



SACSESS – the EURATOM FP7 project on actinide separation from spent nuclear fuels

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Abstract. Recycling of actinides by their separation from spent nuclear fuel, followed by transmutation in fast neutron reactors of Generation IV, is considered the most promising strategy for nuclear waste management. Closing the fuel cycle and burning long-lived actinides allows optimizing the use of natural resources and minimizing the long-term hazard of high-level nuclear waste. Moreover, improving the safety and sustainability of nuclear power worldwide. This paper presents the activities striving to meet these challenges, carried out under the Euratom FP7 collaborative project SACSESS (Safety of Actinide Separation Processes). Emphasis is put on the safety issues of fuel reprocessing and waste storage. Two types of actinide separation processes, hydrometallurgical and pyrometallurgical, are considered, as well as related aspects of material studies, process modeling and the radiolytic stability of solvent extraction systems. Education and training of young researchers in nuclear chemistry is of particular importance for further development of this field.

Key words: actinide separation • minor actinides • nuclear fuel reprocessing • partitioning • solvent extraction • pyrochemical separations

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Introduction

Advanced nuclear fuel cycles of the future rely on an optimized recycling of actinides to make a more efficient use of resources and a better management of the nuclear waste. Fissionable material is re-used instead of being finally disposed of, thus minimizing uranium consumption as well as the volume, heat load and long-term radiotoxicity of the highly radioactive nuclear waste (Fig. 1). Plutonium is already being separated from spent nuclear fuel (SNF), together with uranium, in the PUREX process and recycled into MOX fuel. To provide further reduction of radiotoxicity and the heat load of the highly radioactive waste, the strategy of partitioning and

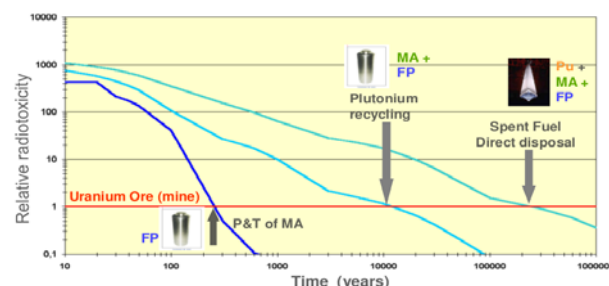


Fig. 1. The decrease in the radiotoxicity of nuclear waste as a function of time for various options of SNF management. Reprinted from Ref. [1], with permission from Elsevier.

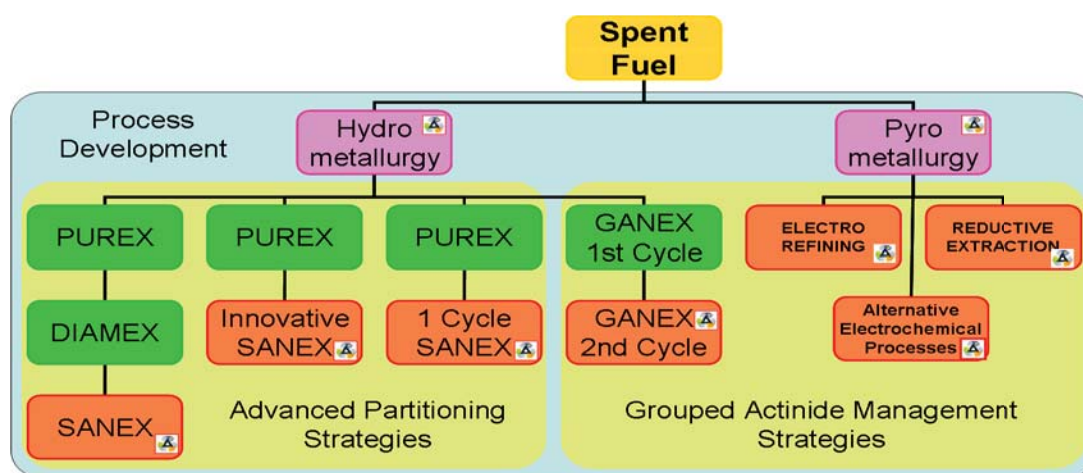


Fig. 2. Scheme of various options of SFN management. Reprinted from the Ref. [1], with permission from Elsevier.

transmutation (P&T) of minor actinides (MA = Np, Am, Cm,...) [2] is the most promising option for the management of SNF, enhancing the safety of nuclear energy. Transmutation can be achieved by high energy neutrons that transform these elements into much shorter-lived and stable nuclides. Their initial separation from fission products (FP) of high neutron cross sections (reactor poisons) is indispensable for the transmutation to be efficient.

Two technologies are being studied to achieve actinide separation:

- Hydrometallurgy – based on liquid-liquid (aqueous/organic) extraction processes, of ca. 70 years of research and development and a long-lasting proven experience at the industrial level. Hydrometallurgy can allow either the heterogeneous or the homogeneous recycling of the actinides, depending on the processes developed (Fig. 2).
- Pyrometallurgy – processes of pyrochemical separation, first studied over half a century ago for the treatment of spent fuel from molten salt reactors and breeder reactors. At the end of the 1980s, the interest renewed for treating metallic fuel in the integral fast reactor concept, but without reaching the level of industrial development. Pyrometallurgy is mainly studied for the homogeneous recycling of actinides (Fig. 2).

The Safety of Actinide Separation Processes (SACSESS) Project is a Euratom FP7 collaborative project (2013–2016) dealing with the safety aspects of hydrometallurgical and pyrometallurgical processes of actinide separation, developed within the previous Euratom projects [1, 3]. SACSESS provides a structured framework to enhance the fuel cycle safety associated with P&T of MA. In addition, safety studies are performed for each selected process (hydrometallurgical and pyrometallurgical, Fig. 2) to identify weak points which are to be studied further. These data are used to optimize flowsheets and process operation conditions.

SACSESS generates fundamental safety improvements for the future design of an advanced processing unit. It thus is an essential contribution to the demonstration of the potential benefits of actinide partitioning to the safe management of the long-lived waste.

Hydrometallurgy

Within FP7-ACSEPT, several hydrometallurgical options for separating transuranium elements have been developed and demonstrated through hot-tests to complement (heterogeneous recycling) or to replace (homogeneous recycling) the well-known PUREX process (Fig. 3).

These aqueous partitioning processes involved new extractants or complexing ligands and new diluents [2]. SACSESS addresses the safety issues required under operational conditions or maloperation, which implies a better understanding of the chemical systems involved and the need to enhance the process operation at the industrial level. Issues such as chemical and radiolytic stability, impact of degradation products, downstream effects, loading issues, etc. are studied since they affect safety and performance of aqueous separation processes.

The particular solvent extraction systems under study are:

- CyMe₄-BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2'-bipyridine) based systems, selectively extracting An(III) in r-SANEX or 1c-SANEX processes, either directly from the PUREX raffinate or from the An(III) + Ln(III) product solution coming from the DIAMEX or TODGA systems [4, 5];
- TODGA (N,N,N',N'-tetraoctyldiglycolamide) based systems – co-extracting An(III) and Ln(III) in i-SANEX or GANEX processes [6];
- water soluble hydro-BTP [2,6-bis(5,6-di-(sulphophenyl)-1,2,4-triazin-3-yl)-pyridine] based systems, selectively stripping An(III) from the loaded TODGA phase in the i-SANEX or GANEX processes [7, 8].

French expertise gained at the turn of the centuries allowed us to limit the number of long-lived MA (and fission products) which should be transmuted to americium merely [9] in order to avoid the presence of neutron-emitting curium in the fuel fabrication [10]. That is because the high neutron dose and heat generation from curium-containing transmutation targets would require special shielding. On the other hand, the short half-life (18 y) of the major

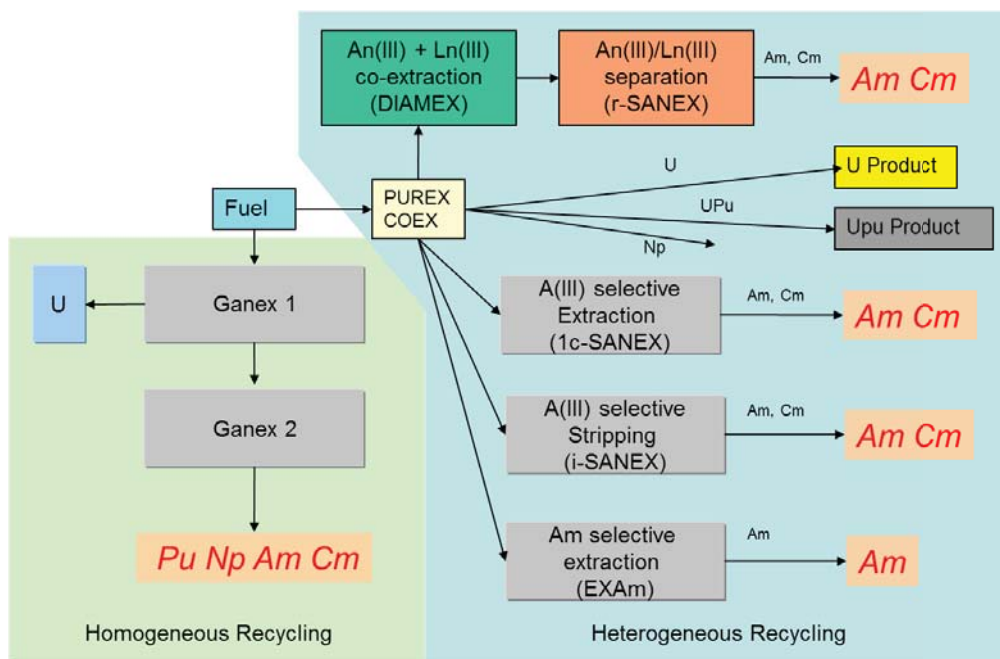


Fig. 3. Hydrometallurgical processes under studies in ACSEPT and SACSESS.

isotope ^{244}Cm enables disposal of Cm together with the fission products in the glass canisters. The activity and heat load of Cm will decay during the interim storage time before deep geological disposal. This implies the necessity to separate Am(III) not only from chemically similar lanthanide fission products, but also from much more similar Cm(III) [11–13]. The separation of only trivalent americium from the PUREX high active raffinate (EXAm concept), not previously studied in European projects, is now developed in SACSESS.

Modeling

Safely and fully assessing hydrometallurgical separation processes requires a reliable modeling of the different steps of these processes. Reliable models of the separation processes based on a multiscale modeling approach and on trustworthy experimental data are developed. On-line monitoring required for process control is also developed.

One of the approaches studied is the theoretical modeling of the chemical systems and processes with the use of quantum chemical calculations. Such calculations are helpful for a better understanding of the role of the molecular and electronic structure of highly effective N-donor and O-donor ligands for the An(III)/Ln(III) separation, and of the origin of the selectivity in the separation processes [14, 15].

Radiolytic stability

Solvent extraction systems used for SNF reprocessing are exposed to high doses of ionizing radiation. Thus, when designing a new system it is necessary to demonstrate not only its good extraction properties, but also sufficient radiolytic stability of the extractants and

diluents, and how the extraction properties change upon irradiation. Radiolytic degradation results in the consumption of the extracting agent and in the production of degradation products, affecting important parameters of solvent extraction systems such as distribution ratios, selectivity, loading capacity, phase disengagement times etc. [16].

The long-term use of the chemical systems involved must be assessed to warrant their safety, not only during normal operation, but also in the case of maloperations. SACSESS investigates the stability of solvent extraction systems towards irradiation and chemical degradation by nitric acid. Degradation products do form even in the most stable systems; these are identified and their impact on the properties of solvent extraction systems is assessed.

Pyrochemistry

High-temperature methods of reprocessing SNF, still under research and development, are an alternative for solvent extraction. Two options are usually studied: electrochemical methods in molten salts (electrorefining, electrowinning,...) and chemical methods. In this case, instead of aqueous and organic solvents, molten salts and molten metals (pure or eutectics) are used. The challenge is to perform a selective extraction of actinides from spent liquid fuel in order to recover the fissile material and to separate the minor actinides from fission products [17, 18]. The process involves several chemical steps based on redox and acido-basic properties of various elements contained in the SNF.

Pyrochemical processes are obvious when dealing with molten salt reactor containing a liquid fuel but such processes have also been particularly studied and developed for solid metallic fuel reprocessing. Announced more compact than aqueous methods, pyrochemistry could allow SNF reprocessing at

are co-organized with other European projects such as ASGAR, TALISMAN [22] and CINCH (Cooperation in Education and Training in Nuclear Chemistry) [23, 24], resulting in a powerful network.

Conclusions

Research towards more sustainable nuclear power, allowing a safe long-term management of the current nuclear waste, is of high priority. SACSESS, among several successful European projects (ASGAR, TALISMAN and CINCH), partially funded by the EC under the 7th and previous framework programmes, is paving the way to future demonstration. From initial concepts established about 20 years ago to the recent assessment of reliable flowsheets, huge progress is made. New challenges need to be addressed when shifting towards implementation. Foreseen is a selection of the most appropriate technique(s) to be matured. Hopefully, by the end of the project, a new process flowsheet based on the EXAm concept will complete the tool box of the actinide separation processes, given a full set of options for the stakeholders. In the next step, an integration of these processes in the whole back-end of the fuel cycle will be performed, ‘from fuel to fuel’, linking the separation and fuel communities.

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References

1. Bourg, S., Hill, C., Caravaca, C., Rhodes, C., Ekberg, C., Taylor, R., Geist, A., Modolo, G., Cassayre, L., Malmbeck, R., Harrison, M., de Angelis, G., Espartero, A., Bouvet, S., & Ouvrier, N. (2011). ACSEPT – Partitioning technologies and actinide science: Towards pilot facilities in Europe. *Nucl. Eng. Des.*, 241, 3427–3435. DOI: 10.1016/j.nucengdes.2011.03.011.
2. Salvatores, M., & Palmiotti, G. (2011). Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges. *Prog. Part. Nucl. Phys.*, 66, 144–166.
3. SACSESS report summary, http://cordis.europa.eu/result/rcn/158019_en.html.
4. Modolo, G., Wilden, A., Geist, A., Magnusson, D., & Malmbeck, R. (2012). A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate. *Radiochim. Acta*, 100, 715–725. DOI: 10.1524/ract.2012.1962.
5. Wilden, A., Modolo, G., Schreinemachers, C., Sadowski, F., Lange, S., Sypula, M., Magnusson, D., Geist, A., Lewis, F. W., Harwood, L. M., & Hudson, M. J. (2013). Direct selective extraction of actinides(III) from PUREX raffinate using a mixture of CyMe₄BTBP and TODGA as 1-cycle SANEX solvent. Part III: Demonstration of a laboratory-scale counter-current centrifugal contactor process. *Solvent Extr. Ion Exch.*, 31, 519–537. DOI: 10.1080/07366299.2013.775890.
6. Modolo, G., Asp, H., Schreinemachers, C., & Vijgen, H. (2007). Development of a TODGA based process for partitioning of actinides from a PUREX raffinate. Part I: Batch extraction optimization studies and stability tests. *Solvent Extr. Ion Exch.*, 25, 703–721. DOI: 10.1080/07366290701634578.
7. Wilden, A., Modolo, G., Kauffholz, P., Sadowski, F., Lange, S., Sypula, M., Magnusson, D., Muellich, U., Geist, A., & Bosbach, D. (2015). Laboratory-scale counter-current centrifugal contactor demonstration of an innovative-SANEX process using a water soluble BTP. *Solvent Extr. Ion Exch.*, 33, 91–108. DOI: 10.1080/07366299.2014.952532.
8. Carrott, M., Geist, A., Hérès, X., Lange, S., Malmbeck, R., Miguiditchian, M., Modolo, G., Wilden, A., & Taylor, R. (2015). Distribution of plutonium, americium and interfering fission products between nitric acid and a mixed organic phase of TODGA and DMDHEMA in kerosene, and implications for the design of the “EURO-GANEX” process. *Hydrometallurgy*, 152, 139–148.
9. Poinssot, C., Rostaing, C., Baron, P., Warin, D., & Boullis, B. (2012). Main results of the French program on partitioning of minor actinides, a significant improvement towards nuclear waste reduction. *Procedia Chem.*, 7, 358–366. DOI: 10.1016/j.proche.2012.10.056.
10. Rostaing, C., Poinssot, C., Warin, D., Baron, P., & Lorrain, B. (2012). Development and validation of the EXAm separation process for single Am recycling. *Procedia Chem.*, 7, 367–373.
11. Modolo, G., Kluxen, P., & Geist, A. (2010). Demonstration of the LUCA process for the separation of americium(III) from curium(III), californium(III), and lanthanides(III) in acidic solution using a synergistic mixture of bis(chlorophenyl)dithiophosphinic acid and tris(2-ethylhexyl)phosphate. *Radiochim. Acta*, 98, 193–201. DOI: 10.1524/ract.2010.1708.
12. Bollesteros, M. -J., Calor, J. -N., Costenoble, S., Montuir, M., Pacary, V., Sorel, C., Burdet, F., Espinoux, D., Hérès, X., & Eysseric, C. (2012). Implementation of americium separation from a PUREX raffinate. *Procedia Chem.*, 7, 178–183.
13. Chapron, S., Marie, C., Arrachart, G., Miguiditchian, M., & Pellet-Rostaing, S. (2015). New insight into the americium/curium separation by solvent extraction using diglycolamides. *Solvent Extr. Ion Exch.*, 33(3), 236–248.
14. Narbutt, J., Wodyński, A., & Pecul, M. (2015). The selectivity of diglycolamide (TODGA) and bis-triazine-bipyridine (BTBP) ligands in actinide/lanthanide complexation and solvent extraction separation – a theoretical approach. *Dalton Trans.*, 44(6), 2657–2666. DOI: 10.1039/c4dt02657h.
15. Bryantsev, V. S., & Hay, B. P. (2015). Theoretical prediction of Am(III)/Eu(III) selectivity to aid the design of actinide-lanthanide separation agents. *Dalton Trans.*, 44(17), 7935–7942. DOI: 10.1039/c4dt03275f.
16. Mincher, B. J., Elias, G., Martin, L. R., & Mezyk, S. P. (2009). Radiation chemistry and the nuclear fuel cycle. *J. Radioanal. Nucl. Chem.*, 282, 645–649.
17. Inoue, T. (2002). Actinide recycling by pyro-process with metal fuel FBR for future nuclear fuel cycle system. *Prog. Nucl. Energy*, 40, 547–554.
18. Koyama, T., Sakamura, Y., Iizuka, M., Kato, T., Murakami, T., & Glatz, J. -P. (2012). Development of pyro-processing fuel-cycle technology for closing actinide cycle. *Procedia Chem.*, 7, 772–778.
19. Soucek, P., Malmbeck, R., Nourry, C., & Glatz, J. -P. (2011). Pyrochemical reprocessing of spent fuel by

- electrochemical techniques using solid aluminium cathodes. *Energy Procedia*, 7, 396–404.
20. Chmielewski, A. G. (2008). Nuclear fissile fuels world-wide reserves. *Nukleonika*, 53(Suppl. 2), S11–S14.
21. <http://asgardproject.eu/>
22. www.talisman-project.eu
23. <http://cinch-project.eu/>
24. John, J., Lehto, J., Koivula, T., & Omtvedt, J. P. (2015). Cooperation in education and training in nuclear- and radiochemistry in Europe. *J. Radioanal. Nucl. Chem.*, 304, 459–466.