

# The EURO-GANEX process: current status of flowsheet development and process safety studies

Robin Taylor, Mike Carrott, Hitos Galan, Andreas Geist, Xavier Hères, Chris Maher, Chris Mason, Rikard Malmbeck, Manuel Miguirditchian, Giuseppe Modolo, et al.

▶ **To cite this version:**

Robin Taylor, Mike Carrott, Hitos Galan, Andreas Geist, Xavier Hères, et al.. The EURO-GANEX process: current status of flowsheet development and process safety studies. Procedia Chemistry, 2016, 21, pp.524 - 529. 10.1016/j.proche.2016.10.073 . cea-03541219

**HAL Id: cea-03541219**
**https://cea.hal.science/cea-03541219**

Submitted on 24 Jan 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 21 (2016) 524 – 529

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

# The EURO-GANEX process: current status of flowsheet development and process safety studies

Robin Taylor*[a], Mike Carrott[a], Hitos Galan[b], Andreas Geist[c], Xavier Hères[d], Chris Maher[a], Chris Mason[a], Rikard Malmbeck[e], Manuel Miguirditchian[d], Giuseppe Modolo[f], Chris Rhodes[a], Mark Sarsfield[a], Andreas Wilden[f]

[a]*National Nuclear Laboratory, Central Laboratory, Seascale, CA20 1PG, United Kingdom*
[b]*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid 28040, Spain*
[c]*Karlsruher Institut für Technologie, Institut für Nukleare Entsorgung, Karlsruhe, Germany*
[d]*Radiochemistry and Processes Development Department, CEA, Nuclear Energy Division, Marcoule, France*
[e]*European Commission, Joint Research Centre, Institute for Transuranium Elements (ITU), Karlsruhe, Germany*
[f]*Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung (IEK-6), Nukleare Entsorgung und Reaktorsicherheit, 52425 Jülich, Germany*

**Abstract**

A new hydrometallurgical grouped actinide extraction process has been developed to separate the transuranic actinide ions from dissolved spent fuel solution (after an initial uranium extraction cycle). This "EURO-GANEX" process is aimed towards the homogeneous recycling of plutonium and minor actinides in a future closed fuel cycle. The separation process is based on the co-extraction of actinides and lanthanides from aqueous nitric acid into an organic phase followed by selective co-stripping of actinides. A suitable organic phase has been formulated and distribution ratios determined for lanthanides, actinides and some problematic fission products under extraction and stripping conditions. The process flowsheet has been proven on surrogate feed solutions as well as with spent fast reactor fuel; excellent recoveries of the actinides and good decontamination factors from the lanthanides and other fission products were obtained. A variation on the EURO-GANEX flowsheet (the "TRU-SANEX" process) has now been designed to produce separate Pu+Np and Am+Cm products for heterogeneous recycling. Progress on underpinning process chemistry and safety studies as well as flowsheet tests are summarized.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of ATALANTE 2016

* Corresponding author. Tel.: +44-19467-79000; fax: +44-19467-79007.
*E-mail address*: robin.j.taylor@nnl.co.uk.

1876-6196 © 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.073

*Keywords:* GANEX; TODGA; plutonium; flowsheet

## 1. Introduction

One option for the management of used nuclear fuel is to reprocess the fuel so the actinides can be recycled and residual high level waste immobilized for disposal. This closed fuel cycle may have significant benefits over the direct disposal of used fuel due to the substantially improved utilization of resources and reduction in the footprint of the disposal facility required. To fully realize potential benefits from the closed fuel cycle, however, requires the introduction of fast reactors as well as significant improvements in reprocessing. Industrial scale reprocessing is presently dominated by the PUREX process which was designed in the mid-20$^{th}$ century to produce separate pure uranium and plutonium products. Whilst the PUREX process has been hugely successful in reprocessing spent fuel to date, it is unlikely to be acceptable in its current form in advanced closed fuel cycles due to concerns regarding costs, environmental impacts, secondary wastes and proliferation. Radical improvements to the PUREX process and/or alternative actinide separation processes are, therefore, subjects of international interest. In this regard, one objective of the European Union's 7$^{th}$ Framework Programme ACSEPT and SACSESS projects (2008-2012 and 2013-2016 respectively) was to develop a new hydrometallurgical based process that is aimed towards the homogeneous recycling of plutonium and minor actinides (MA) in a fast reactor based fuel cycle. This grouped actinide extraction (GANEX) process was expected to deliver benefits in process safety, waste management and proliferation resistance whilst recovering all actinides for recycling [1-3].

## 2. Concept

The GANEX process assumes there is an initial uranium extraction process (GANEX-1) to reduce the heavy metal content of the dissolved spent fuel solution and simplify separations on the highly active (HA) aqueous stream [4]. The subsequent separation needs to fully recover all transuranic (TRU) actinides (present in oxidation states from III to VI), preferably without use of redox reagents and using CHON molecules only. Ideally, this will be in a single solvent extraction cycle and will be compatible with the use of small footprint centrifugal contactors that enable intensified mixing and settling of phases. The concept selected is illustrated in Fig. 1. Basically, this involves co-extraction of actinides and lanthanides from the GANEX-1 aqueous product, leaving the remaining fission products in the aqueous raffinate, followed by selective co-stripping of actinides and finally lanthanide stripping, with the solvent raffinate cleaned up before recycling back into the process. The fission product (HA) and lanthanide containing raffinates are converted to suitable solid waste forms for disposal whilst the actinide product is converted to an oxide ready for fuel manufacturing.

## 3. Process chemistry

The preferred solvent extraction system for the GANEX process was based on aqueous nitric acid and an organic phase containing the ligand *N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) that had previously been shown to have many excellent properties for MA separations [5]. However, as the GANEX process is aimed towards reprocessing thermal mixed oxide and fast reactor fuels, it needs to be capable of handling high concentrations of Pu, typically 5-20 wt.%HM (HM: heavy metal), and early tests showed that TODGA had a very low capacity for Pu; indeed, a solid precipitate formed at the solvent/aqueous interface. Various modifiers were tested before a suitable "GANEX solvent" formulation of 0.2 mol/L TODGA and 0.5 mol/L *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexyloxyethyl) malonamide (DMDOHEMA) was selected [6]. This solvent was a compromise between high actinide/lanthanide distribution ratios, loading capacity, physical properties and ease of backwashing extracted metal ions. The boundary for third phase formation was shown to vary linearly with initial $HNO_3$ concentration in the aqueous phase and for 10 g/L Pu content in the feed solution, the concentration selected for demonstrating the process, the capacity of the solvent was shown to be sufficient for aqueous phases ≤6 mol/L $HNO_3$ [7].

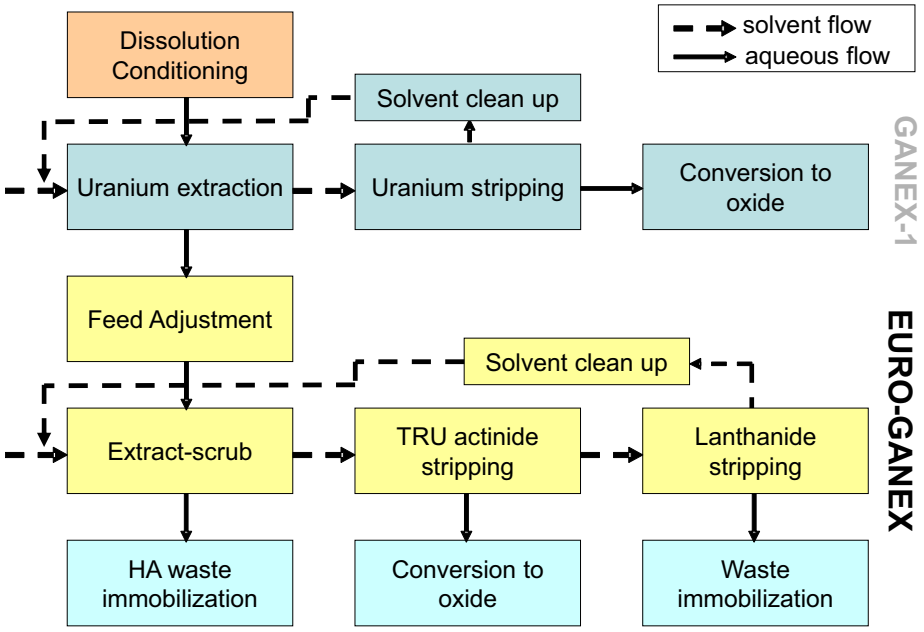



Fig. 1. Schematic of the overall GANEX process for spent fuel reprocessing showing GANEX-1 and EURO-GANEX solvent extraction cycles.

Distribution ratios for lanthanides and actinides (Pu, Am, Cm) into the GANEX solvent reach very high values above 3 mol/L $HNO_3$ (>>100), the region anticipated for the extract section of a flowsheet [7]. Lighter lanthanides are less extracted than heavier ones though. The measured distribution ratios confirmed that under extract-scrub conditions in a flowsheet the actinides and lanthanide ions will be efficiently extracted into the organic phase.

A number of fission and corrosion products (Fe, Sr, Tc, Mo, Ru, Zr, Pd) were identified as potentially as potentially extractable in the GANEX process and their behaviours were examined in some detail, including the determinations of distribution ratios at varying acidities [8]. An effective aqueous phase "hold back" ligand, 1,2-cyclohexanediaminetetraacetic acid (CDTA), was developed to inhibit the extraction of Zr and Pd [9]. Batch tests on a HA raffinate (HAR) simulant showed that species such as Ag, Cs, Ni, Rb, Rh, Sn, Sb, Te and Cu were not extracted but Sr, Fe, Mo, Ru, Tc and, to a lesser extent Se, Cd and Ba, were extracted. However, whilst Sr and maybe Mo could be removed by low acid scrubbing, Tc and Ru extraction remained problematic. Possible Fe accumulation in the extract-scrub section was also a concern and a capacity of 13 g/L Fe at ~4 mol/L $HNO_3$ was obtained before third phase formation. It was shown that iron extraction was primarily by DMDOHEMA whereas Tc extraction is mainly due to TODGA.

As it can exist in three easily inter-convertible oxidation states in $HNO_3$ that have differing extractabilities into organic phases, neptunium control in solvent extraction processes is known to be difficult, often leading to split routing in flowsheets [10]. Specific studies of the extraction of Np(IV), (V) and (VI) ions into the GANEX solvent were, therefore, made, including some efforts into understanding the influences of the individual organic ligands, TODGA and DMDOHEMA. Extraction into the GANEX solvent followed the order Np(IV)>>Np(VI)>>Np(V) although even Np(V) exhibits distribution ratios >1 above 3 mol/L $HNO_3$. Interestingly, Np(V) was shown to be quickly disproportionated in the organic phase to Np(IV) and Np(VI), particularly at high acidities, and this was suggested to be a feasible means of enhancing Np extraction [11].

Initial studies showed that acetohydroxamic acid (AHA) effectively backwashed Pu and Np at low acidities, although Pu backwashing was very sensitive to acidity [6, 11]. Analogous to applications in an Advanced PUREX process [12], Pu(IV) and Np(IV) are stripped by formation of hydrophilic AHA complexes whereas Np(VI) is stripped by rapid reduction to Np(V) by AHA. Separation of trivalent actinides from lanthanides is more difficult and for this purpose a novel aqueous phase sulphonated-bistriazinylpyridine ($SO_3$-Ph-BTP) ligand was developed for

applications in the GANEX process and the related innovative-SANEX process [13]. Distribution ratios for the full range of lanthanides plus Am and Pu were determined at trace metal concentrations with 0.02 mol/L $SO_3$-Ph-BTP and separation factors of >100 were obtained in nitric acid solutions below ~0.6 mol/L. With process level concentrations of Pu (1-10 g/L), the distribution ratios and separation factors for Am, Pu and Eu (typical lanthanide) were shown to be dependent on a range of factors (Pu and ligand concentrations, acidity and AHA concentration). Data were accumulated to aid flowsheet design [8].

Extraction of acid by the organic phase needs to be well understood because it causes a decrease in free ligand concentration, thus influencing metal ion extraction, and acid carryover in the organic phase can particularly affect the efficiency of stripping operations that must be performed at low acidity. A model for nitric acid extraction into TODGA, based on experimental distribution ratios, was first reported in [14] and refined in [15]. The model was fitted by 1:1 to 4:1 $(HNO_3)_x(TODGA)_y$ complexes and equilibrium constants were determined. The model was valid between 0.1-7 mol/L $HNO_3$ and 0.05-0.4 mol/L TODGA at ambient temperature. Additional $HNO_3$ distribution data with DMODHEMA have now been accumulated and a model for the combined TODGA/DMDOHEMA solvent is under evaluation.

As part of recent process safety and industrialization orientated studies, the radiolytic degradation of the organic and aqueous phases are being investigated with two objectives: (i) determination of radiolytic degradation products and their impacts on process performance and (ii) generation of hydrogen. As TODGA and DMDOHEMA are amides, radiolysis ruptures the amidic C-N bond to give the corresponding amine and carboxylic acids [16, 17]. γ-radiolysis studies show that with doses >1000 kGy, there is a significant decrease in TODGA concentration and nine degradation products have been characterized, all of which have low distribution ratios for Am and Eu. A protective effect of nitric acid was found [18]. Preliminary results suggest that hydrogen generation from α-radiolysis of the organic phase is primarily linked to the alkane diluent rather than TODGA content of the solvent.

## 4. Flowsheet testing

Based on the process chemistry studies summarized above, flowsheets were designed and tested. Carrott *et al*. reported a test on a surrogate feed solution that contained 10 g/L Pu as well as Np, Am, a range of lanthanides and some other fission products [19]. The flowsheet used CDTA in the extract-scrub to suppress Zr and Pd extraction and a split actinide strip with feeds of:

1. 0.091 mol/L $SO_3$-Ph-BTP + 1 mol/L AHA in 0.5 mol/L $HNO_3$ fed to stage 24
2. 0.018 mol/L $SO_3$-Ph-BTP + 1 mol/L AHA in 0.5 mol/L $HNO_3$ fed to stage 28

Very good recoveries of Am and Pu were obtained but ~30 % Np was lost to the aqueous raffinate and ~7 % of Eu (taken as a model lanthanide) was found in the actinide product. Modelling of the flowsheet using the PAREX code [20] showed that profiles could be simulated reasonably well and thus PAREX was used to improve the flowsheet design prior to a "hot test" with irradiated fuels. Specifically, the acidity of the aqueous feed (GANEX-1 product) was raised to 5.9 mol/L $HNO_3$ to enhance Np extraction and the split actinide strip was consolidated into a single strip solution of 0.055 mol/L $SO_3$-Ph-BTP and 1 mol/L AHA in 0.5 mol/L $HNO_3$.

The hot test used some legacy fast reactor carbide fuel from Dounreay that was initially oxidized and dissolved before a U extraction cycle (GANEX-1) was run to produce the feed for the EURO-GANEX test. The feed was adjusted to 10 g/L Pu, acidity increased to 5.9 mol/L and CDTA (0.055 mol/L) added. As the HA cell only contained 16 stages of centrifugal contactors, the test was split into two parts: (i) extract-scrub and (ii) stripping. Excellent results were obtained with >99 % recovery of transuranic actinides (Np, Pu, Am) in the actinide product with <0.1 % contamination by lanthanides [21]. Some key results from the hot and surrogate tests are compared in Table 1.

As part of process safety investigations, a potentially severe maloperation of the extract-scrub flowsheet (Fig. 2) was identified using a systematic safety review process developed under the SACSESS project [22] in which the scrub acidity is reduced by a factor of 10. This maloperation was tested experimentally and the flowsheet was shown to be robust to hazardous Pu accumulations.

Recently, a variation of the EURO-GANEX flowsheet has been reported in which separate strip sections using AHA and $SO_3$-Ph-BTP are employed to produce separate Pu+Np and MA (Am+Cm) products [23]. The flowsheet was

tested using a surrogate feed solution and generally performed well, comparable to the EURO-GANEX flowsheet tests. There was a small amount of cross contamination between Pu+Np and MA products but this was not considered significant. This option (termed "TRU-SANEX" as it also similar to the innovative-SANEX process [13]) enables application of the GANEX process to heterogeneous recycling scenarios and addresses one criticism of the GANEX process – that it produces a transuranic product stream that is relatively large due to the Pu content but would need to be handled remotely in the downstream fuel fabrication plant due to the presence of highly radioactive Cm. This issue incidentally, highlights, a need to develop future closed fuel cycles in an integrated fashion rather than different parts of the cycle optimizing their operations in isolation.

Table 1. Comparison of surrogate and hot EURO-GANEX flowsheet tests.

| | Surrogate test | Hot test |
|---|---|---|
| Pu recovery in extract-scrub (%) | 99.999 | 99.99 |
| Am recovery in extract-scrub (%) | 99.99 | 99.99 |
| Np in HAR (%) | 29 | 0.07 |
| Np in TRU actinide product (%) | 41.7* | 99.91 |
| Ln in TRU actinide product (%) | 6.7 (based on Eu) | 0.06 |
| Am in TRU actinide product (%) | 99.4** | 99.90 |
| Pu in TRU actinide product (%) | 99.99** | 99.85 |

*Low Np recovery is due to low mass balance of 66 % reported in [19]; this was attributed to Np accumulation in the extract-scrub section).

**Calculated with respect to mass balance across products and raffinates

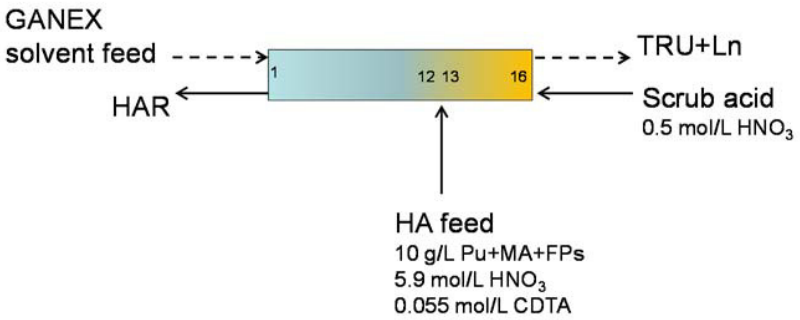



Fig. 2. EURO-GANEX extract-scrub flowsheet as configured for the hot test.

## 5. Conclusions

Significant progress has been made towards the design of a GANEX process capable of recycling spent nuclear fuels containing high levels of Pu as well as minor actinides. Further efforts to optimize the flowsheet design and understand the basic process chemistry, as well as process safety studies, are ongoing but there are promising indications that the EURO-GANEX or TRU-SANEX processes (when coupled to an initial uranium extraction cycle) could eventually become viable alternatives to the established PUREX process for fuel reprocessing in future closed fuel cycles.

## Acknowledgements

Financial support for this work was from European Framework Projects "ACSEPT" (FP7-CP-2007-211 267) and "SACSESS" (FP7-FISSION-2012-323282), the UK Department of Energy and Climate Change, National Nuclear Laboratory (Strategic Research Programme, Aqueous Recycle project), Sellafield Ltd. and the Nuclear Decommissioning Authority.

## References


1. Taylor R, editor. *Reprocessing and Recycling of Spent Nuclear Fuel*. Oxford: Woodhead Publishing; 2015.
2. Bourg S, Hill C, Caravaca C, Rhodes C, Ekberg C, Taylor R, Geist A, Modolo G, Cassayre L, Malmbeck R, Harrison M, de Angelis G, Espartero A, Bouvet S, Ouvrier N. ACSEPT--Partitioning technologies and actinide science: Towards pilot facilities in Europe. *Nuclear Engineering and Design* 2011;**241**:3427-3435.
3. Nash KL, Lumetta GJ, editors. *Advanced separation techniques for nuclear fuel reprocessing and radioactive waste treatment*. Oxford: Woodhouse Publishing Ltd.; 2011.
4. Miguirditchian M, Sorel C, Camès B, Bisel I, Baron P. Extraction of uranium (VI by N,N-di(2-ethylhexyl)isobutyramide (DEHIBA): from the batch experimental data to the countercurrent process. In B. A. Moyer, editor. *Solvent extraction: fundamentals to industrial applications. Proceedings ISEC 2008 International Solvent Extraction conference.* Montreal, Canada: Can. Inst. Min. Metall. Pet.; 2008. p. 721-726.
5. Ansari SA, Pathak P, Mohapatra PK, Manchanda VK. Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning. *Chemical Reviews* 2012;**112**:1751-1772.
6. Brown J, McLachlan F, Sarsfield MJ, Taylor RJ, Modolo G, Wilden A. Plutonium loading of prospective grouped actinide extraction (GANEX) solvent systems based on diglycolamide extractants. *Solvent Extraction and Ion Exchange* 2012;**30**:127-141.
7. Bell K, Carpentier C, Carrott M, Geist A, Gregson C, Hérès X, Magnusson D, Malmbeck R, McLachlan F, Modolo G, Müllich U, Sypula M, Taylor R, Wilden A. Progress towards the development of a new GANEX process. *Procedia Chemistry* 2012;**7**:392-397.
8. Carrott M, Geist A, Hères X, Lange S, Malmbeck R, Miguirditchian M, Modolo G, Wilden A, Taylor R. Distribution of plutonium, americium and interfering fission products between nitric acid and a mixed organic phase of TODGA and DMDOHEMA in kerosene, and implications for the design of the "EURO-GANEX" process. *Hydrometallurgy* 2015;**152**:139-148.
9. Sypula M, Wilden A, Schreinemachers C, Malmbeck R, Geist A, Taylor R, Modolo G. Use of polyaminocarboxylic acids as hydrophilic masking agents for fission products in actinide partitioning processes. *Solvent Extraction and Ion Exchange* 2013;**3**:748-764.
10. Taylor RJ, Gregson CR, Carrott MJ, Mason C, Sarsfield MJ. Progress towards the Full Recovery of Neptunium in an Advanced PUREX Process. *Solvent Extraction and Ion Exchange* 2013;**31**:442-462.
11. Carrot MJ, Gregson CR, Taylor RJ. Neptunium Extraction and Stability in the GANEX Solvent: 0.2 M TODGA/0.5 M DMDOHEMA/Kerosene. *Solvent Extraction and Ion Exchange* 2012;**31**:463-482.
12. Birkett JE, Carrott MJ, Fox OD, Jones CJ, Maher CJ, Roube CV, Taylor RJ, Woodhead DA. Recent Developments in the Purex Process for Nuclear Fuel Reprocessing: Complexant Based Stripping for Uranium - Plutonium Separation. *Chimia* 2005;**59**:898-904.
13. Wilden A, Modolo G, Kaufholz P, Sadowski F, Lange S, Sypula M, Magnusson D, Müllich U, Geist A, Bosbach D. Laboratory-Scale Counter-Current Centrifugal Contactor Demonstration of an Innovative-SANEX Process Using a Water Soluble BTP. *Solvent Extraction and Ion Exchange* 2014;**33**:91-108.
14. Bell KJ, McLachlan F, Geist A, Modolo G, Taylor RJ. Nitric acid extraction into TODGA based solvents. *Procedia Chemistry* 2012;**7**:152-159.
15. McLachlan F, Greenough K, Geist A, McLuckie B, Modolo G, Wilden A, Taylor R. Nitric acid extraction into the TODGA/TBP solvent. *Solvent Extraction and Ion Exchange* 2016.
16. Mincher BJ. Chapter 8 - Radiation chemistry in the reprocessing and recycling of spent nuclear fuels. In Robin Taylor, editor. *Reprocessing and Recycling of Spent Nuclear Fuel.* Oxford: Woodhead Publishing; 2015. p. 191-211.
17. Berthon L, Charbonnel M-C. Radiolysis of solvents used in nuclear fuel reprocessing. In B. A. Moyer, editor. *Io Exchange and Solvent extraction:a Series of Advances.* Montreal, Canada: CRC press; 2009. p. 429-513.
18. Galán H, Núñez A, Espartero AG, Sedano R, Durana A, de Mendoza J. Radiolytic Stability of TODGA: Characterization of Degraded Samples under Different Experimental Conditions. *Procedia Chemistry* 2012;**7**:195-201.
19. Carrott M, Bell K, Brown J, Geist A, Gregson C, Hères X, Maher C, Malmbeck R, Mason C, Modolo G, Müllich U, Sarsfield M, Wilden A, Taylor R. Development of a new flowsheet for co-separating the transuranic actinides: the "EURO-GANEX" process. *Solvent Extraction and Ion Exchange* 2014;**32**:447-467.
20. Sorel C, Dinh B, Montuir M, Pacary V, Roussel H, Baron P. The PAREX code: a powerful tool to model and simulate solvent extraction operations. In *Uranium 2010, 3rd international conference on uranium*. 2010. Saskatoon, Canada: Metall. Soc. Can. Inst. Min. p.643-652.
21. Malmbeck R, Carrott MJ, Geist A, Hérès X, Magnusson D, Miguirditchian M, Modolo G, Sorel C, Taylor RJ, Wilden A. The hydrometallurgical co-separation of neptunium, plutonium, americium and curium by the EURO-GANEX process. In *Internat. Solvent Extr. Conf. (ISEC 2014)*. 2014. Würzburg, Germany p.39-44.
22. Carrott M, Flint L, Gregson C, Griffiths T, Hodgson Z, Maher C, Mason C, McLachlan F, Orr R, Reilly S, Rhodes C, Sarsfield M, Sims H, Shepherd D, Taylor R, Webb K, Woodall S, Woodhead D. Spent fuel reprocessing and minor actinide partitioning safety related research at the UK National Nuclear Laboratory. *Actinide and Fission Product Partitioning and Transmutation, Thirteenth Information Exchange Meeting.* Seoul, Korea: OECD-NEA; 2015. p. 391-403.
23. Carrott M, Maher C, Mason C, Sarsfield M, Taylor R. "TRU-SANEX": a variation on the EURO-GANEX and i-SANEX processes for heterogeneous recycling of actinides Np-Cm. *Separation Science and Technology* 2016;**Under review**.