohexanone diluents", *Radiochimica Acta* 100(10), 747–751 (2012), published in issue October 2012 and on the web on 10 April 2012– DOI: 10.1524/ract.2012.1949
- ✓ Modolo G., Wilden A., Geist A., Magnusson D., Malmbeck R., "A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate", *Radiochim. Acta* 100 (8-9, Plutonium Futures), 715-725 (2012), published on the web on 13 August 2012 - DOI: 10.1524/ract.2012.1962

### **I.1.20 Journal of Radioanalytical and Nuclear Chemistry (2011 Impact factor: 1.520)**

- ✓ P. Souček, R. Malmbeck, E. Mendes, C. Nourry, J.-P. Glatz., "Exhaustive electrolysis for recovery of actinides from molten LiCl-KCl using solid aluminium cathodes", *J Radioanal Nucl Chem* 286(3) 823–828 (2010), published in issue on 1 December 2010 and on the web on 29 August 2010 - DOI : 10.1007/s10967-010-0739-6
- ✓ Anna Fermvik, "Comparison of the effect of alpha and gamma radiolysis on the extraction of americium by C5-BTBP in cyclohexanone", *J Radioanal Nucl Chem* 289(3) 811–817 (2011), published in issue on 1 September 2011 and on the web on 20 May 2011 - DOI 10.1007/s10967-011-1163-2
- ✓ Aneheim E., Ekberg C., Littley A., Löfström-Engdahl E., Skarnemark G., "Technetium chemistry in a novel group actinide extraction process", *Journal of Radioanalytical and Nuclear Chemistry* 2012, published on the web on 18 July 2012 – DOI: 10.1007/s10967-012-1928-2
- ✓ Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Gunnar Skarnemark, "A reinterpretation of C5-BTBP extraction data, performed in various alcohols", *J Radioanal Nucl Chem* 2012, published on the web on 17 August 2012 - DOI 10.1007/s10967-012-1976-7
- ✓ Straka M., Korenko M., Szatmary L., "Electrochemistry of praseodymium in LiF-CaF<sub>2</sub>", *J Radioanal Nucl Chem*, 289(2) (2011) 591-593, published in issue on 1 August 2011 and on the web on 11 May 2011 – DOI: 10.1007/s10967-011-1128-5

### **I.1.21 Radiation Physics and Chemistry (2011 Impact factor: 1.227)**

- ✓ Ekberg C., Aneheim E., Fermvik A., Skarnemark G., "Using <sup>211</sup>At as internal alpha radiolysis source allowing for simple detection of radiolysis products", *Radiation Physics and Chemistry*, **79**, 454-456, (2010) – DOI: 10.1016/j.radphyschem.2009.10.003.

### **I.1.22 Separation Science & Technology (2011 Impact factor: 1.088)**

- ✓ Emma Aneheim, Christian Ekberg, Mark R.S. Foreman, Elin Löfström-Engdahl, Nathalie Mabile, "Studies of a solvent for GANEX applications containing CyMe<sub>4</sub>-BTBP and DEHBA in Cyclohexanone", *Separation Science and Technology*, 47 (5) 663-669, 2012, published in issue on 06 Apr 2012, published on the web on 06 Dec 2011 - DOI: 10.1080/01496395.2011.627908

### **I.1.23 Progress in Nuclear Energy (2011 Impact factor: 0.849)**

- ✓ H. Daniels, S. Neumeier, A.A. Bukaemskiy, G. Modolo, D. Bosbach, "Fabrication of oxidic uranium-neodymium microspheres by internal gelation", *Progress in Nuclear Energy* 57 (2012) 106-110,

published in issue May 2012 - DOI: 10.1016/j.pnucene.2011.12.016

### **I.1.24 Nuclear Engineering and Design (2011 Impact factor: 0.765)**

- ✓ Bourg S., Hill C., Caravaca C., Rhodes C., Ekberg C., Taylor R., Geist A., Modolo G., Cassayre L., Malmbeck R., Harrison M., de Angelis G., Espartero A., Bouvet S., Ouvrier N., "ACSEPT - Partitioning technologies and actinide science: Towards pilot facilities in Europe", Nuclear Engineering and Design 241(9), 3427-3435, (2011), published in issue September 2011 - DOI: 10.1016/j.nucengdes.2011.03.011

## **I.2 Dissemination Activities**

### **I.2.1 First level Conferences (for ACSEPT dissemination of knowledge)**

#### **235<sup>th</sup> National Meeting of the American Chemical Society, New Orleans, USA, 6-10 April 2008**

##### **Oral presentation on invitation:**

- ✓ J. F. Desreux, D. Braekers, C. Peters, "Nuclear magnetic resonance and actinide ions",

#### **2<sup>nd</sup> International Nuclear Chemistry Congress, Cancun, Mexico, 12-18 April 2008**

##### **Poster presentation:**

- ✓ Retegan, T. et al.: "CHON-principle, a viable alternative for separating the actinides from lanthanides for further transmutation",
- ✓ D. Braekers, C. Peters, J. F. Desreux: "Nuclear magnetic resonance studies of solutions of actinide ions and their complexes. A contribution of NMR to radiochemistry".

#### **Atalante 2008 International Conference, 19-22 May 2008, Montpellier**

##### **Oral presentations + proceedings:**

- ✓ S. Bourg, E. Tournon, C. Caravaca, C. Ekberg, E. Gaubert, C. Hill, "ACSEPT: A New FP7-Euratom Collaborative Project in the Field of Partitioning Processes for Advanced Fuel Cycles",
- ✓ M-C. Charbonnel, N. Boubals, T-H. Vu, L. Couston, F. Arnaud, "Thermodynamic and structural description of europium complexation in 1-octanol solution",
- ✓ S. Trumm, P.J. Panak, M.R.St.J. Foreman, T. Fanghänel, A. Geist, "TRLFS studies on the complexation of Cm(III) and Eu(III) with BTBP ligands in organic solution",
- ✓ D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo D. Serrano-Purroy, C.Sorel, "Demonstration of Minor Actinide separation from a genuine PUREX raffinate by TODGA/TBP and SANEX reprocessing",
- ✓ G. Modolo, H. Vijgen, A.G. Espartero, P. Prados and J. de Mendoza, "Partitioning of Minor Actinides from High Active Raffinates using Bis-Diglycolamides (BisDGA) as new efficient Extractants",
- ✓ G. Benay, G. Modolo, A.C. Robisson, S. Grandjean, "Microspheres Prepared by Internal Gelation for Actinide Co-Conversion - Influence of Organic Precursors in Initial Solution on Structure during Thermal Treatment",
- ✓ E. Mendes, L. Cassayre, R. Malmbeck, P. Souček, R. Jardin, J.-P. Glatz, "Recovery of Actinides from Actinide-Aluminium Alloys: Chlorination Route".

##### **Posters + proceedings:**

- ✓ L'Hermite D., Bourg S., "LIBS : a new analytical technique for molten salt analysis",
- ✓ K. Chuchvalcova Bimova, R. Tulackova, M. Straka, M. Keppert, F. Lisy, P. Soucek, "Study of electrochemical separation in molten fluoride salt media",
- ✓ D. Magnusson, B. Christiansen, J.-P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy, C. Sorel, "Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors",
- ✓ A.C. Robisson, J. Dauby, S. Grandjean, G. Benay, G. Modolo, "Actinide co-conversion by internal gelation".

**EUROMAR, Saint Petersburg, Russia, 6-11 July 2008**

**Poster presentation:**

- ✓ D. Braekers, C. Peters, G. Vidick, J. F. Desreux, "NMR studies of solutions of actinide ions and their complexes. relaxation and spectroscopy".

**IPRC 2008 International Pyroprocessing Research Conference, Jeju Island, Republic of Korea, 24-27 August 2008.**

**Oral presentations:**

- ✓ L. Cassayre, C. Caravaca, R. Malmbeck, M. Harrison, G. De Angelis and S. Bourg, "Pyrochemistry within the FP7 Acept Project".

**EUCHEM 2008 Conference 24-29 August 2008, Copenhagen**

**Poster presentation:**

- ✓ K. Chuchvalcova Bimova, R. Tulackova, M. Straka, F. Lisy, "Electrochemical Separations of Actinides and Lanthanides in Molten Fluoride Media".

**NRC7 – 7<sup>th</sup> International Conference on Nuclear and Radiochemistry, Budapest, Hungary 24-29 August 2008**

**Oral presentation**

- ✓ E. Mendes, P. Souček, R. Malmbeck, C. Caravaca, J.-P. Glatz, "Study of thermodynamic properties of Np-Al alloys in molten LiCl-KCl eutectic".

**ISEC'08, International Solvent Extraction Conference), Tucson, Arizona, USA, 15-19 September 2008**

**Oral presentations & Proceedings:**

- ✓ M-C. Charbonnel, N. Boubals, T-H.Vu, L. Couston, F. Arnaud, "Thermodynamic and structural description of europium complexation in 1-octanol solution", Proceedings, 1043-1048,
- ✓ Fermvik A., et al., "The effect of irradiation on extraction of various metals by C5-BTBP, Solvent Extraction: Fundamentals to Industrial Applications", Proceedings, Vol 1 551-556,
- ✓ G. Modolo, H. Vijgen, R. Malmbeck, D. Magnusson, C. Sorel (key note talk), "Partitioning of trivalent actinides(III) from a PUREX Raffinate using a TODGA based solvent extraction process",
- ✓ G. Modolo, M. Sypula, A. Geist, C. Hill, C. Sorel, R. Malmbeck, D. Magnusson, M.R.St.J Foreman, "Development and Demonstration of a new SANEX-Process for Actinide(III)/ Lanthanide(III) Separation using a mixture of CyMe<sub>4</sub>BTBP and TODGA as selective extractant".

**10<sup>th</sup> IEMPT, OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mito, Japan, 6-10 Oct. 2008**

**Oral presentations & Proceedings:**

- ✓ Stéphane Bourg, Concha Caravaca, Christian Ekberg, Clément Hill, Chris Rhodes, "ACSEPT, a new step in the future demonstration of advanced fuel processing",
- ✓ G. Modolo, M. Sypula, A. Geist, C. Hill, C. Sorel, R. Malmbeck, D. Magnusson, M.R.S. Foreman, "Development and demonstration of a new SANEX process for An(III)/Ln(III) separation using a mixture of CyMe<sub>4</sub>-BTBP and TODGA as selective extractant",
- ✓ Tadafumi Koyama, Takanari Ogata, Tadashi Inoue, "Recent Development of Pyrochemical Processing and Metal Fuel Cycle Technology in CRIEPI".

**Posters & Proceedings:**

- ✓ Espartero A.G., Prados P., Murillo M.T., Sánchez-Quesada J., Iglesias-Sánchez J.C., Núñez A., de Mendoza J., "Stability against hydrolysis and radiolysis of BIS-DGAs UAM-069 and UAM-081 for the co-extraction of actinides(III) and lanthanides(III) from high level wastes issued from PUREX process",

- ✓ Xavier Hérès, Christian Sorel, Clément Hill, Pascal Baron, "A new concept for An(III)/Ln(III) separation using TODGA extractant",
- ✓ E. Aneheim, C. Ekberg, A. Fermvik, M. St.J. Foreman, J-O. Liljenzin, T. Retegan, G. Skarnemark, "Partitioning and Transmutation research at Chalmers University of Technology",
- ✓ E. Aneheim, C. Ekberg, A. Fermvik, M. St.J. Foreman, T. Retegan, G. Skarnemark, "Development of Equipment for Pilot Scale Tests of Processes for Partitioning and Transmutation",
- ✓ K. Chuchvalcová Bímová, M. Straka, R. Tuláčková, "Electroseparation studies of the actinides and lanthanides in molten fluoride media".

#### **2008 Joint Symposium on Molten Salts (MS8). October 19-23, 2008. Kobe (Japan).**

##### **Oral presentations & Proceedings::**

- ✓ Fabre S., Cabet C., Cassayre L., Chamelot P., Finne J., Massot L., Noël D., "Corrosion of nickel base alloys in molten fluoride salts",
- ✓ M. Straka, K. Chuchvalcova Bimova, R. Tulackova, F. Lisy, "Actinides and Lanthanides electrochemical Separations in molten fluoride Media",
- ✓ G. De Córdoba et al., "Determination of the activity coefficient of americium in liquid aluminium by electrochemical methods".

#### **Junior Scientist Conference " Science and Technology for the Future", Wien, 16-18 November 2008**

##### **Poster presentation:**

- ✓ S. Trumm, P.J. Panak, A. Geist, R. Klenze, Th. Fanghänel, "Complexation of Cm(III) and Eu(III) with extracting agents for the partitioning & transmutation strategy".

#### **ACHEMA 2009 Kongress, Frankfurt/M., 11–15.5.2009**

##### **Oral presentation:**

- ✓ A. Geist, G. Modolo, R. Malmbeck, "Actinides(III)/lanthanides(III) separation using CyMe<sub>4</sub>-BTBP – lab-scale tests".

#### **ICAPP'09, Tokyo, 10-14 May 2009**

##### **Oral presentation & Proceedings:**

- ✓ Stéphanie Fabre, Jörgen Finne, Pierre Chamelot, Laurent Cassayre, Laurent Massot, Celine Cabet, Fanny Balbaud-Célérier, "Corrosion of metallic materials for molten salt reactors".

#### **MRS'09, 33<sup>rd</sup> International Symposium on Nuclear Waste Management, St Petersburg, 24-29 May 2009**

##### **Poster presentation & Proceedings**

- ✓ G. De Angelis, I. Bardez-Giboire, M. Mariani, M. Capone, M. Chartier, and E. Macerata, "Synthesis and characterization of sodalite as matrix for conditioning chloride spent salts from pyroprocesses", Paper CP-10.

#### **4<sup>th</sup> European Young Investigators Conference 2009, June 18-21, Slubice, Poland**

##### **Poster:**

- ✓ Agnieszka Sulich, Jan Grodkowski, Jacek Mirkowski, Rafal Kocia, Mark Foreman, "Pulse radiolysis of CyMe<sub>4</sub>-BTP and CyMe<sub>4</sub>-BTBP in octanol".

#### **7<sup>th</sup> European Commission Conference on Euratom Research and Training in Reactor Systems (FISA) on Nuclear Engineering and Design, Prague, Czech Rep., JUN 22-24, 2009**

##### **Oral presentations:**

- ✓ Bourg S., Hill C., Caravaca C., Rhodes C., Ekberg C., Taylor R., Geist A., Modolo G., Cassayre L., Malmbeck R., Harrison M., de Angelis G., Espartero A., Bouvet S., Ouvrier N., "ACSEPT - Partitioning technologies and actinide science: Towards pilot facilities in Europe".

### **ACTINIDES 2009, San Francisco, 12–17 July, 2009**

#### **Oral presentations:**

- ✓ L. Berthon, N. Zorz, B. Gannaz, S. Lagrave, T. Retegan, A. Fermvik, C. Ekberg, "Use of Electrospray Ionization Mass Spectrometry for the characterization of actinide complexes in solution",
- ✓ S. Trumm, M.A. Denecke, P.J. Panak, Th. Fanghänel, A. Geist, "Structural investigations on actinide(III)-BTBP and lanthanide(III)-BTBP 1:2 complexes in organic solution",
- ✓ P.J. Panak, A. Skerencak, V. Neck, S. Trumm, A. Geist, M.A. Denecke, "Speciation of actinides by time-resolved laser fluorescence spectroscopy",
- ✓ Jamie Brown, Michael Carrott, Danny Fox, Chris J. Maher, Chris Mason, Fiona McLachlan, Mark J. Sarsfield, Robin J. Taylor, Dave A. Woodhead, "Screening of TODGA/TBP/OK Solvent Mixtures for the Grouped Extraction of Actinides",
- ✓ Jean F. Desreux, Damien Braekers and Geoffrey Vidick, "Nuclear Magnetic Resonance Spectroscopy and Relaxivity of the Actinide ions and their Complexes".

### **238<sup>th</sup> ACS National Meeting, Washington 16-19 August 2009**

#### **Oral presentations:**

- ✓ Ekberg et al., "General presentation of ACSEPT",
- ✓ Fermvik Anna, Aneheim Emma, Ekberg Christian, "Identification of degradation products from irradiated C5-BTBP and their influence on the extraction of actinides and lanthanides",
- ✓ Aneheim Emma, Fermvik Anna, Foreman Mark R. S., " Fission product suppression and extraction in a proposed GANEX process",
- ✓ G. Modolo, A.Geist, R. Malmbeck, "Actinide(III) recovery from high active waste solutions using innovative partitioning processes".

### **Global 2009, Paris, France, September 6-11, 2009**

#### **Oral presentations + proceedings:**

- ✓ Stéphane Bourg, Concha Caravaca, Christian Ekberg, Clément Hill, Chris Rhodes, "ACSEPT, Toward the Future Demonstration of Advanced Fuel Treatments",
- ✓ Xavier Hérès, Christian Sorel, Manuel Miguirditchian, Béatrice Camès, Clément Hill, Isabelle Bisel, Denis Espinoux, Catherine Eysseric, Pascal Baron, Brigitte Lorrain, "Results of recent counter-current tests on An(III)/Ln(III) separation using TODGA extractant", paper 9384,
- ✓ S. Grandjean, B. Arab-Chapelet, A-C. Robisson, S. Picart, C. Léorier, N. Herlet, J.-P. Dancausse, "TRU recycling: recent experiments and results for the conversion of minor actinides into oxide", Paper 9446,
- ✓ Malmbeck R., et al., "Recovery of MA using a CyMe<sub>4</sub>BTBP based SANEX solvent",
- ✓ Nourry C., et al., "Study of thermodynamic properties of Pu-Al alloys in eutectic LiCl-KCl",
- ✓ Souček P., et al., "Recovery of Actinides from Spent Nuclear Fuel by Pyrochemical Reprocessing",
- ✓ Souček P., et al., "Separation of Uranium from Uranium-Aluminium Alloys by Chlorination",
- ✓ G. Modolo, P. Kluxen, A. Geist, "Selective separation of americium(III) from curium(III), californium(III), and lanthanides(III) by the LUCA process", Paper 9336,
- ✓ A. Geist, G. Modolo, "TODGA Process Development: an Improved Solvent Formulation", Paper 9193,
- ✓ Mike Carrott, Danny Fox, Chris Maher, Giuseppe Modolo, Fiona McLachlan, Mark Sarsfield, Robin Taylor, Dave Woodhead, "Extraction and stripping of actinides in TBP and TODGA/TBP systems for advanced fuels processing", Paper 9033,
- ✓ M. Straka, M. Korenko, F. Lisý, "Development of electrochemical separation methods in molten fluoride salts FLINAK and FLIBE",
- ✓ J. Svedkauskaite-LeGore, N. Kivel, I. Günther-Leopold, "Real Time Measurement of Fission Products Released from Spent Nuclear Oxide Fuel by Thermal Treatment", paper 9249,

### **APSORC'09, 4<sup>th</sup> Asia-Pacific Symposium on Radiochemistry, 29.11– 4.12.2009, Napa, CA, USA**

#### **Presentation & Proceedings**

- ✓ John J., Šuláková J., Šebesta F., Klímek F., Mareš K.V, Hudson M.J., Foreman M.R.S., "Am/Eu

Chromatographic Separation with New Solid Extractants based on BTBPs".

### **239<sup>th</sup> ACS National Meeting, San Francisco, March 21–25, 2010**

#### **Oral presentations:**

- ✓ Stéphane Bourg, "ACSEPT, an actinide science community in Europe as the legacy of Charles Madic",
- ✓ Emma Aneheim, Anna Fermvik, Christian Ekberg, Mark Foreman, "Development of a GANEX type extraction system",
- ✓ Emma Aneheim, Anna Fermvik, Christian Ekberg, Elin Löfström-Engdahl, Mark Foreman, "Partitioning and Transmutation in Scandinavia - Chalmers Group",
- ✓ C. Bessada, O. Pauvert, D. Zanghi, A.-L. Rollet, V. Sarou-Kanian, M. Gobet, G. Moussaed, A. Rakhmatullin, M. Salanne, C. Simon, H. Matsuura, "In situ experimental approach of the speciation in molten lanthanide and actinide fluorides combining NMR, EXAFS and Molecular Dynamics",
- ✓ A. Geist, "Investigating the An(III)/Ln(III) selectivity of N-donor extracting agents – the BTP case",
- ✓ Giuseppe Modolo, Andreas Geist, Rikard Malmbeck, "Separation of Am(III) from Cm(III) and Ln(III) using aromatic dithiophosphinic acid",
- ✓ J. F. Desreux, G. Vidick, N. Bouslimani, L. Frank, M. J. Hudson, L. M. Harwood, "NMR investigation of the lanthanide complexes with bis-triazine ligands: Solution structure and extraction properties",
- ✓ J. F. Desreux, G. Vidick, N. Bouslimani, "NMR Spectroscopy and relaxivity of the actinide ions and of their complexes: In search of covalency effects".

### **1<sup>st</sup> AIWO ACSEPT International Workshop, Lisbon, 31 March – 2 April 2010,**

#### **Oral presentation:**

- ✓ Löfström-Engdahl E., Aneheim E., Ekberg C., Foreman M., Skarnemark G., "Diluent effects in solvent extraction",
- ✓ I. Spendlikova, P. Distler, J. John, F. Sebesta, F. Lewis, L.M. Harwood, M.J. Hudson, "Study of Extraction Properties of Pyridine Molecules in Various Diluents",
- ✓ Sypula, M., Wilden, A., Schreinemachers, C., Modolo, G., "Separation of An(III) from PUREX raffinate as an innovative-SANEX process based on a mixture of TODGA/TBP",
- ✓ Wilden A., Sypula M., Schreinemachers C., Kluxen P., Modolo G., "1-cycle SANEX process development studies performed at Forschungszentrum Jülich",
- ✓ Daniels H., Neumeier S., Modolo G., "Synthesis of Uranium-based Microspheres for Transmutation of Minor Actinides",
- ✓ A. Deptula, M. Brykala, W. Lada, T. Olczak, D. Wawszczak, G. Modolo, H. Daniels, A.G. Chmielewski, "Synthesis of uranium oxides by Complex Sol-Gel Process (CSGP)",
- ✓ Fiona MacLachlan, "Extraction Studies of Potential Solvent Formulations for the GANEX Process",
- ✓ Trong-Hung VU, Jean-Pierre SIMONIN, "Kinetics of extraction of Eu<sup>3+</sup> ion by TODGA and CyMe<sub>4</sub>-BTBP studied using the RMC technique",
- ✓ Nourry C., et al., "Electrochemistry of uranium in molten fluorides",
- ✓ J. Svedkauskaite-Le Gore, N. Kivel, I. Günther-Leopold, "A high temperature heating device for the study of fission product release",
- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, G. Modolo, M. Sypula, J. F. Desreux, N. Bouslimani and G. Vidick, "Studies on the Interaction of a Novel 6,6''- bis(1,2,4-triazin-3-yl)-2,2':6',2''-terpyridine Ligand with Lanthanide(III) Ions and Americium(III)",
- ✓ G. Vidick, N. Bouslimani and J. F. Desreux, "Nuclear magnetic resonance applied to actinide ions and their complexes: in search of covalency effects".

#### **Poster presentation/**

- ✓ W. P. Oziminski and J. Narbutt, "Theoretical Modelling of Europium and Americium(III) Complexes with BTBP Ligands",
- ✓ C. Lourenço, J.M. Carretas, I. Paiva, J. Marçalo et al. "Actinide Sciences at ITN – Basic Studies in Chemistry with Potential Interest for Partitioning, Fuel Fabrication and More".

**ENC 2010 European Nuclear Conference, 30 May – 2 June 2010, Barcelona, Spain**

**Oral presentation:**

- ✓ S. Bourg, "ACSEPT: A European Project For A New Step In The Future Demonstration of Advanced Fuel Processing".

**Plutonium Futures 2010 - "The Science" –September 19-23, 2010 Keystone, Colorado**

**Oral presentations:**

- ✓ Robin Taylor, Fiona McLachlan, Mark Sarsfield, "Plutonium extraction chemistry in diglycolamide based solvents for the GANEX process".

**NuMat 2010, 4-7 Oct.2010, Kalsruhe**

**Oral presentations:**

- ✓ C. Bessada et al., "In situ experimental approach of the speciation",
- ✓ M. Gibilaro, L. Cassayre, L. Massot, P. Chamelot, R. Malmbeck, O. Dugne, "Investigation of UO<sub>2</sub> direct electrochemical reduction in LiF-CaF<sub>2</sub>",
- ✓ Soucek P., et al., "Study on Properties of Actinide-Aluminium Alloys in Molten LiCl-KCl",
- ✓ Nourry C., et al., "Electrochemistry of Uranium in Molten Fluoride Salts",

**Poster presentation/**

- ✓ M. Korenko, M. Straka, F. Lisý, "Electrochemical Separation of Uranium from Molten System FLiNaK - UF<sub>4</sub>".

**11<sup>th</sup> IEMPT, OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, San Francisco, 1–4 November 2010**

**Oral presentations and Proceedings:**

- ✓ S. Bourg, C. Hill, C. Caravaca, Ch. Rhodes, Ch. Ekberg, "ACSEPT – Progresses in advanced partitioning and challenges for the future"
- ✓ Emma Aneheim, Christian Ekberg, Anna Fermvik, Mark R.S. Foreman, "Development of a novel GANEX process",
- ✓ A. Wilden, M. Sypula, G. Modolo, A. Geist, "One-cycle SANEX process development studies and lab-scale demonstrations",
- ✓ Jan Uhlír, "Current progress in R&D on pyrochemical partitioning technology in the Czech Republic",
- ✓ Koichi Uozumi, Masatoshi Iizuka, Tsuyoshi Murakami, Tadashi Inoue, Tadafumi Koyama, Michel Ougier, Rikard Malmbeck, Jean-Paul Glatz, "Pyropartitioning experiment to recover TRU from high-level liquid waste".

**Poster:**

- ✓ A. Geist, U. Müllich, G. Modolo, A. Wilden, "Selective aqueous complexation of actinides with hydrophilic BTP and BTBP: towards improved i-SANEX processes",
- ✓ C. Nourry, L. Cassayre, R. Malmbeck, E. Mendes, P. Souček, J-P. Glatz, "Chlorination Route for recovery of Actinides from Actinide-Aluminium Alloys".

**IPRC 2010 Internat. Pyroprocess Research Conference, 29 Nov.–3 Dec. 2010, Dimitrovgrad, Russia**

**Oral presentation:**

- ✓ S. Bourg, "Pyroprocessing achievements in the field of the ACSEPT Project",
- ✓ G. De Angelis, M. Capone, A. Manniello, M. Mariani, E. Macerata, C. Conti, "Different methods for conditioning chloride salt wastes from pyroprocesses".

**MS9, 9<sup>th</sup> International Symposium on Molten Salts Chemistry and Technology, 5-9 June 2011, Trondheim, Norway**

**Oral presentations**



- ✓ C. Bessada, O. Pauvert, L. Maksoud, D. Zanghi, V. Sarou-Kanian, M. Gobet, A.L. Rollet, A. Rakhmatullin, M. Salanne, C. Simon, D. Thiaudiere, H. Matsuura, "In situ experimental approach of speciation in molten fluorides: a combination of NMR, EXAFS and Molecular Dynamics" (plenary lecture),
- ✓ Straka M., Lisy F., Szatmary L., "Electrodeposition of Uranium by Pulse electrolysis in Molten Fluoride Salts", Molten Salts 9, 5.-9.6 2011, Trondheim, Norway.

### **ISEC 2011, 19<sup>th</sup> International Solvent Extraction Conference, 17.-21.10.2011, Santiago de Chile, Chile**

#### **Oral presentations and Proceedings**

- ✓ Aneheim E., Mabile N., Ekberg C., "Exchange of TBP for a Monoamide Extraction Ligand in a GANEX Solvent - Advantages & Disadvantages", Proceedings, ed. F. Valenzuela, B. Moyer, Chapter 3, Nuclear Fuel Reprocessing, pp 65,
- ✓ Löfström-Engdahl E., Aneheim E., Mabile N., Ekberg C., Skarnemark G., "Solvent effects on the extraction rate in proposed GANEX processes", Proceedings, ed. F. Valenzuela, B. Moyer. Chapter 3, Nuclear Fuel Reprocessing, pp 70,
- ✓ Ana Núñez, Hitos Galán, Amparo González-Espartero, Berta Camafort, Javier de Mendoza and Rosa Sedano, "Radiolytic Stability of TODGA-Characterisation and Quantification of Degradation Compounds",
- ✓ A. Geist, U. Müllich, G. Modolo, A. Wilden, "Actinide(III)/lanthanide(III) separation via selective aqueous complexation of actinides(III) in nitric acid",
- ✓ A. Wilden, M. Sypula, G. Modolo, A. Geist, "Direct Actinide(III) separation from PUREX raffinate using a BTBP/TODGA solvent",
- ✓ Andreas Geist, Udo Müllich, Andreas Wilden, Steve Gülland and Giuseppe Modolo, "C5-BPP-a new highly selective extractant for the separation of trivalent actinides from lanthanides",
- ✓ J. F. Desreux, G. Vidick and N. Bouslimani, "NMR investigation of the lanthanide and actinide complexes of bis-triazine extracting agents", Proceedings F. Valenzuela L., B. A. Meyer, Eds. p. 133.

#### **Poster presentation and Proceedings**

- ✓ Sypula M., Wilden A., Modolo G., Geist A., "Innovative SANEX process for actinide(III) separation from PUREX raffinate using TODGA-based solvents",
- ✓ Jean-Pierre Simonin and Trong-Hung Vu, "Kinetics of extraction of europium(III) ion by various extractants for nuclear applications",
- ✓ Teodora V. Retegan, Christian Ekberg and Anna Fermvik, "Modification of extraction kinetics of C2-BTBP and CyMe<sub>4</sub>-BTBP by addition of tert-butyl to the core molecule".

### **Global 2011, Makuhari, Japan, 11-16 December 2011**

#### **Oral presentations and Proceedings**

- ✓ S. Bourg, S. Bouvet, C. Caravaca, L. Cassayre, G. de Angelis, C. Ekberg, A.G. Espartero, A. Geist, Ph. Guilbaud, M. Harrison, F. Klaassen, R. Malmbeck, G. Modolo, N. Ouvrier, C. Rhodes, R. Taylor, "ACSEPT – The Current European Project on Actinide Separation", Proceedings Paper Nr 357353,
- ✓ Mareš K.V., John J., Šebesta F., "Decontamination of Spent DIAMEX Solvents containing Contaminants difficult to strip", Proceedings p. 105,
- ✓ Magnusson D., Geist A., Wilden A., Modolo G., Malmbeck R., "Computer Code Development for Flow-Sheet Design and Modeling with Verification Towards a Novel Partitioning Process", Proceedings Paper Nr 355757.

### **NFCC'2012, Nuclear Fuel Cycle Conference 2012, Manchester, UK, 23-25 April 2012**

#### **Oral presentation and Proceedings**

- ✓ S. Bourg, S. Bouvet, L. Cassayre, G. de Angelis, C. Ekberg, A.G. Espartero, A. Geist, P. Guilbaud, M. Harrison, R. Malmbeck, G. Modolo, N. Ouvrier, C. Rhodes, R. Taylor, "ACSEPT - reprocessing for advanced fuel cycles",
- ✓ Wilden A., Schreinemachers C., Sadowski F., Gülland S., Sypula M., Modolo G., Magnusson D., Geist A., Lewis F. W., Harwood L. M., Hudson M. J., "Demonstration of a 1-cycle SANEX Process for

the Selective Recovery of Trivalent Actinides from PUREX Raffinate Using a CyMe<sub>4</sub>BTBP/TODGA Solvent",

- ✓ M. Brykała, A. Deptuła, W. Łada, T. Olczak, A.G. Chmielewski, "Synthesis of Uranium Dioxide Microspheres by Water and Nitrate Extraction from Uranyl-Ascorbate Sols",
- ✓ K. Bell, C. Carpentier, M. Carrott, A. Geist, C. Gregson, X. Heres, D. Magnusson, R. Malmbeck, G. Modolo, U. Müllich, M. Sypula, R. Taylor, A. Wilden, "Towards a new GANEX 2<sup>nd</sup> cycle process for the co-separation of TRU",
- ✓ Robin Taylor, "Advanced fuel recycling processes" (keynote speaker),
- ✓ N. Shcherbina, N. Kivel, I. Günther-Leopold, D. Kulik, "Inductive heating for partitioning of fission products from spent nuclear fuel".

#### **Poster presentation**

- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.-H. Vu, J.-P. Simonin, "From BTBPs to BTPPhens: Improving the Properties of Actinide-Selective Solvent Extraction Reagents by Ligand Pre-Organization".

#### **Plutonium Futures – the Science, Cambridge, 15-20 July 2012**

##### **Oral presentations and Proceedings**

- ✓ M.J. Carrott, P.M.A. Cook, O.D. Fox, C.J. Maher, C. Mason, S.L.M. Schroeder, "The dissolution kinetics of (U,Pu)O<sub>2</sub> in nitric acid",
- ✓ Chris Mason, Katie Bell, Jamie Brown, Michael Carrott, Andreas Geist, Colin Gregson, Chris Maher, Rikard Malmbeck, Giuseppe Modolo, Mark Sarsfield, Robin Taylor, Louise Walton, "Development and Testing of a GANEX Flowsheet".

#### **IPRC 2012, International Pyroprocessing Research Conference Fontana, Wisconsin, USA, 26-29 August 2012**

##### **Oral presentations**

- ✓ G. De Angelis, C. Fedeli, M. Capone, M. Da Ros, F. Giacobbo, E. Macerata, M. Mariani, "Synthesis of sodalite from nepheline for conditioning chloride salt wastes",
- ✓ L. Cassayre, R. Malmbeck, M. Harrison, G. DeAngelis, C. Caravaca, S. Bourg, "Pyrochemical Separation of Spent Nuclear Fuel: Advances in the frame of the European ACSEPT Project",
- ✓ E. Mendes, H. Boussier, A. Laplace, J.F. Vigier, M. Miguiriditchian, "Development Status on the Pyrochemistry R&D Program at CEA".

#### **ATALANTE 2012, 4<sup>th</sup> International Conference on Nuclear Chemistry for Sustainable Fuel Cycles**

##### **Oral presentations and Publications in Procedia Chemistry**

- ✓ Stephane Bourg, Christophe Poinssot, Andres Geist, Laurent Cassayre, Chris Rhodes, Christian Ekberg, "Advanced Reprocessing Developments in Europe Status on European Projects ACSEPT and ACTINET-I3",
- ✓ Aneheim E., Bauhn L., Ekberg C., Foreman M., Löfström-Engdahl E., "Extraction experiments after radiolysis of a proposed GANEX solvent – the effect of time",
- ✓ E. Löfström-Engdahl, E. Aneheim, Ch. Ekberg, M. Foreman, G. Skarnemark, Z. Hájková, B. Grüner, "The Extraction of Silver and the effect of Diluent, Ligand side group and Solvent composition",
- ✓ Ana Núñez, Amparo Glez Espartero, Hitos Galán, "Optimization studies of the An(III) and Ln(III) extraction and back-extraction from a PUREX raffinate by bisDGA compounds",
- ✓ Hitos Galán, Ana Núñez, Amparo Glez Espartero, Rosa Sedano, Aritz Durana, Javier de Mendoza, "Radiolytic Stability of TODGA: Characterization of Degraded Samples under Different Experimental Conditions",
- ✓ Wilden A., Modolo G., Sypula, M., Geist A., Magnusson D., "The Recovery of An(III) in an innovative-SANEX process using a TODGA-based solvent and selective stripping with a hydrophilic BTP",
- ✓ Björn B. Beele, Udo Müllich, Felicitas Schwörer, Andreas Geist, Petra J. Panak, "Systematic Modifications of BTP-type Ligands and Effects on the Separation of Trivalent Lanthanides and Actinides",
- ✓ Steve Drewery, Erik Heeres, Steve Percival, Chris Rhodes, Mitch St George, Erwin Wilbers, David A.

Woodhead, "Experimental and Modelling Studies of Mass Transfer in Centrifugal Contactors",

- ✓ M.J. Carrott, P.M.A. Cook, O.D. Fox, C.J. Maher, S.L.M. Schroeder, "The chemistry of (U,Pu)O<sub>2</sub> dissolution in nitric acid",
- ✓ Colin Gregson, Colin Boxall, Michael Carrott, Scott Edwards, Mark Sarsfield, Robin Taylor, David Woodhead, "Neptunium (V) Oxidation by Nitrous Acid in Nitric Acid",
- ✓ K. Bell, C. Carpentier, M. Carrott, A. Geist, C. Gregson, X. Hérès, D. Magnusson, R. Malmbeck, F. McLachlan, G. Modolo, U. Müllich, M. Sypula, R. Taylor, A. Wilden, "Progress towards the development of a new GANEX process",
- ✓ Katie J. Bell, Fiona McLachlan, Andreas Geist, Giuseppe Modolo, Robin J. Taylor, A. Wilden, "Nitric acid extraction into TODGA based solvents",
- ✓ N. Shcherbina, N. Kivel, I. Günther-Leopold, "Effect of redox conditions on the fission products release from irradiated oxide fuel",
- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, A. Wilden, M. Sypula, G. Modolo, T.-H. Vu, J.-P. Simonin, G. Vidick, N. Bouslimani, J. F. Desreux, "From BTBPs to BTPPhens: The Effect of Ligand Pre-Organization on the Extraction Properties of Quadridentate Bis-Triazine Ligands",
- ✓ E. Mendes, O. Conocar, A. Laplace, N. Douyère, M. Miguiditchian, "Assessment of the Complete Core of the Reference Pyrochemical Process developed by the CEA",
- ✓ Noël Ouvrier, Hubert Boussier, "Recycling of MgO, Mo & ZrO<sub>2</sub> based Actinide-Bearing Matrices: Assessment of Reprocessing Feasibility & Waste Production",
- ✓ T. Koyama, Y. Sakamura, M. Iizuka, T. Kato, T. Murakami, J.-P. Glatz, "Development of Pyro-processing Fuel Cycle Technology for Closing Actinide Cycle",

#### Oral presentations

- ✓ Distler P., John J., Šťastná K., Lewis F.W., Harwood L.M., Hudson M.J., "Kinetic effects in the Am/Eu Separation with BTBP-Ligands",
- ✓ Neumeier S., Daniels H., Schreinemachers C., Modolo G., Bosbach D., Leturcq G., Grandjean S., "The co-conversion of minor actinides in uranium based fuel by internal gelation",
- ✓ A. Sulich, J. Grodkowski, J. Mirkowski, R. Kocia, M. J. Foreman, "Research on radiation chemistry of selected substances applied in SANEX process",
- ✓ W. P. Oziminski, J. Narbutt, "Solvent extraction selectivity of BTBP ligands for Am(III) over Eu(III) ions. Quantum mechanical study".

#### Poster presentation and publication in Procedia Chemistry

- ✓ Magnusson D., Geist A., Wilden A., Modolo G., Malmbeck R., "Flow-sheet design for an innovative SANEX process using TODGA and SO<sub>3</sub>-Ph-BTP",
- ✓ Roland Meier, Pavel Souček, Rikard Malmbeck, Thomas Fanghänel, "Recycling of Uranium from Uranium-Aluminium alloys by Chlorination with HCl(g)",
- ✓ G. De Angelis, C. Fedeli, A. Manniello, M. Da Ros, F. Giacobbo, E. Macerata, M. Mariani, "Conditioning of chloride salt wastes from pyroprocesses through the pressureless consolidation process",
- ✓ Martin Straka, Lorant Szatmáry, "Electrochemistry of Selected Lanthanides in FLiBe and Possibilities of their Recovery on Reactive Electrode",
- ✓ H. Boussier, F. Peron, "Hydrofluorination Device with "In Situ" HF Generation".

#### Poster presentation

- ✓ D. L'Hermite, C. Quéré, M. Tabarant, A. Laplace, F. Peron, T. Vercouter, "Toward in-situ measurements of liquid by LIBS for fuel reprocessing",
- ✓ Hitos Galán, Geoffrey Vidick, Nouri Bouslimani, Jean F. Desreux, "NMR Analysis of the Complexation of Ln and An Ions by TODGA and BTTP extractants".
- ✓ Mareš K.V., John J., Šebesta F., Vlk M., Svobodová T., "Decontamination of Spent Diamex Solvent containing Contaminants difficult to strip",
- ✓ B. Zielinska, J. Narbutt, F. W. Lewis, L. M. Harwood, M. J. Hudson, "Selective stripping of

americium(III) over europium(III) with a novel hydrophilic bis-triazine-bipyridine derivative",

- ✓ Koubský T., Kalvoda L., Dráb M., "Ab-initio simulations of chemical stability of the bis-DGA-type molecule and its degradation products",
- ✓ S. Scaravaggi, E. Macerata, M. Galletta, E. Mossini, M. Giola, M. Mariani, "Hydrophilic 1,10-phenanthroline derivatives for the An selective stripping in the i-SANEX and GANEX processes",
- ✓ Stefano Scaravaggi, Michele Galletta, Mario Mariani, "Lipophilic 1,10-phenanthroline derivatives for the An/Ln separation in the SANEX process",
- ✓ Célia Lourenço, Ana F. Lucena, José Manuel Carretas, Bernardo Monteiro, Isabel Paiva, Joaquim Marçalo, Nicole Zorz, Laurence Berthon, "Gas-phase studies of the relative affinities of N- and O-donor bases toward Ln(III) and An(III) ions".

### **12<sup>th</sup> IEMPT, OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation Prague, 24–27 September 2012**

#### **Oral presentations and Proceedings**

- ✓ Stephane BOURG, Andreas Geist, Laurent Cassayre, Chris Rhodes, Christian Ekberg "ACSEPT – a successful story in actinide separation process development in EUROPE",
- ✓ P. Soucek, R. Malmbeck, J.-P. Glatz, " Co-processing of actinides in nuclear fuel cycles",
- ✓ Masatoshi Iizuka, Takanari Ogata and Tadafumi Koyama, "Recent P&T Related Activities in CRIEPI: Development of Pyrochemical Processing and Metallic Fuel Technologies",
- ✓ Robin Taylor, Francis Livens, Andy Mount, Laurence Harwood, Chris Rhodes, Bruce Hanson, "Status of Advanced Reprocessing and Minor Actinide Partitioning Research in the UK".

#### **Posters & Proceedings**

- ✓ A. Geist, U. Müllich, D. Magnusson, G. Modolo, "A kinetic study on the extraction of americium(III) into CyMe<sub>4</sub>-BTBP",
- ✓ D. Magnusson, A. Geist, R. Malmbeck, U. Müllich, "Loading and flow-rate dependence of the transfer rates in a centrifugal contactor using organic ligand CyMe<sub>4</sub>-BTBP",
- ✓ Szatmáry, L., Straka, M., Lisy F., "Pulse Electrolysis of Uranium in Molten Fluoride Salts",
- ✓ Martin Straka, Lórant Szatmáry, František Lisý, " Electrochemistry of selected lanthanides in LiF-BeF<sub>2</sub> system".

## **I.2.2 Second level Conferences (for ACSEPT dissemination of knowledge)**

### **Int. Conference Poster: SNE-TP General Assembly 26 November 2008, Brussels, Belgium)**

#### **Poster presentation:**

- ✓ S. Bourg, C. Caravaca, C. Ekberg, C. Hill, C. Rhodes, "From EUROPART to ACSEPT, a new step in the future demonstration of advanced fuel treatment".

### **27<sup>th</sup> Meeting of the Japan Association of Solvent Extraction, Tokyo, Japan, 11-12 October 2008.**

#### **Oral presentations & Proceedings:**

- ✓ A. Geist, "What drives the An(III)/Ln(III) selectivity of N-donor SANEX extracting agents?",
- ✓ G. Modolo, "Development and demonstration of processes for the partitioning of trivalent actinides from high level liquid wastes".

### **7<sup>th</sup> International SF-ICP-MS Conference", New Brunswick (USA), 8-12 September 2008**

#### **Oral presentation (no proceedings):**

- ✓ J. Svedkauskaite-LeGore et al., "Online monitoring of fission products released from nuclear fuel samples by ICP-MS".

### **European Winter Conference on Plasma Spectrochemistry", Graz (Austria), 15-20 February 2009**

**Poster Presentation:**

- ✓ I. Günther-Leopold, J. Svedkauskaite-Le Gore, N. Kivel, "Online ICP-MS detection of the thermal release of fission products from nuclear fuel samples".

**3<sup>rd</sup> Seminar on Advanced ORIENT Cycle, Tohoku University, Sendai, Japan, 30 October 2009**

**Oral presentation:**

- ✓ C. Hill, X. Hérès, C. Sorel, M. Montuir, M. Mirguiditchian, B. Camès, I. Bisel, D. Espinoux, C. Eysseric, P. Baron, B. Lorrain, "Results of recent counter-current tests on An(III)/Ln(III) separation using TODGA extractant", Proceedings JAEA-Review 2009-062 p 92-108 March 2010.

**16<sup>th</sup> Radiochemical Conference, Marianske Lazne, 18-23 April 2010**

**Oral presentation:**

- ✓ P. Distler, J. John, L.M. Harwood, F.W. Lewis, M.J. Hudson, "The Liquid-Liquid Extraction of Minor Actinides with CyMe<sub>4</sub>-BTBP in Selected Diluents".

**CIMTEC 2010 12<sup>th</sup> International Conference on Modern Materials and Technologies, June 13-18, Montecatini, Italy**

**Oral presentation:**

- ✓ Modolo G., Bosbach D, Geist A., Malmbeck R., "Recovery of Long-lived Minor Actinides from High Active Waste Solutions using Innovative Partitioning Processes",
- ✓ Daniels H., Neumeier S., Bukaemskiy A. A., Modolo G., Bosbach D., "Co-Conversion of actinides into a uranium-matrix".

**DAE-BRNS Biennial symposium on Emerging Trends in Separation Science and Technology, Kalpakkam, India, March 1-4, 2010**

**Oral presentation:**

- ✓ W. Verboom, "Synthesis and evaluation of ligands for nuclear waste treatment".

**217<sup>th</sup> ECS Meeting 25-30-04-2010 Vancouver Canada**

**Oral presentation**

- ✓ C. P. Fabian, C. Caravaca Moreno, C. Griffith, V. Luca and G. Lumpkin, "Electrochemical Behavior of Zirconium in LiCl - KCl Eutectic Molten Salt".

**218<sup>th</sup> ECS Meeting 10-15/10/2010 Las Vegas, USA**

**Oral presentation and Publication in ECS Transactions**

- ✓ Catherine Bessada, Olivier Pauvert, Didier Zanghi, Anne-Laure Rollet , Vincent Sarou-Kanian, Mallory Gobet, Georges Moussaed, Aydar Rakhmatullin, Mathieu Salanne, Christian Simon , Haruaki Matsuura, "In situ experimental approach of the speciation in molten lanthanide and actinide fluorides combining NMR, EXAFS and Molecular Dynamics", ECS Transactions 2010 33 (7), 361-369 - DOI: 10.1149/1.3484794

**I3<sup>rd</sup> International Conference on Uranium, August 15-18, 2010, Saskatoon (Canada)**

**Oral presentations and Proceedings:**

- ✓ A. Deptula, M. Brykala, W. Lada, T. Olczak, D. Wawszczak, G. Modolo, H. Daniels, A.G. Chmielewski, "Synthesis of uranium dioxides by Complex Sol-Gel Processes (CSGP)".

**International Youth Nuclear Congress, Cape Town, South Africa, 12-18 July 2010**

**Oral presentations and Proceedings:**

- ✓ M. Gibilaro, L. Cassayre, P. Chamelot, R. Malmbeck, O. Dugne, P. Allegri, "Electrochemical reduction of solid UO<sub>2</sub> in molten fluoride salts".

**11th Eurasia Conference on Chemical Sciences, Dead Sea, Jordan, 6th-10th October 2010**

**Oral presentation:**

- ✓ L. M. Harwood, "Studies on Ligands for Selective Actinide Extraction".

**ANUP 2010 (Asian Nuclear Prospects), Chennai, India**

**Oral presentation:**

- ✓ Soucek P., et al., "Pyrochemical Reprocessing of Spent Fuel by Electrochemical Techniques Using Solid Aluminium Cathodes".

**24<sup>th</sup> European Colloquium on Heterocyclic Chemistry, Vienna University of Technology, Vienna, Austria, 23-27 August 2010.**

**Oral presentation:**

- ✓ L. M. Harwood, M. J. Hudson, F. W. Lewis, "Studies on Ligands for Selective Actinide Extraction".

**Poster presentation/**

- ✓ F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, G. Modolo, M. Sypula, J. F. Desreux, N. Bouslimani, G. Vidick, "Synthesis, Solvent Extraction and Trivalent Metal Ion Complexation Studies of a Novel Bistriazinylterpyridine Ligand".

**MARC IX conference (Methods & Application of Radioanalytical Chemistry), Hawaii, March 2012.**

**Poster presentation**

- ✓ N. Kivel, N. Shcherbina, I. Günther-Leopold: "Development of a high temperature treatment device for spent nuclear fuel".

**TMS 2011 (The Minerals, Metals & Materials Society) Feb27-Mar3, San Diego, USA**

**Oral presentation:**

- ✓ L. Cassayre, M. Gibilaro, J. Pivato, O. Dugne, L. Massot, P. Chamelot, "Direct electroreduction of oxides in molten fluorides".

**European Winterconference on Plasma Spectrochemistry, Zaragoza (Spain), 30<sup>th</sup> January – 4<sup>th</sup> February 2011**

- ✓ I. Günther-Leopold, N. Kivel, N. Shcherbina: "Study of the fission product release from nuclear fuel samples using an inductive heating device and online ICP mass spectrometric detection".

**6<sup>th</sup> Jordanian International Conference of Chemistry, Yarmouk, Jordan, 19-21 April 2011**

**Plenary Lecture**

- ✓ L. M. Harwood, "Studies on Ligands for Selective Actinide Extraction".

**5<sup>th</sup> European Young Investigators Conference (EYIC), Slubice, Poland/Frankfurt(Oder), Germany; 22-26/06/2011**

**Poster presentation**

- ✓ A. Sulich, J. Grodkowski, J. Mirkowski, R. Kocia, M. Foreman, "Benzophenone as a probe in the pulse radiolysis of cyclohexanone and 1-octanol, diluents for procedures in minor actinides extraction".

**14<sup>th</sup> Blue Danube Symposium on Heterocyclic Chemistry, Podbanské, Slovakia, 26-29 June 2011**

**Plenary Lecture**

- ✓ L. M. Harwood, "Studies on Ligands for Selective Actinide Extraction".

**15<sup>th</sup> International Scientific Conference, Siberian State Aerospace University, Krasnoyarsk, 2011**

**Oral presentation and Proceedings**

- ✓ T. Koubsky, "Simulation of chemical stability of UAM-069 and one of the degradation products".

**SESTEC 2012, Mumbai India), February 27-March 1 2012**

**Invited lecture**

- ✓ W. Verboom, "Development of different types of novel ligands for nuclear waste treatment".

**NCR-8, EuCheMS International Conference on Nuclear and Radiochemistry, Como, Italy, 16-21 September 2012**

**Oral presentations and Proceedings**

- ✓ J. Narbutt, W. P. Oziminski, "Selectivity of bis-triazinyl bipyridine ligands for americium(III) in Am/Eu separation by solvent extraction. Quantum mechanical study", Book of Abstracts (M. Bonardi, Ed.), p. 91.

**I.2.3 Thesis**

- ✓ Fermvik A.: "The effect of radiolysis of BTBP type molecules on Distribution ratios", Thesis for the degree of Licentiate, Chalmers University of Technology, ISSN: 1652-943X (2008).
- ✓ Magnusson D.: "Recovery Processes of Actinides from Genuine Spent Nuclear Fuel using TODGA and BTBP Extractants", PhD. Thesis, Chalmers University of Technology, Gothenburg, ISBN 978-91-7385-203-6 (2008).
- ✓ Retegan T.: "Investigations of Solvent Systems based on BTBP-class Ligands for the Separation of Actinides from Lanthanides", PhD Thesis, Chalmers University of Technology, ISBN: 978-91-7385-239-5 (2009).
- ✓ Fabre Stéphanie: "Behaviour of metals and alloys in molten fluoride media", University Paul Sabatier of Toulouse, PhD thesis, publicly defended on 25 September 2009, Toulouse, France.
- ✓ Huguet Anne: "Actinide-Lanthanide separation by an electrolytic method in molten salt media: feasibility assessment of a renewed liquid cathode", University Joseph Fourier of Grenoble, PhD thesis publicly defended on 04 Dec 2009.
- ✓ Aneheim E.: "Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel", Thesis for the degree of doctor of philosophy, ISBN 978-91-7385-751-2, Chalmers University of Technology, 2012.
- ✓ Núñez Ana: "Study of new ligands applied to hydrometallurgical separation processes for advanced nuclear fuel cycles" in the Autónoma University of Madrid.
- ✓ Mareš K.V.: "Study of the Possibility to Decontaminate Spent Solvents Issuing the DIAMEX and/or SANEX Processes", Diploma thesis, Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Prague 2011, 75 pp.

## **II SECTION B: APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS & EXPLOITABLE FOREGROUND**

### **II.1 Applications for Patents, Trademarks, Registered Designs**

- ✓ A. Deptuła, M. Brykała, W. Łada, D. Wawszczak, T. Olczak, A.G. Chmielewski, "Method for preparing of uranium dioxide in the form of spherical and irregular grains", Polish Patent PL389385 (27-10-2009), Russian Federation Patent RU2010136670 (2010), Belarus Patent 20101305 (2010), Ukraine Patent 201010756 (6-09-2010), European Patent EP2316794 (2011).
- ✓ L. M. Harwood, M. J. Hudson, F. W. Lewis, "Synthesis of Ligands for use in Actinide Extraction", UK Patent GB 0922588.9 (23-12-2009), World Patent WO2011077081 (2011), US Patent US2012264935 (2012), European Patent EP2516378 (2012).