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WPASR 7

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WPASR7

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WP1**INTRODUCTION**

WP1 aims at investigating the solution and extraction chemistry of key fission products. This research is important to improve the actinide/fission product separation and then to further optimize the separation processes. It includes extraction chemistry of problematic fission products (Task 1.1) and the optimization of scrubbing steps during co-extraction (Task 1.2).

MAIN RESULTS**TASK 1.1**

Completed

TASK 1.2

Completed

LIST OF PUBLICATIONS

Dirks et al. “Raman and DFT study of ruthenium(III) nitrosyl nitrate complexes in nitric acid solution with variable nitrous acid concentrations” submitted to Dalton Transaction.

International Conference on Development and Applications of Nuclear Technologies, NUTECH-2020, Warsaw, 4-7 Oct. 2020; <http://www.nutech2020.pl>: section report: Optimizing the separation of fission product technetium in the process of recycling actinides from spent nuclear fuel, I. Herdzik-Koniecko, M. Rejnis-Strzelak, J. Narbutt

CONCLUSIONS

Since the start of the GENIORS project the planned actions related to the fission product chemistry (Task 1.1) were carried out and reported in D1.1. The work on Task 1.2 was reported in deliverable D1.2.

WP2**INTRODUCTION**

The general objective of WP2 is to ensure a safe long-term performance of a chemical system submitted to radiation. To understand and improve the degradation of the ligands as well as of the extraction systems is the main goal. Solvent degradation may lead to many undesirable effects, for that, the identification of losses of efficiency, the behaviour troublesome degradation products or any mal operation situation due to degradation are the key issues. Work is divided in four task: T21 Radiolysis & degradation products; T22 Destruction of organics; T23 Gas generation and T24 Radiolysis modelling.

MAIN RESULTS**TASK 2.1 RADIOLYSIS & DEGRADATION PRODUCTS (TASK LEADER: JULICH)****MANPOWER**

11.2 mp (2.4 pm CTU, 3.3 pm IIC, 2.0 pm CIEMAT, 3 pm Juelich and 0.5 pm POLIMI) were reported this semester.

MAIN PROGRESSES

Stability studies of diglycolamides:

TODGA:

Within the GENIORS – DOE collaboration JUELICH contributed to a publication in Phys. Chem. Chem. Phys. regarding the scavenging effect of 1-octanol for radicals formed in TODGA solvents. As a conclusion of the work, the presence of 1-octanol in irradiated organic-only solution has been shown to enhance the degradation rate of TODGA in n-dodecane. This is attributed to the energetically favourable reaction between TODGA and the 1-octanol radical, which may be produced by both direct alcohol radiolysis, or by reaction with the n-dodecane radical cation. Further, scavenging capacity calculations showed that the yield of 1-octanol radicals produced by reaction with the n-dodecane radical cation was much higher than the yield of radical cation reaction with TODGA directly. Thus, the higher yield of 1-octanol radicals produced by this reaction pathway increased the rate of TODGA degradation. However, in the presence of 1-octanol and an aqueous HNO_3 phase the rate of TODGA degradation was lower than for the pure organic solution. This is attributed to HNO_3 and H_2O in the organic phase extracted as TODGA/1-octanol adducts which interfere with the hydrogen atom abstraction process between the 1-octanol radical and TODGA. This result is fortuitous for the use of TODGA in UNF reprocessing, which is conducted in highly radioactive mixed phase solutions.

mTDDGA:

The radiolysis of mTDDGA was further studied as part of Juelich-SCK•CEN collaboration. Solutions of cis-mTDDGA were irradiated in BRIGITTE at SCK CEN up to 1200 kGy for solutions of 0.05 mol L⁻¹ cis-mTDDGA in n-dodecane, in contact with 4 mol L⁻¹ HNO₃ and 16 mmol L⁻¹ Nd to study the effect of Nd-loading on the dose constant. Also samples were irradiated to evaluate the effect of washing steps after irradiation. A washing method still needs to be selected (based on others' experience for the EURO-GANEX process). (Julich)

Extraction experiments with 3 of 5 degradation compounds synthesized by the University of Twente were conducted:

The DC RE1911 (N,N-didecylpropionamide) did not show a very strong metal complexantion. The effect on the extraction behavior of an irradiated mTDDGA solvent would probably be limited since there is only significant extraction at very high ligand and nitric acid concentrations. The extraction of Pu should not be a problem since this is what is required in the EURO-GANEX process. Data on extraction of FP will be obtained later.

The screening test of DC RE1913 (N,N-didecyl-2-hydroxypropanamide) showed that this degradation compound of mTDDGA mainly extracts Pu. Issues for fission products might arise for Mo (precipitation) and Zr (extraction). However, these effects might be limited in the presence of masking agents such as CDTA.

For the screening test of DC RE1915 (N,N-didecyl-2-((1-(decylamino)-1-oxopropan-2-yl)oxy)propanamide), which lost an alkyl chain but still has the original diglycolamide backbone as the core of its structure, Pu is the best extracted element. For the fission products, especially the distribution ratio of Pd seems elevated. However, for this element the mass balance was extremely low (<10%), which strongly indicates the formation of precipitation. Extraction increased as the concentration of RE1915 increased; however, at higher concentrations than 0.1 mol L⁻¹, there is a clear kink in the curves visible. This is also the point at which precipitation was visually observed at the interphases. Interestingly, the only element which is almost not affected is Pu.

Stability studies of BTBP and BTPPhen:

During this semester, CTU and IIC have continued the studies of CyMe₄-BTBP in fluorinated diluents:

The extraction of Am(III) and Eu(III) was performed by CTU for the CHALMEX systems (0.01 M CyMe₄-BTBP in 70% FS-13/30% TBP; 4 M HNO₃) after irradiation at different temperatures (15, 25, 35, and 45 °C) in two different settings: only a solvent or solvent in contact with nitric acid (usually 4 M HNO₃). The presence of aqueous phase proved significant effect on stability towards radiation, which remains comparatively high in the range of HNO₃ concentrations from 2 to 8M. In contrast, no significant effect on decrease of stability was observed in the temperature interval from 15 to 45°C towards applied irradiation doses. The quantification studies performed by IIC corroborated that presence of aqueous

phase in the system clearly increases the stability of the ligand. On the other hand, the effect of temperature on degradation in the interval from 15° to 45°C was low at all monitored irradiation doses. But also, there is almost no effect of increased HNO₃ concentration in the aqueous phase.

IIC has continued with the analysis and isolation of CyMe₄-BTBP DCs from the concentrated samples irradiated at Chalmers facilities (1200 kGy). The information from NMR spectra was complemented with results from MS, LC-MS and HPLC. More detailed evaluation of the data enabled to propose probable structures of several degradation products present in each series.

Studies of SO₃PhBTP and SO₃PhBTP stripping or masking agents:

CIEMAT has continued with activities to analyse quantitatively the degraded aqueous phases containing AHA or SO₃-Ph-BTP. After setting up the methodology to measure and quantify the remaining concentration of SO₃-Ph-BTP by Raman spectroscopy, quantitative studies of irradiated aqueous phases have been carried out. Particularly, it has been analysed the resistance to radiation of extractants involved in the aqueous phase of Euro-GANEX process, AHA and SO₃-Ph-BTP. As conclusion of this study it can be said that greater robustness of the system is found when both molecules are irradiated together. A manuscript has been written with the full results of the study.

CTU and IIC have also addressed the effects of the irradiation of tetrasulfonated BTBP and BTP samples (i-SANEX systems conditions) at different temperatures (15, 25, 35, and 45 °C) in two different settings: only the aq. solvent or solvent in contact with the organic phase. Some temperature effect was observed only for SO₃-Ph-BTP at higher doses, particularly under conditions of irradiation without contact with organic phase. On the other hand, the stability of SO₃-Ph-BTP in the presence of organic phase proved closely parallel that of SO₃-Ph-BTBP irradiated under identical conditions, although the SO₃-Ph-BTBP system seems to be more stable than SO₃-Ph-BTP system.

Studies of PTD stripping agent:

In order to complete the studies of PTD stability towards radiolysis, POLIMI has continued working on the identification of the new degradation products (DPs) and the on impact of their presence on the extracting performances of the irradiated stripping phases. To this purpose, POLIMI has tested some degradation products synthesised by UNIPR on the basis of the hypotheses formulated thanks to the HPLC-ESI-MS investigations. The compounds that resulted soluble (DP#1 and monoPTD) were tested under the same experimental conditions of PTD. Results shows that only DP#1, which results from the radiation-induced loss of the lateral chain and preserves the complexing core, still keeps an affinity for Am cations even if it exhibits an overall worsening of the extracting properties of the original PTD structure. From the previous studies, the percentage of DP#1 in the mixture increases with increasing the absorbed dose and consequently it is reasonable to expect that at a certain point its worse stripping performances contribute to affect the overall performances of the PTD stripping phase.

DIFFICULTIES

Most of difficulties reported affecting to task 2.1 are due the situation provokes by COVID-19. As consequence, D2.1 has been postponed until 01-2021:

Activities related to realistic stability studies of CDTA aqueous phases could not be addressed. (CIEMAT)

No DCs or adducts of BTBP neither BTPPhen available for experiments yet. (CTU)

Due to technical problem to the HPLC-MS equipment, POLIMI has not yet started the HPLC-MS analyses to confirm the identity of the PTD degradation products observed in the irradiated PTD solutions. (POLIMI)

ACTION PLAN

All activities related to task 2.1 must be finished in the next semester. D2.1 has been postponed until 01-2021

CIEMAT: Summarization of the results achieved in T2.1 for the presentation in Deliverable D2.1.

CTU: Completion of the studies and evaluation of the results obtained in the 7th period. Summarization of the results achieved in T2.1 for the presentation in Deliverable D2.1. Preparation of manuscripts for publication of the results in dedicated scientific journals.

IIC: We plan to summarize and update results from isolations of degradation products by HPLC and all analyses performed under this Project. Also material from other partners for Deliverable D2.1. will be collected and organized and this Deliverable will be written and submitted. Expected date is January 31st 2021.

POLIMI: HPLC-MS analyses to confirm the identity of the PTD degradation products present in the irradiated PTD solutions and to enable a quantitative analysis will be completed.

JUELICH: Further radiolysis data will be evaluated with mTDDGA and the radiolysis modelling studies will be continued.

TASK 2.2 DESTRUCTION OF ORGANIC (TASK LEADER: CEA)

Task 2.2 is now completed

TASK 2.4 RADIOLYSIS MODELLING (TASK LEADER: CTU)

MANPOWER

2.0 pm realized this semester by CTU

MAIN PROGRESSES

Modelling studies of the radiolysis of water soluble diglycolamides: (2.0 pm, CTU)

The theoretical study of TMDGA, TEDGA, Me-TEDGA, and Me₂-TEDGA dissolved in water has been continued. The works have been focused on determination of QM and MD-based chemical stability indicators relevant for the selected hydrophilic DGA derivatives, analysis of an acidic environment impact on values of the calculated indicators and verification of the obtained theoretical findings against known experimental data.

Radical Fukui function (FF) has been identified as the QM indicator showing the best agreement with the experimental data, in concert with the expected radical-initiated decay mechanisms. Main maxima of volumetric radical FF are localized close to H atom adjacent to the ether bond. Stability enhancement in acidic environment is suggested by the normalized values shown in histogram. Additional radical FF maxima located in vicinity of the amide groups show no systematic trend.

Extensive MD simulations (quantified by the calculated temporal rate of conformation changes (L, [ps⁻¹])) followed by statistical conformation analysis have been performed. In general, a good qualitative agreement is found between the calculated parameter L and the observed decomposition rates (d, k) taken from previous experimental studies within the project.

DIFFICULTIES

Convergence problems persist occurring in case of DFT calculations of transient states for the reaction pathways involving a hydroxyl radical attack on the studied hydrophilic DGA derivatives. Extremely flat potential surface around the corresponding saddle points has been identified as the probable reason. (CTU)

ACTION PLAN

CTU: Completion of the studies and evaluation of the results obtained in the 7th period. Summarization of the results achieved in T2.1 for the presentation in Deliverable D2.1. Preparation of manuscripts for publication of the results in dedicated scientific journals.

Juelich: the radiolysis modelling studies will be continued.

LIST OF PUBLICATIONS

Paper published:

1. Geist, A.; Berthon, L.; Charbonnel, M.-C.; Müllich, U., Extraction of nitric acid, americium(III), curium(III), and lanthanides(III) into DMDOHEMA dissolved in kerosene. *Solvent Extr. Ion Exch.* 2020, 38 (7), 681–702.
2. Weißling, P.; Schenk, T.; Braun, F.; Beele, B. B.; Trumm, S.; Trumm, M. Schimmelpfennig, B.; Schild, D.; Geist, A.; Panak, P. J., Trivalent actinide ions showing tenfold coordination in solution. *Inorg. Chem.* 2020, 59 (17), 12410–12421.
3. T.H. Vu, J.-P. Simonin, A.-L. Rollet, R.J.M. Egberink, W. Verboom, M.C. Gullo and A. Casnati, Liquid/liquid extraction kinetics of Eu(III) and Am(III) by extractants designed for the industrial reprocessing of nuclear wastes, *Ind. Eng. Chem. Res.* 2020, 59, 13477-13490.

4. Sánchez-García, I; Bonales, L.J.; Galán, H.; Perlado J.M.; Cobos. J. Radiolytic Degradation of sulfonated BTP and acetohydroxamic acid under Euro-GANEX conditions. *Radiation Physics and Chemistry*. 177 (2020) 109094.
5. Horne, G. P.; Zarzana, C.; Rae, C.; Cook, A. R.; Mezyk, S. P.; Zalupski, P.; Wilden, A.; Mincher, B. J. Does Addition of 1-Octanol as a Phase Modifier Provide Radical Scavenging Radioprotection for N,N,N',N'-tetraoctyldiglycolamide (TODGA)? *Phys. Chem. Chem. Phys.* 2020, 22, 43, 24978-24985. DOI:10.1039/D0CP04310A.

Conferences:

1. M. Mindová, P. Distler: Influence of gamma-radiation on extraction properties of CyMe4-BTBP on Ln(III) and An(III) extraction. In: Proc. Jaderná energetika v pracích mladé generace – 2019, Brno, 2020, p. 123–127. ISBN: 978-80-02-02895-6.
2. J. Šebesta, P. Distler, J. John: Study of the influence of radiation on properties of systems that use hydrophilic masking agents and TODGA in organic phase. In: Proc. Jaderná energetika v pracích mladé generace – 2019, Brno, 2020, p. 128–133. ISBN: 978-80-02-02895-6.
3. M. Mindová, P. Distler, J. John, D. Bovol, B. Grüner: Characteristics of extraction properties of the CHALMEX process for Am(III) and Eu(III) separation, In: Proc. 72nd Congress of the Czech and Slovak Chemical Societies. Prague, 6-9 September 2020; Czech Chemical Society Symposium Series, Vol 18, No 4 (2020), p. 157 (poster presentation, in Czech) ISSN 2336-7210.
4. J. Šebesta, P. Distler, J. John, D. Bovol, B. Gruner: Characteristics of separation systems using hydrophilic masking agents for minor actinoids and lanthanoids extraction into TODGA. In: Proc. 72nd Congress of the Czech and Slovak Chemical Societies. Prague, 6-9 September 2020; Czech Chemical Society Symposium Series, Vol 18, No 4 (2020), p. 157–158 (poster presentation, in Czech) ISSN 2336-7210.
5. J. Luštinec: Application of quantum simulations for characterizing the stability of organic extraction ligands. In: Proceedings of the 9th SSC SSP, CTU in Prague, FNSPE, Prague 2020.

Thesis:

1. M. Mindová: Characteristics of extraction systems based on lipophilic extracting agents for minor actinoids and lanthanoids separation. MSc. Thesis, CTU in Prague, FNSPE, Prague 2020, 72 pp.(supervisor P. Distler).
2. J. Šebesta: Characteristics of extraction systems based on hydrophilic masking agents – TODGA intended for minor actinoids and lanthanoids separation. MSc Thesis, CTU in Prague, FNSPE, Prague 2020, 113 pp. (supervisor P. Distler).

CONCLUSIONS

After 42 months of GENIORS project more that 100% of WP2 have been reached. During this semester, although the situation provokes by COVID-19 pandemic has continued, it has been reported a more than optimal development of the experimental and reporting activities. Particularly, this semester has

been reported 13.2 pm has been reported, distributed between task2.1 and task2.4. It must be mentioned again that it has been a delay in the supplying of degradation compounds and some experimental work in task 2.1.

D2.1 Stability and safety studies of hold extraction systems (1 for each CyMe4BTBP, HidroBTBP, TODGA & PTD) has been postponed to 2021-1-31, when all activities related to WP2 must be finished. Only to those activities involved in irradiation loops work could continue, since there will be included in *D 5.2 Impacts of solvent degradation and recycle on the GANEX process (31-5-2021)*.

WP3

INTRODUCTION

The aim of this work-package is to improve the understanding and optimization of the reference chemical systems for advanced solvent extraction separation processes: grouped separation of the actinides (EURO-GANEX), separation of the minor actinides (i-SANEX), or separation of americium only (EURO-EXAM). It includes (i) the understanding of extraction chemistry to support concept process flowsheets (Tasks 3.1 & 3.3), (ii) the acquisition of extraction data to support the conception of process flowsheets (Task 3.2), and (iii) the identification of process options for clean-up of solvents to allow recycle on plant (Task 3.4).

MANPOWER

The amount of person.month (pm) realized in WP3 for each partner and each semester is summarized in the table below.

	HYPARS							Total Realized	
	1	2	3	4	5	6	7	(pm)	(%)
CEA	0	4	7	6	0	1	0	18	151%
CIEMAT	1.5	1.5	1	1	1.25	0	2	8.25	65%
CNRS	0	0	4.75	2.2	0.3	0	0	7.25	121%
ICHTJ	3.5	4.6	9	7.45	3.4	3	7.6	38.55	92%
JUELICH	0	0	3.9	1.8	0	0.5	3	9.2	105%
KIT	6	1.25	1.6	1.7	2.5	2.5	7	22.55	110%
NNL	0.4	0.1	0.88	1.14	0.2	0.47	0.48	3.67	75%
POLIMI	2	7	9.5	6	1.5	0.3	0.5	26.8	131%
UNIPR	2	2	3	2	2	2.1	0	13.1	100%
TOTAL	15.4	20.45	40.63	29.29	11.15	9.87	20.58	147.37	105%

MAIN RESULTS

TASK 3.1 OPTIMISATION OF SYSTEMS (TASK LEADER: POLIMI)

MANPOWER

8.5 pm realized this semester (JUELICH, KIT, POLIMI).

71.95 pm realized since the beginning of the project, corresponding to 92.2% of the 78 pm

planned for the complete project.

MAIN PROGRESSES

- The optimal composition of a EURO-GANEX solvent using cis-mTDDGA and PTD was evaluated at JUELICH with regards to the irradiation test loop experiments.
- The Cm(III) and Eu speciation with cis- and trans-mTDDGA was studied by TRLFS at KIT
- A batch of TEDGA (approx. 7 g) was synthesised and the Am(III) and Ln(III) speciation with TEDGA was studied by NMR at KIT
- POLIMI has worked to support the scale up process of the PTD synthesis. The extracting performances of several PTD batches with different purity provided by UNIPR were evaluated. Good results have been obtained: the 25 g PTD batch showed the same extracting behavior of the highly purified PTD, thus demonstrating the successful scale up of the PTD synthesis.

TASK 3.2 DISTRIBUTION DATA AND CHEMICAL MODELLING (TASK LEADER: KIT)

MANPOWER

9.6 pm realized (ICHTJ, KIT)

35.25 pm realized since the beginning of the project, corresponding to 259.2% of the 13.6 pm planned for the complete project.

MAIN PROGRESSES

- A batch of PTD (approx. 0.5 g) was synthesised.
- An and Ln distribution data for a EURO-GANEX/PTD system were determined. PTD shows promise as a CHON stripping agent for the EURO-GANEX process for selectively stripping actinides from a loaded TODGA/DMDHEMA solvent. and potentially replace SO₃-Ph-BTP.
- Quantum-mechanical studies were conducted on the effect of aryl substituents in DTA ligands on the stability of Am(III) and Eu(III) complexes with these ligands. The calculations of the energies of complex formation were carried out after optimizing (in the gas phase) the structures of nine pairs of large (up to 340 atoms) [Me(R₄DGA)₃]³⁺ (Me = Am or Eu) complexes with the R₄DGA ligands containing various n-alkyl and aryl substituents R. Since the results obtained are not conclusive, the calculations are repeated after optimization of the structures of the [Me(R₄DGA)₃]³⁺ complexes as solutes in water.

DIFFICULTIES

No delivery of an expected new T-DGA batch by TWENTE to ICHTJ, due to the Covid-19 epidemic.

ACTION PLAN

This project has received funding from the EURATOM research and training programme 2014-2018 under grant agreement No 755171. The content of this deliverable reflects only the author's view. The European Commission is not responsible for any use that may be made of the information it contains.

- Completion of quantum-mechanical research on the influence of aryl substituents in DTA ligands on the stability of Eu and Am(III) complexes with these ligands. Preparing the publication.
- Continuation of the experiments on the formation of the assumed heteroleptic complexes of Eu and Am(III), $[M(T-DGA)(SO_3-Ph-BTP)]^-$, but only when a new T-DGA batch is delivered

TASK 3.3 PHYSICO-CHEMICAL & LOADING (TASK LEADER: CIEMAT)

MANPOWER

0 pm realized during this semester

27.15 pm realized since the beginning of the project, corresponding to 79.9 % of the 34 pm planned for the complete project.

TASK 3.4 SOLVENT CLEAN-UP & RECYCLE (TASK LEADER: NNL)

MANPOWER

2.48 pm realized (CIEMAT, NNL)

13.02 pm realized since the beginning of the project, corresponding to 60.6 % of the 21.5 pm planned for the complete project.

MAIN PROGRESSES

- Activities related to the influence and clean-up of TODGA detrimental DCs
 - o Recycling studies of the irradiated TODGA-based solvent at irradiation loop at Náyade facility.
- A review has been carried out at NNL to summarise previous experience and identify options that have been employed for the clean-up and recycle of solvent in process flowsheets. The review is being checked & revised ready for adding to the deliverable report

DIFFICULTIES

- The planned stay of Iván Sánchez at NNL Central Lab to complete Euro-GANEX loading capacity stability studies is still delayed due to COVID-19 situation.
- Some activities have suffered small delays due to the new personal organization at CIEMAT to follow the COVID-19 protocols.

ACTION PLAN

- Assessment of implications for the accumulated dose to solvent in the process flowsheet.
- When traveling is allowed again:
 - o Loading capacity studies of degraded Euro-GANEX solvent and influence of CDs on Pu extraction/stripping (CIEMAT in collaboration with NNL).
 - o Am loading capacity of irradiated samples (CIEMAT in collaboration with KIT-INE).
- Completion of deliverable report D3.4

LIST OF PUBLICATIONS

Publications:

1. Geist, A.; Berthon, L.; Charbonnel, M.-C.; Müllich, U., Extraction of nitric acid, americium(III), curium(III), and lanthanides(III) into DMDOHEMA dissolved in kerosene. *Solvent Extr. Ion Exch.* 2020, 38 (7), 681–702.
2. Weßling, P.; Schenk, T.; Braun, F.; Beele, B. B.; Trumm, S.; Trumm, M.; Schimmelpfennig, B.; Schild, D.; Geist, A.; Panak, P. J., Trivalent actinide ions showing tenfold coordination in solution. *Inorg. Chem.* 2020, 59 (17), 12410–12421.

CONCLUSIONS

The continuity of actions was maintained in this workpackage. However, some experiments were suspended due to the COVID19 lockdown.

Three of the four deliverables planned in this workpackage have been finished.

After 42 months, 147.37 pm have been realized within WP3, corresponding to 100.2% of the 147.1 pm planned for the whole project.

WP4

INTRODUCTION

The main objectives of the WP solid/liquid interface chemistry is to better understand the phenomena occurring at the solid/liquid interfaces during spent nuclear fuel reprocessing in order to support potential processes. It is divided in two main topics. The first is devoted to dissolution step (Task 4.1). It will be examined not only considering direct interactions between the chemical species coming from the solid and the solution, but also through the development of catalytic reactions at the interface. The second topic is focused on the conversion of actinides by precipitation of original precursors coming from new chemical processes based on wet chemistry routes (Task 4.2). The total man power (pm) dedicated to WP4 (Tasks 4.1 and 4.2) are summarized in the table below

Partner	Total planned	WPASR # 1	# 2	# 3	# 4	# 5	# 6	# 7
CNRS/ICSM	38.5	1.6	2.2	7.7	8.4	9.9	7.2	7.9
CEA	15.4	0.0	3.0	3.0	1.0	6.0	6.0	6.0
SCK.CEN	20.0	2.5	2.5	2.5	2.5	2.5	2.5	2.5
UNIMAN	11.0	0.0	0.0	6.0	6.0	0.0	0.0	0.0
Total	84.9	4.1	7.7	19.2	17.9	18.4	15.7	16.4

MAIN RESULTS

TASK 4.1 STUDY OF THE SOLID/LIQUID INTERFACES DURING DISSOLUTION [1-48] TASK LEADER : CNRS

MANPOWER

Expected effort for the period 0 men.month

Actual effort spent during the period 0 men.month

MAIN PROGRESSES

The D7.1 report on dissolution model was written and validated

DIFFICULTIES

None

ACTION PLAN

No more work except writing of an article

TASK 4.2 STUDY OF THE SOLID/LIQUID INTERFACE DURING CONVERSION [1-48] TASK LEADER : SCK.CEN

MANPOWER

Expected effort for the period 1.5 men.month

Actual effort spent during the period 0.69 men.month

MAIN PROGRESSES

Initial tests on destruction of ligands at high temperatures ('boiling tests') have started. Electrochemical destruction studies are being planned. Latest batch of oxalate solubility studies have been completed (further data on Nd as an analogue for Am). Some additional tests identified as necessary to fill in gaps. Pu tests due to start

DIFFICULTIES

Experimental work is behind schedule due to COVID-19 delays.

A request has been made to delay D7.2 to month 48

ACTION PLAN

Complete boiling tests. Start & complete electrochemical tests. Write report D7.2

TASK 7.3

MANPOWER

Expected effort for the period 0 men.month

Actual effort spent during the period 0 men.month

MAIN PROGRESSES

No significant progress obtained in this Task during this semester

DIFFICULTIES

None

ACTION PLAN

D7.3 report to be written by end of 2020.

TASK 7.4 CHARACTERIZATIONS

MANPOWER

Expected effort for the period 0 men.month

Actual effort spent during the period 0 men.month

MAIN PROGRESSES

No work this semester

DIFFICULTIES

None

ACTION PLAN

Do a demonstration EURO-GANEX product finishing campaign (taking the EURO-GANEX product from solution to oxide via the oxalate co-precipitation route), characterize the MOX powder product. Write report D7.4.

LIST OF PUBLICATIONS

None

CONCLUSIONS

During this semester, work on task 7.2 has resumed and has to be finished next semester, as a demo EURO-GANEX product finishing campaign and the characterization of the MOX powder product in order to write the deliverables D7.2 and D7.4. D7.3 is planned to be written before end of year.

WP5

TASK 5.1

MANPOWER

- Jülich: 0 pm
- CNRS: 0 pm
- CEA: 1 pm
- CIEMAT: 2 pm
- KIT: 1.5 pm
- ULANC: 6 pm

MAIN PROGRESSES

- ULANC:
 - RDC extraction data has been analysed using a series of models, allowing for the deconvolution of the roles played by the chemical complexation and physical mass transfer in the overall kinetics of the extraction process.
 - RDC studies have been extended to include the measurement of extraction kinetics of Nd(III) by TODGA. $D(\text{Nd(III)})$ is five times that of $D(\text{Ce(III)})$, indicating more favourable thermodynamics for Nd(III) extraction. As before, Nd(III) extraction by non-pre-contacted TODGA was followed by UV-VIS spectrophotometry using the distinct 585 nm peak.
 - As in the Ce(III)/TODGA and Ce(IV)/TBP systems, the cross-membrane extraction fluxes counter-intuitively increase with decreasing membrane rotation rate, suggesting that the Nd(III) extraction occurs by a similar mechanism – specifically the the MTWCR (Mass Transfer With Chemical Reaction) mechanism, already known for UO₂²⁺/TBP extraction. The key steps of this are as follows:
 - Extractant partitioning from the organic into the aqueous phase;
 - Complexation with metal in zone adjacent to interface on aqueous side
 - Partitioning of complex back into organic phase from aqueous.
 - A maximum interfacial flux of $15 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ is observed at low shear rate (RDC rotation rate of 1 Hz)
 - The mathematical model of extraction was refined previously (see HYPAR6) to include:
 - A new boundary condition allowing for a non-zero concentration of complex at phase interface; and
 - the stoichiometry of the complex.
 - Fit of the Nd(III)-TODGA extraction data to model indicates that a key parameter is the rate of complexation in the aqueous phase, the value of which is found to be $640 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
 - This defines a key reaction zone thickness in the aqueous phase of 0.3 mm. High shear rates (RDC rotation rates > 10Hz) result in the diffusion of the complex to aqueous bulk very effectively competing with diffusion of complex through membrane into organic phase.
- CEA:

- Kinetics data acquisition: The single drop device in glove box has been repaired but its sealing has still to be checked.
- Collecting data related to the treatment of highly concentrated solutions of Am.
- CIEMAT:
 - Ongoing activities to finish the analysis of the first Euro-GANEX irradiation loop at Náyade facility:
 - Quantitative analysis of organic and aqueous phases by HPLC-MS and Raman, respectively.
 - Additional experiments to understand and check EURO-GANEX test loop results.
 - Preparation of methodology and set up for new-GANEX irradiation loop at Náyade facility. First analysis of m-TDDGA and PTD by HPLC-MS and Raman spectroscopy.
 - Two papers under preparation.
- KIT:
 - The stability of the Pu(IV) loading capacity against both α - and γ - radiolysis for the TODGA/DIPB and the cis-mTDDGA/Exxsol D80 solvents have been studied. Both solvents were shown to be stable for up to 5 months of α -irradiation (corresponding to an absorbed dose of 279 kGy). After 10 months of α -irradiation (2322 kGy for cis-mTDDGA/Exxsol D80, 563 kGy for TODGA/DIPB) both solvents showed precipitation, irrespective of contact with acid or not.
 - γ -irradiations were performed at SCK-KIT and loaded with 36 g/L Pu(IV) and analysed at KIT. No 3rd phase formation or precipitation was observed, and the organic Pu concentration was constant as a function of dose, again showing its stability towards γ -radiolysis.

DIFFICULTIES

- JÜLICH:
- ULANC: Lab closure from March-August 2020 due to covid-19 lockdown restrictions in the UK, resulting in significant delays in experimental work including the intended kinetic extraction experiments on TWENTE's mTDDGA sample. Modelling work has continued on the lanthanide extraction kinetics by TODGA using existing data.
- CEA: Kinetics data acquisition: The preliminary acquisitions performed in 2019 with a microfluidics device did not allow to get accurate results of the Eu(III), Fe(III) and Gd(III) kinetics transfer. Thus, the next experiments will be carried out in gloves box, with spiked solutions, using the single drop device. However, because the mTDDGA solvent was never studied with this setup, all the experimental parameters (injection flow rate, drop residence time,...) have to be determined.
- CIEMAT: Some delays experienced due to the pandemic

ACTION PLAN

- JÜLICH:
- ULANC:

- Following the success of the Nd(III) modelling run, a greater bank of RDC extraction data may now be imported into the model for the purposes of parameter estimation. Principal datasets to be modelled going forward include:
 - TBP/Ce(IV) PUREX analogue system [1] – dataset already exist
- Continue the study of the Nd(III)-TODGA system, concentrating on:
 - Extraction studies as a function of [TODGA] so as to determine the order of the extraction process with respect to ligand concentration;
 - Extraction studies using pre-contacted aqueous and organic phases; to date, our experiments on the i-SANEX system have concentrated on un-pre-contacted phases.
- Commence RDC studies of the trivalent lanthanide / mTTDGA extraction system
- CEA: A test of radiolytic stability of the EURO-GNAEX solvent is planned next February on the Marcel irradiation loop in Marcoule. Extracting molecule = cis m-TDDGA, An stripping agent = PTB.
- CIEMAT: New-GANEX test loop at Náyade facility and preparation of D5.2.

TASK 5.3

MANPOWER

NNL: 0.44 pm

JUELICH: 0.2 pm

ULEEDS: 1 pm

MAIN PROGRESSES

- NNL:
 - The models of trivalent MA/Ln extraction into the i-SANEX solvent are being checked.
 - Experimental design software has been used to identify new data required for the models.
- ULEEDS:
 - Completed the development of a working CFD model of a simplified ACC configuration using new multiphase modelling technique.
 - Daniel Theobald has successfully defended his PhD thesis on PSEC modelling.
 - Work is continuing on the development of the ACC model to include mass transfer funded by the UK Advanced Fuel Cycle Programme.
- JUELICH: A videoconference call was attended discussing the planning of the irradiation loop tests on 8 August 2020. As a results JUELICH received a portion of the large cis-mTDDGA batch synthesized at Oak Ridge to evaluate the best chemical conditions to be tested in the irradiation loop tests. Details are reported in domain 1, WP 3.

ACTION PLAN

NNL: Complete checking, add new data if available to models and write deliverable report.

LIST OF PUBLICATIONSCIEMAT

I. Sánchez-García, H. Galán, J.M. Perlado and J. Cobos. “Development of experimental irradiation strategies to evaluate the robustness of TODGA and water-soluble BTP extraction systems for advanced nuclear fuel recycling” Radiation Physics and Chemistry 177 (2020) 109094.

I. Sánchez-García, H. Galán, A. Núñez, J.M Perlado and J. Cobos. “Development of a gamma irradiation loop to evaluate the performance of a EURO-GANEX process”. Industrial & Engineering Chemistry Research. Submitted.

ULEEDS

Theobald, Daniel W.; Hanson, Bruce ; Fairweather, Michael ; Heggs, Peter J. “Implications of hydrodynamics on the design of pulsed sieve-plate extraction columns: A one-fluid multiphase CFD model using the volume of fluid method”, March 2020, Chemical Engineering Science, Elsevier Ltd, Volume 221

A. De Santis, M. Colombo, B. C. Hanson , M. Fairweather, “A generalized multiphase modelling approach for multiscale flows”, J. Comp. Phys (JCOMP-D-20-00923R1 under review)

WP6

INTRODUCTION

The objectives of WP6 are to optimise the efficiencies and safety of separation processes developed under the SACSESS project (*i.e.* i-SANEX, EURO-GANEX, EXAm, CHALMEX). The main emphasis is on process development through flowsheet testing. WP6 focuses on optimisation of the reference separation processes, particularly where significant simplification is possible or replacement of non-CHON ligands by CHON molecules can be proposed. It also includes extension of process envelopes to more challenging GenIV feeds and integration of the minor actinide SX cycles with upstream and downstream stages, particularly where interfaces may cause issues.

MAIN RESULTS

MANPOWER

A total of 18.2 person-months has been reported split into 10.1 person-months for Task 1 (CHALMERS, ICHTJ, JUELICH, NNL), and 8.1 person-months for Task 2 (JUELICH, UNIPR). This represents an increase on semester 6 which reported 16.6 person-months suggesting a degree of recovery from the COVID-19 emergency that shut down laboratory work in 2020. However, greater efforts are to be expected in the final semester to meet the outstanding deliverables.

	task 1		task 2	
	expected	achieved	expected	achieved
CEA				
CHALMERS	6	6		
CIEMAT				
ICHTJ	0	2.6		
JRC				
JUELICH	0	0.2	5	5
KIT	1.8	0	0.4	0
NNL	2	1.3		
POLIMI				
UNIPR			0	3.1
total	9.8	10.1	5.4	8.1

TASK 6.1: HOMOGENEOUS RECYCLING

MAIN PROGRESSES

OPTIMIZING ACTINIDE / TECHNETIUM SEPARATION BY SOLVENT EXTRACTION

Long lived fission product technetium-99 of high fission yield must be separated from actinides in hydrometallurgical reprocessing of spent nuclear fuel. However, pertechnetate anion – the most stable form of Tc in HNO_3 solutions is easily co-extracted with the actinides into the organic phase used in the process, which causes problems with its further separation. Tests of the EURO-GANEX solvent extraction recycling of transuranides (TRU) from irradiated fast reactor fuel showed that a significant part of Tc passed with uranium to the organic phase containing the amide extractant DEHiBA in the 1st cycle of the process, but most of Tc went with TRU to the 2nd cycle where Tc accompanied the actinides and lanthanides extracted into the organic phase by the TODGA and DMDOHEMA extractants, to be probably found in the spent organic solvent together with some U ($<4 \cdot 10^{-5}$ mol/L) and traces of TRU and Ln [1].

Attempts to reduce technetium and obtain non-extractable hydrophilic complexes of its low valent forms, well separated from the actinides were rather unsuccessful except from the work by Czerwinski et al. who used acetohydroxamic acid (AHA) as the reducing and complexing agent for Tc, which formed a hydrophilic $\text{Tc(II)-nitrosyl-AHA}$ complex, $[\text{TcII}(\text{NO})(\text{AHA})_2\text{H}_2\text{O}]^+$ [2]. Because of a very slow kinetics of Tc(VII) reduction at room temperature the authors worked at 95°C and at a high AHA concentration (4 mol/L) to accelerate the process. Unfortunately, so harsh conditions seem to be hardly acceptable for technological solvent extraction work with highly radioactive material.

However, we found this process to be efficient for technetium separation from Am(III) in the EURO-GANEX system [3], and examined the possibility to alleviate the harsh conditions of Tc(VII) reduction [4]. We also considered the possibility of directing all or most of the Tc to the loaded organic solvent, followed by selective stripping of the reduced Tc to an aqueous phase, remaining uranium in the organic solvent [5].

In the current reporting period we analyzed the problem in details. Literature data indicate that the transfer of significant amounts of Tc(VII) to the loaded solvent in the system 1 M DEHiBA in kerosene / HNO_3 is impossible due to low distribution ratios, $D(\text{TcVII}) < 1$, even in the presence of uranyl nitrate up to 120 g U/L [6]. Our preliminary experimental data indicate that even in the system 1 M DEHiBA in kerosene / 120 g U/L 0.3 M HNO_3 , where we could expect the highest $D(\text{TcVII})$ and low $D(\text{UVI})$ values, $D(\text{TcVII}) \approx 0.8$ which does not allow to efficiently separate Tc(VII) from uranium.

Therefore, the technetium should rather be entirely routed to the aqueous raffinate of the 1st GANEX cycle, used then as feed in the 2nd cycle, as it was foreseen for the hot test of the EURO-GANEX process [1]. However, the results of the hot test were inconsistent with the simple physicochemical model of Tc(VII) behaviour in the 1st GANEX cycle. Only 75% of the Tc was found in the highly active raffinate, while the remainder, almost 25% of the Tc, was transferred to the loaded organic phase [1].

In our opinion, this inconsistency may be due to an unverified assumption that the hydrazine scrubbing of the loaded DEHiBA/kerosene solvent leaves technetium in a form which is hardly extractable to the organic phase. Such a model either assumes that the reduction of Tc(VII) with hydrazine [7] (which begins in the scrubbing section) is very slow, perhaps accompanied by re-oxidation of Tc(IV,V) to Tc(VII) , or it neglects the extraction by DEHiBA of the reduced forms of Tc in the system studied. However, according to [8], Tc(V) formed in HNO_3 solutions of SNF by slow reduction of Tc(VII) with hydrazine is stabilized by an excess of a tetravalent cation, in particular the fission product Zr(IV) , when the zirconyl ion forms a stable mixed complex with two dioxotechnetium(V) cations.

According to our hypothesis, partial replacement of the hydrating water molecules by DEHiBA present in the organic phase may render this complex amphiphilic, allowing part of the Tc to be transferred to the organic

phase. To check this assumption, we intend to verify the data obtained on the basis of VIS spectrometric studies (absorption maximum of Tc(V) at 473 nm) reported in [8], and to conduct further tests to clarify whether this (or a similar) Tc(V) complex is to some extent extracted by DEHiBA. If the answer obtained is positive, we will support our earlier [5] proposal to modify the 1st GANEX cycle to prevent the Tc transfer to the DEHiBA solvent. To achieve this goal, we intend to replace the scrubbing of the loaded DEHiBA phase with hydrazine in 1.5 M HNO₃ [1] by scrubbing it with dilute AHA in 0.5 - 1 M HNO₃ at room temperature. Under these conditions, Np(VI) reduced by AHA to Np(V), Pu(IV) complexed by AHA and Tc(VII) not reduced by AHA [4,5] would be found in the aqueous raffinate, leaving U(VI) in the organic phase (as tested for UREX+ [9]). The research will be complemented by tests to see whether the presence of small amounts of AHA in the raffinate may interfere with the subsequent extraction of Np and Pu in the 2nd cycle of the EURO-GANEX process.

CONCLUSIONS

The problem of how and in which cycle of the EURO-GANEX process should technetium and actinides be separated remains unresolved. Our analysis suggests to choose the option of routing all the Tc present in the HNO₃ solution of spent nuclear fuel to the 2nd cycle of the process. Further experiments will be decisive in this matter and perhaps will suggest minor improvements to the flow-sheet of the process.

REFERENCES

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6. P. Moeyaert, T. Dumas, D. Guillaumont, K. Kvashnina, C. Sorel, M. Miguiditchian, P. Moisy and J.-F. Dufrêche, Modeling and speciation study of uranium(VI) and technetium(VII) coextraction with DEHiBA. *Inorg. Chem.*, 2016, 55, 6511–6519.
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8. Ya.A. Obruchnikova, K.E. German, V.F. Peretrushin, M.V. Logunov, M.N. Mashkin and I.G. Tananayev, Behavior of technetium in a nitric acid solution containing hydrazine nitrate and multivalent metal cations (Th and Zr) [in Russian] (2014), *Voprosy radiatsionnoj bezopasnosti (Radiation Safety)*, No 2, 15-19.
9. R.S. Herbst, P. Baron, M. Nilsson, (2011). Standard and advanced separation: PUREX processes for nuclear fuel reprocessing, in: K.L. Nash and G.J. Lumetta (Eds.), *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*. Woodhead Publishing Ltd., pp. 141–175.

PLUTONIUM LOADING EXPERIMENTS WITH MTDDGA

Further batch tests have been performed to confirm the Pu loading and third phase boundary for the new GANEX solvent system, based upon the modified diglycolamide mTDDGA. Initial batch tests showed that with a lower concentration of extractant, 0.1M m-TDDGA, third phase formation was observed when the Pu loading exceeded the concentration for the formation of the 1:3 complex. Consequently, there was a concern that third phase formation may be masked by the dark colour of the solvent phase obtained with 0.3M and 0.5M mTDDGA. Therefore, some of the tests were repeated to confirm whether a third phase was present at the high Pu loadings achieved with 0.3M and 0.5M mTDDGA. The maximum Pu loading achieved without third phase formation in the solvent is summarised in table 1.

Table 1. Summary of maximum Pu loading for cis-mTDDGA in odourless kerosene

Initial [HNO ₃]aq	[Pu] _{org} g/l		
	0.1M mTDDGA	0.3M mTDDGA	0.5M mTDDGA
1	*		
2	15		
3	13.6		
4	9.4		55
5	8.3	40	55
6	8.3		50
7	8.3		45

Note: * - precipitation occurred at all Pu concentrations tested.

- At lower concentrations of the extractant (0.1M m-TDDGA) third phase formation was observed when the Pu loading of the solvent exceeded the limit for the formation of the 1:3 complex.
- Precipitation was observed with 0.1M mTDDGA at low nitric acid concentration (1M HNO₃), even with Pu concentration as low as 2.5 g/l.
- At higher concentrations of the extractant (0.3M and 0.5M mTDDGA) the high Pu loadings achieved imply that formation of the 1:2 complexes occurs without third phase formation.
- The Pu loading tests indicate that a solvent composition between 0.3M and 0.5M mTDDGA could provide a suitable alternative to the current EURO-GANEX solvent system.

Figure 1 compares the UV-Vis spectra for the Pu loaded solvent phase (mTDDGA) with the aqueous Pu(IV) spectrum in 5M nitric acid and the UV-Vis spectrum for Pu in the EURO-GANEX solvent (0.2M TODGA/ 0.5M DMDOHEMA). The spectrum for Pu in 5M nitric acid shows the characteristic absorption peaks for Pu(IV). As expected, the spectra for Pu in the solvent phase exhibit shifts in the intensity and position of the absorption peaks in compared to the aqueous spectrum. However, the peaks are broadly consistent with the presence of Pu(IV) in the solvent.

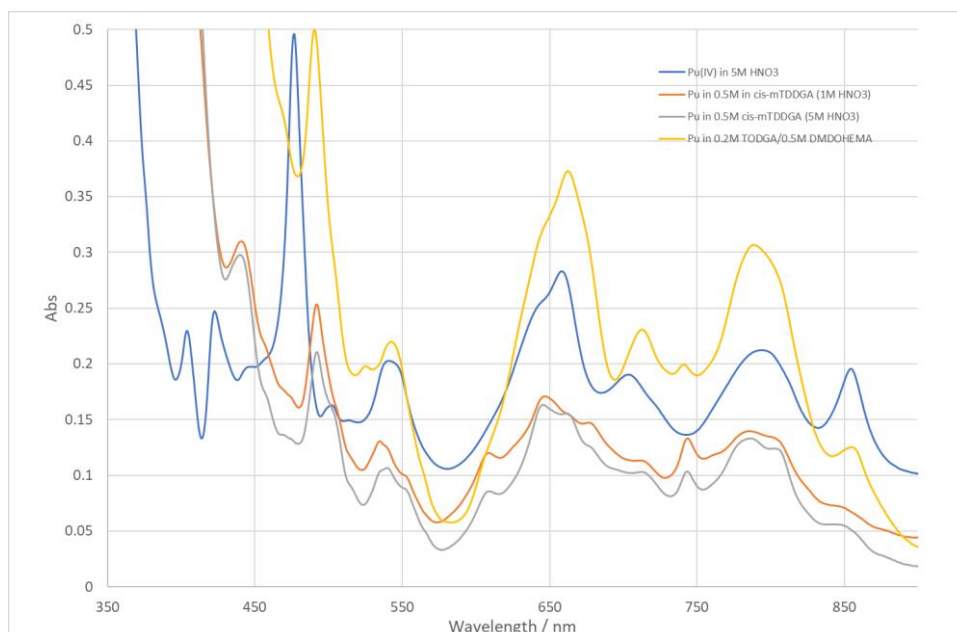


Figure 1. UV-Vis spectra for Pu in nitric acid and GANEX solvents (mTDDGA and TODGA/DMDOHEMA)

There are a number of other tasks that are currently in progress or planned to continue optimisation of the EURO-GANEX process, including:

- Extraction behaviour of Tc. In the PUREX process the extraction behaviour and control of Tc is affected by the co-extraction of TcO_4^- with both U and Pu. Therefore, experiments are in progress to assess the co-extraction of Tc with Pu in the EURO-GANEX process in order to develop options for the control of this species in the flowsheet.
- The use of PyTriDiol (PTD) has been shown to provide an alternative CHON option to the sulphonated BTP complexants for the selective separation of minor actinides and lanthanides. Further tests will be performed to optimise the conditions for the selective separation of Pu and minor actinides (Am) from lanthanides in the presence of flowsheet levels of Pu (10 to 20 g/l Pu loading in solvent phase).
- Np extraction and control in both the PUREX and GANEX process is complicated as Np may be present in a number oxidation states, Np(IV), Np(V) or Np(VI), which exhibit different extraction behaviour. Therefore, a series of batch experiments will be also be carried out to evaluate the extraction and routing of Np in the GANEX process using the alternative mTDDGA extractant.

SYNTHESIS OF PTD

The properties of PTD have been largely investigated in order to open the possibility of employing the ligand in the i-SANEX process at industrial scale. The MA selectivity has been demonstrated by extraction tests performed at Radiochemistry and Radiation Chemistry Lab of Politecnico di Milano and at CEA facilities. Furthermore, TRLFS experiments performed at KIT have confirmed MA selectivity. Hydrolytic and radiolytic stability was demonstrated by solvent extraction experiments, HPLC-MS and

NMR analysis performed both at POLIMI and UNIPR. More recently, in 2018, single stage centrifugal contactor experiments with PTD have been conducted at FZJ. The encouraging results obtained from these tests demonstrated the applicability of PTD complexing agent at industrial scale. Nevertheless, an effective use at industrial level requires further experiments of plant simulations and huge quantity of ligand. In order to obtain a comprehensive overview necessary for industrial application a consistent simplification of the synthesis in order to obtain the target molecule in an easier, faster and economically more convenient way is needed.

The common procedure for the synthesis of PTD is described in the scheme below, and was usually carried out on a 2.0-2.5 g scale. The first step is a Sonogashira reaction between the 2,6-dibromopyridine and trimethylsilylacetylene, both commercially available. For this cross-coupling we used $\text{Pd}(\text{PPh}_3)_4$ and CuI as catalysts and diisopropylamine as a base in toluene. The intermediate **5** is obtained pure after purification by chromatography. The deprotection step is settled by the usual procedure using potassium carbonate and methanol. The 2,6-diethynylpyridine, intermediate **6**, is light and air sensitive so it should be immediately used as soon as it is produced and purified. Finally, the target molecule PTD is obtained under classical CuAAC reaction conditions starting from 2,6-diethynylpyridine and 3-azidopropan-1-ol aside synthesized. The crude is purified by chromatography in 70/80% yield. The only commercially available reagents of the reported synthesis are the 2,6-dibromopyridine, the trimethylsilylacetylene and 3-chloropropanol. As described above, the synthetic route requires at least three purification steps. The first is needed to remove the excess of trimethylsilyl acetylene and the monofunctionalised pyridine from compound **5**, a second step is needed to purify the deprotected diacetylene **6** while a third column chromatography is used to isolate the target compound from the salts formed during the click reaction. In a joint study with Polimi, it was shown that PTD not purified in the last step from inorganic salts could result in remarkably lower D_{Am} and SF values.

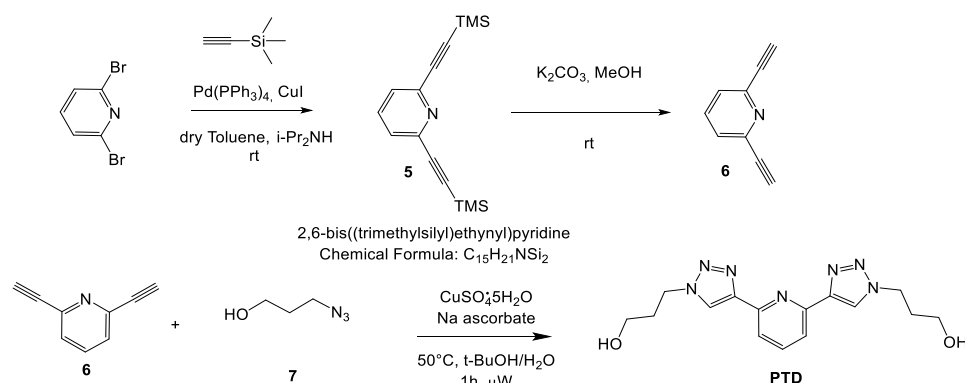


Figure 1. Synthesis of PTD on a 3 gram scale

In view of a possible scale up of the synthesis three main points/elements must be considered:

- reduce the purification steps (in the reported synthesis three flash column chromatographies were reported)
- possibly substitute chromatography with purification procedure more compatible with large quantity of materials, i.e. crystallizations
- simplify the synthetic pathways (reducing the number of reaction setup and workup procedures)
- minimize decomposition of compound **3** (unstable to light and air)
- minimize the amount of azide **4** present in concentrated/neat conditions, being the azide a potential hazard (potentially explosive when heated in conc. solutions or neat)

- minimize the amount of $\text{Pd(PPh}_3)_4$ since it is rather expensive
- PTD is needed quite pure to ensure high SF

The proposed strategy to achieve these issues is the three steps, one pot approach, herein described. This approach was firstly tested using 10 g of 2,6-dibromopyridine as starting material and then with 25 g batches (Figure 2).

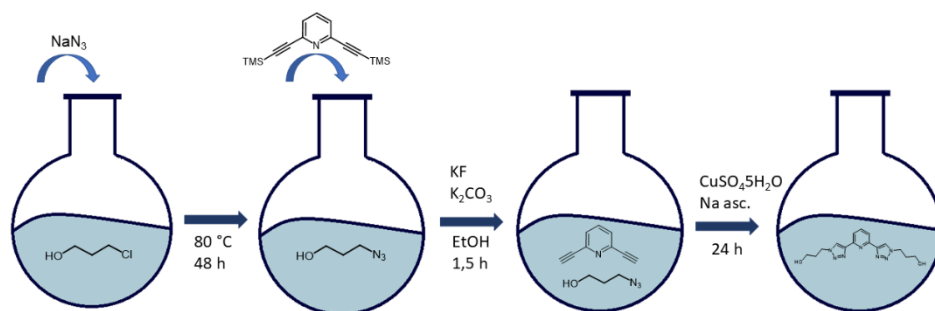


Figure 2. PTD large scale synthesis (25g scale) through the “three steps, one pot” procedure

In a round bottom flask 3-chloropropan-1-ol and NaN_3 in 1:3.5 molar ratio were dissolved in water (0.25 l). The mixture was heated up to 80 °C and stirred for 48 hours. Care must be taken as a condenser has not been used. The reaction mixture was cooled to room temperature whereupon KF , K_2CO_3 , 2,6-bis((trimethylsilyl)ethynyl)pyridine **5** and ethanol (0.25 l) were added sequentially. The mixture was stirred until the deprotection is completed. It is possible to heat the reaction mixture up to 35-40°C in order to shorten the reaction time. The reaction progression is checked by TLC and it usually indicates that the reaction is over after 1.5 hour. The 2,6-bis((trimethylsilyl)ethynyl)pyridine is not soluble in the solvent mixture while the deprotected intermediate is. Sodium ascorbate and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were added to the mixture at room temperature. Whereupon, the mixture was stirred for one day checking the progression of the reaction by TLC (DCM/MeOH 9:1). Considering the O_2 sensitivity of the Cu (I) added in the last step it is advisable to use PTFE gaskets to seal the flask. If the solution turns green, it means that the copper has been oxidized and it is necessary to add sodium ascorbate. The reaction was quenched by evaporating the ethanol under reduced pressure. Acetone is then added to precipitate the inorganic salts which are filtered off. Whereupon, the mixture was completely dried under reduced pressure. Acetone was added and the mixture was sonicated at 30 °C in order to fully dissolve the solid. An orange suspension of inorganic salts was formed and filtered off. The mixture was dried to obtain the product as a light brown solid. In this way the product could be obtained without further purification in 85% yield. The 2,6-bis((trimethylsilyl)ethynyl)pyridine used in the described three steps, one pot procedure was aside synthesized according to the first step of the scheme in Figure 1. Intermediate **5** is usually purified by a filtration on silica giving 90 % yield. Some experiments in order to develop a more suitable purification system have been made. The best one was a crystallization in cold MeOH. However, this method lowers the yield because of the high solubility of the compound in the used solvent.

Samples of the different batches (different ratio between reagents and different purification methodologies) were sent to POLIMI in order to assess where the level of impurities could have been considered acceptable for the process separations. Results are collected in Table 1.

Table 1: Different PTD batches with indication of the quantities of starting material (synthesis scale), method of purification and solvent used in the purification. For every batch are reported the ratio

between D_{Am} , D_{Eu} and $SF_{Eu/Am}$ of large scale samples versus highly purified PTD samples used as references. A values of 1 means there is no observable difference between the property of the large scale batch compared to the highly purified PTD, values of 0.9 means the large scale batch has an efficiency/selectivity 90% compared to highly purified PTD and so on.

PTD batch (Code)	Synthesis Scale	Purif. Method	Solvent used	$D_{Am}/D_{Am\ ref}$	$D_{Eu}/D_{Eu\ ref}$	$SF_{Eu/Am} / SF_{Eu/Am\ ref}$
RA 131 G	25 g	1° cryst	MeOH	1.0	0.9	0.9
RA 131 V	25 g	2° cryst	MeOH	0.9	0.9	1.0
RA 119	5 g	Crude		1.0	0.9	0.9
RA 117 CRIST	5 g	Cryst	CH ₃ CN	0.9	0.8	0.9
RA 117 DIFF	5 g			0.9	0.7	0.7
RA 117 sox-dcm	5 g	Soxhlet washing	CH ₂ Cl ₂	0.9	0.7	0.7
RA 115 grezzo	5 g	Crude		1.4	1.2	0.9
RA 115 FIL2	5 g	Cryst	CH ₃ CN	1.2	1.0	0.8
RA 115 silice	5 g	Silica pad	acetone	1.2	1.2	1.0

As observed from the table, samples named RA131, obtained starting from 25 g of 2,6-dibromopyridine behave both in distribution and separation from 90% to 100% as the highly purified sample of PTD taken as reference. This obviously means that the scale-up synthesis developed in this semester gave sample rather pure and that can be used for further and large scale process experiments.

Moreover, this large scale synthesis solved several problems and allows to:

- avoid three expensive and time-consuming column chromatography and thus reduce the number of chromatographic purification steps to only a fast one, for the purification of the protected diethynyl pyridine
- substitute the final chromatographic purification on PTD with a simple precipitation with methanol
- simplify the synthetic pathways (reducing the number of reaction setup and workup procedures). Apart from the first Sonogashira coupling all the other steps are driven in a single vessel just adding the reagents after a proper time.
- minimize decomposition of compound **3** (unstable to light and air)
- minimize the amount of potentially explosive azide **4** present in concentrated solution
- minimize the amount of Pd(PPh₃)₄ since it is rather expensive
- obtain PTD at a sufficient degree of purity to allow large scale separation test

Large samples of this compound RA131 were sent to INL, CEA, CIEMAT and JUELICH for an irradiation loop test.

CHALMEX PROCESS

The work on masking agents has been continued in the last term of 2020. The focus has been on carboxylic acids as also investigated by Sypula et al.¹ Although some of the masking agents performed in accordance with literature, none of the carboxylic acids reduce the extraction of the problematic fission products to a greater extent than the currently used bimet and mannitol, see Table 2.

Earlier efforts on exchanging TBP with DEHiBA (Figure 2) have been resumed. A fresh batch of DEHiBA has been produced in-house, and screening studies have been started with Am/Eu extraction and hydrolytic stability. The results can be seen in

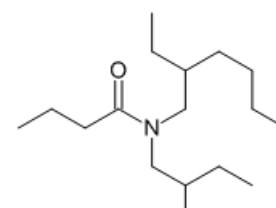


Figure 2. The molecular structure of DEHiBA.

Table 2. The distribution ratios of problematic fission products both for pristine aqueous phase, and in the presence of different masking agents with concentration 20 mM.

	107Ag	111Cd	105Pd	90Zr	95Mo	52Cr	57Fe	63Cu	60Ni
Pristine	>100	>100	14.8	1.7	45	0.10	0.25	73	76
EDTA	>100	>100	11.6	0.37	74	0.10	0.28	13	83
HEDTA	>100	>100	>100	43	>100	0.13	0.28	14	80
DTPA	>100	1.5	>100	40	>100	0.16	0.29	13	76
CDTA	>100	>100	12	0.25	70	~0		~0	>100
Bimet	0.00	>100	0.23	3.66	6.92		1.94	>100	49
Mannitol	>100	>100	7.53	7.24	6.70	0.00	1.12	1.34	43

Table 3. The distribution ratios (D) for Am and Eu extraction in different solvents. "Solvent" refers to a solution containing 10 mM CyMe4-BTBP, 30% v/v DEHiBA and 70% v/v FS-13. It is clear that the DEHiBA solvent yields significantly lower D(Am) values than the TBP-CHALMEX solvent (D(Am)=29). It is also apparent that the solvent degrades over quite a short time span (5 days) and that DEHiBA does not extract americium. Plutonium extraction experiments will be conducted in the next reporting period.

¹ Michal Sypula, Andreas Wilden, Christian Schreinemachers, Rikard Malmbeck, Andreas Geist, Robin Taylor & Giuseppe Modolo (2012) Use of Polyaminocarboxylic Acids as Hydrophilic Masking Agents for Fission Products in Actinide Partitioning Processes, Solvent Extraction and Ion Exchange, 30:7, 748-764, DOI: [10.1080/07366299.2012.700591](https://doi.org/10.1080/07366299.2012.700591)

Table 3. The distribution ratios (D) for Am and Eu extraction in different solvents. "Solvent" refers to a solution containing 10 mM CyMe4-BTBP, 30% v/v DEHBA and 70% v/v FS-13.

	Pre-equilibrated	Age	D(Am)	D(Eu)
Solvent	No	Fresh	3.81	0.17
Solvent	No	5 days	2.99	0.15
Solvent	Yes	Fresh	2.37	0.11
Solvent	Yes	5 days	1.17	0.09
DEHBA + FS-13	Yes	Fresh	0	0
DEHBA + FS-13	No	Fresh	0	0

Some efforts have also been spent on mapping the physical properties of the CHALMEX solvent(s). Some experiments are still pending due to lack of diluent.

Table 4. Physical properties of different solvents.

		T> 27 deg C	T>29 deg C	
Solvent	Pre-equilibrated w/	ρ -avg (g/cm ³)	Surface tension	Interfacial tension
TBP	-	0.9705	27.2517	
FS-13	-	1.406	22.9272	
TBP	4 M HNO ₃	0.9965		
TBP	MQ	0.959		19.454
30% TBP, 70% FS-13	-	1.2535		
30% TBP, 70% FS-13	4 M HNO ₃	1.2565		14.7779
CHALMEX	4 M HNO ₃	1.269		
4 M HNO ₃	-	1.122	55.687	

BIMET-PALLADIUM COMPLEXATION CHEMISTRY

Investigations into the bimetal-palladium complex formation has been initiated. Initial extraction experiments were performed using Aliquat 336 in ethyl benzene to establish the ionic nature of the complex. Since Aliquat 336 is an anionic exchanger, extraction by this molecule implies a cationic complex between bimetal and palladium. The first extraction tests showed D-values ranging from D=5 to infinite D-values, with little to no reproducibility. It was realised it was probably due to the kinetics of the Pd-bimetal complex formation, so extractions were done systematically after different Pd-bimetal reaction times. For reaction times up to 20 minutes, the Pd remaining in the aqueous phase was still below the detection limit, yielding infinite D-values. Experiments with longer reaction times (up to 24 hours) have been done, but results are pending due to maintenance of the ICP-OES.

The dependency of Pd extraction on bimetal concentration has also been established, see Figure 3.

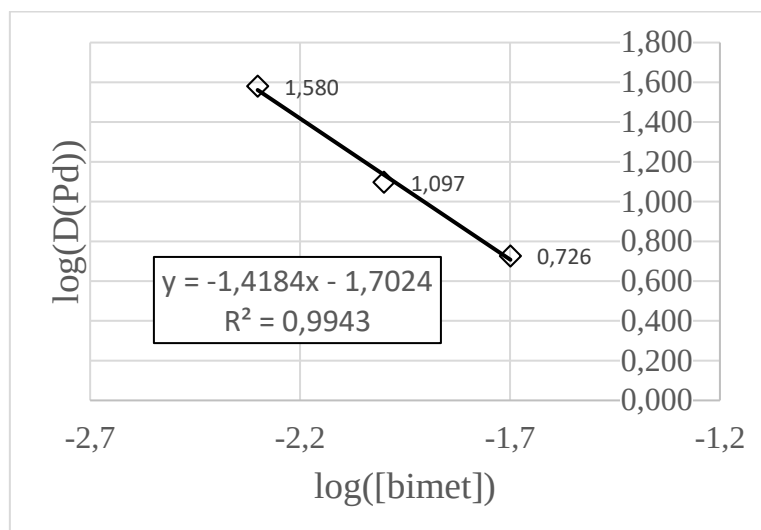


Figure 3. The logarithmic distribution ratio (D) of palladium versus the logarithmic bimet concentration.

6.2 HETEROGENEOUS RECYCLING

I-SANEX PTD DEMONSTRATION

A countercurrent i-SANEX process was demonstrated using PyTri-Diol (PTD, Figure 4) for the An(III) selective stripping. The solvent was the same as tested in the first i-SANEX process, 0.2 mol L⁻¹ TODGA (Figure 4) + 5%_{vol.} 1-octanol in TPH.^[21] The CHON compliant PTD was shown to be a promising replacement for the non-CHON compliant SO₃-Ph-BTP.^[18-20] CDTA was used to mask Zr and Pd extraction in the feed.^[22]

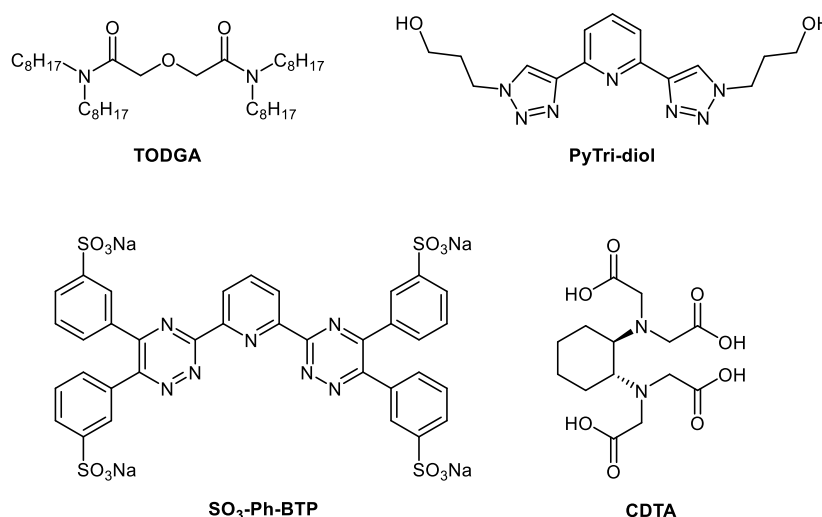


Figure 4. Chemical structures of TODGA, PyTri-diol, SO₃-Ph-BTP, and CDTA.

A 16-stage flow-sheet was calculated at KIT for the An(III) selective stripping and Ln(III) re-extraction sections. Due to the limited number of available contactors in our laboratory, only the An(III) selective stripping and Ln(III) re-extraction sections were tested. As the extraction and scrubbing sections of the

PTD i-SANEX test were identical to the original i-SANEX test^[21] and did not involve the use of the new hydrophilic stripping agents, it was decided to prepare the loaded organic phase by a series of batch contacts. Analyses of the loaded organic phase showed a composition well comparable to the original i-SANEX test. Similarly, the Ln(III) stripping was not tested, as it was demonstrated successfully in the original i-SANEX test.^[21] Figure 5 shows the series of batch contacts for the preparation of the loaded organic phase and the flowsheet of the i-SANEX test.

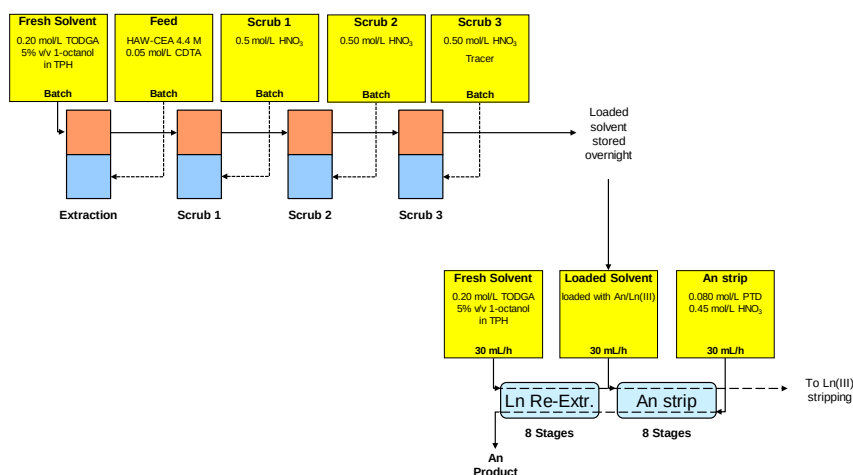


Figure 5. Flowsheet of the PTD i-SANEX test.

The full evaluation of the analytical data obtained from the centrifugal contactor test is currently carried out. All results will be given in the next HYPAR and a full paper will be prepared to be published. Nevertheless, preliminary data showed in Figure 6 shows very good An(III)/Ln(III) selectivity and the demonstration test is believed to successfully show that PTD is a good candidate to replace SO₃-Ph-BTP in the i-SANEX process. Probably PTD can also be used as a replacement in other processes, e.g. the EURO-GANEX process.

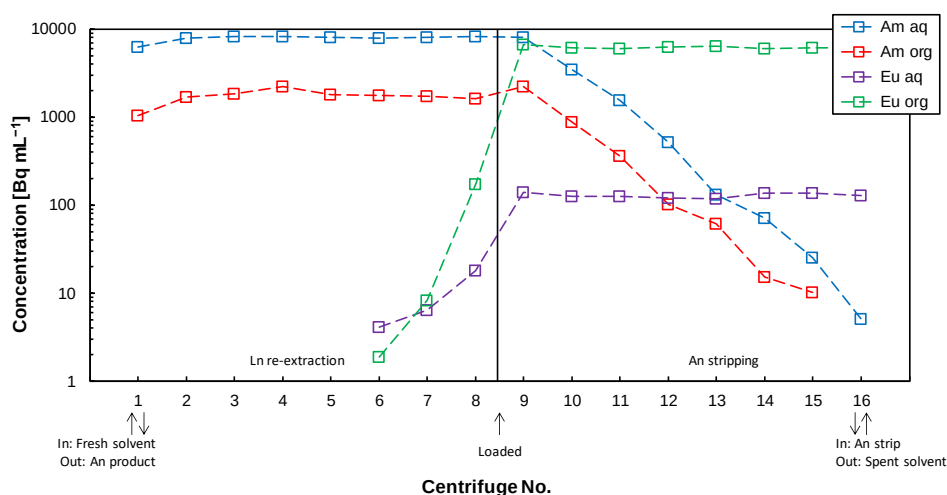


Figure 6. Am and Eu stage profiles of the PTD i-SANEX demonstration test (data from gamma spectroscopy).

CONCLUSIONS

Key technical highlights this semester include:

- A review of Tc behaviour and optimised strategies to ensure it is fully directed to the GANEX-1 aqueous product, i.e. EURO-GANEX feed, for decontamination in the EURO-GANEX cycle.
- Further data establishing the 3rd phase boundary for the m-TDDGA ligand.
- A scaled up « three step, one pot » synthesis for PTD has been developed to help meet demand for the ligand.
- Work is continuing on the CHALMEX process focused on hold back agents, replacing TBP with DEHiBA and solvent properties measurements.
- An i-SANEX flowsheet test was conducted with spiked feeds to investigate the replacement of the sulphonated BTP with PTD for selective minor actinide stripping. Only the actinide stripping section was run countercurrent in centrifugal contactors. Promising results were obtained and data are being analysed.

It appears overall that, although delivery will surely be challenging, there is sufficient progress being made to meet deliverables D6.2 and D6.3 as planned (month 48) and despite the impacts of the COVID-19 emergency in 2020 that are continuing into 2021.

WP7

INTRODUCTION

The objective of WP7 is to provide relevant dissolution and conversion processes linkable with the separation processes. When necessary, interfaces between dissolution/separation and separation/conversion are considered. For dissolution, the focus is put on the completion of data relevant for defining a dissolution model. The conversion issues of solutions from SX-process are the development of safe synthesis routes, the destruction of prejudicial organics from SX-process and characterization of synthesized MABB precursors. The workpackage is divided into 4 tasks: Task7.1 on dissolution, Task7.2 on destruction of organics, Task7.3 on development of safe synthesis routes and Task7.4 on characterization of MABB precursors

MAIN RESULTS

TASK 7.1

MANPOWER

Expected effort for the period 1.8 men.month

Actual effort spent during the period 1.8 men.month

MAIN PROGRESSES

The D7.1 report on dissolution model was written and validated

ACTION PLAN

No more work except writing of an article

TASK 7.2

MANPOWER

Expected effort for the period 1.5 men.month

Actual effort spent during the period 0.04 men.month

MAIN PROGRESSES

No significant progress this semester. Experimental programme has been planned and awaiting restart of laboratory operations

DIFFICULTIES

All laboratory work has been suspended due to COVID-19. Planned experiments to study the effect of complexants upon the precipitation of Pu oxalate have been postponed.

Abstract submitted to ATALANTE 2020. Conference has been cancelled due to COVID-19 impacts

A request has been made to delay D7.2 to month 48

ACTION PLAN

Additional batch tests will be performed to evaluate the effect of acetic acid (AHA decomposition product) and PTD upon the precipitation of Pu oxalate.

TASK 7.3

No significant progress obtained in this Task during this semester

TASK 7.4 CHARACTERIZATIONS

No work in this Task during this semester

CONCLUSION

During this semester, no progress was obtained in WP7 except achievement of D7.1.

WP8**INTRODUCTION**

This WP addresses the industrialisation and scale up of some of the chemical projects studied in GENIORS. To develop processes towards industrialisation studies that consider the holistic impacts of the flowsheet are necessary. The tasks in this work package seek to assess and illustrate the holistic effects on the nuclear fuel cycle that occur from fundamental changes to the chemistry at the heart of its key processes. Appropriate technology deployment and consideration of potential issues and impediments to industrialisation will also be assessed.

MAIN RESULTS**TASK 8.1 TO 8.3**

completed

TASK 8.4**MAIN PROGRESS**

Construction of the main Sim Plant tool (waste evaluation) is complete, simulating the reprocessing flowsheet and waste treatment operations. The tool compares the Advanced PUREX and THORP processes to arrive at characterised waste volumes and number of waste containers generated. These are compared normalised to the electricity produced from the fuel. The Euro-GANEX flowsheet has undergone modifications to update the chemistry (separation and decontamination factors) to align with the latest knowledge.

ACTION PLAN

The conversion of the Euro-GANEX flowsheet into the Sim Plant format, enabling it to be compared to the PUREX and Advanced PUREX flowsheets.

Running the Euro-GANEX flowsheet in the Sim Plant tool and production of the final report detailing comparisons will then take place.

TASK 8.5

completed

CONCLUSIONS

Expert input is needed. The initial findings should be validated.

WP9

INTRODUCTION

Work Pack 9 aims to develop an emerging process towards industrialisation it is essential to understand from the outset what the safety implications of the process are and where efforts need to be focused to understand further the risks which need to be mitigated through flowsheet design and engineering. This work package aims to study these requirements for both normal and mal-operations across the fuel cycle from head end dissolution through to powder formation for fuel manufacture.

MAIN RESULTS

TASK 9.2

MANPOWER

IRSN – 1.3 pm

MAIN PROGRESSES

TASK 9.2-A: PRELIMINARY HAZARD ANALYSIS FOCUSING ON CRITICALITY SAFETY

Subtask 1: Carrying out of an independent safety review based on the Euro-GANEX plant design and process flowsheet provided by NNL (WP8) “NNL Euro-GANEX flowsheet and process data” (PD06 - Deliverable 8.1 – NNL 14620 - version 1 issued on 06/15/2018).

This preliminary criticality safety review is almost finished but must take into account results obtained with the new density laws. Other hazards safety review is in progress.

This work is based upon IRSN’s knowledge and experience of reprocessing of FR MOX fuels in Marcoule and La Hague plants and is mainly focused on criticality safety. Nevertheless, besides criticality, areas/hazards for consideration, even to a greater or lesser extent, are also radiation protection, materials selection/corrosion, flammability and explosion, chemical compatibility, thermal stability/reactivity, radiolysis, radioactive decay heat and management of liquid and gaseous effluents. This work covers the operations from head-end section to co-conversion unit and considers the interface between each process step.

Depletion calculations have been performed for a realistic initial composition of MOX fuel and an Astrid reactor and post-processed. These results allow IRSN to compare the amount of U, Pu, Am and Cm of this calculation to the NNL Euro-GANEX flowsheet and process data. Based on these results (particularly the isotopic composition of U, Pu, Cm and Am), simple criticality calculations have been performed in order to determine minimal critical dimensions/properties (for example: cylinder diameter, plate thickness, amount of water, concentration) of different fissile media and have been compared with those of the fissile media encountered in La Hague plants to confirm the industrial applicability of the proposed control methods for the different

parts of the Euro-GANEX process. Some complementary calculations were done to evaluate the safety issues of some potential incidental situations in the chemical separations unit considering, in particular, the separation of actinides (for example, Cm from Am if chemically or physically credible).

Depletion calculations have been performed. Most of the criticality calculations, except those with new extractants and diluents, have been done and used in the criticality safety analysis. A preliminary draft of the safety review including criticality has been written but must be completed with criticality results obtained with new extractants and diluents and with other hazards review and then undergo an internal review

Subtask 2: Assessment of the compatibility of the process and potential technology with the flows of actinide material to be treated, taking into account the criticality constraints

IRSN has performed several depletion calculations for MOX fuel in fast reactors in order to estimate the isotopic composition of Am, Cm, Pu. In this part, the impact of the following hypothesis are studied: the initial composition of MOX fuel (in particular Pu/UPu, Pu isotopic composition, the eventual presence of Cm or Am) and the irradiation conditions (burn-up, depletion time). The results of all depletion calculations considering various initial compositions of MOX fuel will confirm conclusions of step 1 or the need of new criticality calculations (for example in case the Cm amount could be higher depending of the initial composition of MOX fuel). Depletion calculations have been performed and must be post-processed to extract the range of variation for each isotope of interest for criticality safety. Results have still to be introduced in deliverable 9.2.

TASK 9.2-B: CRITICALITY STUDIES (VERIFICATION OF THE BOUNDING NATURE OF WATER MODERATION WITH REGARD TO NEW EXTRACTANTS AND DILUENTS)

Subtask 2: Apply the previous methodology to the different Euro-GANEX solvents

Thanks to the help of the project partners, most data could be obtained. The bulk theoretical densities of the extractants and diluents could be retrieved for the three steps of the GANEX process. Measurements of these densities versus temperature allowed determining the behaviour versus temperature. In addition, some measurements of the mixtures with concentrations in fissile species corresponding to the specifications of the process were provided by the partners. It allowed IRSN verifying the validity of its volume additive laws in the concentration range of the process. IRSN has therefore established volume additive density laws in the concentration ranges of the Euro-GANEX process and compare criticality values with the ones obtained for water as a solvent.

The comparison of criticality standards for the different solvents versus water has been initiated showing that water is quite often conservative. However, it could not necessarily be the case for the solvents of step 2 without considering acidity. The report describing this task should follow.

ACTION PLAN

Task 9.2-a / Subtask 1: Finish the independent Euro-GANEX safety review based on NNL Euro-Ganex

Task 9.2-a / Subtask 2: Continuation of the post-processing of depletion calculations for FR MOX fuel and use it in deliverable 9.2

Task 9.2-b / Subtask 2: Finish to produce comparison of standard critical values with “new” density laws and density law of water (January 2021) to use it in deliverable 9.2

TASK 9.3

MANPOWER

ULanc – 6pm

MAIN PROGRESS

- Trans-1,2-diaminocyclohexane-N,N,N',N'-tetraaceticacid (CDTA) has been definitively shown to act a corrosion inhibitor under both normal and maloperational (> 1V) conditions. The ability for CDTA to extend the region of passivity and reduce transpassive currents can also been determined for solutions irradiated to a maximum absorbed gamma dose of 1.6 MGy.
- In tandem, stainless steel pieces irradiated in nitric acid and CDTA solutions of the concentrations appropriate for the EURO-GANEX 2nd cycle, showed a greater resistance to intergranular attack with the addition of CDTA, compared to nitric sans CDTA. This effect is most likely due to one or both or two effects.
 - a. CDTA is adsorbing at the steel surface, said adsorption providing a degree of protection to the Cr₂O₃ passivation layer, preventing oxidative attack.
 - b. The presence of CDTA may suppress nitrous acid production – either via providing a substrate that the nitrous participate with in nitrating reactions or by the provision of CDTA radical species during irradiation that interrupt nitrous production
- • It is important to note that this irradiation experiment was performed using an argon headspace. There is evidence in the literature that lack of O₂ will result in greater yields of highly corrosive species formed during the radiolytic breakdown of nitric acid.
- • The next gamma irradiation experiment will assess whether this corrosion inhibition holds, or is enhanced under oxic conditions
See ULanc HYPAR for full details.

ACTION PLAN

- Continuation of electrochemical corrosion assessment of stainless steels in GANEX inventory permutations.
- Continuation of electrochemical corrosion assessment of gamma irradiated solutions of CDTA, AHA and SO₃-Ph-BTP
- Continuation of surface analysis of 304L steel flags irradiated in acidic solutions of CDTA, AHA and SO₃-Ph-BTP

WP10

The objective of WP10 is to integrate the work done in GENIORS in a more global approach by creating synergies with other European and international initiatives and by involving the stakeholders. This is done via Clustering Events and Stakeholders Events.

MAIN RESULTS**TASK 10.1 CLUSTERING EVENTS****MANPOWER**

Globally on track.

MAIN PROGRESS

D10.2: Deliverable was written and finalized.

D10.3: Clustering Event “ATALANTE 2021” was defined and supposed to be organized in June 2021. However, due to Covid-19 pandemic, the conference was cancelled again.

D10.4: Clustering Event “Partitioning meets Conditioning” was defined. However, due to Covid-19 pandemic, organization of this event is problematic. Options were evaluated how to still organize this event.

DIFFICULTIES

D10.3 – Clustering Event “ATALANTE 2021” – cancelled due to Covid-19 pandemic.

D10.4 – Clustering Event “Partitioning meets Conditioning” – not (yet) planned nor organized due to Covid-19 pandemic.

ACTION PLAN

Re-evaluate options to organize two remaining Clustering Events (SCK CEN and CEA).

TASK 10.2 STAKEHOLDERS EVENTS**MAIN PROGRESS**

D10.5: Deliverable was written and finalized

DIFFICULTIES

D10.5: Deliverable was written and finalized

D10.6 – Stakeholders Event 2 – not (yet) planned due to Covid-19 pandemic.

ACTION PLAN

Re-evaluate options to organize the remaining Stakeholders Event (CEA).

CONCLUSIONS

Summary status of organizing Clustering/Stakeholders Events:

2 Clustering Events (D10.1 – “Partitioning meets Transmutation” and D10.2 – “INSPYRE summer school”) and 1 Stakeholders Event (D10.5 – “Partitioning meets Transmutation”) have been organized.

2 Clustering Events and 1 Stakeholders Event are still to be organized. Options for Clustering Events 3 (related to D10.3) and 4 (related to D10.4) and Stakeholders Event 2 (related to D10.6) need to be re-evaluated due to the current Covid-19 pandemic.

WP12

INTRODUCTION

This work package covers Training and Education and Knowledge Management. Work on the tasks has largely proceeded as planned.

MAIN RESULTS

TASK 12.1

MANPOWER

ULEEDS: 0.1pm

MAIN PROGRESSES

To date there have been 10 awards approved, six secondments and four travel bursaries, with a total value of €16190. However, due to travel restrictions in place, four of these awards are on hold, so the total amount spent is €11455. Therefore, €3810 remains for new awards.

Name	Institution	Project	Type	Place	Amount awarded	Comments
Ivan Sanchez Garcia	CIEMAT	Gas generation in TODGA-DMDHEMA/AHA-SO ₃ PhBTP systems	Secondment	NNL	€ 2,500	On hold - until end 2020/start 2021
Magdalena Rejnis-Strzelak	Institute of Nuclear Chemistry and Technology, Warsaw	TRLFS investigations on the Cm ³⁺ and Eu ³⁺ complexes with an SO ₃ -Ph-BTP4- ligand in aqueous HNO ₃ solutions	Secondment	KIT-INE	€ 1,780	On hold - possibly Spring 2021
Annalisa Ossola	Politecnico di Milano	Investigation on loading capability and speciation of PyTri-Diol under process conditions	Secondment	CEA	€ 2,500	Completed & report received
Daniel Theobald	University of Leeds	Computational Engineering for Nuclear Solvent Extraction Equipment	Travel bursary	Waste Management 2019, Phoenix, Arizona	€ 1,000	Completed & report received
Thea Lyseid Authen	Chalmers University of Technology	Process development of the Chalmers Ganex process	Travel bursary	Fifteenth NEA IEMPT, Manchester, UK	€ 982	Completed & report received
Thea Lyseid Authen	Chalmers University of Technology	Process development of the Chalmers Ganex process	Secondment	Forschungszentrum Jülich	€ 1,780	Completed & report received
Nigel Lucas	Edinburgh University	The Electrochemical Removal of Neutron Poisons from molten salts for applications in Gen IV nuclear reactors and nuclear waste recycling	Travel Bursary	Processes: Flow-sheets & Simulation Workshop, Milan, Nov 4-6 2019	€ 750	Completed & report received
Thea Lyseid Authen	Chalmers University of Technology	Process development of the Chalmers Ganex process	Secondment	Forschungszentrum Jülich	€ 1,533	Completed & report received
Maria Gallo	Universita di Parma		Secondment	CEA	€ 2,500	Unable to undertake due to Covid-19. May submit new proposal for Twente
Alex Fells	University of Leeds	Experimental validation of a computational fluid dynamics model of a pulsed sieve-plate extraction column.	Travel bursary	CEA	€ 865	Unable to undertake due to Covid-19 - may reschedule?
TOTAL so far					€ 16,190	
Remaining funds including on hold/postponed					€ 3,810	
Remaining funds excluding on hold/postponed					€ 8,545	

DIFFICULTIES

Travel restrictions due to Covid are preventing the funds from being used.

ACTION PLAN

Continue to encourage applications to the fund and consider alternatives.

TASK 12.2

This task is complete.

TASK 423

MANPOWER

ULEEDS: 0.10 pm

MAIN PROGRESSES

The course outline has been created and the script/content of the packages is being developed with Leeds Digital Education Service.

ACTION PLAN

Continue to develop the course script/content.

Produce draft package on PUREX by 31st January 2021.