Abstract

Nuclear energy has more than ever to demonstrate that it can contribute safely and on a sustainable way to answer the international increase in energy needs. Actually, in addition to an increased safety of the reactors themselves, its acceptance is still closely associated to our capability to reduce the lifetime of the nuclear waste, to manage them safely and to propose options for a better use of the natural resources. Spent fuel reprocessing can help to reach these objectives. At the European level, ACSEPT and ACTINET-I3 have worked together to improve our knowledge in actinide chemistry and advanced separation process development.

Keywords: ACSEPT, ACTINET-I3, aqueous reprocessing, pyrometallurgy, transnational access, EURATOM projects

1. Introduction

Nuclear energy has more than ever to demonstrate that it can contribute safely and on a sustainable way to answer the international increase in energy needs. Actually, in addition to an increased safety of the reactors
themselves, its acceptance is still closely associated to our capability to reduce the lifetime of the nuclear waste, to manage them safely and to propose options for a better use of the natural resources. Spent fuel reprocessing can help to reach these objectives. But this cannot be achieved only by optimizing industrial processes through engineering studies. It is of a primary importance to increase our fundamental knowledge in actinide sciences in order to build the future of nuclear energy on reliable and scientifically-founded results, and therefore meet the needs of the future fuel cycles in terms of fabrication and performance of fuels, reprocessing and waste management. It also requires ensuring the top level European expertise in this field by developing the skills of the young researchers in nuclear sciences in Europe through a training and education program.

This paper describes the facilities open for transnational access within ACTINET-I3 and highlights the main ACSEPT achievements. Actions in terms of training and education are also emphasized.

2. ACTINET-I3 Transnational access

In order to keep a leading position in the field of nuclear energy – both in terms of safety and efficient use of natural resources – Europe needs to reinforce its expertise and to prepare the next generation of scientists and engineers who will be able to contribute to develop actinide management strategies based on sound scientific bases. However, because most actinides are radioactive, their study requires specific tools and facilities that are only available in a limited number of laboratories in Europe. It is therefore strategic to coordinate the existing Actinide infrastructures in Europe and to strengthen the community of European scientists working on actinides.

The establishment of a Network of Excellence – ACTINET – was a first step in this direction, achieved under the 6th Framework Programme (FP6). As a second step, the objective of the present FP7-Integrated Infrastructure Initiative (I3) ACTINET-I3 is to reinforce the networking of existing European infrastructures in actinide sciences, and to facilitate their efficient use by the European scientific community (Figure 1).

![Image](image.png)

Figure 1: The ACTINET-I3 Initiative

The first objective is to pool selected parts of the major facilities of some large European institutes (CEA, ITU, KIT, HZDR, and PSI) and to operate this pool as a multi-site user facility, in order to make it accessible through a competitive selection of joint projects. University of Manchester, KTH and CNRS contribute also to this initiative to help improving the networking between pooled facilities and users.

The pooled facilities are laboratories that allow the handling of radioactive material at various levels of activity (from dilute solutions to high concentrations of actinides and spent nuclear fuel) and under specific conditions (inert gas boxes), with access to analytical techniques and specific characterization methods (elementary and isotopic analysis, laser spectroscopy, synchrotron radiation etc.).

The ACTINET-I3 research projects potentially address all the major fields of basic actinide sciences, keeping in mind the potential applications for the production of nuclear fission energy and the safety of nuclear waste disposal, and include:

- Physics and chemistry of actinide compounds.
- Chemistry of actinides in solutions and at interfaces.
- Theoretical chemistry of actinides.
Analytical methods development.  
To date, more than one hundred Joint Research Projects carried out in these facilities have been granted by ACTINET-I3

3. Separation process developments

For more than four years, in the continuation of previous FP4 (NEWPART), FP5 (PARTNEW, CALIXPART, PYROREP) and FP6 (EUROPART) European projects, ACSEPT works at developing actinide separation processes from the basis chemistry approach to the process demonstration in hot-labs. A consortium of 34 Partners gathers its skills to address the different issues related to these developments from the fuel dissolution to the fuel refabrication (Figure 2).

3.1. Recent Achievements

3.1.1. Aqueous reprocessing

A part of the work is dedicated to spent fuel dissolution. Conceptual studies of potential chemical treatment options (direct dissolution or pre-treatment) for the dissolution of various types of spent nuclear fuels from current and next generation reactors were performed and the potential chemical treatment options (direct dissolution or pre-treatment) were studied. Recently MOx dissolution tests were performed to assess the role of HNO₃ concentration on dissolution. The effect of HNO₃ upon the rate of dissolution was observed to be small at nitric acid concentration < 5 mol/L. However, above 6 mol/L HNO₃ increasing HNO₃ concentration was observed to significantly increase the rate of dissolution.
Actually, basic research activities are prerequisite to the development of efficient separation processes. In ACSEPT, new ligands were designed, synthesised and assessed towards their complexing and extracting properties. So far, approx. 140 new compounds have been synthesized and screened following standardized protocols. 75% of these compounds are lipophilic extracting agents whereas the remaining 25% are hydrophilic complexing agents. Few of the new extracting agents showed to have properties better than the current reference SANEX extracting agent, CyMe4-BTBP (Figure 4). Through ACTINET-I3, these ligands are studied more deeply to try to understand the selectivity drivers of such ligands.

![Figure 4. Organic molecules selected for further studies within ACSEPT](image)

In the next step, optimized flow-sheets were developed and implemented in cold and spiked tests before being run on genuine spent fuel feeds in hot cells. Up to now, two hot-tests were successfully carried out within ACSEPT (r-SANEX at ITU and i-SANEX at CEA) as well as a spiked test on the 1c-SANEX concept. Currently a GANEX 2nd cycle process based on TODGA + DMDOHEMA in kerosene to co-extract actinides and lanthanides from the 1st cycle raffinate, followed by selective actinides back-extraction using two complexing agents in nitric acid is under development.

In addition to the above studies, methods not handling powders have been studied for actinide fuel material synthesis: co-precipitation, sol-gel processes and infiltration of solid sorbents impregnated with actinide extracting agents such as TODGA. The activities cover basic studies, such as the chemical speciation of polyactinide solutions (oxidation state monitoring) or the thermodynamic and kinetics of actinide co-conversion into polyactinide solids to understand and improve the co-conversion processes.

### 3.1.2. Pyro reprocessing

In this domain, the objective is to make advances beyond the current state of the art in pyrochemical separation processes for homogeneous recycling strategies. The four main steps of a process (head-end, core process, salt treatment for recycling and waste conditioning) are studied. In addition, process modelling, materials and engineering studies are performed in the cross-cutting activity domain.

As far as fuel dissolution is concerned, a lot of data have already been available in chloride but less in fluoride media. Some effort was put on the latter. The electrorefining process is dedicated to metallic fuels. In a double strata concept, it could be of interest to go from an oxide fuel to a metallic one to make the link between the two strata. Thus direct electroreduction from oxide to metal is studied. To enhance core process performance and to simplify salt purification, volatile fission products removal prior to the core process by thermal treatment is studied.

The main part of the work was the development of core processes involved in pyrochemical separation of actinides. Two reference technologies have been identified and selected as promising for a global actinide
management in previous projects: liquid-liquid reductive extraction in molten fluoride and electorefining of actinides onto solid aluminium cathodes in molten chloride (Figure 5). The exhaustive electrolysis has been studied to yield “quantitative” recovery of actinides. Implemented after the electorefining, it allows the actinides remaining in the salt to be recycled in the process before the salt purification step (removal of all the fission products) Another objective was to recover pure actinides from the metallic aluminium phase, which is a common step for the two reference processes. Major progress has been made in this field from both solid and liquid aluminium phases. In addition, the development of alternative electrochemical processes in fluoride media was continued. One study was dedicated to the recovery of minor actinide from PUREX raffinate: the performances of a liquid-liquid reductive extraction in molten chloride/liquid cadmium were measured by CRIEPI in collaboration with ITU.

Secondary waste minimization requires the treatment of salt before it can be recycled. Progress was made in the decontamination of spent chloride salts. Zeolite ion-exchange filtration and phosphate or carbonate precipitation were selected for efficient salt clean-up. In precipitation processes, studies are carried out to replace phosphate and carbonate by a gaseous reagent that allows the minimisation of the salt inventory in the loop and consequently the reduction of the amount of waste. In molten fluoride, the distillation of the reference molten salt LiF-AlF₃ allowed the salt to be decontaminated and recycled in the process.

Specific wastes have also to be managed. Synthesis, characterization and leaching of sodalite clearly demonstrated that this material is not relevant for the confinement of high active waste. Alternatively, studies are undergoing to obtain a chloroapatite phase as a material for incorporating alkaline, alkaline-earth and rare earth elements. The immobilisation of noble fission products (Pd, Mo, Ru, Rh, Tc, etc.) via the formation of solid solutions in Cu/Ni, Cu/Sn, and Al based alloys were studied.

3.1.3. Cross-cutting activities

Engineering and systems studies have been performed on aqueous and pyrochemical separation processes, paving the way to a future demonstration at a pilot level. This was achieved by creating feedback between technical domains in order to help achieving optimisation and rationalisation of research efforts. Conceptual studies were performed to identify the most promising hydrometallurgical and pyrometallurgical process options and to down select options.

Whereas process operation and online monitoring are well developed for hydrometallurgical processes, this is not the case in pyrometallurgy. Thus, on-line monitoring and corrosion in molten salts were studied in ACSEPT. Regarding hydrometallurgical processes, work on scaling up centrifugal contactors was performed.

ACSEPT contributed also to the FP7 FAIRFUELS project by performing a feasibility study on the fabrication of a minor actinide-bearing pin in the framework of the MARIOS program.

Another part of the work was an assessment of the reprocessibility of different types of minor actinide bearing targets (MgO, Mo, UO₂ based). This study led to implement a part of the FP7 ASGARD project.
3.1.4. Training and education

ACTINET-I3 and ACSEPT contribute to develop the integration of European education and training in the field actinide chemistry, to combat the decline in student numbers, teaching establishments and young researchers. thus providing the necessary competence and expertise for a sustainable development of nuclear energy. It provides an infrastructure which supports co-operative work among the European nuclear community.

ACSEPT supports the funding of post-doctoral students (two students funded on the first half of the project), the exchange of students between partners (2–3 month stays) and helps students attending conferences, ACSEPT training sessions or summer schools. ACTINET-I3 organises yearly Summer-Schools and sponsors international conference that offer travel grants to students.

In September 2012, ACSEPT and ACTINET-I3 sponsored the ATALANTE 2012 International Conference on nuclear chemistry for sustainable fuel cycles.

4. Conclusion

Thanks to ACTINET-I3 and ACSEPT, FP7 EURATOM Fission has contributed largely to the development of a European nuclear chemistry community. Researches from universities have had access to top level hot labs or beam lines and have contributed to the development of advanced fuel cycle separation processes. The ACTINET-I3 Joint Research Activity is carried out in close connection with ACSEPT and allows us to go deeply in the understanding of such complexes. Last but not least significant efforts were made for dissemination activity and training of students, helping developing nuclear skills in Europe.

With these technical advances, it should be possible to propose options to Governments, European utilities as well as technology providers. A technically feasible strategy for recycling actinides will certainly produce positive arguments. European decision makers and public opinion could be convinced that alternative solutions to nuclear waste management are now available.

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