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GENIORS

WPASR 5

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Summary

WPASR

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CONTENT

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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).

The total man power (pm) dedicated in WP1 to semester 1-5 is summarized in Table 1.

Partner	WP1 effort	HYPAR 1 realised	HYPAR2 realised	HYPAR3 realised	HYPAR4 realised	HYPAR5 realised
CEA	7.9	0	0	3	4	3
ICHTJ	9.00	0	1.2	3	1	4
JUELICH	9.80	0	1	2	2	1
KIT	5.90	1	0.25	0	0.3	1.25
TWENTE	1.8		180h (1)	270h (1.5)	300 (1.7)	218 (1.2)
UREAD	5.8	0	0	0	0	0
Total	**40.2**	**1**	**3.45**	**9.5**	**9**	**10.45**

Table 1: Manpower (in pm) devoted to WP1

MAIN RESULTS

TASK 1.1

MANPOWER

9.45 pm was realized this semester by CEA, ICHTJ, KIT and TWENTE. After 5 semester 87.1 % of efforts planned for the complete project (Task 1: 37.2 pm) were realized.

MAIN PROGRESSES

Extraction and speciation of Ruthenium (Comparison of solvent extraction systems) CEA

In current PUREX processes, ruthenium is known for its unusual behavior in solvent extraction scrubbing cycles. TODGA and MOEHA globally extract ruthenium in the same order of magnitude as TBP and clearly below a distribution ratio of 1 which promote the use of such solvent to separate ruthenium from uranium. Once ruthenium nitrosyl complexes are extracted into the organic phase, they are notably hard to remove in scrubbing stages at low nitric acid concentrations. Overall, the ruthenium extraction was studied for different extraction system showing all promising in means of ruthenium selectivity (low D_{Ru}). Nevertheless, the retention mechanism identified already for TBP is also evidenced for the other studied extracting molecule (TODGA-MOEHA). From the speciation

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analysis already reported, CEA described the similarity in the ruthenium extraction process for the three studies system. The ruthenium is extracted as a nitrosyl complex through H-bonds. Our latest experiment shows that nitrite ligand are also important because it may strongly interact with ruthenium complexes and are indeed affecting the ruthenium distribution ratio. This effect is one clue to explain the ruthenium retention mechanism but as already mentioned, there is still no fully satisfying explanation to explain the variation observed for DRu in the stripping steps.

Extraction studies of technetium into TODGA system (ICHTJ)

Solvent extraction separation of Am(III) from weight amounts of technetium(VII) (99TcO4–) was examined in the system with TODGA extractant, modelling the second cycle of EURO-GANEX process. Attempts to modify a known high-temperature method of reducing Tc(VII) to Tc(II) by acetohydroxamic acid (AHA) in HNO3 solutions [Czerwinski et al., 2008] were undertaken in order to alleviate the harsh conditions (4 M AHA, 95 °C) of this slow process of reduction, followed by formation of a non-extractable hydrophilic complex of Tc(II). A wide range of the parameters affecting the Tc(VII) reduction (AHA concentration, temperature and time) has been determined at various steps of the extractive separation. Unfortunately, the low but still non-equilibrium DTc values obtained in our tests are unattainable in fast counter-current processes carried out at moderate temperatures. Moreover, inability to separate the reduced Tc(II) from Np and Pu (both being also reduced by AHA to non-extractable forms) limits the developed method of separating Am(III) from Tc to systems with no Pu and Np, e.g. the raffinate from the advanced PUREX process. The method may also be used at an elevated temperature for technetium removal from uranium containing solvents in certain sections of the EURO-GANEX process.

C.M. Gong, W.W. Lukens, F. Poineau, K.R. Czerwinski (2008). Reduction of pertechnetate by acetohydroxamic acid: formation of [TcII(NO)(AHA)2(H2O)] and implementations for the UREX process. Inorg. Chem. 47, 6674–6680.

Sr(II) loading into TODGA dissolved in DIPB/octanol (KIT)

Sr(II) is less extracted with the DIPB-based solvent compared to the TPH/octanol based solvent; distribution ratios for non-loading conditions are lower by a factor of approximately 9. The Sr distribution data show a maximum at an initial HNO_3 concentration of ≈ 3 mol/L, as already observed with the 1-octanol/TPH diluent. For a TODGA concentration of 0.5 mol/L and HNO_3 concentrations greater than 0.7 mol/L, Sr(II) distribution ratios are greater than 1.

A simple slope analysis of the distribution data was performed. The slope of lg $D_{Sr(II)}$ vs. lg [TODGA] decreases from 4 (for 0.5 mol/L HNO_3) to ≈ 3 (for 1–2 mol/L HNO_3). The value of 2.3 (4.6 mol/L HNO_3) must not be stressed since the prerequisites for applying slope analysis are definitely not met for such conditions. Slopes significantly greater than three have also been observed for the extraction of Am(III) into TODGA in DIPB (1). This deviation from the spectroscopically verified formation of 1:3 complexes may be explained by outer sphere complexation by a fourth TODGA molecule. A similar mechanism may be assumed for the extraction of Sr(II) at lower nitric acid concentrations.

(1) Weßling, P.; Müllich, U.; Guerinoni, E.; Geist, A.; Panak, P. J., Application of aromatic TODGA solvents for An(III) and Ln(III) extraction requiring no modifier to suppress third phase formation. Hydrometallurgy 2019, (submitted).

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TASK 1.2

1 pm was realized this semester by JUELICH for writing the deliverable D1.2. The work devoted to Task 1.2 was realized within the fourth semester and is reported in WP3, since it relates more to solvent extraction chemistry. A modified DGA was recently proposed by the TWENTE group, in which of one or two methyl groups to the central methylene carbon atoms of the TODGA molecule leads to a reduction of the extraction efficiency for An(III) and Ln(III). The reduction in extraction efficiency leads to overall reduced distribution ratios of all tested metal ions, including some unwanted fission product such as Sr(II). The reduced Sr(II) extraction is beneficial as a co-extraction in a solvent extraction process could be avoided, while an efficient extraction of the desired An(III) and Ln(III) is still achieved. Furthermore, this might be a benefit, as the stripping behaviour might be improved, even at moderate nitric acid concentrations. A systematic investigation on the extraction behaviour of the different diastereomeric forms of mTDDGA was carried out. Beside the extraction of actinides and lanthanides also the non-lanthanide fission products were in the focus of this research. The behaviour of fission products in this modified DGA system is reported in D1.2: Identification of optimized conditions for effecter fission product masking/ scrubbing.

LIST OF PUBLICATIONS

T. Dirks, T. Dumas, P. L. Solari, and M.-C. Charbonnel, Ruthenium nitrosyl structure in solvent extraction systems: A comparison of tributyl phosphate (TBP), tetrabutyl urea (TBU), N-methyl, N-octyl ethylhexanamide (MOEHA) and N, N, N', N' tetraoctyldiglycolamide (TODGA), Ind. Eng. Chem. Res., Just Accepted Manuscript • DOI: 10.1021/acs.iecr.9b02555 • Publication Date (Web): 18 Jul 2019.

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

M. Rejnis-Strzelak, I. Herdzik-Koniecko, J. Narbutt, Attempts to isolate technetium in the process of separating actinides from spent nuclear fuel (in Polish). Poster S16 P10, 62nd Meeting of the Polish Chemical Society, Warsaw, September 2-6, 2019; Abstracts, p. S16-25.

Weßling, P.; Müllich, U.; Guerinoni, E.; Geist, A.; Panak, P. J., Application of aromatic TODGA solvents for An(III) and Ln(III) extraction requiring no modifier to suppress third phase formation. Hydrometallurgy 2019, (submitted).

CONCLUSIONS

Since the start of the GENIORS project most of 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 initiated by Jülich and further results will be reported in HYPAR6. The deliverable D1.2 was finalized too.

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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 loses 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

5.7 mp (1.8 pm CTU, 2.7 pm IIC, 0.2 pm CIEMAT and 1 pm Juelich) were reported this semester.

MAIN PROGRESSES

Stability studies of BTBP and BTPhen:

During this semester, it has been continued the stability studies $CyMe_4$-BTBP and $CyMe_4$-BTPhen in fluorinated diluent by CTU. The systems for Am(III) and Cm(III) extraction based on $CyMe_4$-BTBP and $CyMe_4$-BTPhen in fluorinated diluent BK1 were evaluated for their stability against gamma radiation taking into account the contact with an 1 mol/L HNO_3 aqueous phase. For both systems, the presence of HNO_3 during irradiation improved their radiation stability. $CyMe_4$-BTPhen was found to be significantly less stable than $CyMe_4$-BTBP, however, the degradation compounds/adducts formed extract Am(III) and Cm(III) to a certain extent. In general, the trends observed for Am/Cm separation factors were similar to those observed earlier for the Am(III) and Eu(III) extraction.

IIC has continued with the analysis and isolation of degradation products from the irradiated samples of $CyMe_4$-BTBP at Chalmers facilities and Czech Technical University. The previously pre-separated fractions from large irradiated samples of Ganex solvent (70% FS-13, 30% TBP, 1200 kGy), octanol+TBP (300 kGy) at Chalmers were used. Additionally, new pre-separations were performed for the sample in FS-13 (700 kGy). A new semi-preparative HPLC method was developed and its performance was verified on the all three series of samples, inclusive recovery of solid degradation compounds (DCs) from aqueous buffer. MS and ^{1}H NMR spectra of collected fractions were recorded for a better identification, though still persists some uncertainty about concrete structures.

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In the case of irradiated samples from Czech Technical University, the analyses of 1.0 mM $CyMe_4$-BTBP and $CyMe_4$-BTPhen in new fluorinated BK-1 solvent showed a fast degradation of the molecule even at low doses. Several degradation products were also identified. Good insight into composition of degradation product could be gained from application of tandem LC-MS method.

Stability studies of diglycolamides:

- *TODGA-based systems:*

Ongoing activities about relevant-process conditions to simulate the degradation of a full Euro-GANEX system (TODGA-DMDOHEMA/AHA-SO_3PhBTP) have been performed by CIEMAT and reported in WP5, therefore the quantitative analysis by HPLC-MS of TODGA DCs is discussed there.

- *mTDDGA :*

The radiolysis of mTDDGA was further studied and has been continued as part of Juelich-SCK•CEN collaboration. It was found that mTDDGA shows a slightly lower dose constant (*d*) than TODGA, i.e. mTDDGA is slightly more stable than TODGA against radiolysis. Compared to TODGA, mTDDGA shows a slightly lower dose constant. This observation is in line with what could be expected from the results of previous work of Galán et al. [[i]] in which double methylated TODGA derivates showed a lower dose constant. Additionally, the increase in *d* value for samples in contact with 2.5 mol/L HNO_3 solution reported previously was not observed here, but remained almost constant. Radiolysis products were identified and semi-quantified. And in general the findings above agree with previous experimental results studies [i, [ii],[iii]] on the radiolysis of similar diglycolamide.

The diastereochemically pure cis-mTDDGA was also studied, results are still pending.

Stability studies of stripping or masking agents:

Ongoing activities to analyse quantitatively the degraded aqueous phases containing AHA or SO_3-Ph-BTP by HPLC-MS and spectroscopies techniques are under progress at CIEMAT.

SO_3PhBTP:

Ongoing activities about relevant-process conditions to simulate the degradation of a full Euro-GANEX system (TODGA-DMDOHEMA/AHA-SO_3PhBTP) have been performed by CIEMAT and reported in WP5. Therefore the quantitative analysis of AHA as a function of time of the stability studies and the estimation of SO_3PhBTP concentration as function of the dose (by the correlation between D_{Am} values) is reported there.

SO_3BTPhen:

Extraction systems for *i*-SANEX process with the masking agent SO_3BTPhen in aqueous phase, to suppress Am(III) and Cm(III) extraction into TODGA solution, were tested for their behaviour under irradiation (doses up to 300 kGy) under different nitric acid concentrations by CTU. The trend in $SF_{Cm/Am}$ values was similar to the trend of values of $SF_{Eu/Am}$ reported in the previous HYPAR4, i.e. a gradual

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decrease of the separation factors with increasing dose was observed. Up tp 100 kGy and 200 kGy, the values of D_{Cm} remain almost the same for 0.25 mol/L HNO_3. Significant changes in all D values were observed at the absorbed dose of 300 kGy.

DIFFICULTIES

No major difficulties have been reported, although there were some delays affecting to task1:

- Technical problems with HPLC-MS equipment and the provision of TODGA necessary for the abovementioned tests (POLIMI).
- No DCs or adducts of BTBP neither BTPhen available for experiments yet (CTU).
- Extensive decommissioning and refurbishment of UREAD synthetic laboratory that has lasted 3.5 months causing delays in moving to our new refurbished lab prolonging our recommencement of work (UREAD).

ACTION PLAN

CIEMAT: Ongoing activities to perform quantitative studies of degraded aqueous phases containing AHA or SO_3PhBTP by HPLC-MS and spectroscopies technics. To compare the dose rate apply in the gamma irradiation facilities at CIEMAT and SCK.CEM. Ongoing activities regarding realistic stability studies of CDTA aqueous phases

CTU: Studies of the temperature dependence of the radiation degradation for both *r*-SANEX and *i*-SANEX extraction systems.

IIC: The work on separation of DCs from their mixtures by HPLC and identification of their structures by NMR and other methods will be continued, particularly a larger scale separations will be performed with recovery of larger amounts of pure DCs for NMR and crystallization- possible X-ray characterizations. The sample irradiated in neat FS-13, where separations have been more demanding due to interferences with solvent peak and deeper degradation will be studied in more details. However, for this new amount of irradiated sample will be needed.

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, as well as some liquid-liquid extraction tests.

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

UREAD: LCMS of the irradiated samples, full analysis of the irradiated samples by NMR. Synthesis of the degradation adducts. Synthesis of $CyMe_4$-BTBP for CTU.

TASK 2.2 DESTRUCTION OF ORGANIC (TASK LEADER: CEA)

MANPOWER

2 pm realized this semester (2 pm CEA).

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MAIN PROGRESSES

Thermal decomposition of organic phases in contact with nitric acid at high acidity and high temperature has been studied by TSU calorimeter (non-adiabatic calorimeter) to evaluate the reactivity of chemical systems during the concentration operations for the recovery of nitric acid in nuclear fuel reprocessing plants. The influence of γ-radiolysis of TODGA solutions has been also considered.

- The reactivity of TODGA solutions in TPH is higher than neat TODGA, behaviour already seen with other extractants as TBP. The presence of TPH and also octanol lead to lower reaction start-up temperatures.
- All the degraded solutions of TODGA in TPH have the same behaviour as the non-irradiated solutions. An irradiation dose up to 600 kGy has no impact on the reactivity of the 0.1 or 0.2 mol/L TODGA solutions in TPH equilibrated with 2.5 mol/L HNO_3.
- On the contrary, with neat TODGA equilibrated with 11 M nitric acid a decrease in reactivity has been measured after irradiation. This decrease in reactivity could be explained by the decrease of the concentration of the amide function in favor of less reactive functions with regard to nitric acid, and/or to a loss of potential energy of the chemical system due to the breaking of chemical bonds by radiolysis or hydrolysis. Nevertheless, these hypotheses have to be checked by more detailed studies.

To obtain thermokinetics data of the reaction experiments were also realized with neat TODGA in contact with nitric acid at different concentrations.

- The enthalpy of the reaction increases 3 times for TODGA compared with TBP, which could come from the fact that the TODGA molecule has 3 times more carbons than TBP, each carbon can produce energy by reacting with nitric acid to form CO_2. Further investigations on the final composition could be performed to better explain the behavior.
- The acidity has also an influence on the activation energy, the pre-exponential factor, and on the reaction rate characterized by the rate of rise in temperature and pressure.
- The rates in temperature and pressure increase also quasi-linearly with the quantity of introduced TODGA

ACTION PLAN

CEA: Residual aqueous phase and gas phase analyses are planned to determine an overall apparent stoichiometry of the decomposition reaction of TODGA by nitric acid.

TASK 2.3 GAS GENERATION (TASK LEADER: POLIMI)

MANPOWER

0 pm were realized this semester.

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MAIN PROGRESSES

D.4 Impacts on process safety of gas generation has been prepared and it is currently under review.

There was no additional experimental work.

DIFFICULTIES

No major difficulties have been reported, although there were some delays affecting to task3:

- Stability studies as part of NNL-CIEMAT collaboration were delayed.

TASK 2.4 RADIOLYSIS MODELLING (TASK LEADER: CTU)

MANPOWER

2 pm realized this semester (1.5 pm CTU and 0.5 pm Juelich).

MAIN PROGRESSES

Modelling studies of the radiolysis of lipophilic diglycolamides: (0.5 pm, Juelich)

The radiolysis mechanism of TODGA and mTDDGA is being further studied using computational methods to enhance the fundamental understanding. For that density functional theory (DFT) calculations with the PBE functional were conducted to obtain reaction profiles for hydrogen abstraction mechanism as main hydrolysis pathway.

Initially, gas phase entropy terms were employed to come to this result. This led to similar results as shown in literature, with decreasing Gibbs free energies for every reaction step. At the moment, work is being done to implement liquid phase entropy [iv] terms into these calculation. This might have a great influence on the simulated reaction, since the second step is only favourable because of the increase in entropy (which is most pronounced for the gas phase). Energy calculations of the transition states will be attempted with nudged elastic band (NEB) simulations.

Modelling studies of the radiolysis of water soluble diglycolamides: (1.5 pm, CTU)

The theoretical study of TMDGA, TEDGA, Me-TEDGA, and Me2-TEDGA dissolved in water has been continued along the two planned pathways: (i) ab-initio QM simulations by DFT method and (ii) conformational analysis by MD followed by statistical analysis of the obtained trajectories.

As for lipophilic DGA, an indirect radiolysis route is assumed with the main cause of degradation reactions assigned to the chemical interaction between the ligand and free radicals, in this case •OH or H• created through radiolysis of surrounding water molecules.

Detailed DFT simulations of degradation reaction pathways have been performed on set of models including alternative nitric acid representations. Analysis of the obtained result is currently in progress.

Conformational analysis of DGA derivatives in aqueous solutions performed by classical simulation methods is under progress. The theoretical analysis is running focused on the links between the selected statistical conformational indicators, MD simulation parameters and settings, the

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intramolecular bonds electronic properties, and the analyzed molecular bonds energetics in solution. The results will be summarized in the next ordinary report.

ACTION PLAN

D2.5 Molecular modelling of particular degradation mechanism of extracting and complexing agents (31-5-2020, CTU).

CTU: a) Analysis of the obtained DFT results followed by their discussion and comparison with available experimental data. Estimation and discussion of statistical significance of the obtained theoretical figures of merit (stability indicators, energy values related to analysed reaction kinetics) with respect to the applied theory level. b) Completion of MD calculations providing the trajectories of the investigated ensembles in the conformation space suitable for further statistical analysis. Launch of the analysis performed by means of the improved evaluation SW code. Continuation of the quest focused on the theoretical interpretation of the obtained conformation data.

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

LIST OF PUBLICATIONS

Publications :

1. I. Sánchez-García, H. Galán, J. M. Perlado and J. Cobos. Stability studies of GANEX system under different irradiation conditions." *EPJ Nuclear Sci. Techno*, **2019**, 5, 19.
2. A. Afsar, P. Distler, L. M. Harwood, J. John, J. S. Babra, Z.Y. Selfe, J. Cowell, J. Westwood. Separation of minor actinides from lanthanides using immobilized ligand systems: the role of the counterion. *Heterocycles*, **2019**, 99(2), str. 825–833.
3. P. Distler, K. Stamberg, J. John, L. M. Harwood, F. W. Lewis. Thermodynamic Parameters of Am(III), Cm(III) and Eu(III) Extraction by CyMe4-BTPhen in Cyclohexanone from HNO_3 Solutions. *The Journal of Chemical Thermodynamics*, **2019**. DOI: 10.1016/j.jct.2019.105955.
4. G. Horne, A. Wilden, et al. *Dalton Trans*. **2019**, 48, 17005–17013, DOI: 10.1039/C9DT03918J.

Conferences:

Oral communications:

1. Hitos Galán, Ana Núñez, Iván Sánchez, Joaquín Cobos. "Aspectos radiolíticos que afectan al desarrollo del reprocesado del combustible nuclear" SNE 2019 (Spanish Nuclear Society), September 2019, Vigo, Spain.

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CONCLUSIONS

After 30 months of GENIORS project it has been reached 94.8 (+10 synthesis) pm of the 107 pm dedicated to WP2. In general it can be reported a more than optimal development of WP2 activities, particularly this semester has been reported 9.7 pm distributed between task1, task2 and task 4, since activities about task3 have been completed. Nevertheless it should be mentioned that it has been a delay in the supplying of degradation compounds.

D.2.2 Stability studies of stripping agents is already finished and *D2.4 Impacts on process safety of gas generation is under review*; however, *D2.3 Destruction of organic* has been postponed to 2020-5-31 to allow some partners finish the activities related to. *D2.5 Molecular modelling of particular degradation mechanism of extracting and complexing agents* should be prepared in the following semester.

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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.

	HYPAR					Total Realized	
	1	2	3	4	**5**	(pm)	(%)
CEA	0	4	7	6	0	17	142.86%
CIEMAT	1.5	1.5	1	1	1.25	6.25	49.21%
CNRS	0	0	4.75	2.2	0.3	7.25	120.83%
ICHTJ	3.5	4.6	9	7.45	3.4	27.95	66.55%
JUELICH	0	0	3.9	1.8	0	5.7	64.77%
KIT	6	1.25	1.6	1.7	2.5	13.05	63.35%
NNL	0.4	0.1	0.88	1.14	0.2	2.72	55.51%
POLIMI	2	7	9.5	6	1.5	26	127.45%
UNIPR	2	2	3	2	2	11	83.97%
TOTAL	15.4	20.45	40.63	29.29	11.15	116.92	83.28%

MAIN RESULTS

TASK 3.1 OPTIMISATION OF SYSTEMS (TASK LEADER: POLIMI)

MANPOWER

3.3 pm realized this semester (CNRS, POLIMI, UNIPR).

61.85 pm realized since the beginning of the project, corresponding to 79.3 % of the 78 pm planned for the complete project.

MAIN PROGRESSES

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- New batches of PTD were produced. Two samples were sent to CEA: 1) for kinetic measurements under Euro-Ganex conditions with mTDDGA behaviour; and 2) for calorimetric studies of lanthanide and Americium salts.
- 2.57 g of PTEH was synthesised
- The analysis of all the data and spectra obtained by means of TRLFS, ESI-MS and NMR investigations on PTEH solutions was completed:
- Preliminary studies were performed by Electrospray Ionization Mass Spectrometry to qualitatively investigate PTEH complexes with La(III) and Eu(III) metal cations.
- The ligand speciation and the complexation mechanism with Cm(III) and Eu(III) by TRLFS experiments.
- NMR investigations were performed titrating $Ln(NO_3)_3$ salts. This confirms that the aromatic coordinating core is the most sensitive part of the PTEH structure towards metal cations.
- Studies have been performed in order to assess the purity level easily achievable during the synthetic procedure and high enough to guarantee the complexation performances of PTD in the process.

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

MANPOWER

5.9 pm realized (KIT, ICHTJ)

20.65 pm realized since the beginning of the project, corresponding to 151.8 % of the

13.6 pm planned for the complete project.

MAIN PROGRESSES

- Extraction of HNO_3 and Am(III) into a TODGA-diisopropyl benzene (DIPB) solvent was continued (distribution ratios as function of HNO_3 and TODGA concentrations)
- In some solvent extraction systems, heteroleptic complexes of certain metals are formed, containing two different ligands that compete for the metal cation: a lipophilic extractant and a hydrophilic stripping agent. The presence of these lipophilic complexes in the organic phase worsens the effectivity of separation of metals by selective stripping of that which forms such heteroleptic complex. In order to better understand this phenomenon we studied solvent extraction of Am(III) and Eu(III) in the model system containing a tripodal-DGA (T-DGA) extractant in 1-octanol solution and a hydrophilic stripping agent SO_3-Ph-BTP in aqueous phase: 0.3 M HNO_3 + 0.7 M $NaNO_3$. Previously, we concluded on the existence of heteroleptic complexes, $M(T\text{-}DGA)(SO_3\text{-}Ph\text{-}BTP)^-$, in the organic phase of this system. Preliminary analysis of the dependences of the distribution ratios of the metals on the concentrations of T-DGA (0.02, 0.04 M and preliminary data for 0.062 M) and of SO_3-Ph-BTP ($5\cdot10^{-6}$ to $4\cdot10^{-2}$ M) indicates for significant differences in the stability of these heteroleptic

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complexes, depending on the concentration of T-DGA. A hypothesis has been put forward to explain these differences.

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

MANPOWER

0.5 pm realized (POLIMI)

24.45 pm realized since the beginning of the project, corresponding to 71.9 % of the 34 pm planned for the complete project.

MAIN PROGRESSES

The studies on the possible solubility (in the aqueous phase) of the species formed when cations are complexed by PTEH have been continued taking into account the speciation results obtained in task 3.1.

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

MANPOWER

1.45 pm realized (CIEMAT NNL)

pm realized since the beginning of the project, corresponding to 46.4 % of the 21.5 pm planned for the complete project.

MAIN PROGRESSES

The radiation dose model has been developed and presented at GENIORS/DOE radiation chemistry meeting in France. The model can now be used to look at effects of dose from future spent fuels on solvents used in GENIORS processes and implications for solvent degradation, clean up and recycling

Ongoing activities about the influence and clean-up of TODGA detrimental DCs:

- Influence of detrimental DCs (2-hydroxy-N,N-dioctylacetamide, XII (DOHyA); N,Ndioctyl acetamide, XIII (DOAA)) on the extraction of Ln/An/FP of TODGA systems.
- Review of boiling point range of compounds present in a degraded TODGA- based solvent.

DIFFICULTIES

The secondment of Ivan Sanchez-Garcia from CIEMAT to NNL was long delayed due to administrative issues at CIEMAT. His security clearance has to be re- established before NNL can proceed further.

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ACTION PLAN

NNL & CIEMAT are in regular discussions to try and resolve this issue.

LIST OF PUBLICATIONS

Publications:

1. Weßling, P.; Trumm, M.; Macerata, E.; Ossola A.; Mossini E.; Gullo, M. C.; Arduini, A.; Casnati, A.; Mariani M.; Adam, C.; Geist, A.; Panak, P. J. Activation of the Aromatic Core of 3,3'-(Pyridine2,6-diylbis(1H- 1,2,3-triazole- 4,1-diyl))bis(propan-1-ol) - Effects on Extraction Performance, Stability Constants, and Basicity Inorg. Chem. 2019, 58 (21), 14642-14651.
2. Weßling, P.; Müllich, U.; Guerinoni, E.; Geist, A.; Panak, P. J., Application of aromatic TODGA solvents for An(III) and Ln(III) extraction requiring no modifier to suppress third phase formation (submitted).
3. 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 (submitted).
4. J. Narbutt, "Solvent Extraction for Nuclear Power", Chapter 24 (invited) in: *Handbooks of Separation Science: Liquid-Phase Extraction*, (C.F. Poole, Ed.). Elsevier, 2019, pp. 725-744.
5. Ł. Steczek, J. Narbutt, M.-Ch. Charbonnel, P. Moisy: "Solvent extraction investigations on Pu(IV) and Th(IV) complexes with hydrophilic SO_3-Ph-BTP and SO_3-Ph-BTBP ligands", *Solv. Extr. Ion Exch*., 37, 259-268 (2019). DOI: 10.1080/07366299.2019.1639366.
6. L. Klass, A. Wilden, F. Kreft, C. Wagner, A. Geist, P. J. Panak, I. Herdzik-Koniecko, J. Narbutt, G. Modolo, Evaluation of the hydrophilic complexant *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) and its methyl- substituted analogues in the selective Am(III) separation. *Solvent Extr. Ion Exch.*, 37, 297-312 (2019). DOI:10.1080/07366299.2019.1651039

CONFERENCES:

1. J. Narbutt, Solvent extraction of americium from spent nuclear fuel and closing the fuel cycle - new perspectives for development of nuclear energy (in Polish). Section lecture S16 WS03, 62nd Meeting of the Polish Chemical Society, Warsaw, September 2-6, 2019; Abstracts, p. S16-6
2. Gullo, M.C.; Ossola, A.; Mossini, E.; Arduini, A.; Sansone, F.; Scaravaggi, S.; Boubals, N.; Charbonnel, M.C.; Mariani, M.; Macerata, E.; Casnati A.: Poster at the International School on Organic Synthesis A. Corbella ISOS 2019, Gargnano (Bs), Italy, 9th-14th June 2019: "Pyridine2,6-bis(1H-1,2,3-triazol-4-yl): a selective chelating unit for Minor Actinide extraction from radioactive wastes".
3. P. Kowalski et al. E-MRS Fall Meeting and Exhibit, Warsaw, Poland, 16-19 September 2019, conference presentation.
4. A. Wilden et al. GDCh Wissenschafsforum Chemie, Aachen, Germany, 15-18 September 2019, poster presentation

CONCLUSIONS

All of the actions in this workpackage are going on as planned.

After 30 months, 116.92 pm have been realized within WP3, corresponding to 79.5 % of the

147.1 pm planned for the complete project.

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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	WPASR 2	WPASR 3	WPASR 4	WPASR 5
CNRS/ICSM	38.5	1.6	2.2	7.7	8.4	9.9
CEA	15.4	0.0	3.0	3.0	1.0	6.0
SCK.CEN	20.0	2.5	2.5	2.5	2.5	2.5
UNIMAN	11.0	0.0	0.0	6.0	6.0	0.0
Total	**84.9**	**4.1**	**7.7**	**19.2**	**17.9**	**18.4**

MAIN RESULTS

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

MANPOWER

4.6 pm (CNRS) – 6 pm (CEA) ⇒ Total : 10.6 pm

MAIN PROGRESSES

Three main actions have been developed in the field of task T4.1.

Multiparametric study of the dissolution of $(U,Ce)O_2$ and $(U,Ln)O_{2-x}$ solid solutions – CNRS/ICSM

In order to develop the multiparametric dissolution tests, the preparation then characterization of a large defined panel of uranium-lanthanide solid solutions was performed since 2018. Several kinds of powdered and sintered samples were prepared with this aim.

In order to study the impact of the lanthanide mole loading on the chemical durability of $U_{1-x}Nd_xO_{2-y}$, $U_{1-x}Gd_xO_{2-y}$ and $U_{1-x}Ce_xO_2$, several dissolution tests were performed in static conditions in 2 $mol.L^{-1}$ HNO_3 at room temperature (or at 60°C) for few days. During this time, aliquots were regularly taken off and then the elemental release in solution were analyzed.

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For homogeneous $U_{1-x}Ce_xO_2$ samples, uranium and cerium were released almost congruently during all the dissolution tests. Indeed, at room temperature, the evolution of all the normalized mass losses exhibited a similar behavior with a two-steps evolution. The first one was associated to surface driving reactions. During the second step (catalyzed controlling mechanism), the evolution of the standardized mass loss then became non linear, and corresponded to the fast release of the cations in solution. At room temperature, the normalized dissolution rates obtained for uranium-lanthanide solid solutions were found to be higher than for the pure end members, with slight variations versus the chemical composition. When making the dissolution tests at higher temperature (i.e. 60°C), the first step was not observed anymore. At this temperature, the full dissolution of the materials was obtained after less than 15 minutes, with a significant decrease of the normalized dissolution rates when incorporating lanthanide elements in the materials.

For heterogeneous sintered samples, the dissolution became uncongruent, with a preferential release of cerium compared to uranium, surely due to the presence of Ce(III) in the prepared pellets. Simultaneously, the chemical durability of the samples was decreasing compared to homogeneous samples. Additionally, the duration of the induction period was shortened and then the samples were dissolved more rapidly.

Innovative dissolution routes for highly plutonium doped $(U,Pu)O_2$ and $(U,Pu,MA)O_2$ samples – CEA

Two different populations of particles were obtained after grinding CeO_2 samples. Their characterization (STEM ad EELS) highlighted the presence of dislocations in the initial platelet fragments and of nanoparticles partly reduced (i.e. presence of Ce^{3+}). The core of the nanoparticles was composed by Ce^{4+} while the shell revealed the presence of Ce^{3+} (which could be responsible for the increase of the dissolution kinetics). The samples were thus submitted to multiparametric dissolution tests, varying the milling time, the grinding energy, the time of residence in the grinding chamber. The increase of the grinding time led to that of the dissolution rate, with a greater effect on the first stage of dissolution (and surely due to the presence of more nanoparticles). The first stage was assigned to the presence of Ce^{3+} in the material. Other experiments keeping constant the grinding energy with extending grinding time or residence time showed an impact on the material (i.e; on the SSA value). However, the dissolution obtained after 1400 minutes were found to be of the same order of magnitude.

Dissolution and leaching investigations on CeO_2 and UO_2 – UNIMAN

A reproducible method for the preparation of micron-thick film spent nuclear fuel (SNF) model was developed. “Virgin” (20% MOX) and “spent” (80 GWd/tU burnup MOX) MO_2 SNF models, adapted from the GENIORS SFR SNF composition have been successfully prepared. Four “core” chemistries have been explored with various surrogates for uranium and plutonium : pure cerium compounds (Ce = U & Pu); cerium-thorium compounds (Ce = U, Th = Pu); uranium-cerium compounds (U = U, Ce = Pu); and uranium-thorium compounds (U = U, Th = Pu). The “virgin” derivatives contained 80% of primary and 20% of secondary metals whereas the “spent” derivatives contained 73% of primary metal, 12% of secondary metal and a variety of simulated FPs, MAs, and metallic ε-particles. These samples were prepared at high temperatures and under reducing atmosphere (Ar + 5% H_2). The full samples matrix

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has been subjected to 100 kGy γ-irradiation at DCF, and the Ce matrix to up to 200 kGy α-irradiation. Dissolution studies will be undertaken upon completion of characterization (XRD, SEM, TRLFS, XAFS/XANES). Leaching and dissolution studies of U- and Th-bearing samples will be investigated under simulated SNF storage conditions. *However, it is important to mention that additional dissolution tests should be developed in more aggressive media, representative of reprocessing steps.*

DIFFICULTIES

The primary challenges encountered thus far have stemmed from the difficulty in adaption of thin film (nm-thick) oxide preparation PAD methods to micron-thickness for generation of controllable high-quality crack-free films. Through incorporation of a PAD template with drop-casting of the metal precursor and desired dopants, controlled evaporation and low-temperature calcination, we are able to reproducibly prepare high-quality films of desired phase and approximately 5 micron thickness. Secondary challenges in transferring the developed techniques to the UO_2 system were encountered due to the closure of the active laboratories at the University's School of Chemistry for refurbishment and delays in acquiring and approval of new laboratory space for active work to proceed. This has now been addressed and active work has commenced. U- and Th- containing samples have been prepared based on the previous method. Some challenges have been encountered in the availability of XPS, XANES and EXAFS techniques due to movement of analytical equipment and personnel within the university, and the necessary containment requirements for handling radioactive materials.

ACTION PLAN

CNRS/ICSM: Dissolution tests were developed on various powdered and sintered samples of $U_{1-x}Nd_xO_{2-y}$, $U_{1-x}Gd_xO_{2-y}$ and $U_{1-x}Ce_xO_2$ solid solutions in 2 mol.L^{-1} HNO_3 at room temperature and 60°C. They will be completed during the next semester. Complementary operando experiments will be monitored by ESEM in order to underline the preponderant mechanism occurring at the interface during dissolution tests.

CEA: The study of the effect of the energy of grinding on dissolution linked to the quantity of crystalline defects brought by the grinding step will be continued. The mechanisms associated to the enhancement of the dissolution kinetics (i.e. the individual role of Ce^{3+}, on the one hand, and of dislocations, on the other hand) will be elucidated. Additional experiments coupling dissolution and grinding will be also carried out.

UNIMAN: Leaching/dissolution studies of the U- and Th- containing samples are to be investigated under simulated SNF storage conditions, as previously described. Irradiation studies are ongoing at DCF. The described sample matrix has been exposed to 100 kGy of γ irradiation, and α irradiation is pending, awaiting upgrades to the accelerator at DCF.

Complementary dissolution tests should have to be performed in more aggressive conditions to be more representative of reprocessing processes.

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LIST OF PUBLICATIONS

Int. Conference Oral:

New insights in the description of the dissolution of actinide dioxides : better understanding for their reprocessing, N. Dacheux, INSPYRE First Summer School, Delft, 13-17 mai, 2019 / *Given*

Contribution of the coupling milling / dissolution on the dissolution of oxides, J. Hidalgo, P. Roussel, T. Delahaye, G. Leturcq, J.L. Rouviere, EMRS Spring Meeting 2019, Nice, 27-31 mai 2019 / *Given*

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

MANPOWER

5.3 pm (CNRS/ICSM) + 2.5 pm (SCK.CEN) ⇒ Total : 7.8 pm

MAIN PROGRESSES

Four main actions have been developed in the field of task T4.2.

Studies of non-powder routes for the synthesis of MOX fuels materials, potentially bearing minor actinides and blanket fuel materials – SCK.CEN

U/Ce particle fabrication via internal gelation. The ammonium diuranate (ADU) microspheres, prepared via internal gelation, undergo a thermal treatment to form the desired product. Firstly, a calcination in air is carried out, within this step, the ADU releases water and ammonia, followed by a conversion via UO_3 to α-U_3O_8. A second thermal treatment step in a reducing environment leads to the desired UO_2 or $U_{1-y}Ce_yO_{2\pm x}$ as final product.

For un-doped material, a detailed investigation of the reactions occurring during the calcination was carried out. ADU microspheres prepared by internal gelation were compared to ADU powder prepared by a typical ammonium diuranate precipitation reaction. The samples could be assigned to $3UO_3{\cdot}2NH_3{\cdot}4H_2O$ (microspheres) and $3UO_3{\cdot}NH_3{\cdot}5H_2O$ (powder). A combination of simultaneous thermal analysis, evolved gas analysis and non-ambient XRD techniques was used to characterize and investigate the thermal decomposition behavior. The results were partially described in previous *Half Yearly Partner Activity Reports* and were now summarized in a manuscript, entitled "*The conversion of ammonium uranate prepared via sol-gel synthesis into uranium oxides*", which was recently accepted for publication in *Nuclear Engineering and Technology* (doi: 10.1016/j.net.2019.11.004, open access, license: CC BY-NC-ND). The outcome of this study and the resulting data serve as reference for the thermal treatment of Ce-doped microspheres, prepared by internal gelation. The data-set was published individually and is available for download from the repository *Zenodo* (doi: 10.5281/zenodo.3250894, open access, license: CC BY-NC-SA). A further manuscript about the synthesis of Ce-doped material by internal gelation, using Ce^{III} and Ce^{IV} as dopant precursors, which

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was also described in previous *Half Yearly Partner Activity Reports*, is currently in preparation. The paper focusses on the influence of the dopant precursors' oxidation state. Additionally, a comparison of Ce and Nd as dopant is carried out.

There was also some practical work carried out within this reporting period. The thermal decomposition of the hydrolysis precipitates, introduced in *HYPAR4*, was studied using TG-DSC and EGA-MS analyses. The processing of the resulting data is currently ongoing and a submission of the outcome in two individual manuscripts is envisaged, one dealing on the hydrolysis precipitation itself, and a second one on the thermal decomposition in air, as well as a comparison to the thermal decomposition of the un-doped and doped ADU microspheres prepared by internal gelation.

Moreover, an *in-situ* high-temperature scanning electron microscopy (HT-SEM) study of un-doped and 10 % doped ADU microspheres, prepared by internal gelation, was carried out in collaboration with the *Laboratory for the Study of Matter in Environmental Conditions* at the *Institut de Chimie Séparative de Marcoule* (ICSM). HT-SEM analyses of the samples synthesized at SCK•CEN were performed simulating both mentioned steps of the thermal treatment. The aims were to monitor pore formations and a possible phase segregation for the doped material during the calcination, while the growth of crystals was of interest during the sintering step. Additionally, the shrinkage of the microspheres during the individual treatment steps, and the formation of (partially temporary) cracks on the particles surface, could be observed.

Hydrothermal precipitation of uranium oxides for simplified fuel fabrication – CNRS/ICSM

The direct precipitation of uranium oxides has been undertaken under hydrothermal conditions through the *in situ* conversion of uranium oxalate. Below 180°C, $U(C_2O_4)_2.nH_2O$ was formed whereas $UO_{2+x}.nH_2O$ was prepared above this temperature. Moreover, HERFD-XANES showed that the O/U stoichiometry was affected by the temperature and typically ranged from 2.4 up to 210°C to 2.1 between 220 and 250°C. SEM observations revealed the loss of the classical square platelet shape of the oxalate, while the evaluation of the residual carbon and water contents led to values significantly lower than that usually obtained through thermal conversion. Additionally, the pH control allowed to optimize the uranium precipitation yield and to orientate the morphology towards agglomerated microspheres. From the multiparametric study of the hydrothermal conversion, crystalline $UO_{2+x}.nH_2O$ samples were obtained after only 1 hour of heat treatment at 250°C (5 hours being necessary to improve the crystallinity of the powders). Nevertheless, the samples obtained after 1h were found to be highly oxidized (O/U ≈ 2.6), which suggested that the conversion mechanism should be based on the oxidative decomposition of the initial U(IV) oxalate, then on the hydrothermal reduction of uranium thanks to organic species in solution. Finally, first results concerning the preparation of $U_{1-x}Ce_xO_2$ mixed oxides were obtained and showed that the recovery of uranium was quantitative through a heat treatment of 24 hours at 250°C and pH = 5 whereas cerium recovery depended on the cerium content in the starting mixtures could be obtained. Also, preliminary studies regarding the sintering capability of the powders have been undertaken thanks to dilatometry tests.

Innovative precursors for morphology-controlled UO_2 and $(U,Ln)O_2$ oxides – CNRS/ICSM

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$UO_{2+x}.nH_2O$ microspheres were obtained through hydrolysis of uranium(IV) in the presence of aspartic acid under hydrothermal conditions (160°C). A multi-parametric study involving time, temperature, concentration of the reactants was then undertaken. It showed that a 50% excess in aspartic acid led to monodisperse powders. The addition of mechanical stirring during the hydrothermal process allowed to accurately control the average diameter of the particles produced (400 – 2500 nm range). For all the conditions tested, the characterization of the powders showed the formation of fluorite type $UO_{2+x}.nH_2O$ samples with traces of residual organics at the surface. Both water and residual organics were eliminated by heating at 600°C. This latter did not alter the shape of the particles and allowed the preparation of size-controlled UO_{2+x} microspheres. Complementary FIB experiments further confirmed the absence of porosity within these particles. Finally, preliminary tests concerning the synthesis of mixed $(U,Ce)O_{2+x}$ particles were undertaken and showed the formation of microspheres up to 10 mol.% in cerium. The first dilatometric experiments aiming to evaluate the sintering capability of these solids are now under progress.

Conversion of uranium nitrate into uranium oxide by Solution Combustion Synthesis –CNRS/ICSM

The solution combustion synthesis (SCS reaction) of metal nitrate to oxide is a self-propagating reaction of an organic fuel with a metal nitrate dissolved in water. In a first stage, this reaction was employed with an actinide surrogate element. The conversion of $Gd(NO_3)_3$ to Gd_2O_3 was obtained with glycine and citric acid as fuel, for a heating temperature of 300°C. Under these conditions, for a fuel / $Gd(NO_3)_3$ stoichiometric ratio, the monoclinic phase Gd_2O_3 was obtained with a high specific surface area (10-20 m^2/g), a small amount of residual carbon and a good crystallinity. The ignition of the precursors leading to the conversion nitrate / oxide, was observed at a temperature of about 210°C.

The conversion of uranyl nitrate into UO_2 was obtained using citric acid or glycine as fuel, for a richness (ratio $UO_2(NO_3)_2$ /fuel), respectively equal to 1 and 1.7. For the other richness values, a mixture of U_3O_8 and UO_{2+x} was obtained. The reaction was successfully extended to the $U_xCe_{1-x}O_2$ solid solutions. The powders obtained have interesting characteristics (15-25 m^2/g), and their sintering was successfully carried out.

ACTION PLAN

SCK.CEN: During the next semester, the processing of the data resulting from all analyses will be carried out within this semester. Finalization of the manuscripts will be performed on the fabrication of doped particles using internal gelation, on the one hand, and on the hydrolysis of uranium-lanthanide mixtures by thermal decomposition of urea (Ce, Nd), on the other hand.

CNRS/ICSM: Direct precipitation of oxides under hydrothermal conditions will be continued on $U_{1-x}Ce_xO_{2-y}$ mixed oxides. Sintering of uranium oxides obtained through hydrothermal conversion of oxalate will be studied through dilatometry and establishment of sintering map. The experimental protocol developed for the conversion of uranyl nitrate to uranium dioxide and of gadolinium nitrate to gadolinium oxide by Solution Combustion studies will be completed/extended for uranium-cerium bearing solid solutions.

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LIST OF PUBLICATIONS

Publications:

Synthesis of size-controlled UO_2 microspheres from the hydrothermal conversion of U(IV) aspartate, V. Trillaud, J. Maynadié, J. Manaud, J. Hidalgo, D. Meyer, R. Podor, N. Dacheux, N. Clavier**,** *CrystEngComm*, 2018, 20, 7749 (Front Cover paper).

Conversion of actinide nitrate surrogates into oxide using combustion synthesis process: A facile approach, J. Monnier, E. Welcomme, S. Chandra Mohan, J. Causse, X. Deschanels. *J. Nucl. Mater.*, 2019, 525, 14.

Hydrothermal conversion of uranium(IV) oxalate into oxides : a comprehensive study, J. Manaud, J. Maynadié, A. Mesbah, M.O.J.Y. Hunault, P. Martin, M. Zunino, D. Meyer, N. Dacheux, N. Clavier, *Inorg. Chem.*, 2020, 59, 3260.

The conversion of ammonium uranate prepared via sol-gel synthesis into uranium oxides, C. Schreinemachers, G. Leinders, G. Modolo, M. Verwerft, K. Binnemans, T. Cardinaels, *Nuclear Engineering and Technology*, 2019, doi: 10.1016/j.net.2019.11.004 (in press)

Int. Conference Oral:

Caractérisation *in situ* par MEBE-HT et MET-HT du premier stade du frittage de UO_2, V. Trillaud, R. Podor, C. Ricolleau, N. Dacheux, N. Clavier**,** Journées de la division Chimie du Solide de la SCF, Montpellier, 8-10 november 2017 / *Given*

Synthèse directe par voie hydrothermale d'oxydes d'uranium hydratés UO_2, nH_2O, J. Manaud, J. Maynadié, D. Meyer, N. Dacheux, N. Clavier**,** JECRRC, Strasbourg, 28 may – 1 june 2018 / *Given*

Solution combustion synthesis of gadolinium oxide nanopowders: Influence of the fuel on the properties of the material, J. Monnier, X. Deschanels X., C. Rey, E. Welcomme, CIMTEC, Pérouse, 4-8 June 2018 / *Given*

Caractérisation in situ par MEBE-HT et MET-HT du premier stade du frittage de UO_2, V. Trillaud, R. Podor, C. Ricolleau, N. Dacheux, N. Clavier, Matériaux 2018, Strasbourg, 19-23 november 2018 / *Given*

Wet chemistry route to uranium oxide microspheres as reference materials for nuclear safeguards, N. Clavier, J. Maynadié, V. Trillaud, J. Manaud, L. Sangély, T. Tranpaphan, N. Dacheux**,** MRS Fall Meeting 2018, Boston, 26-30 November 2018 / *Given*

Voies humides originales pour la precipitation directe d'oxydes d'actinides, N. Clavier, J. Manaud, V. Trillaud, J. Maynadié, A. Mesbah, N. Dacheux, Journées plénières du GdR SCINee, Lyon, 22-23 janvier 2019 / *Given*

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Synthèse de nanoparticules d'oxydes de gadolinium et d'uranium par combustion en solution : effet des paramètres du procédé sur le matériau, J. Monnier, X. Deschanels, C. Rey, E. Welcomme, Journées du GFC 2019, Montpellier (France), 12-14 Mars 2019 / *Given*

New insights in the description of the dissolution of actinide dioxides : better understanding for their reprocessing, N. Dacheux, INSPYRE First Summer School, Delft, 13-17 mai, 2019 / *Given*

Study of UO_2 sintering first stage by in situ HT-ESEM, V.. Trillaud, R. Podor, N. Dacheux, N. Clavier, EMRS Spring Meeting 2019, Nice, 27-31 mai 2019 / *Given*

Multiparametric study of the hydrothermal conversion of uranium(IV) oxalate, J. Manaud, J. Maynadié, D. Meyer, A. Mesbah, N. Dacheux, N. Clavier, EMRS Spring Meeting 2019, Nice, 27-31 mai 2019 / *Given*

Contribution of the coupling milling / dissolution on the dissolution of oxides, J. Hidalgo, P. Roussel, T. Delahaye, G. Leturcq, J.L. Rouviere, EMRS Spring Meeting 2019, Nice, 27-31 mai 2019 / *Given*

In situ high temperature electron microscopy observation of sintering first stage of MO_2 (M = Ce, Th, U) microspheres, N. Clavier, V. Trillaud, G.I. Nkou Bouala, J. Léchelle, N. Dacheux, R. Podor, PACRIM13, Okinawa, 27 octobre – 1 novembre 2019 / *Given*

Direct synthesis of morphology-controlled UO_{2+x} through hydrothermal conversion of uranium(IV) carboxylates, J. Manaud, V. Trillaud, J. Maynadié, A. Mesbah, N. Dacheux, R. Podor, N. Clavier, PACRIM13, Okinawa, 27 octobre – 1 novembre 2019 / *Given*

Conversion nitrate – oxyde par combustion en solution, J. Monnier, C. Rey, E. Welcomme, X. Deschanels, Sol_Gel, Tours, 7-9 octobre 2019 / *Given*

CONCLUSIONS

Several complementary ways of preparation of precursors were already developed or are now under progress. They were (are) able to provide a large variety of oxide based materials (Ce, U-Ce, U-Ln, U doped with FP) exhibiting various compositions, microstructures, crystal defects due to milling of to radiation damages, ... This spread panel of materials allowed to develop various dissolution experiments in order to access multiparametric expression of the dissolution rates. Only few difficulties are encountered by the partners for both tasks : T4.1 and T4.2.

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WP5

TASK 5.1

MANPOWER

- Jülich: 0 pm
- CNRS: 0 pm
- CIEMAT: 4.5 pm
- ULEEDS: 0 pm
- ULANC: 0 pm
- CEA: 3 pm

MAIN PROGRESSES

- CEA:
  - Kinetics data acquisition: Due to the unavailability of the single drop device in glove box and the molecules amount required by this technique, preliminary acquisitions were performed with a microfluidics device. The initial system to be studied TODGA (5% octanol) was set aside in favour of the DGA system proposed for the irradiation loops benchmark. Thus, mass transfer kinetics of Eu(III), Fe(III) and Gd(III) at 10-3 M in HNO3 3M extracted with mTDDGA 0.5M in TPH was carried out.
- CIEMAT:
  - Ongoing activities for the implementation of the irradiation loop at Náyade facility:
    - First dynamic experiment of TODGA-based solvent irradiation loop: DAm and DEu measurements; quantification of remaining TODGA concentration and its DCs.
    - Synthesis and purification of ne batches of TODGA and new improvements of the design of the loop
  - Ongoing activities about relevant-process conditions to simulate degradation:
    - Analysis of a full Euro-GANEX system submitted to radiation (TODGADMDOHEMA / AHA- SO3-Ph-BTP):
    - Quantitative analysis by HPLC-MS of TODGA DCs.
    - Quantification of AHA as a function of time of stability studies.
    - Estimation of SO3-Ph-BTP concentration by the correlation between DAm values.

DIFFICULTIES

- CEA:
  - Kinetics data acquisition: Because the microfluidics setup is not yet available in glove box, the aqueous stream was not spiked with radiotracers. Even with a 10-3 M concentration in the feed concentration of the extracted cations is too low to be accurately exploited.
- CIEMAT:
  - DCs of DMDOHEMA are not available to complete the quantification of Euro-GANEX degraded solvent.

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ACTION PLAN

- CEA:
  - Kinetics data acquisition: Extraction of the Eu(III), Fe(III) and Gd(III) at higher cations concentratio (1, 10 and 20 g.L-1) and/ or with slower velocities will be performed. Determination of mass transfer coefficients of Eu(III) in the stripping conditions of new Euro-GANEX (PTD solution and mTDDGA solvent) with the microfluidics device or the single drop technic.
  - The system to test was chosen in June 2019. Some data are available but acquisitions are still in progress. Model development will start in 2020.
- CIEMAT:
  - EURO-GANEX irradiation loop at Nàyade facility
- CNRS:
  - The results about kinetics will be gathered by the present partner CNRS-PHENIX in the next deliverable D5.1 due at month 30.

TASK 5.3

MANPOWER

- Jülich: 0.5 pm
- CEA: 0 pm
- KIT: 0
- NNL: 1.40 pm

MAIN PROGRESSES

- NNL:
  - Paper on extraction of HNO_3 into TODGA/octanol published in Solvent Extraction and Ion Exchange
  - Ongoing modelling of trivalent MA/Ln extraction into i-SANEX solvent. Experimental design software is used to identify data required for modelling efforts.
  - A young generation researcher is being trained in developing solvent extraction models using gPROMS.
- Jülich: No actions

ACTION PLAN

- NNL
  - Define data requirements for process model development
  - Draft sections of the paper on work to date
- Jülich:
  - An i-SANEX process flow-sheet (PTD) will be developed in collaboration with PoliMilano, KIT, based on the results of single centrifugal contactor tests. The flow-sheet will be tested in our centrifugal contactor battery

LIST OF PUBLICATIONS

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David Woodhead, Fiona McLachlan, Robin Taylor, Udo Müllich, Andreas Geist, Andreas Wilden, Giuseppe Modolo, Nitric Acid Extraction into a TODGA Solvent Modified with Octanol, Solv. Extr. Ion Exch. 37(2), 173-190 (2019).

Iván Sánchez-García, Hitos Galán, Jose Manuel Perlado and Joaquín Cobos. Stability studies of GANEX system under different irradiation conditions." EPJ Nuclear Sci. Techno, 2019. In press. DOI: 10.1051/epjn/2019049.

P. Kowalski et al. E-MRS Fall Meeting and Exhibit, Warsaw, Poland, 16-19 September 2019, conference presentation.

A. Wilden et al. GDCh Wissenschafsforum Chemie, Aachen, Germany, 15-18 September 2019, poster presentation

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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

TASK 1.1: HOMOGENEOUS RECYCLING

MANPOWER

A total of 15.6 person-months has been reported split into 7.1 person-months for Task 1 (CHALMERS, NNL), and 8.5 person-months for Task 2 (JUELICH, UNIPR, CEA, POLIMI). This represents a slight decrease on semester 4 which reported 17.3 person-months reflecting decisions taken at the Antwerp workshop that GENIORS focuses more on basic chemistry of the extraction processes and less on flowsheet testing due to the lack of basic knowledge of some of the extractants, e.g. m-TDDGA.

	task 1		task 2	
	expected	achieved	expected	achieved
CEA	0	0	2	2
CHALMERS	5	5	0	0
CIEMAT	0	0	0	0
ICHTJ	0	0	0	0
JRC	no Hypar	no Hypar	no Hypar	no Hypar
JUELICH	0	0	0	3
KIT	1.8	0	0.4	0
NNL	2.5	2.1	0	0
POLIMI	0	0	0.3	0.5
UNIPR	0	0	0	3
total	9.3	7.1	2.7	8.5

MAIN PROGRESSES

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ALSEP PROCESS DEMONSTRATION

An ALSEP process demonstration was run in the JUELICH centrifugal contactor setup. The flow-sheet in shown in Figure 1. Due to the limited number of available stages, the test was split into two parts and run on consecutive days. On the first day the extraction and scrubbing stages were tested and the loaded solvent was collected and stored overnight. On the next day the loaded solvent was used as the organic feed. On both days the experiments were run until steady state was reached. During the first day the test was continued until enough loaded solvent for the second day was collected. The outlets of the centrifugal contactor battery (raffinate, loaded solvent, An product, Ln product, and spent solvent) were monitored by sampling and quick gamma measurements of Am-241 and Eu-152.

After stopping the tests (stopping pumps and contactors), the contents of the mixing chambers were transferred to test tubes and centrifuged to achieve quantitative phase separation. Both phases were samples and analysed by gamma and alpha spectroscopy, and ICP-MS analysis. The stage profiles for Am and Eu are shown in Figure 2 and for Am and Cm in Figure 3. Figure 4 shows the corresponding distribution ratios.

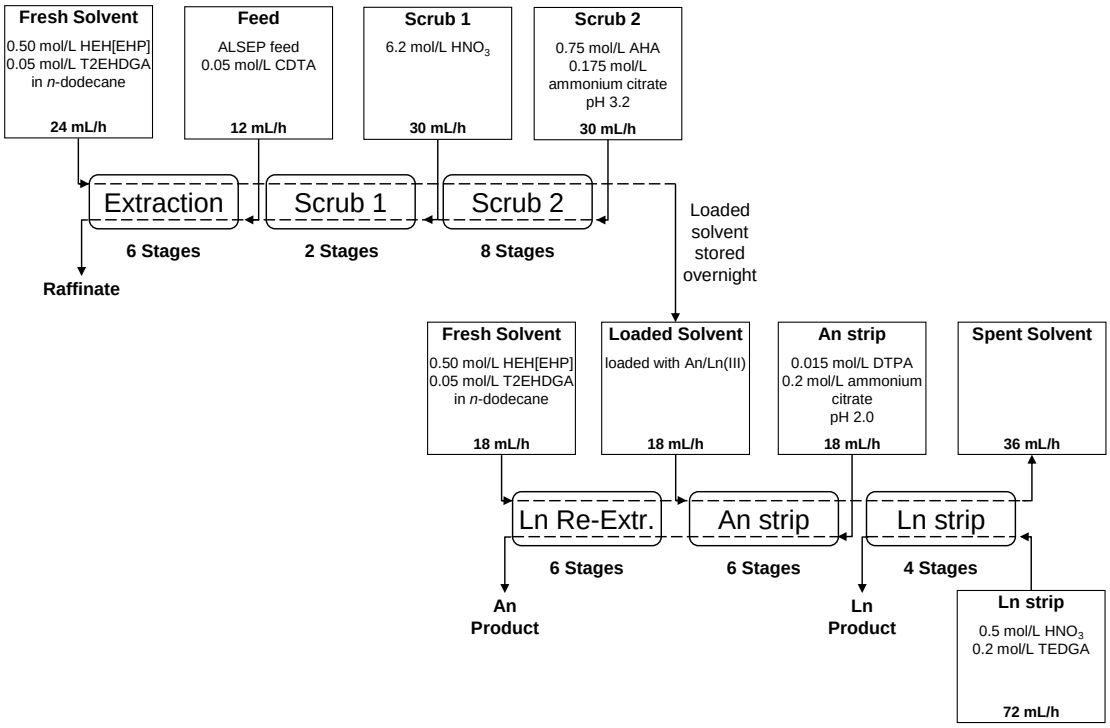

Figure 1. Flow-sheet of the ALSEP process demonstration.

Am, Cm and Eu were well extracted and stayed in the organic phase during the scrubbing steps. The An/Ln separation stages worked well, as Am and Cm were mostly routed to the An product, while Eu was nearly quantitatively routed to the Ln product. A slight Am and Cm recycling was observed in the Ln re-extraction section, presumably due to a slight pH change in stages 17-22 from pH 1.7 to pH 1.9. This pH change was caused by the acidic extractant introduced with the fresh solvent which had not been pre-equilibrated. The pH values in the An stripping section (stages 23-28) were relatively constant at pH 1.9 – 2.0. The pH values or H^+ concentrations in the individual aqueous phases of the stage samples were measured using a pH-meter or titrated against standardised 0.1 mol L^{-1} NaOH solution. The measured pH values or H^+ concentrations are shown in Figure 5.

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The An product was fairly clean with only very low contaminations (detailed analysis follows). However, a little fraction of Am and Cm (ca. 5%) were routed to the Ln product. Apparently, the number of An stripping stages was too low to achieve a quantitative An/Ln separation, as also visible in the Am and Cm stage profiles.

The Ln stripping with TEDGA worked very well and four stages were sufficient for a good clean-up of the solvent.

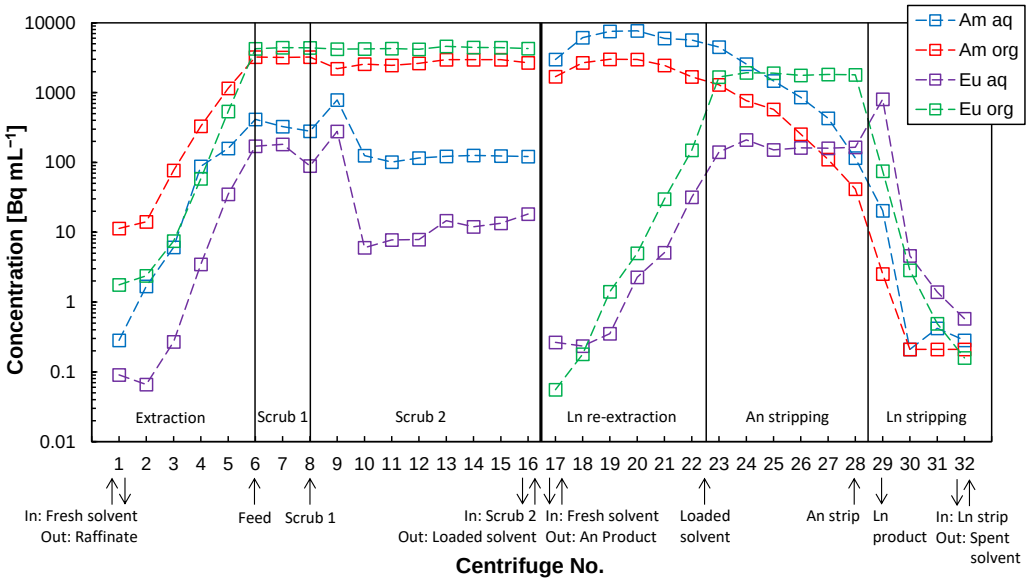

Figure 2. Am and Eu stage profiles of the ALSEP demonstration test (data from ICP-MS measurements).

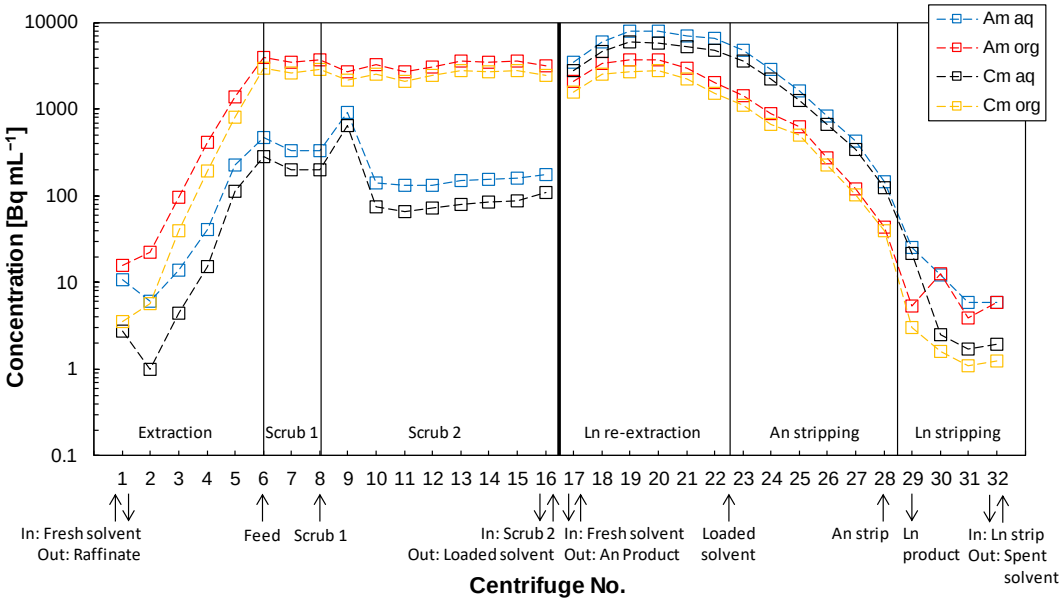

Figure 3. Am and Cm stage profiles of the ALSEP demonstration test (data from alpha spectrometry).

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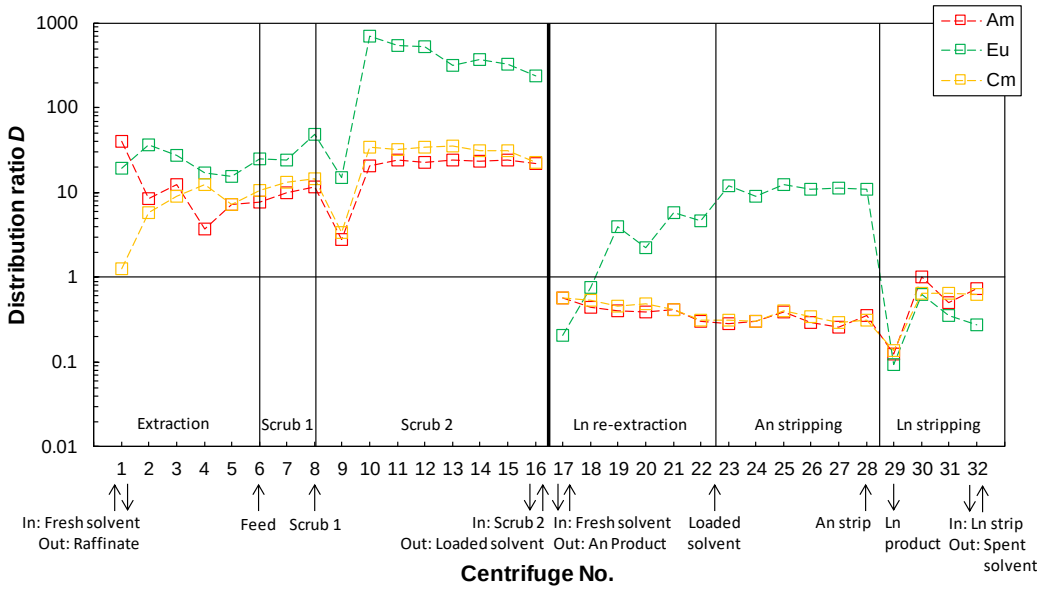

Figure 4. Am, Cm and Eu distribution ratios in the stages of the ALSEP demonstration test (Am, Eu data from ICP-MS measurements, Cm data from alpha spectrometry).

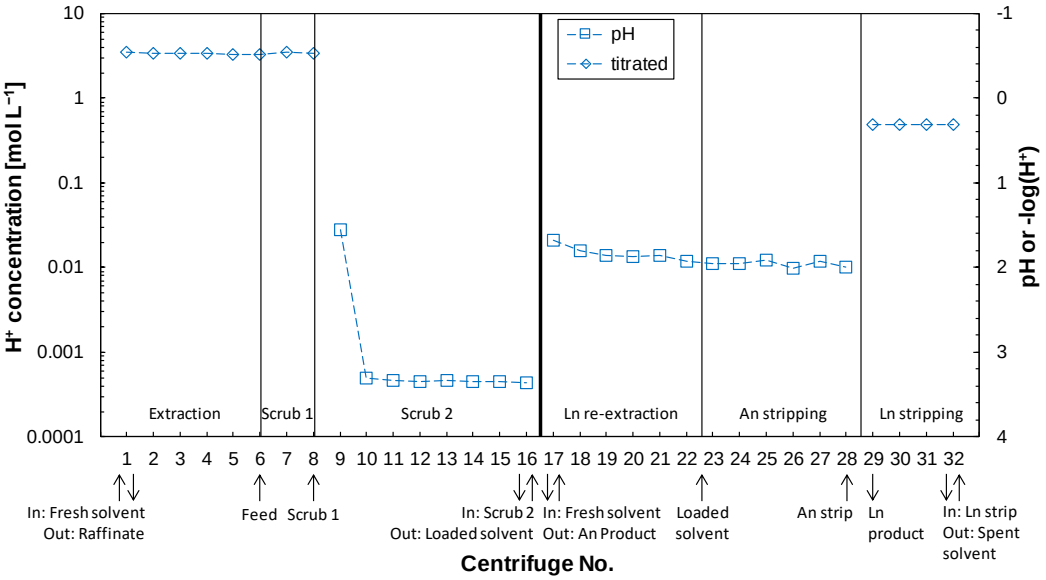

Figure 5. Measured pH values or titrated H^+ concentration in the stages of the ALSEP demonstration test. Note that the right y-axis is plotted upside down.

First evaluation of the ICP-MS data shows, that all non-Ln fission products were routed to the raffinate. Pd and Zr masking in the feed with CDTA was effective, and the Mo scrubbing also worked well. The heavier lanthanides (Pr, Nd, Sm, Eu, Gd) and Yttrium were mainly routed to the Ln product, while the lighter lanthanides (La, Ce) were also partly found in the raffinate.

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EXAM DEVELOPMENT (TPAEN STUDIES)

One option for the americium alone separation form a PUREX raffinate would be to use TODGA extractant to co-extract lanthanides (Ln), Am and Cm in a first step, and then strip selectively Am from other elements in a second stripping step.

For this purpose, the solvent TODGA 0.2 M in TPH with 5% n-octanol was selected in combination with TPAEN selective complexing agent.[1] The main limitation of this option is the low solubility of TPAEN ligand in nitric acid medium. Other complexing agents are currently studied in the framework of GENIORS like SO_3-Ph-BTBP and PTD derivatives. The objective of the present study is to compare the performances of new DGAs extractants to TODGA. For this purpose, 5 new diglycolamide extractants (DGAs) were synthesized in our laboratory [2]: 3 are unsymmetrical DGAs (EDdDGA, PyrrDdDGA and iPDdDGA), and 2 are symmetrical (iBDdDGA and PDdDGA) but with different alkyl chains compared with TODGA (Figure 6). The study of iBDdDGA and iPDdDGA will allow to evaluate the influence of branched alkyl chains on actinides and lanthanides extraction, while PyrrDdDGA presents a cyclic pyrrolidine amine on one side. And finally, PDdDGA and EDdDGA are analogs of TODGA with only linear alkyl chains but with a different repartition of carbon atoms symmetrically (PDdDGA) or unsymmetrically (EDdDGA) positioned on the DGA function.

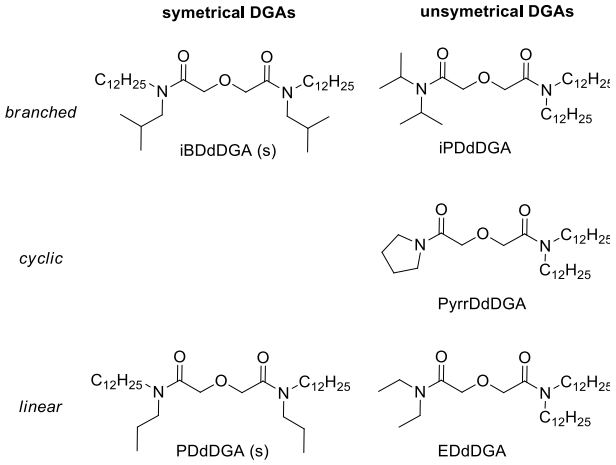

Figure 6: Structures of new DGAs.

For extraction tests, each DGA extractant was dissolved at 0.1 M in TPH with 10% octanol.

Extraction: Each organic phase was first contacted with an aqueous solution with traces amounts (200 kBq/mL) of ^{241}Am, ^{152}Eu and ^{244}Cm in 1 M HNO_3 (O/A = 1, 30 minutes, 25°C) by means of a vortex shaker equipped with a thermostated cell.

Stripping: Each loaded solvent was then sampled and contacted with a stripping solution containing TPAEN ligand 2.5 mM in 0.1 M HNO_3 (pH=1). (O/A = 1, 30 minutes, 25°C).

Organic and aqueous phases at equilibrium were analyzed by alpha and gamma spectrometry to determine distribution ratios of each radio-nuclide.

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Results reported in Figure 7 indicate that new DGAs except symmetrical iBDdDGA are stronger extractants compared to TODGA with distribution ratios higher than 1000 in those conditions (the remaining activity in the aqueous phase at equilibrium was too low to determine the D values with accuracy). Whereas, the iBDdDGA analogue with two branched *iso*-butyl chains shows lower distribution ratios (D<1000) but sufficiently high to allow co-extraction of Am, Cm and Eu at 1M HNO_3. During the stripping step with TPAEN at lower nitric acid concentration, Am distribution ratios remain too high for the following analogs: EDdDGA, PyrrDdDGA and PDdDGA. Indeed with Am distribution ratios higher than 5, it is not possible to obtain efficient stripping of americium, even by decreasing the extractant concentration since we are already working with 0.1 M. On the contrary, branched analogues (unsymmetrical iPDdDGA and symmetrical iBdDGA) show distribution ratios of Am lower than 1.

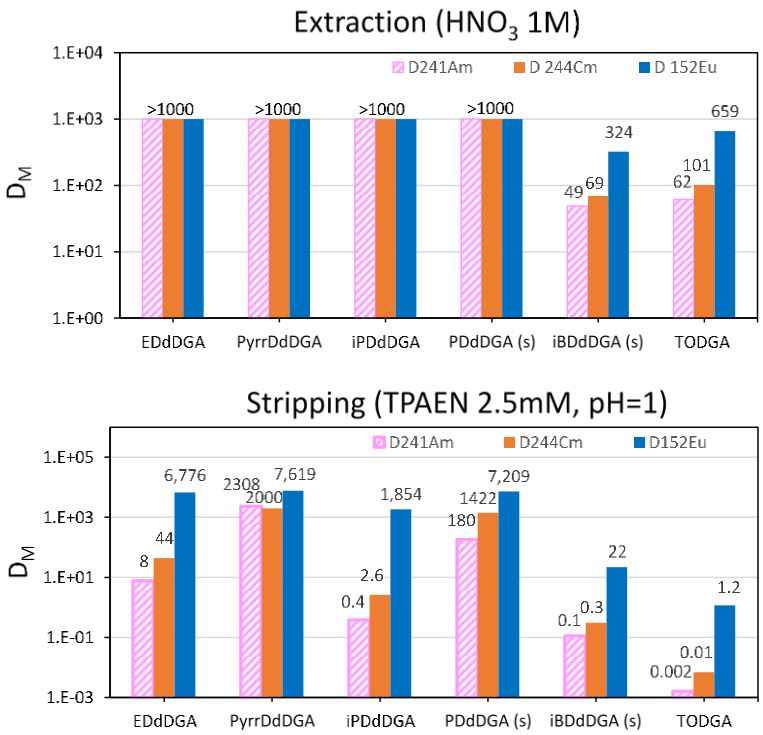

Figure 7: Distribution ratios of ^{241}Am, ^{244}Cm and ^{152}Eu for each DGA extractant 0.1 M in TPH with 10%$_{vol.}$ *n*-octanol during extraction from 1 M HNO_3 and then stripping with a 2.5 mM solution of TPAEN at pH=1 (O/A = 1, 30 minutes, 25°C).

As reported in Table 1, the unsymmetrical iPDdDGA analogue shows improved selectivities compared with TODGA (both Cm/Am and Eu/Am selectivities are improved), while symmetrical iBDdDGA gives lower selectivities.

Extractant	$SF_{Cm/Am}$	$SF_{Eu/Am}$
iPDdDGA	6.8	707
iBDdDGA (s)	2.7	71
TODGA	4.3	168

Table 1: Cm/Am and Eu/Am separation factors during Am stripping step

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To conclude, among new DGAs analogues evaluated in this work, only iPDdDGA could be an interesting candidate for an Am selective stripping process. Compared with TODGA, it would allow to improve the Am selectivity. Nevertheless, those results should be reinforced by additional experimental data. The light lanthanides extraction should be evaluated since La/Am and Ce/Am separations were an issue when trying to develop a process with TODGA/TPAEN system. Moreover, iPDdDGA is a stronger extractant compared with TODGA and it would be necessary to work at a lower concentration of extractant in TPH to allow Am stripping. Then the loading capacity should be checked in extraction conditions to avoid third phase formation. Few additional DGAs analogues (with branched alkyl chains and/or unsymmetrical structure) will be evaluated in the next semester.

After solubility issues observed with TPAEN complexing agent in the past, efforts should be continued to work on a new complexing agent for Am stripping with a higher solubility in the aqueous phase.

[1] Marie C., Kaufholz P., Vanel V., Duchesne M.-T., Russello E., Faroldi F., Baldini L., Casnati A., Wilden A., Modolo G., Miguirditchian M., Development of a Selective Americium Separation Process Using H_4TPAEN as Water-Soluble Stripping Agent. Solvent Extraction and Ion Exchange 2019, 37 (5), 313-327.

[2] Andreiadis E., Mossand G., Rinsant D., Duchesne, M.-T., Amphiphilic Asymmetrical Diglycolamides and Use Thereof for Extracting Rare Earth Metals from Acidic Aqueous Solutions, Patent 2019, WO/2019/197792.

CHALMEX STUDIES

Initial studies on the complexation of troublesome fission products using bimet and mannitol showed unexpected results in the complexation of Pd (Figure 8). Earlier studies have shown efficient complexation of Pd using bimet, and it was suspected that the stock of bimet available had degraded, resulting in reduced Pd complexation efficiency.

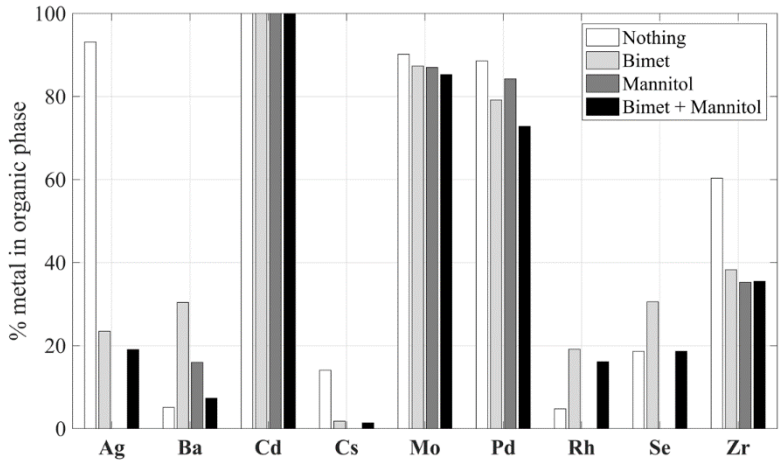

Figure 8: Complexation of troublesome fission products using mannitol and bimet produced no later than 2013.

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A new batch of bimet was produced in-house. The fresh bimet showed expected ability to complex Pd (Figure 9). The combination of mannitol and bimet significantly reduces the extraction Pd, Ag, Cs and Zr.

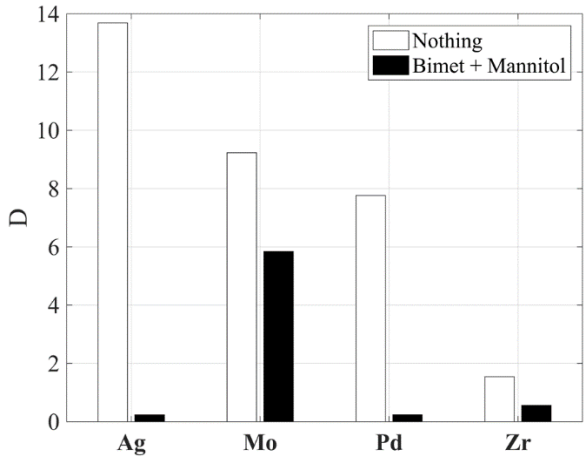

Figure 9 : Complexation of troublesome fission products using mannitol and a fresh batch of bimet.

The extraction of americium, europium and plutonium was also investigated as a function of nitric acid concentrations. The results can be seen in Figure 10. On contrary to plutonium extraction, both americium and europium extraction decreases with increased acid concentration. The reason for this behaviour is unclear: protonation of the organic phase could explain this phenomenon, although earlier studies have found protonation not to occur to any significant extent. Further studies to determine the mechanism is thus needed.

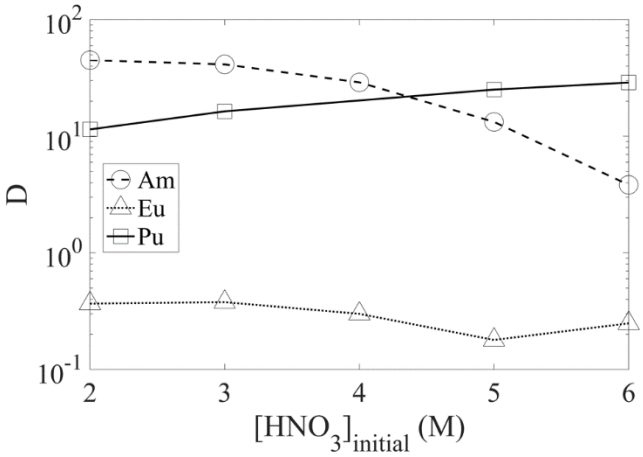

Figure 10: The distribution ratios of Am, Eu and Pu as a function of initial nitric acid concentration.

Experiments were done to see if increasing the nitrate concentration of the solution could be used as a way of boosting the americium extraction by the solvent. The results are presented in Figure 10. There is a clear linear dependency of the americium extraction on the nitrate concentration in the aqueous phase (R^2=1) (initial HNO_3 concentration was 1M). By increasing the nitrate concentration to

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approximately 4M (from 1M), the distribution ratio of Am is increased from ~20 to ~80, while the distribution ratio of Eu is still kept below 1.

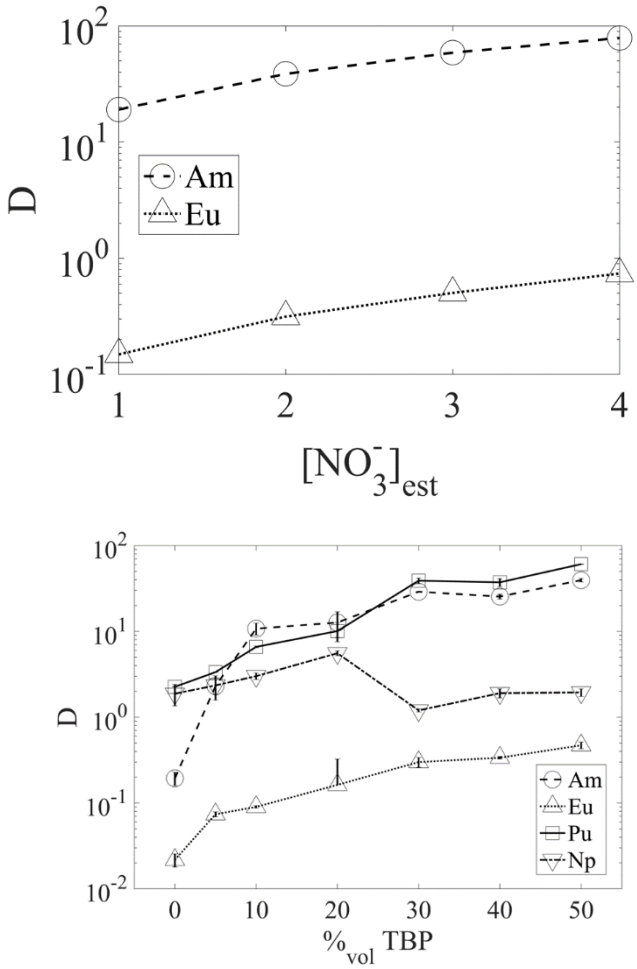

Figure 11: The extraction of the minor actinides as a function of TBP concentration. CyMe4-BTBP concentration was 10 mM, and the aqueous phase was 4 M HNO3.

Solvent optimisation experiments have been performed to supplement earlier experiments and to complete data set needed for publication. The concentration of both extractants (TBP and $CyMe_4$-BTBP) were investigated. The optimal concentration of TBP was decided to be 30%$_{vol}$, which was decided to optimise the Np/Eu separation factor (Figure 4). The reason for the extraction behaviour of Np is unclear and need to be further investigated.

The extraction as a function of $CyMe_4$-BTBP concentration was also investigated at different TBP concentrations (Figure 5). It was found that the distribution ratios of europium and neptunium are inverted at higher Cy'Me4-BTBP concentrations. This inversion also occurs at lower ligand concentrations for systems with higher TBP concentrations.

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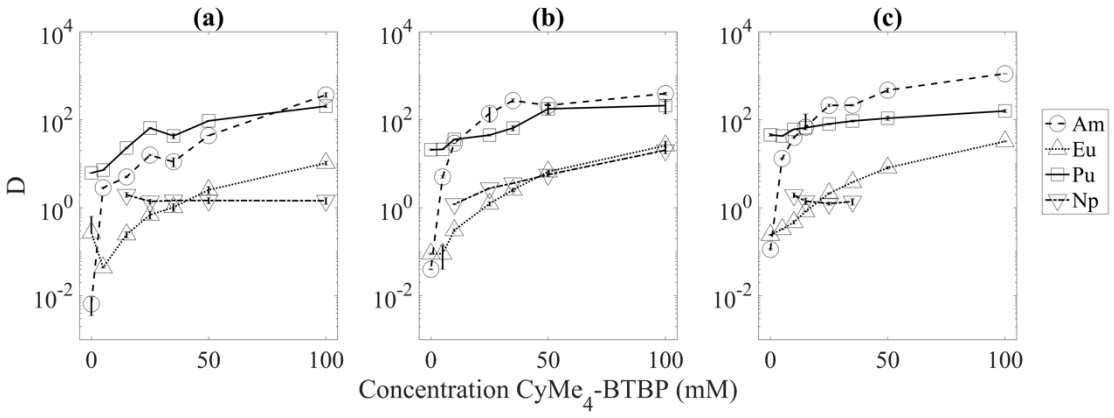

Figure 12: The extraction of Am, Eu, Pu and Np as a function of CyMe4-BTBP concentration for solvents with a) 15%vol TBP, b) 30%vol TBP and c) 50%vol TBP.

CONCLUSIONS

The work package concerns flowsheet development of key processes for homogeneous and heterogeneous recycling so it is expected that most studies will commence in the 2nd half of the project. Few significant delays or causes for concern were raised by the partners in the HYPARs.

A key highlight is Deliverable D6.1 "Assessment of applications of PTD in i-SANEX and EUROGANEX processes" has been submitted and validated.

Manpower on the WP was similar (slight decrease) from semester 5. In the last semester good progress has been made on the CHALMEX process and CEA have synthesised and screened several new DGA molecules for an improved EXAM flowsheet. A key achievement, linked to the US-DOE-GENIORS collaboration, is that JUELICH have tested an ALSEP flowsheet with initial indications suggesting good fission product decontamination.

However, progress needs to be accelerated on EURO-GANEX and AMSEL process development in semesters 6-7.

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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

No work performed during this semester

TASK 7.2

MANPOWER

Expected effort for the period 0.2 men.month

Actual effort spent during the period 0.2 men.month

MAIN PROGRESSES

The work has just started at the very end of the period

TASK 7.3

No work in this Task during this semester

D7.3 report to be written by early 2021.

TASK 7.4 CHARACTERIZATIONS

No work in this Task during this semester

CONCLUSION

During this semester, no progress was obtained in WP7.

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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 asses 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

TASK 8.4

MANPOWER

None

MAIN PROGRESSES

Functional specifications for the Sim Plant model and user interface have been issued, providing clarity and direction to the ongoing development work. These documents clearly state what success will look like and provide a metric to which we can monitor our progress. In addition, guidelines have been established for process modellers working on the Sim Plant project such that all flowsheets and models developed are compatible with one-another.

The existing Excel-based Sim Plant HLW calculations have been converted into Gproms modelling software to enable better compatibility between current and future NNL models and flowsheets.

The Advanced PUREX and THORP PUREX reprocessing flowsheets have been constructed in gPROMS software to provide a baseline and comparison with the Euro-GANEX process.

Constructed an Excel-based front-end tool which links data output from FISPIN spent fuel inventory modelling code with the Sim Plant front end (The reprocessing flowsheet fuel feed). This removes a lot of manual work reducing time restrictions and data transfer errors.

The solid ILW, liquid effluent and Aerial effluent treatment routes on the Sellafield site have been researched and models have been constructed and combined with the existing HLW model.

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Therefore, the Sim plant model is almost at a point where the entire waste route process can be modelled from a flowsheeting perspective. Efforts will be directed to constructing footprint and volume assessments from February 2020.

This was a knowledge capture exercise coordinated through the Sim Plant project team. Early career scientists and engineers were invited.

ACTION PLAN

Capability to simulate a flowsheet from spent fuel to waste container. Further development of Sim Plant for plant footprint and plant sizing to begin (funded by UK leverage).

TASK 8.5

MANPOWER

1.5 pm has been reported.

MAIN PROGRESSES

- Desk research has been performed.
- D8.3 has been analysed and scenarios have been revaluated.
- Interview questions have been prepared.
- Initial contribution from EDF and NNL have been acquired.

DIFFICULTIES

- Decline in nuclear energy interest in the EU resulted in abandoning the fast reactor project, namely ASTRID by CEA. This adversely affect the implementation of scenarios that were developed for the transmutation of the most radiotoxic elements from spent fuel.
- Difficult to access to the interviewee from Orano which is a contributor for the report.

ACTION PLAN

- Interviews will be taken place in the coming days.
- During next workshop, the results will be discussed.
- New interviewee and expert inputs will be needed. Thus, attendance to various GEN IV conferences and other related events can be targeted.

CONCLUSIONS

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

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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

D10.3 - ATALANTE 2020 is defined and will be organised in June 2020.

D10.4 - Clustering Event "Partitioning meets Conditioning" will be organised in October/November 2020. Scope, agenda and venue are being defined.

DIFFICULTIES

D10.2 – Clustering Event "INSPYRE summer school" – still to be written.

TASK 10.2 STAKEHOLDERS EVENTS

No progress this period.

CONCLUSIONS

Progress of organizing Clustering/Stakeholders Events is on track: 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. Clustering Events 3 (related to D10.3) and 4 (related to D10.4) are scheduled for 2020. Stakeholders Event 2 (related to D10.6) is foreseen at the end of the project in 2021.

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WP12

INTRODUCTION

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

MAIN RESULTS

TASK 421

MANPOWER

ULEEDS: 0.37pm

MAIN PROGRESSES

Two secondments and one travel bursary have been awarded – bringing the total awarded to date to €12,825.

ACTION PLAN

Continue to encourage applications to the fund.

TASK 422

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 30th May 2020.

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