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Actinide reCycling by SEParation and Transmutation

Rapports

Informations projet

ACSEPT

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Final Report Summary - ACSEPT (Actinide reCycling by SEParation and Transmutation)

Executive Summary:
All along the last four 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 us MOX dissolution or co-conversion into solid forms suitable for fuel fabrication.
In the field of pyrochemical process development, two reference core 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

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 usage 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:

- hydrometallurgical processes that benefit from more than 60 years of research and developments 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 build 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. The selective stripping which was studied earlier within a European framework, was be 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 lesser difficulties. The group separation process concepts was 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 be 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 materials 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 relevantof 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. Conceptual reviews as well as system studies were carried out, which led for apart to the implementation of an experimental program within FP7 ASGARD. 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.

Project Results:

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 (UOx or MOx) 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. 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 transuraium 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 (14N) fuels produce large quantities of 14C, requiring increased abatement efficiencies to minimise environmental impact
- Nitride (15N) fuels may require 15N recovery on economic grounds; however, direct dissolution causes isotopic mixing during dissolution with 14N 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 3H, 14C, 129I and noble gases (85Kr, 133Xe) for abatement. A process step prior to dissolution is the only viable option to abate some radionuclides, such as 3H, 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 15N 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 a electrochemically generated reagent that acts as a catalyst with a high standard electropotential, such as Ce4+, Co3+ or Ag2+, 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 106Ru, into the off-gas system, which would require very high abatement efficiencies.

These issues were further considered in order to outline flowsheets for advanced dissolution processes. The most significant conclusion from this work is 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 fuels reprocessing.

III.1.1.3 Practical oxide dissolution studies

Uranium dioxide (UOx) and mixed uranium plutonium oxide (MOx) 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 MOx.

The dissolution of uranium dioxide in nitric acid is known to occur in nitric acid 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 MOx has a further complication; that is as MOx is manufactured by the mechanical blending of uranium and plutonium oxides, MOx 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 MOx 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 Ag2+ MEO.

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

Batch dissolution experiments using ca. 5 % Pu MOx powders and pellets were undertaken to investigate the role of nitrous acid in the dissolution in nitric acid. Experiments with high surface area MOx powders largely at low temperature have confirmed the significant role nitrous acid plays, Figure 1. The results of these experiments have been used to derive a dissolution kinetic rate expression. Experiments with low surface area MOx 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 MOx. 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 MOx fuel.

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 Ag2+ and shows the generation, steady state and decomposition (after the current is turned off) of Ag2+. After cell characterisation plutonium dioxide powder dissolution experiments were undertaken. These experiments included in-line determination of Ag2+ and dissolved plutonium concentrations, which have previously only been published by at-line analysis. Comparison of the Ag2+ 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 Ag2+ 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 HNO3), 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 HNO3 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 extracts directly only the actinides from the 1st 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)2-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; tBuCyMe4-BTBP and MeCyMe4-BTBP compared to CyMe4-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.

Figure 2: Am(III) and Eu(III) extraction into CyMe4-BTPhen (filled symbols) or CyMe4-BTBP solution (open symbols), distribution ratios (DAm(III), circles; DEu(III), triangles) as a function of nitric acid concentration.

Organic phase, 10 mmol/L CyMe4-BTPhen in 1 octanol or 10 mmol/L CyMe4-BTBP
+ 0.25 mol/L DMDOHEMA in 1 octanol. Aqueous phase, 241Am(III) + 152Eu(III) in HNO3.

III.1.2.2.1 Lipophilic extracting agents

Among the lipophilic compounds able to separate Am(III) from Eu(III) in the organic phase, CyMe4-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) and with extraction kinetics faster than the current reference molecule, CyMe4-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 CyMe4-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 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, SO3-Ph-BTP and SO3-Ph-BTBP. These ligands do in fact complex Am(III) selectively over Eu(III) in a nitric acid aqueous phase ([HNO3] > 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: SO3-Ph-BTP (left) and SO3-Ph-BTBP (right).

Figure 5. Effect of SO3-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, 241Am(III) + 152Eu(III) in HNO3, with (filled symbols, solid lines) or without (open symbols, dashed lines) 9 mmol/L SO3-Ph-BTP.

SO3-Ph-BTP and SO3-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 HNO3, 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 SO3-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 < [HNO3] < 0.6 mol/L, DAm(III) < 1 and DEu(III) > 1. The separation factor SFEu/Am is in the range of 250–1000 (as compared to SFEu/Am ≈ 7 without SO3-Ph-BTP, being the selectivity of TODGA). Similar results were achieved with SO3-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 (SFEu/Am = 80–110, DAm < 1 in combination with a TODGA organic phase), but is also efficient at higher acidities ([HNO3] = 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 SO3-Ph-BT(B)P, it is does not contain sulphu, which is an advantage with respect to the generation of secondary waste.

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 CyMe4-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) (CH2-N-Et3X)2-BT that was demonstrated to be a good masking agent for nickel, palladium and silver.

Figure 7: BIMET (left) and (CH2-N-Et3X)2-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, 3 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 CyMe4-BTPhen (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 CyMe4-BTPhen, 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, CyMe4-BTPhen 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 CyMe4-BTBP + 5 mmol/L TODGA in kerosene/1 octanol (40:60 vol.). Oxalic acid and L-cysteine were used to supress 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 SO3-Ph-BTP as stripping agents for Am(III) and Cm(III). In both cases HNO3 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) (SFLa(III),Ce(III)/Am(III) < 2).

The SO3-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 SO3-Ph-BTP in HNO3, Am(III) and Cm(III) are stripped (i.e. DAm(III),Cm(III) < 1) while Ln(III) stay in the organic phase (i.e. DLn(III) > 1) for 0.2–0.8 mol/L HNO3. The minimum separation factor is SFLa,(III)/Am(III),Cm(III) ≈ 50. Stripping kinetics is fast.

III.1.3.2.3 GANEX systems

Two systems for the GANEX 2nd 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 1st cycle raffinate, similar to the 1c SANEX process. The CHALMEX solvent is a solution of 10 mmol/L CyMe4-BTBP + 30 % vol. TBP (or DEHBA) in cyclohexanone. Compared to 1 octanol, a cyclohexanone diluent makes for better solubility of CyMe4-BTBP and for faster extraction kinetics. The combination of CyMe4-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 1st 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 HNO3). 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 SO3-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.

The radiolytic stability of CyMe4-BTBP was studied by gamma and alpha irradiation. Gamma irradiation with doses of several 100 kGy caused severe degradation of CyMe4-BTBP in different diluents not contacted with nitric acid. However, extraction properties remained practically unaffected when solutions of CyMe4-BTBP in contact with nitric acid were irradiated to approximately 200 kGy, see Figure 8.

A comparison of alpha and gamma irradiation of CyMe4-BTBP (in presence of HNO3) showed slightly less degradation by alpha irradiation (7.9•10−4 kGy−1) than by gamma irradiation (1.1•10−3 kGy−1). Investigating radiolytic stability using gamma radiation is therefore (at least in this system) conservative.

Figure 8: Gamma irradiation of 0.01 M CyMe4-BTBP + 30% TBP in cyclohexanone in contact with 4 M HNO3. Dose rate approximately 0.9 kGy/h for 235U and 237Np; approximately 18 kGy/h for 152Eu, 238Pu and 241Am extraction (lines added to guide the eye).

III.1.3.3.2 TODGA

An exhaustive characterisation of degraded TODGA solutions through a qualitative and quantitative was developed and performed. 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 tests 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

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

A spiked 1c SANEX test was performed using the system developed in ACSEPT (see III.1.3.2.1). A flowsheet 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.

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 (Figure 11).

Before the hot EURO-GANEX process test a GANEX 1st cycle process had to be run to prepare the genuine feed solution. 117 g fast reactor fuel was dissolved in 6 mol/L HNO_3. U was extracted from this solution in a GANEX 1st 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_3 and used as feed solution in the hot EURO-GANEX test.

The hot NNL-GANEX test (see Figure 11) was run on two consecutive days (day 1, extraction/scrubbing; day 2, stripping). Analytical results are not yet available.

Figure 11. EURO-GANEX flow-sheet for the hot test.

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 in contact with HNO_3 and versus radiation. 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 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 Nd3+, Pu3+ and Am3+ 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 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 crystallinty and finally the integrity of the microspheres was observed.

Concerning the optimisation of thermal treatment it was found that a reduction to UO2 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 UO3 to U3O8.

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 Pu3+ (5 – 45 mol%) and Am3+ (10 mol%) microspheres was successfully. From 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)O2 and (U/Am)O2 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 the Institute of Nuclear Chemistry and Technology 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 UO3,

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 UO2. The CSGP process can be used to synthesize UO2 doped with Nd (as minor actinides surrogate), as irregularly shaped powders or spherical particles. Neodymium oxide was homogenously distributed in the UO2 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 DMDBTDMA (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, ICHTJ 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 UO2 microspheres containing trivalent actinides 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 UO2 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 dropping 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 Selektor (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 CO2 atmosphere. The final product of incineration (UO2) 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 TiO2 only a partial reduction of TiO2 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 UO2, 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 Li2O 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 proceses 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 ($CaCl_2$ 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_2, but also carbides at the cathode, or a Pt anode which is subject to a noticeable corrosion). A complete conversion into metal for Fe_3O_4, SnO_2, and TiO_2 was achieved at 750-850 °C. UO_2 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_3 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_2 in fluoride melts, was finally not successful in the case of UO_2: 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 has been 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 Np, Pu and Am in molten LiCl-KCl has been investigated on reactive solid Al electrodes at temperatures 400 - 550 °C. The composition and structure of the An-Al alloys have been investigated by XRD and SEM-EDX. All studied actinides have shown very similar characteristics on Al and the formation of An-Al alloys has been detected at potentials more positive than reductions of An to the pure metals (under-potential deposition effect). The observed deposition potentials E(M3+/M0-Al) at 450 °C are -2.25V -2.38V -2.43V and -2.48V vs. Cl-/Cl2 reference for M = U, Np, Pu and Am, respectively. The structures of the deposits have been evaluated. While granular deposits with relatively high porosity have been obtained in case of U, dense deposits with only small cracks filled with salt have been observed for the Np and Pu. The alloys have been composed mainly of AnAl3 (major for U, Np and Am) and AnAl4 (major for Pu) compounds. In addition, Zr electro-chemical behaviour during the electrorefining process of An-Zr based fuel has been 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 mA/cm2. 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 in order to evaluate feasibility of the process for purification of the salt from electrorefining. A dedicated experimental set-up has been designed, manufactured and successfully tested 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 have been carried out in molten LiCl-KCl electrolytes, followed by an experiment focused on a complete recovery of all actinides with certain portion of Ln in a multistage electrolysis. The first experiments have been carried out with melts containing only UCl3 and a mixture of UCl3-NdCl3 at a mass ratio of approximately 1:1. Almost all U has been 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 mA·cm-2·wt.%(U)-1, respectively, to keep selectivity. In the final experiment, Pu and Np have been completely recovered from an electrolyte containing 3 times higher concentration of Nd than the initial content of the An. Concentration of An has been decreased from 2.1 down to 0.7 wt.% during selective part of the experiment, when the current density was above -2.0 mA·cm-2. Then co-deposition of actinides and Nd has been carried out up to recovery of all actinides with average current density > -4.0 mA·cm-2.

III.2.2.2 Evaluation of the electrochemical processes in molten fluorides

In order to develop a novel separation processes based on electrochemical methods in fluoride melts, the knowledge of fluoride systems has to be expended. Dedicated experimental set-ups have been designed and manufactured, electrochemical behavior of uranium and selected relevant elements in LiF-CaF2 and LiF-NaF-KF melts has been studied and recovery of uranium by electrolysis using pulsed current technique in molten fluorides using reactive Ni cathode has been investigated. Negative influence of oxygen contamination has been experienced and preliminary tests of oxygen catching ability of ZrF_4 have been performed. Possibilities of a liquid Bi cathode in molten fluorides have been evaluated and the relevant anodic reaction has been 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 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. An electrochemical cell for the experimental work in molten fluorides has been built and commissioned in ANSTO.

The electrochemical behaviour of U(III) has been studied in molten LiF-CaF_2 at 1083 K on inert W and reactive Ni electrodes. Electrorefining of uranium plate in a melt containing Gd(III) ions has been performed and selective reduction of U(0) on Ni electrode has been achieved. Mechanism of uranium nucleation during the electrolysis on inert electrode has been 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 LiF-NaF-KF-UF_4, LiF-NaF-UF_4 and LiF-CaF_2-UF_4 systems on Ni working electrode have been carried out initially using potentiostatic technique. To improve the uranium recovery yield, pulse-current electrolytic experiments have been 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 have been obtained on all electrodes. Electrolysis by pulsed current has been 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 has been focused to 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 has been decided that the experiments would be performed using a liquid metal cathode. The validation experiments have been carried out in molten chlorides with the aim of future adaption of the method for the fluoride salts.

An electrode has been 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 has been developed. A specific furnace made of transparent envelops has been 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 has been successfully carried out, including potentiostatic electrolysis of Nd. The observations have been in good agreement with the theory.

The next step will consist of transposing the electrode to the fluoride media, where no visualization of the drop is possible. An investigation of the interfacial tension between LiF-CaF_2 and liquid Bi at 810°C will be necessary to set correctly the experimental parameters. An experiment is planned in LiF-CaF_2 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 for estimation of 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) has been carried out. The experiment has consisted of preparation of the initial material and its reductive extraction using a Li-Cd alloy as an 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 have been added to the raffinate. About 520g of the HLLW has been prepared containing 8400µg/g of uranium, 600µg/g of TRUs, and 2000µg/g of FPs including 870µg/g of rare-earth FPs. The raffinate has been 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 has been 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 has been loaded in a MgO crucible together with pure Cd metal. The reductive extraction has been carried out at 500°C using step by step addition of Cd-Li alloy containing 0.685wt.% of Li. The reduced An have been 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 has been 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 has been investigated in ITU for recovery of An from the An-Al alloys formed during the electrochemical separation processes. The chlorination route consists in three steps: Vacuum distillation for removal of the salt adhered on the electrode, chlorination of the An-Al alloys by Cl2(g) or HCl(g) and sublimation of the formed AlCl3. A thermochemical study has been performed and it has shown a thermodynamic feasibility of all three steps. On the basis of the calculated conditions, experiments using pure UAl3 alloy have been carried out to evaluate and optimise the chlorination step using both proposed chlorination agents. The work has been focused mainly on the determination of the optimal working temperature, providing complete chlorination of the alloy without formation of volatile UCl5 and UCl6. A very efficient chlorination (up to 99.8% conversion) with no volatilisation of U has been achieved by Cl2(g) already at 150°C. A major part of AlCl3 (between 85% and 94%) has been removed already during the chlorination. The chlorination by HCl(g) enabled higher reaction temperatures, which indicated higher process rates. A complete conversion of UAl3 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 has been 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 has been predicted (salt composition, working temperature 700°C). The first experiments have led to the optimization of both the experimental set-up and the experimental conditions. CaCl2-LiCl (70-30 mol%) salt has been selected and a ratio AlCl3/An = 6–7 has been 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 has been 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 pyroreprocessing 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-AlF3 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-AlF3 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 AlF3, 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/AlF3 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 LnOCl or Ln2O3.

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)
Ion-exchange (zeolites)			
Hybrid aqueous closed loop			
Precipitation (carbonates/phosphates)			
Precipitation (oxygen sparging)			
Precipitation (wet argon sparging)			
Electrolysis			
Li-Reduction			
Melt crystallisation			

Fully effective, demonstrated at lab-scale (>90% efficient)
Partially effective, demonstrated at lab-scale (10-90% efficient)
Slightly effective, demonstrated at lab-scale (<10% efficient)
Ineffective, demonstrated at lab-scale (0% efficient)
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 CO2 laser heating device for NMR experiments up to 1500°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: LaF3-AF (A=Li, Na, K, Rb and Cs), LaF3-LiF-CsF, LaF3-LiF-CaF2, LaF3-LiF-CaO, LaF3-LiF-La203, LaF3-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 19F, 23Na, 85Rb, 133Cs and 139La. In LaF3-AF-CsF and LaF3-AF-CaF2 systems, the coordination number of lanthanum cation ranges from 6 to 8 depending on the LaF3 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 LaF3-LiF-CaO yields to a displacement of the proportion dissolved versus precipitated LaOF.

The effects of adding 3% of BaF_2 in the molten 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 RbCl, CsCl and $SrCl_2$ have been parameterized. These can be used to study the effect of adding these fission products to the 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 penalty for the obtainment of 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 ≥ 96%. About 25 pellets were realized, in order 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, in order to determine the initial dissolution rate. It can be estimated between 12 and 16 g/m2/d, which is a too high value for a high level wastes 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). The results, reported as both tables and graphs, show a significant release of the elements, especially at 90°C. 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 SOD.BG appears more compact and quite hard to break with respect to the SOD.GF 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.

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

The potentialities of other oxychloride phases, like chloroapatite, $Ca10(PO4)6Cl2$, and chlorospodiosite, $Ca2PO4Cl$, 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 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 r0 (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 $CO2$ 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 around 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 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 recover 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 Li12[(AlO2)12(SiO2)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. 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 131Xe/132Xe with the uncertainties of ± 0.5at.% if the experimental error associated with the isotopic analysis is assumed to be ±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 ~1 at.%. Assuming the fission gas amount released from the fuel pins can be measured with the uncertainty of a few percent including measurement error, it is expected that the actinide composition in the fuel can be predicted with accuracy of ±~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, F2, 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 NiF2 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 to support the development of the science being developed within the project. This work was performed by NNL with deliverable 3.1.5 being delivered 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 was 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.

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 to show the pilot plant operations, 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.

III.3.2 Science and Engineering Integration

Work Package 3.2 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

This task was focussed on online monitoring for molten salts processes. 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)) were developed by CEA teams. In the frame of a PhD thesis, UEdin manufactured and characterized microelectrodes to in situ analysis in molten salt.

LIBS device development

CEA teams adapted the LIBS for working with molten salt by modifying the laser wavelength and designing a cell with a 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 LiF-AlF_3-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 occurred during this project indicates a lack of robustness of this device for the use with molten salts.

Microelectrodes development

UEDIN manufactured and characterized microelectrodes to use them in molten salt (LiCl-KCl at 450°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 Sm(III)/Sm(II) and 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 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 works 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: NO2-/NO3- in acid) and stripping/plating (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 HNO3 being studied at varying flowrates and phase ratios. 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 O/A 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-1) and the corrosion is limited by corrosion product diffusion in the melt.
- The corrosion current densities vary with the composition of the fluoride mixture: icorr (LiF-NaF) < icorr (LiF-CaF2) < icorr (LiF-AlF3) 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 2 mol.kg-1 of Li2O 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-electrolyzes 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 UO2 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 UO2 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)O2-x fuel pellets. On the basis of an analysis of the target characteristics and a bibliographical study on the behaviour of helium in a UO2 matrix, the following targets have been set for MARIOS:

- Chemical composition Am0.15U0.85O1.94 (with 100% Am-241)
- Pellets with increased open porosity (density 82.5%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 ~1021 atoms/cm3

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 an estimated He production after of 7•1020 atoms/cm3. 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 UO2 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 UO2-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 UO2, to 10 times more containers with AVM glass, and to 75 times more containers with R7T7 glass. The reprocessing in dilution in the European reprocessed fuel reduces the waste production to twice as many containers than the UO2 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 following ranking was deduced for minor actinide bearing matrices, from better to worse: 1. UO2-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.

Potential Impact:
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, 1cycle 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 technically feasible recycling of actinides strategy 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 are now technologically feasible,
• One of the identified major difficulties for nuclear energy production, 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 10th 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), 10th IEMPT (2), MS8 (Japan) (3) & 235th ACS Meeting (1).
On the second period, three oral talks were given on the organization and objectives of ACSEPT at FISA 2009 (Czech Republic), ACS238 (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 GLOBAL2009 (France) (11), ACTINIDES 2009 (USA) (4), & 238th ACS Meeting (3).
On the third period, general presentations of ACSEPT were given at 239th ACS Meeting, 11th IEMPT (USA), IPRC 2010 (Russia), ENC 2010 (Spain). 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 239th ACS Meeting (7), 11th IEMPT (3), NuMat 2010 (Germany) (5), Plutonium

Futures 2010 (USA) (1). The 1st ACSEPT International Workshop was organised in Lisbon, Portugal, from March 29th to April 2nd 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 ICAPP 2011 (France), GLOBAL 2011 (Japan), NFCC'2012 (UK), ATALANTE 2012 (France), ICAPP 2012 (USA), IEMPT12 (Czech Rep.),. 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), GLOBAL 2011 (2), 12th IEMPT (4), MS9 (Norway) (2), Plutonium Futures (UK) (2), NFCC'2012 (6) and a huge participation at ATALANTE 2012 (20 oral presentations & 12 posters), hosting the 2nd 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 full list is given in the annex.

The different journals involved are: Journal of American Chemical Society (2011 Impact factor: 9.907) (1), Chemistry Communication (6.169) (1), Inorganic Chemistry (4.601) (2), Dalton Transactions (3.838) (6), Electrochemica Acta; (3.832) (1), Organic & Biomolecular Chemistry (3.696) (1), Physical Chemistry Chemical Physics (3.573) (1), 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), Polyhedron (2.057) (1), Journal of Nuclear Materials (2.052) (9), Hydrometallurgy (2.027) (1), Solvent Extraction and Ion Exchange (2.024) (19), Journal of Supramolecular Chemistry (1.960) (1), Journal of Chemical and Engineering data (1.693) Radiochemica Acta (1.575) (10), 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) (1), ECS Transactions (N/A) (1), Energy Procedia (N/A) (2), Procedia Chemistry (N/A) (22).

The average impact factor calculated on publications in Journals whose impact factor is known (72 publications) is 2.419.

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 and Chernobyl 1986 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 to not only 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 exist with other universities and possibly also in other contries. Since the EU framework projects by nature are multi culturral, the students have the possibility to not only meet reserachers 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 trans national 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 for the ACSEPT community and each propossal was thus reviewed by the PCC before any deciscion was taken. In total 11 such inter laboratory visits were performed. The majority (7 out of 11) of these mobility grants were awareded to female scientits. These small projects are listed below

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 CyMe4-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 UCHTJ 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

In a project of the dignity of 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 ACSET partners but also the surrounding scientific community several well-known scientists from different countries contributed, see table below.

First Name Name Institute Country Title of the contribution
Vasiliy Babain Radium Khlopin Institute Russia Fluorinated Diluents for HLW Processing –techological 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 (1st 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
K Nagarajan IGCAR India Pyroprocess Research Activities at IGCAR, Kalpakkam, 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 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 was very high.
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 special lectures were given or training sessions were organized at each ACSEPT meeting. The addressed topics and the contributors are given in the table below. In addition, focused workshops were organized during the half-year meetings to address very specific issued linked to the objectives of the projects, both in hydro and in pyro.

Meeting Contributors Topic
1st 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
1st 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
2nd 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
2nd annual meeting, Lisbon ACSEPT International Workshop
3rd half-year meeting, Petten W. Oziminski, D. Guillaumont, B. Shimmelpfennig, C. Simon, E. Sanchez

(Univ Sevilla, Spain), P. Guilbaud, G. Wipff Computational Chemistry Day
3rd annual meeting, Manchester 13 presentations from ISTC, KAERI and ACSEPT dedicated to students and young scientists ISTC-KAERI-ACSEPT Exchange Meeting
4th 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
4th 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

Another important aspect of dissemination of knowledge is the possibility to present the work performed at international conferences and meetings outside the ASCEPT sphere. 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 we strongly encourage that the younger scientists are present in our 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 accepted 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 here:

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

(ICHTJ) NFCC 2012 Oral “Synthesis of Uranium Dioxide Microspheres by Water and Nitrate Extraction from Uranyl-Ascorbate Sols”

In addition to attendance to these conferences the possibilities to attend the internal ACSEPT training sessions was also given. In order to facilitate attendance participation costs were coved by the DM4 budget after review by the PCC. The attendees for the pyrochemical training session as well as the hydrochemical training sessions are listed in Table Y.

Hydro training session	Pyro training session
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)	

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

IV.3.3 Communication / fostering visibility

Through the participation of both 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 on 20 are directly related to the project, from 12 different websites.

When the keywords are “actinide separation”, ACSEPT is listed two times on the 10 first results (7th and 10th), amongst them, the ACSEPT Homepage (10th).

When the keywords are “actinide recycling”, ACSEPT is listed two times on the 10 first results (2nd and 5th), amongst them, the ACSEPT Homepage (2nd).

When the keywords are “actinide recycling”, ACSEPT is listed two times on the 10 first results (2nd and 5th), amongst them, the ACSEPT Homepage (2nd).

When the keywords are “actinide FP7”, ACSEPT is listed five times on the 10 first results, amongst them, the ACSEPT Homepage (5th).

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...).

List of Websites:
www.acsept.org

Documents connexes

final1-211267-1154907-acsept-final-report.pdf

Dernière mise à jour: 4 Juin 2013

Permalink: https://cordis.europa.eu/project/id/211267/reporting/fr