GENIORS

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WPASR 3

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Summary

WPASR 3

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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 the first 2 semester is summarized in Table 1.

Table 1: Manpower devoted to WP1

Partner	WP1 effort	HYPAR 1 realised	HYPAR2 realised	HYPAR3 realised
CEA	7.9	0	0	3
ICHTJ	9.00	0	1.2	3
JUELICH	9.80	0	1	2
KIT	5.90	1	0.25	0
TWENTE	1.8		180h (1)	270h (1.5)
UREAD	5.8	0	0	0
Total	**40.2**	**1**	**3.45**	**9.5**

MAIN RESULTS

TASK 1.1

MANPOWER

9.5 pm was realized this semester by CEA, ICHTJ,JUELICH, and TWENTE. This is 37.5 % of effort which is planned for the complete project (Task 1: 37.2 pm).

MAIN PROGRESSES

Ruthenium speciation in GANEX 1st Cycle (Monoamide organic phase), CEA

In order to assign the ruthenium speciation in alternative solvent extraction system such as monoamide extracting molecules, a FTIR study similar to the one proposed by Lefebvre et al [1,2] was performed with monoamide ligand. As preliminary experiment, the ruthenium extraction properties were measured with different extracting molecules of the monoamide family. The resulting extraction studies revealed, that the ruthenium speciation in the organic phase by FTIR is easier to achieve for the MOEHA system due to higher D_{Ru} and FTIR detection limits. This ligand was then used as a DEHiBA surrogate and as representative monoamide family member for FTIR measurements. The MOEHA FTIR spectrum obtained after solvent extraction from a 4M nitric acid solution was compared to TBP and TBU organic phase (identical extraction conditions). For the 3 solvent extraction systems, the ruthenium nitrosyl complexes FTIR signal (i.e. nitrosyl vibrations at ν= 1850 - 1950 cm-1, and complexing nitrates at 1531-1481 cm-1 and 1296-1253 cm-1) are identical to those measured in the initial aqueous phase. To confirm this FTIR approach, X-ray absorption spectroscopy were used to compare the ruthenium speciation. The EXAFS spectra again indicate that the ruthenium first coordination sphere is independent of the extracting molecule. For lower acid conditions (HNO_3= 1M), the monoamide system contrast with the TBP one. No ruthenium complexes with hydroxide group were detected in organic phase from the 1M nitric acid experiment.

1. C. Lefebvre, T. Dumas, M. C. Charbonnel and P. L. Solari, Procedia Chem, 2016, 21, 54-60.

2. C. Lefebvre, T. Dumas, C. Tamain, T. Ducres, P. L. Solari and M.-C. Charbonnel, Industrial & Engineering Chemistry Research, 2017, 56, 11292-11301.

Extraction studies of technetium into TODGA system (ICHTJ)

Solvent extraction of technetium(VII) was studied in the two-phase system: TODGA in kerosene vs. aqueous HNO3 solutions. The TcO4– anion is well extracted from this acidic medium, probably as an ion pair with the protonated form of the extractant as the counter-ion. The Actinide/Tc separation in the second cycle of the EURO-GANEX process was examined by the reduction of TcO_4^- with Acetohydroxamic acid (AHA). AHA is a water-soluble organic ligand proposed and studied in details as a reducing agent for Tc(VII) [1]. The desired value D_{Tc} <1 was reached (at trace Tc concentrations) in 0.1 M HNO_3 in the presence of both reducing and stripping agents. The increase in the concentration of DTPA (but not AHA) further decreased the D_{Tc} value. The resulting technetium(II) was complexed by AHA to form the trans-aquanitrosyl-(diacetohydroxamic)-technetium(II) complex, $[Tc^{II}(NO)(AHA)_2H_2O]^+$ which can be studied using UV-vis spectroscopy.

1. 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.

Extraction of Fe(II) into TODGA (FZJ)

The TODGA extraction of ^{55}Fe was studied, as iron is discussed as one of the possibly problematic fission and corrosion products and TODGA is used in the i-SANEX and AMSEL processes. Therefore, the extraction was studied as a function of nitric acid at four different TODGA concentrations. Low distribution ratios were observed under all conditions. Nevertheless, a slight increase in distribution ratios is observed for very low and for higher HNO3 concentrations.

ACTION PLAN

CEA: Future work will involve solvent extraction experiment with second cycle extracting molecules such as TODGA and complementary speciation experiments using electrospray mass spectroscopy. The influence of nitrite ligands on the ruthenium extraction/speciation will be checked since recent experiments demonstrated that ruthenium nitrite complexes, which may form during the spent fuel dissolution, are extremely stable and must not be neglected.

ICHTJ: Studies on solvent extraction separation of technetium (in weight amounts) from americium in the TODGA / HNO_3 extraction system. The effect of temperature on the kinetics of the Tc-AHA complex formation and of solvent extraction (stripping) of the reduced technetium

JUELICH: Further extraction studies will be carried out and organic phases will be analysed by ESI-MS (collaboration with Uni. Hannover).

KIT: Determine Sr(II) distribution data in the TODGA + 5% octanol in TPH / HNO3 system at varied temperature and for Sr(II) loading conditions. Sr(II)/TODGA equilibrium modelling, in collaboration with NNL is planned.

TASK 1.2

No action for this semester

CONCLUSIONS

Since the start of the GENIORS project already 37.5 % of the planned actions related to the fission product chemistry (Task 1.1) were carried out. It is expected that the planned work within Task 1.2 will gain momentum in the next semester.

WP2

INTRODUCTION

The general objective of WP2 is to ensure a safe long-term performance of a chemical system submitted to radiation. To improve the resistance of the ligands as well as of the systems where they are involved will be 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 will be 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

19.35 mp realized this semester (8.0 pm CEA, 0.8 pm CTU, 2.1 pm IIC, 0.75 pm CIEMAT, 0.7 pm Julich, 5 pm POLIMI, 2 UNIPR-synthesis).

MAIN PROGRESSES

Studies of BTBP and BTPhen:

During this third semester, a new procedure for gamma radiation stability testing of hydrophobic ($CyMe_4$-BTBP and $CyMe_4$-BTPhen) and hydrophilic (Sulfonated BTPhen) extraction systems was prepared by CTU. Next semester, extraction properties of selected systems after irradiation by gamma radiation should be reported.

- *Stability studies of $CyMe_4$-BTBP:*

IIC has continued with the analysis by HPLC and MS of $CyMe_4$-BTBP samples irradiated at Chalmers facilities to study their composition and find effective conditions for separation of degradation compounds. Unfortunately, isolations of degradation products from previous series of irradiated $CyMe_4$-BTBP samples had limits due to their presence in low concentrations and thus only low amount of particular products that could be isolated. Therefore, a new series containing three more concentrated samples in (FS-13, FS-13+TBP and octanol+TBP) was irradiated at Chalmers facilities by various doses, depending to actually observed degree of degradation, and analyzed at by HPLC and MS at IIC. The current highly concentrated samples exhibited much lower degree of degradation even at very high doses. The degree of degradation and mutual ratio of degradation products have been found to substantially depending on diluent. The fastest rate of degradation and visible differences in products ratios could be seen for sample in octanol+TBP. The pre-separations have been running in a smaller scale, being enough to obtain relatively good NMR spectra, which is promising for assignment of the structure of degradation products by NMR.

- *Lipophilic PTD, PTEH:*

According to the decision of the Consortium to include the new lipophilic PTD derivative (PTEH) in the objectives of GENIORS project, in continuation of studies already performed, POLIMI has studied the degradation of the PTEH system. Details concerning such experiments are reported as part of WPASR3-WP3, Task 3.1.

Stability studies of diglycolamides:

- *Lipophilic diglycolamides : TODGA based systems*

In connection with experiments done for process development within WP5, CIEMAT has gone further in structural TODGA degradation study under different irradiation conditions (air, argon and air-sparging) and in contact with different aq. phases (0.5 mol/L HNO_3 and 0.018 mol/L SO_3PhBTP in 0.5 mol/L HNO_3). It seems air flow bubbled changes the dominant degradation pathway. This semester CIEMAT has completed the work performed in WP5 by identifying the structure of new possible TODGA DCs formed only when samples have been aerated during the irradiation of org.+aq. phases.

CEA has continued focused on determining the differences between in-situ alpha (provided by the decay of ^{241}Am) and external gamma radiolysis (by a ^{60}Co source) of extractant TODGA and on determining how the degradation products formed affect metal complexation in the organic solvent. This semester CEA has recorded the mass spectra of in-situ alpha irradiated at low and high dose rate (1mM Am, 0.16kGy/hr and 10mM Am, 1.6kGy/hr) up to 400 and 1500 kGy respectively. In-situ alpha irradiated solutions up to 400 kGy contains only hydrolytic degradation compounds that are present also in non-irradiated samples. However, after 500 kGy alpha radiation TODGA stars to split at the C-O ether bond forming the typical degradation compounds with very slightly difference with Am solutions left in contact with nitic acid. Mass spectra of Am-complex formed showed mainly complexation with TODGA, DCs that has lost one octyl group and the carboxylate derivative. Typical TODGA DCs formed by the rupture of ether bond did not show Am complexation. To complement this work, bond dissociation energies of TODGA were calculated.

- *Lipophilic diglycolamides : mTDDGA based systems*

  The radiolytic stability of mTDDGA was studied this semester as part of Julich-SCK•CEN collaboration, as the extractant is discussed to be used in a new GANEX process [i] to replace the mixed TODGA/DMDOHEMA solvent used in the EURO-GANEX process [ii].Gamma irradiation up to 1000 KGy has been carried out for TODGA and mTDDGA samples with and with contact with nitric acid. Additionally, mTDDGA and TPDGA were sent to INL for ^{60}Co gamma irradiation and pulse radiolysis studies. TPDGA was chosen to study the influence of the diluent on radiolysis, as it is soluble in n-dodecane and partially in water. The synthesis of TPDGA was conducted at TWENTE. All irradiated samples will be analyses by JUELICH.

Stability studies of stripping or masking agents:

- *PyTriDiol:*
  A new batch of PyTriDiol was produced by UNIPR to feed the studies carried out by partner. A sample was sent to POLIMI and another to CEA.
  Gamma and alpha irradiations and aged samples of PTD were studied as part of CEA-POLIMI collaboration. For both, alpha and gamma radiation, most of the products appear after 100 kGy and to be the result of H_2 abstraction, OH addition, and NO_3 addition. There were only small difference between compounds form by alpha and gamma radiation and most of them show a strong affinity to Am. The most consistent degradation product formed was the H_2 elimination. Besides, Fukui functions for PTD were calculated to assist in determining degradation product structures.
  During the third semester POLIMI-CEA has also continued the study of PTD degradation by completing the Am and Pu loading experiments with aged and irradiated PTD solutions. Details concerning such experiments are reported as part of WPASR3-WP3, Task 3.3.
- *CDTA :*

  Last year, solutions of CDTA (0.055 mol/L in 4 mol/L HNO_3) were irradiated in presence and absence of a simulated HAR solution by CIEMAT using gamma sources. Using an Euro-GANEX solvent formulation as organic phase, it was checked that Ln(III) extraction is not affected at all by the degradation of CDTA. However, a white precipitate was found just after irradiation of the aqueous phases. The insolubilities seem to be formed by Zr, Pd and degradation compounds from CDTA. During this semester a new series of irradiation experiments have been performed taking into account the real concentration of metals in the feed (100 % HAR solution) and a more realistic estimated doses (0-50 kGy). Besides, parallels experiments are being carried out for EDTA because this compound presents similar properties to CDTA as masking agent and has not a cyclohexyl group in its structure [iii], which could be the responsible of the formation of non-soluble degradation compounds. ICP-MS and gamma spectrometry results are currently under study.

DIFFICULTIES

No major difficulties have been reported. Although there was some delays due to:

- CTU: No $CyMe_4$-BTBP or $CyMe_4$-BTPhen available for experiments during this period. No degradation products/adducts of $CyMe_4$-BTBP and $CyMe_4$-BTPhen synthesized, yet.
- IIC: A series of larger samples expected to be supplied from CTU has been delayed due to low availability of the ligand. Besides one member of IIC team had to be replaced.
- JULICH: Significant differences in comparative irradiation experiments where observed.

ACTION PLAN

CEA: Analysis of the MS2 experiments on PTD.

CIEMAT: On-going activities to perform quantitative studies of SO_3PhBTP and CDTA by HPLC-MS. Assessment of An/Ln/FP extraction by gamma spectrometry and ICP-MS of irradiated CDTA and EDTA masking agents samples. Euro-GANEX stability studies as part of NNL-CIEMAT collaboration.

POLIMI: Irradiation of PTD-TODGA solutions will be repeated and analysed by means of micro GC-MS under optimized conditions.

CTU: Testing of radiation stability of selected extraction systems is planned. If available, testing of extraction properties of radiolysis products synthesized at the University of Reading will start.

IIC: Continuation of larger scale preparative separations of degradation products from currently available high-volume samples. Characterization of $CyMe_4$BTBP DCs by MS and NMR.

JULICH: A validation of the dosimetry for irradiation at SCK-CEN will be conducted. The extraction properties of degradation products of mTDDGA will be studied.

UNIPR: Synthesis of other batches of PTD to allow the acquisition of further extraction data.

TASK 2.2 DESTRUCTION OF ORGANIC (TASK LEADER: CEA)

MANPOWER

3.0 mp realized this semester by CEA.

MAIN PROGRESSES

DGAs:

During this semester CEA has started the studies addressed to deliberate destruction of TODGA and TEHDGA by high acidity (11 M HNO_3) and high temperature by using a calorimeter TSU (Thermal

Screening Unit) and comparing with data obtained for also TBP. From these first results, it seems that the TODGA is more reactive than the TEHDGA and that the ΔTmax and ΔPmax of DGA molecules are higher than TBP. Further experiments will be performed to study the influence of variable chemical conditions

ACTION PLAN

CEA: Further experiments will be performed to study the influence of variable chemical conditions (acidity, presence of degradation products) on the reactivity of DGA systems.

TASK 2.3 GAS GENERATION (TASK LEADER: POLIMI)

MANPOWER

4.66 mp realized this semester (4.16 NNL and 0.5 POLIMI).

MAIN PROGRESSES

Gas generation of TODGA based systems:

During the third semester NNL has continued undertaken irradiations of relevant solvents for the i-SANEX and GANEX processes with He^{2+} ion implantation using the UoM-DCF (University of Manchester Dalton Cumbria Facility) tandem accelerator to measure gas generation during irradiation process. During an initial test in pure n-dodecane was found similar G_{H2} value than those previously obtained by LaVerne; and a linear production of H_2 using beam currents between 1- 5 nA. The similarity and linearity of response demonstrates that the increase in beam current (and therefore dose rate) does not alter the intra-track chemistry of the system and that the rate of stirring is sufficient. Results obtained for the irradiation of i-SANEX and GANEX solvents show clearly that the solvent mixtures suppress the formation of H_2 relative to pure alkane diluents like hexane and dodecane. Besides, they are in agreement with most comparisons between α and ˠ irradiations where ˠ irradiation normally yields less H_2 than α radiation. The G_{H2} values measured also show that the addition of HNO_3 and O_2 to the system suppresses H_2 formation. However, further understanding of the effect of the radiation on the extractant itself is required.

Gas generation of PTD based systems:

During this semester POLIMI has encountered some technical problems with the vials adopted for the gamma radiation treatment of the PTD-TODGA solutions. Some gaseous leakages made necessary to repeat the irradiation experiments.

DIFFICULTIES

NNL has reported delays problems in the measurement of H_2 generation due to viscosity of solvents. Besides his work planned in WP2 is being delayed to fit NNL-CIEMAT scheduling.

During this semester POLIMI encountered some problems in the radiation treatments of the PTD-TODGA extracting system. Unexpectedly, the adopted vials resulted not to suitably avoid gaseous leakages, therefore the radiation treatments have to be repeated.

ACTION PLAN

NNL: Completion of the work, preparation of a report and a paper. Secondment of Iván Sanchez (CIEMAT PhD student) to NNL.
POLIMI: Irradiation of PTD-TODGA solutions will be repeated. When ready the irradiated aqueous and organic phases will be analysed by means of micro GC-MS under optimized conditions.

TASK 2.4 RADIOLYSIS MODELLING (TASK LEADER: CTU)

MANPOWER

3.0 mp realized this semester (2 CTU and 1 Julich).

MAIN PROGRESSES

Modelling studies of water soluble diglycolamides:

The theoretical study of DGA ligands (TMDGA, TEDGA, Me-TEDGA, and Me_2-TEDGA; dissolved in water) was studied by DFT ground-state simulations by CTU following the details of experimental work previously done by Julich [iv]. The calculated Fukui functions were in good correlation with the trend of increased stability with increasing molecular weight. The Fukui charges also brought the explanation why TMDGA most likely does not degrade in the ether group, unlike the other ligands.

Molecular dynamics simulations were started dealing also by CTU with a detail conformation analysis of TEDGA, TMDGA, Me-TEDGA and Me_2-TEDGA molecules in water environment. Remarkable difference in conformation dynamics is observed, with TMDGA and Me_2-TEDGA showing respectively the lowest and highest number of the states in conformation space.

Otherwise, DFT calculations (PBE) were employed to calculate bond dissociation energies of TEDGA by Julich. These were obtained by calculating the difference between the energies of initial end and begin structures of the ligand. Results agreed with Ashleigh Kimberlin data [v], the experimentally observed destabilization of the C-OEther bonds in diglycolamides. The addition of one methyl group to the diglycolamide backbone seems to also destabilize the ether bond on the opposite side of the molecule, which is in agreement with previously observed decreased radiolytic stability of single methylated TODGA [vi].

ACTION PLAN

In the future, Julich will perform calculations of Fukui functions of different diglycolamides (esp. mTDDGA) to give greater inside into the fundamental radiolysis processes. Similar research has previously been conducted by Thomas Koubský for methylated TODGA molecules. [vii]

Regarding conformational analysis, CTU will address the inherent rigidity/flexibility of the molecular frame and the different mean interaction strength with the solvent environment.

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LIST OF PUBLICATIONS

Publications :

1. Koubský, T., Luštinec, J., Application of quantum mechanical simulations for studying the radiolytic stability of prospective extractants in the nuclear fuel cycle, *Journal of Radioanalytical and Nuclear Chemistry*, 2018, DOI 10.1007/s10967-018-6225-2.
2. Koubský, T., Radical degradation of CyMe4-BTBP ligand in hydrometallurgical reprocessing of spent nuclear fuel: A density functional study, *Progress in Nuclear Energy* (submitted).
3. Hallerod J., Ekberg C., Authen T., Bertolo L., Lin M., Grűner B., Švehla J., Wagner C., Geist A., Panak P., Aneheim E. On the Basic Extraction Properties of a Phenyl Trifluoromethyl Sulfone-Based GANEX System Containing CyMe4-BTBP and TBP, *Solvent Extraction-Ion Exchange*, 2018, 36(4), pp. 360-372.
4. Wilden et al. Radiolytic and Hydrolytic Degradation of the Hydrophilic Diglycolamides, *Solvent Extr. Ion Exch.*, 2018, 36, 4, 347-359. DOI:10.1080/07366299.2018.1495384.
5. Eros Mossini, Elena Macerata, Andreas Wilden, Peter Kaufholz, Giuseppe Modolo, Nicolò Iotti, Alessandro Casnati, Andreas Geist & Mario Mariani. Optimization and Single-Stage Centrifugal Contactor Experiments with the Novel Hydrophilic Complexant PyTri-Diol for the i-SANEX Process. *Solvent Extraction and Ion Exchange*, Volume 36, 2018 - Issue 4 (373-386).

Conference paper:

1. V. Babain, M. Alyapyshev, I.G. Voronaev, L. Tkachenko, E.V. Kenf,, M. Mindová, P. Distler, J. John, Fluorinated Carbonates as New Diluents for Extraction of f-Elements, *Czech Chem. Soc. Symp. Ser*. 16 (2018) 135. 18th Radiochemical Conference.
2. P. Distler, A. Afsar, K. Šťastná, J. Westwood, F.W. Lewis, K. Štamberg, L. Harwood, J. John, Partitioning of Minor An(III) and Ln(III) by the 1,2,4-Triazine Extracting Compounds, *Czech Chem. Soc. Symp. Ser.* 16 (2018) 56. 18th Radiochemical Conference.
3. T. Koubský, L. Kalvoda, Application of Molecular Modelling for Studying the Stability of Organic Ligands in Nuclear Fuel Cycle, *Czech Chem. Soc. Symp. Ser.* 16 (2018) 81. 18th Radiochemical Conference.

Oral communications:

1. Verlinden, B. et al. Effect of ionizing radiation on solvent extraction systems for the separation of minor actinides. SCK•CEN Academy PhD day, Mol, Belgium, 19 September 2018.
2. A. Ossola, E. Macerata, E. Mossini, A. F. Folgado de Lucena, F. Galluccio, M. Giola, M. Mariani, Advanced separation strategies for spent nuclear fuel reprocessing studied at Politecnico di Milano Radiochemistry Lab within European Projects. CHERNE 2018 Conference, Macugnaga (I), 29/05-01/06, 2018
3. A. Ossola, E. Mossini, E. Macerata, M. C. Gullo, A. Casnati, M. Mariani, Lipophilic pyridine-2,6-bis(1H-1,2,3-triazol-4-yl) extractant for selective MA(III) extraction in SANEX-like processes. 18th RadChem Conference, Marianske Lazne (CZ), 13-18/05, 2018.

CONCLUSIONS

After 18 months of GENIORS project work it has been reached 64% of the effort dedicated to WP2 and in general it can be reported a more than optimal development of WP2 activities, and this semester has been particularly productive with 30.01 pm. The studies performed with Task1 (*Radiolysis & degradation products*) has reached 78% of the effort dedicated. Activities regarding *destruction of organics* (Task 2, 3 pm) and *gas generation* (Task 3, 4.66 pm) are going on adequately but further studies are needed. *Modelling* studies (Task 4, 3 pm) has cover only 37% of effort dedicate to this activities, however as long the hypothesis are based on experiment results the progress of this task is satisfactory and fit with experimental studies.

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).

MAIN RESULTS

TASK 3.1 OPTIMISATION OF SYSTEMS (TASK LEADER: POLIMI)

MANPOWER

29.25 pm realized this semester (CEA, CNRS, KIT, ICHTJ, JUELICH, POLIMI, UNIPR).

48.35 pm realized since the beginning of the project, corresponding to 62 % of the 78 pm planned for the complete project.

MAIN PROGRESSES

<u>Hydrophilic complexation:</u>

- The synthesis of larger amounts of PTD was carried out in order to obtain the amounts of PTD necessary to study more in details the separation process and in particular the separation of the minor actinides (i-SANEX).
- Microcalorimetry measurements by isothermal titrations have been started in order to determine the stability constants and the associated thermodynamic parameters of PTD complexes with Ln(III) and Am(III) cations.
- Confirmation of the hypothesis that extractable heteroleptic complexes of Am^{3+} and of Eu^{3+} ions with both T-DGA and SO_3-Ph-BTP^{4-} ligands are formed in solvent extraction systems containing these two ligands – lipophilic and hydrophilic. Experimental confirmation of the correctness of the equation derived to describe the metal extraction/stripping in such systems. Formulation of an experimental criterion that allows to distinguish whether the extractable heteroleptic complexes of a metal cation with two different ligands: a lipophilic extractant and a hydrophilic stripping agent; are really formed in a given extraction system containing the two ligands that compete for the metal cation.

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Organic phase:

Extractants: The extractant mTDDGA was studied as a potential candidate to be used in a new GANEX process.

Phase modifiers: Further lipophilic modifiers of the TODGA-containing organic phase were studied, expected to improve the selectivity of Am(III)/Ln(III) stripping in EURO-GANEX systems. However, no satisfactorily effective synergist of the Ln(III) extraction has been found yet.

Diluents: The possibility of using aromatic diluents for a TODGA based GANEX system was assessed. Cm(III) and Eu(III) complexes were identified in an aromatic TODGA solvent

Extraction kinetics:

- The effects of the phase-transfer catalyst TODGA, of CyMe$_4$-BTBP concentration on extraction kinetics were obtained.
- Issued from the extraction of multi-elements at high concentrations performed in separation processes, the kinetics of simultaneous extraction of two radioactive cations (at trace level) were measured. Moreover, the effect of added non-radioactive Eu(III) of different concentrations from 10^{-5}M to 10^{-1}M on ^{152}Eu(III) and ^{241}Am(III) extraction kinetics was investigated.
- Very small even negligible changes of extraction rate k_f with increased temperature (from 22.5°C to 35°C) were observed. However increase in temperature has lowered the distribution ratio, indicating exothermic property of extraction reaction.

DIFFICULTIES

- Extraction kinetics studies: ordering of radioactive Ce(III) was delayed (waiting for safety agency authorisation)

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

MANPOWER

1.75 pm realized (KIT, UNIPR)

6.0 pm realized since the beginning of the project, corresponding to 44.1 % of the 13.6 pm planned for the complete project.

MAIN PROGRESSES

- Extraction of HNO_3, An(III) and Ln(III) into a TODGA-diisopropyl benzene (DIPB) solvent was studied (distribution ratios as function of HNO3 and TODGA concentrations)

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

MANPOWER

7.25 pm realized (CEA, KIT, POLIMI, UNIPR)

17.75 pm realized since the beginning of the project, corresponding to 52.2 % of the 34 pm planned for the complete project.

MAIN PROGRESSES

Loading of TODGA organic phases studies:

- A TODGA-diisopropyl benzene solvent was loaded with La(III)
- Studies coupling experiments with MD simulations for the characterization of the species formed in TODGA, TODGA+octanol and TODGA+DMDOHEMA organic phases have been continued. All solvent extraction experiments have been completed for the extraction of water and $Nd(NO_3)_3$. The solutions have been characterized experimentally using ESI-MS, FT-IR and SWAXS. MD Simulations for organic phases containing $Nd(NO_3)_3$ have been launched and will be analysed in the next months

Loading of aqueous phases containing Py-Tri-Diol as a selective complexing agent:

- A researcher from POLIMI was hosted for two months in the ATALANTE (CEA) facility within the frame of a GENIORS “secondment grant”. The loading capacities of PyTri-Diol solutions (fresh, aged and irradiated solutions) were studied performing batch solvent extraction tests in the EURO-GANEX, iSANEX and PTD-GANEX process conditions.

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

MANPOWER

2.38 pm realized (CIEMAT NNL, POLIMI)

4.38 pm realized since the beginning of the project, corresponding to 20.4 % of the 21.5 pm planned for the complete project.

MAIN PROGRESSES

- TODGA solvent clean-up: studies about the influence of detrimental degradation compound V (diglycolamic acid, DODGAA) on the extraction process: solubility limits in OK and first clean-up experiments
- Radiation dose study started – looking at effects of dose from future spent fuels on solvents used in EURO-GANEX processes and implications for solvent degradation, clean up and recycling

DIFFICULTIES

- Not enough amount of degradation products XII and XIII to perform parallel experiments (Task 3.4)
- Experimental work delayed due to delays in secondment of Ivan Sanchez from CIEMAT (see WP1.2 for more details)

LIST OF PUBLICATIONS

Publications:

1. *2,6-Bis(1-alkyl-1H-1,2,3-triazol-4-yl)-pyridines: Selective Lipophilic Chelating Ligands for Minor Actinides*: Ossola, A.; Macerata, E.; Mossini, E.; Giola, M.; Gullo, M. C.; Arduini, A.; Casnati, A.; Mariani, M., Journal of Radioanalytical and Nuclear Chemistry2018, Volume 318, Issue 3, pp 2013–2022.
2. *Optimization and Single-Stage Centrifugal Contactor Experiments with the Novel Hydrophilic Complexant PyTri-Diol for the i-SANEX Process.* Eros Mossini, Elena Macerata, Andreas Wilden, Peter Kaufholz, Giuseppe Modolo, Nicolò Iotti, Alessandro Casnati, Andreas Geist & Mario Mariani Solvent Extraction and Ion Exchange, Volume 36, 2018 - Issue 4
3. *Solvent extraction investigations on Pu(IV) and Th(IV) complexes with hydrophilic SO3-Ph-BTP and SO3-Ph-BTBP ligands.* Steczek L, Narbutt J, Charbonnel M-Ch, Moisy P. Solvent Extr. Ion Exch. 2019, accepted.
4. *Evaluation of the hydrophilic complexant N,N,N′,N′-tetraethyldiglycolamide (TEDGA) and its methyl-substituted analogues in the selective Am(III) separation.* Klaß L, Wilden A, Sadowski F, Wagner C, Geist A, Panak PJ, Herdzik-Koniecko I, Narbutt J, Modolo G. Solvent Extr. Ion Exch., submitted.
5. *Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA,* Whittaker, D. et al. Solvent Extr. Ion Exch., **2018**, *36*, 3, 223-256. DOI:10.1080/07366299.2018.1464269.

Conferences:

1. 18th Radiochemical Conference RadChem 2018 Poster NFC.L02 (Id: 723) *Lipophilic Pyridine-2,6-Bis(1h-1,2,3-Triazol-4-Yl) Extractant for Selective MA(III) Extraction In SANEX-Like Processes*: Ossola, A.; Mossini, E.; Macerata, E.; Gullo, M. C.; Casnati, A.; Mariani, M. Poster.
2. XII Spanish Italian Symposium on Organic chemistry (SISOC), 2-4 July 2018 Ferrara, Italy, *Pyridine-2,6-bis(1H-1,2,3-triazol-4-yl): a selective chelating unit for Minor Actinide extraction from radioactive wastes*: 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.
3. Merck and Elsevier Young Chemists Symposium (MEYCS), 19-21 November 2018 Rimini, Italy, “*Pyridine-2,6-bis(1H-1,2,3-triazol-4-yl): a selective chelating unit for Minor Actinide extraction from radioactive wastes*” : Gullo, M. C. ; Ossola, A.; Arduini, A. ; Sansone, F. ; Scaravaggi, S. ; Boubals, N. ; Charbonnel, M.-C. ; Mariani, M. ; Macerata, E. ; Casnati, A. Flash presentation.

CONCLUSIONS

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

After 18 months, 76.48 pm have been realized within WP3, corresponding to 52.0 % of the 147.1 pm planned for the complete project.

WP4

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
CNRS/ICSM	38.5	1.6	2.2	7.7
CEA	15.4	0.0	3.0	3.0
SCK.CEN	20.0	2.5	2.5	2.5
UNIMAN	11.0	0.0	0.0	6.0
Total	**84.9**	**4.1**	**7.7**	**19.2**

MAIN RESULTS

TASK 4.1

MANPOWER

3.4 pm (CNRS) – 3 pm (CEA) – 6 pm (UNIMAN) ⇒ Total : 12.4 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 has begun in month 6. The impact of the cerium mole loading on the chemical durability of $U_{1-x}Ce_xO_2$ solid solutions was examined. Uranium and cerium releases were the same during dissolution tests, showing a two-stage evolution. The first was associated to uncatalysed dissolution mechanisms (control by surface driving reactions) while the second was associated to catalyzed mechanisms (fast release of the cations in the solution). For uranium enriched materials, the dissolution seemed to have the same behavior as UO_2 ; the oxidation of uranium controlling the overall dissolution kinetics. In addition, the release of uranium and cerium in solution seemed to be faster when increasing the uranium mole loading in the samples.

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

To study of the solid/liquid interfaces during dissolution, the synthesis of CeO_2 and $Ce_{0.8}Gd_{0.2}O_{1.9}$ samples using oxalic route and calcined at different temperatures was performed to obtain samples exhibiting different levels of crystal defects and morphological parameters. The set-up of the Netzsch microserie grinder was fixed to study the milling/dissolution couplings. CeO_2 samples heated at 1200°C were ground then characterized before and after the grinding step. The dissolution of raw and ground samples of CeO_2 were performed. The grinding step increased the mass of dissolved material for given time and dissolution conditions. This effect was not only limited to the increase of specific surface area.

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) models, i.e. CeO_2 (UO_2 surrogate) containing either Pd ε-particles or fission products (Nd) or both, using polymer assisted deposition (PAD) and subsequent low-temperature calcination was developed. The method was derived from a layer-by-layer (LbL) method based on the work of Liu *et al*. for the synthesis of Ln-doped La and $CePO_4$. Structural characterization and leaching/dissolution studies are under way on CeO_2 model system. Studies into the effect of γ irradiation (up to 100 kGy) on the structure and leaching/dissolution of these films have been initiated.

DIFFICULTIES

Concerning the studies developed at UNIMAN, 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 have been 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.

ACTION PLAN

CNRS/ICSM

The dissolution experiments on $(U,Ce)O_2$ solid solutions were launched in May 2018. The first results obtained will be completed by making complementary dissolution tests (in terms of pH, T, …) in order to access the multiparametric dissolution law. Additional experiments will be devoted to the dissolution of $(U,Ln)O_{2-x}$ solid solutions.

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 initiated.

UNIMAN

Leaching/dissolution studies of both films and bulk samples are being investigated under simulated SNF storage conditions.

The effect of irradiation by α, p (as an n simulant) and γ radiation on the structure and leaching of CeO_2 samples will be explored using the Dalton Cumbria Facility (DCF). Prior to using the accelerator for irradiation, A. Holdsworth will take part in a safety and training course at the DCF site (the "DCF Accelerator Masterclass").

Pending approval for access to the active laboratory, the PAD method developed for the preparation of CeO_2 films will be adapted to the UO_2 system. This will require exploration of a range of U based precursors and calcination conditions for the optimisation of the film preparation. Due to different chemical behaviours of Ce and U +4 oxidation states (oxidizing vs. reducing), a reducing or inert atmosphere will be required for preparation of UO_2. Once the optimal protocol for film preparation has been established, ε-particles and MA simulants will be incorporated as for CeO_2, and characterization undertaken, followed by leaching/dissolution studies and investigation into the effect of irradiation.

TASK 4.2

MANPOWER

4.3 pm (CNRS/ICSM) + 2.5 pm (SCK.CEN) $\Rightarrow$ Total : 6.8 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

The synthesis of Ce-doped particles using Ce(IV) as precursor was tested. Spherical particles were obtained for molar Ce metal fraction up to 10 %. XRD analyses of the dried particles were carried out and the thermal behaviour was studied via TG-DSC. The gelled spheres were thermally treated and the products were analysed using powder XRD. A linearly decrease of lattice parameter with increasing Ce content up to 20% was 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, the usual structure of $U(C_2O_4)_2.2H_2O$ was observed whereas $UO_{2+x}.nH_2O$ was prepared above this temperature. SEM observations of the resulting samples further revealed the loss of the classical square platelet shape of the oxalate, while the evaluation of the residual carbon content led to values significantly lower than that usually obtained through thermal conversion. Additionally, controlling of the pH allowed to optimize the uranium precipitation yield and to orientate the morphology towards agglomerated microspheres. The kinetics of the hydrothermal conversion was also investigated and showed that crystalline $UO_{2+x}.nH_2O$ samples could be obtained after only 1 hour of heat treatment at 250°C. Finally, first results concerning the preparation of $(U,Ce)O_2$ mixed oxides were obtained and showed that the quantitative recovery of both uranium and cerium could be obtained through a heat treatment of 24 hours at 250°C and pH = 4. Further studies will then be devoted to sintering of the samples prepared as well as to the $(U,Ln)O_2$ systems.

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

$UO_2.nH_2O$ 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 size of the particles produced (200 – 1200 nm range). For all the conditions tested, the characterization of the powders showed the formation of fluorite type

$UO_2.nH_2O$ 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 microspheres. Complementary FIB experiments further confirmed the absence of porosity within these particles. Finally, preliminary tests concerning the shaping of the UO_2 microspheres into pellets were undertaken and revealed that green densities up to about 45 %TD can be obtained at 400-600 MPa without crushing the particles. First dilatometric studies are now under progress to evaluate the sintering capability of the compacts.

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. 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.

Preliminary studies on the conversion of uranyl nitrate into uranium oxide were done. In a first step, uranyl nitrate was prepared by dissolution of powdered UO_2 in 5M HNO_3. The solution obtained was heated on a hot plate to dryness to obtain uranyl nitrate crystals. These crystals were dissolved in distilled water and mixed with a quantity of fuel necessary to obtain a ratio fuel/$UO_2(NO_3)_2$ equal to 1 and 1.7. The heating rate was 10°C/min up to 300°C in air atmosphere. Uranium oxide was obtained after these treatments. The ignition temperature observed in these tests was in the range of 180-210°C. The process conditions impacted the nature of the phases obtained, the compound UO_{2+x} was obtained for the ratio (glycine/$UO_2(NO_3)_2$) equal to 1.7 whereas a mixture of UO_{2+x} and U_3O_8 was observed for a ratio of 1. Works are in progress to explain the origin of this difference.

DIFFICULTIES

Concerning the non-powder routes developed by SCK.CEN to prepare MOX fuels, the gelation parameter found to be suitable for the production of Ce doped particles using Ce(III) as precursor do not lead to satisfying products with Ce(IV) as starting material.

ACTION PLAN

SCK.CEN

During the next semester, the prepared samples will be analysed using scanning electron microscopy. The gelation parameter will be optimised for Ce(IV) as precursor and different sintering conditions will be investigated for the particles prepared with Ce(III) as precursor.

CNRS/ICSM

Direct precipitation of uranium oxides under hydrothermal conditions will be extended to $(U,Ln)O_2$ mixed oxides.

The sintering capability of UO_2 microspheres will be extensively studied through dilatometry tests and further SEM examinations.

The experimental protocol developed for the conversion of gadolinium nitrate to gadolinium oxide by Solution Combustion Synthesis has been transposed to uranium oxide powders. Extensive experiments will be developed during the next periods.

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).

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*.

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*

Thermal decomposition and structural changes of lanthanide-doped uranium dioxide particles prepared by internal gelation, C. Schreinemachers, G. Leinders, G. Modolo, M. Verwerft, K. Binnemans , T. Cardinaels; RadChem 2018 - 18th Radiochemical Conference, Marianske Lazne (Czech Republic), 13-18 May 2018 / *Given*

CONCLUSIONS

Several complementary ways of preparation of precursors are now under progress. They are able to provide a large variety of oxide based materials (Ce, U-Ce, U-Ln, U doped with FP) exhibiting various compositions, microstructures, defects, ... This spread panel of materials allowed to start 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.

WP5

MAIN RESULTS

TASK 5.1

MANPOWER

- CIEMAT : 3.25 pm
- ULEEDS: 0.3 (+6) pm
- ULANC: 6 pm

MAIN PROGRESSES

- CIEMAT:
  - Irradiation loop at Nàyade facility:

- ▪ Material evaluation under radiation conditions, organic solvents and high nitric acid concentrations
- ▪ Schematic overview of the current Nàyade loop status
- ○ Simulation of relevant process conditions, ongoing:
- ▪ New irradiation and analysis of samples corresponding to TODGA /SO_3PhBTP system to corroborate data previously obtained and extract final conclusions: qualitative and quantitative analysis by HPLC_MS; extraction behavior of An and Ln after irradiation-
- ▪ Irradiation of samples corresponding to a full Euro-GANEX system (TODGA-DMDOHEMA-AHA-So3PhBTP system)
- ULEEDS
- ○ Development of a numerical method for simulating multiphase flows and implementation within the open-source Computational Fluid Dynamics code OpenFOAM.
- ○ Examination of the capabilities of the above mentioned code in various two and three-dimensional numerical tests and obtained results for a journal paper.
- ○ Creation of the CAD design and the computational mesh of an annular centrifugal contractor. Simulation and analysis of results from simulations of annular centrifugal contractors.
- ○ Participation in meetings inside and outside the university in Antwerp, Belgium for the Geniors meeting and in Idaho, USA, visiting the Idaho National Laboratory.
- ○ Preparation of a journal paper demonstrating the capabilities of the developed method and results providing comparisons and validation.
- ULANC
- ○ Rotating diffusion cell (RDC) studies have been performed to determine the extraction kinetics of La/FPs
- ▪ The primary kinetic limitation was found to be the rate at which TODGA complexes with Ce(III)
- ▪ Indications on a 10 times higher than expected concentration of TODGA at the org/aq interface were found
- ○ The extraction-suppressing effects reported in HYPAR 2, is much diminished below aqueous acidities of 0.7 mol dm^{-3}. Some suppression is still seen for very long RDC run times.

DIFFICULTIES

- ULEEDS: Modelling of multiphase PSPECs is computationally expensive, finding the resources in order conduct studies has been difficult. My availability on the University of Leeds HPC (ARC3) has been throttled due to heavy use, as such progression of models has been limited
- CEA_ temporary unavailability of the single drop experimental device

ACTION PLAN

- CIEMAT
- ○ Continue work on simulating relevant process conditions
- ULEEDS:
- ○ Pulsed column: Continue with original plan outlined in the previous HYPAR report, to conduct an in-depth study comparing the different turbulence (flow) modelling approaches to justify the use of the method chosen (large eddy simulation)
- ○ Centrifugal contactors: Continuation of the development of the numerical method for simulating centrifugal contractors, improving the code. In addition, some more numerical tests for the developed methodology in two and three dimensions will be carried out for the assessment of the new algorithm.

- ULANC
  - Work on validating the new analytical model of the RDC
  - Experiments at lower acidities will be performed
- CEA: work to start ASAP. Determination of mass transfer coefficients of Am and Eu in the stripping conditions of EURO-GANEX.

TASK 5.2

MANPOWER

- UEDIN: 6 pm

MAIN PROGRESSES

- UEDIN:
  - Electrodes redesigned and fabricated: move from Pt single microelectrodes to Pt arrays and Pt arrays with ion exchange membrane
  - Establish suitability of chosen membrane for use in system and its influence of membrane on nitric acid signal
  - Testing of Ce3/4 and Fe2/3 as non-active analogue reactions in nitric acid on initial and redesigned devices
  - Set up collaboration with UREAD to supply ligands for electrochemical testing
  - Initial electrochemical response of exemplar species: free and ligand-bound iron in nitric acid
  - Funding for EPSRC project ATLANTIC secured which will leverage GENIORS funding

DIFFICULTIES

- UEDIN: lab move caused interruptions in labwork for 6 weeks.

ACTION PLAN

- UDEIN:
  - An optimised experimental plan for ligand extraction will be determined and executed, including the extraction monitoring in a range of conditions
  - Test the influence of the presence of organic phase components on electrochemical detection
  - Presentation of data to GENIORS community for discussion, particularly ULEEDS as co-contributor to T5.2, followed by write up data for publication

TASK 5.3

MANPOWER

- NNL: 1.99 pm

MAIN PROGRESSES

- NNL
  - Paper submitted to Solvent Extraction and Ion Exchange
  - Initial phase of modelling of trivalent Ma/Ln extraction into i-SANEX solvent completed

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.

- Workshop held in Manchester to discuss way forward

DIFFICULTIES

- NNL
  - None

ACTION PLAN

- NNL
  - Complete the process model development and validation by performing more experiments
  - Submit a journal paper on a model of trivalent MA(Ln extraction into i-SANEX solvent

LIST OF PUBLICATIONS

David Woodhead, Fiona McLachlan, Robin Taylor, Udo Müllich, Andreas Geist, Andreas Wilden, Giuseppe Modolo, Nitric Acid Extraction into a TODGA Solvent Modified with Octanol, under review Solv. Extr. Ion Exch. (2018)

”A Study of Cerium Extraction Kinetics by TODGA in Acidified and Non-Acidified Organic Solvent Phases in the Context of Fission Product Management”, M.A.Bromley, C.Boxall, Prog.Nucl.Sci.Tech, 5, in press (2018).

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 10.55 person-months has been reported split into 6.5 person-months for Task 1 (JUELICH, KIT, CHALMERS, POLIMI, UNIPR), and 4.05 person-months for Task 2 (JUELICH, POLIMI).

	task 1		task 2	
	expected	achieved	expected	achieved
JRC	0	0	0	0
JUELICH	0	0	2	3.8
KIT	2	2.5	0.375	0
CHALMERS	4	4	0	0
CEA	0	0	0	0
NNL	0	0	0	0
POLIMI	0	0	0.25	0.25
UNIPR	0	3	0	0
total	6	6.5	2.625	4.05

MAIN PROGRESSES

EXTRACTION WITH M-TDDGA (STUDIES AT KIT)

Distribution ratios for An(III) and Ln(III) were acquired with mTDDGA (TWENTE, 95:5) dissolved in kerosene as function of the initial nitric acid concentration (Figure 9). Compared to TODGA in kerosene + 5 vol.% 1-octanol distribution data were found to be rather low, requiring higher nitric acid concentrations to extract Am(III) and Ln(III). This trend had also been observed for methylated and dimethylated TODGA. mTDDGA synthesized at INE shows a diastereomeric composition of 50:50. The fact that only the cis diastereomer extracts was established experimentally. Distribution ratios for the TWENTE compound are larger by a factor 5, which is in good agreement with the relative concentrations of the (better extracting) cis diastereomer being 1.9. Applying the concentration dependency observed for TODGA in TPH/1-octanol (slope ≈2.7, see GENIORS HYPAR2-KIT), a factor of 5.7 is expected.

NEW PYRIDINE TRIAZOLE LIGAND DEVELOPMENT AT UNIPR

A new lipophilic ligand based on the Pyridine Triazole unit was synthesized and test in POLIMI showing interesting properties for its possible use in the EURO-GANEX process. The synthesis was developed in UNIPR while the extraction data were collected in POLIMI. A sample was sent to POLIMI, another one to KIT. Although other lipophilic Pyridine Triazole binding groups were reported in the literature we believed that their inability to extract actinides or lanthanide into organic layer was due not to the inefficiency of binding but to the extremely low solubility of these ligands in organic diluents used (dodecane/kerosene). Starting from this assumption, we planned to synthesise a PyTri derivative bringing branched alkyl chains on the triazole units. We choose the 2-ethyl-hexyl chains since they can be obtained starting from the commercially available and cheap 2-ethyl-hexanol. From this alcohol it was relatively easy to prepare the chloride and to transform this chloride into an azide. The synthesis of the lipophilic ligand named PTEH (Scheme 1) was accomplished by directly clicking this azide derivative 2 onto the 2,6-dialkynyl-pyridine 1. The reactions proceeded smoothly at room temperature in a mixture of DMF/H2O. After 24–72 hs, the ligand was extracted in the organic phase and purified by column chromatography, resulting in yields of 65%. The structure of the final ligands was properly confirmed by NMR and MS spectroscopy.

PTEH was studied in POLIMI showing very interesting extraction properties both in terms of efficiency and selectivity. Solubility was reasonably high especially in mixture of kerosene containing few percentages of octanol. This preliminary results augur well for the application of this CHON ligand in a EURO-GANEX process.

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RADIOLYTIC STABILITY OF THE CHALMEX PROCESS

Table 1 shows the results of the extraction experiments performed on the solvent irradiated to different doses in contact with nitric acid. A decrease in distribution ratio of Am and Eu can be seen for increased doses. Somewhat surprisingly, an opposite trend is seen for both plutonium and neptunium: increased dose gives increased extraction.

Table 1 presents the distribution ratios for the extraction experiments performed on the solvent irradiated in contact with acid, for various dose rates.

Series 1: in contact with nitric acid				
Dose (kGy)	**D(Am)**	**D(Pu)**	**D(Np)**	**D(Eu)**
0	152		3	2.2
25	152	23	3.5	1.4
100	156	41	3.7	1.7
150	146	68	5.3	1.5
350		174		
500	83	212	9	1

However, a distinction between the series irradiated in contact with nitric acid and without nitric acid became clear: the former showed higher distribution ratios overall for all the elements investigated (Pu, Am, Np, Eu), as can be seen when comparing of the chalmex process

Table 1 shows the results of the extraction experiments performed on the solvent irradiated to different doses in contact with nitric acid. A decrease in distribution ratio of Am and Eu can be seen for increased doses. Somewhat surprisingly, an opposite trend is seen for both plutonium and neptunium: increased dose gives increased extraction.

Table 1 or Table 2. It also appears that the solvent irradiated without acid contact show a trend of increasing extraction with dose for americium. Further studies of higher doses are required to conclude however.

Table 2 presents the distribution ratios for the extraction experiments performed on the solvent irradiated without contact with acid, for various dose rates.

Series 2: no acid contact				
Dose (kGy)	**D(Am)**	**D(Pu)**	**D(Np)**	**D(Eu)**
0	152		3	2.2
25	167	24	2.6	1.6
100	179	42	3.1	1.9
150		52		

Finally, a reference series was also investigated, in order to identify any thermal effects on the solvent. The results are presented in Table 3. Here it can be seen that the thermal instability of the solvent have at least some effect on the extraction, though more studies are also required in order to finally conclude.

Table 3 presents the distribution ratios for the extraction experiments performed on the reference series: kept at 50degC for the same time period as the equivalent radiation dose in the GammaCell.

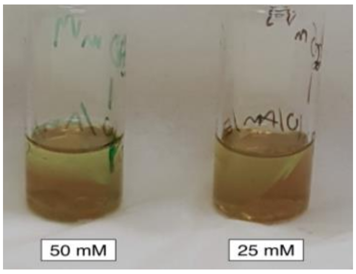
Reference series: 50degC				
Time equivalent to dose (kGy)	**D(Am)**	**D(Pu)**	**D(Np)**	**D(Eu)**

0	152	64	3	2.2
25	138	61	5.9	1.4
100	105	69	11.4	1.4

URANIUM LOADING IN THE CHALMEX PROCESS

The proposed future GANEX process for partitioning and transmutation of used nuclear fuel is based on two extraction steps following fuel dissolution: the extraction of bulk uranium and subsequent co-extraction of all the transuranic elements neptunium, plutonium, americium and curium. A feasibility study on the combined extraction of uranium and subsequent transuranic elements has been performed.

	$[U]_{tot}$ (mol dm^{-3})	$[Pu]_{tot}$ (mol dm^{-3})
50 g U L-1	0.21	0.042
100 g U L-1	0.42	0.042



The system with 100 g U L^{-1}, showed adequate separation factors for CyMe$_4$-BTBP concentration 25 mM, though complete polymerisation of both aqueous and organic phase was observed for extractant concentrations of 50 mM.

By lowering the uranium content, a significant increase in distribution ratios were observed, in particular for CyMe$_4$-BTBP concentration 50 mM. On the contrary to other systems investigated, the neptunium extraction remained high throughout all the systems tested. The oxidation states of both plutonium and uranium were confirmed at +4 and +6 respectively during the extraction, by UV-VIS spectroscopy. This confirms that the Pu and U is extracted by TBP.

DIFFICULTIES

Availability of key ligands such as PTD and m-TDDGA in sufficient quantities has been highlighted as a potential problem (for new EURO-GANEX process development).

ACTION PLAN

The action plan for EURO-GANEX process development has been defined in the minutes of the Antwerp workshop. Plans for the CHALMEX process development are still being developed.

TASK 1.2: HETEROGENEOUS RECYCLING

MANPOWER

	task 1		task 2	
	expected	achieved	expected	achieved
JRC	0	0	0	0
JUELICH	0	0	2	3,8
KIT	2	2,5	0,375	0
CHALMERS	4	4	0	0
CEA	0	0	0	0
NNL	0	0	0	0
POLIMI	0	0	0,25	0,25
UNIPR	0	3	0	0
total	6	6,5	2,625	4,05

A total of 10.55 person-months has been reported split into 6.5 person-months for Task 1 (JUELICH, KIT, CHALMERS, POLIMI, UNIPR), and 4.05 person-months for Task 2 (JUELICH, POLIMI).

MAIN PROGRESSES

AMSEL PROCESS DEVELOPMENT AT JUELICH

In our first two HYPAR reports, the optimization of the AMSEL system was reported, including single centrifugal contactor tests. The aim of the AMSEL process is to selectively separate Am(III) from a high active raffinate solution. The process is based on the i-SANEX process, namely an extraction using 0.2 mol/L TODGA in TPH + 5 vol.-% 1-octanol. The co-extraction of Zr and Pd is prevented using CDTA in the aqueous feed. Stripping of Am(III) is done using a solution of SO_3-Ph-BTBP in nitric acid.

Due to the failure of our ICP-MS equipment, the stable element concentrations could not be determined and reported in the former reports. A new ICP-MS machine was installed in JUELICH recently. As the samples have been stored for later analyses, we can now determine the stable element concentrations in the old samples.

A comparative study of different TODGA batches available in JUELICH was done in batch shaking experiments in the AMSEL system. Figure 1 shows the results and a comparison to literature data. The used TODGA batches were purchased from TechnoComm Ltd. (TODGA1 = older batch, TODGA3 = re-purified “Batch009”), or received from KIT (TODGA2). Generally, the different batches and the literature data (Wagner, C.; Müllich, U.; Geist, A.; Panak, P. J. Selective Extraction of Am(III) from PUREX Raffinate: The AmSel System. Solvent Extr. Ion Exch. 2016, 34, 2, 103-113) are in relatively good agreement.

The Ln(III) extraction pattern shows an unusual behavior, as increasing distribution ratios are observed for the light to medium lanthanides with a maximum between Sm-Gd. Then, the distribution ratios decrease to a minimum around Tm, after which for some TODGA batches a new increase is observed.

Another difference in the behavior of lighter and heavier lanthanides is also observed for the distribution ratios as a function of the HNO_3 concentration, as shown in Figure 2. For the lighter lanthanides a roughly linear relationship is observed, while the heavier lanthanides and Y don’t show that linearity. Currently, the reason for this behavior is unclear.

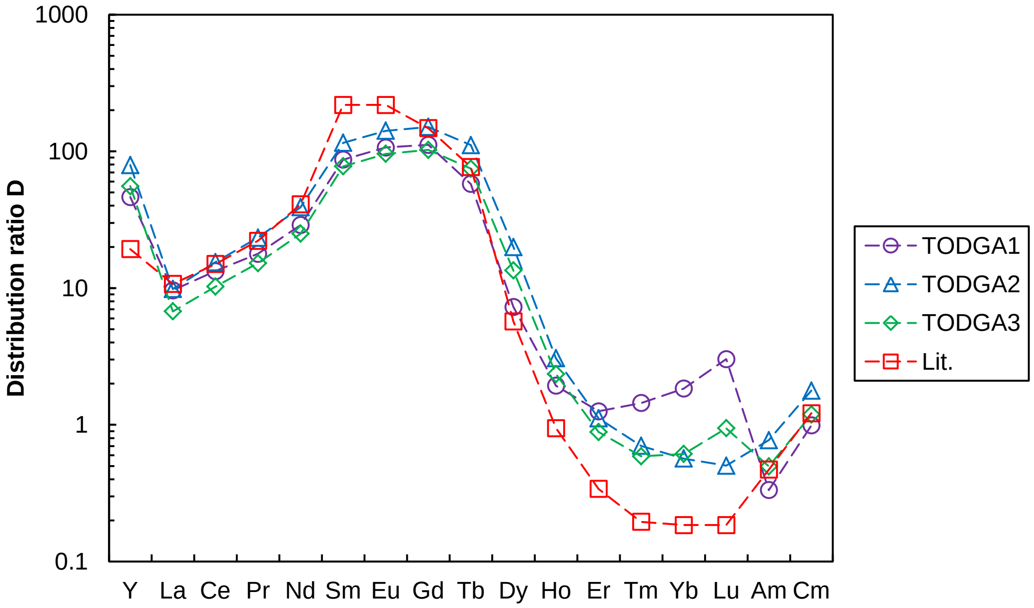
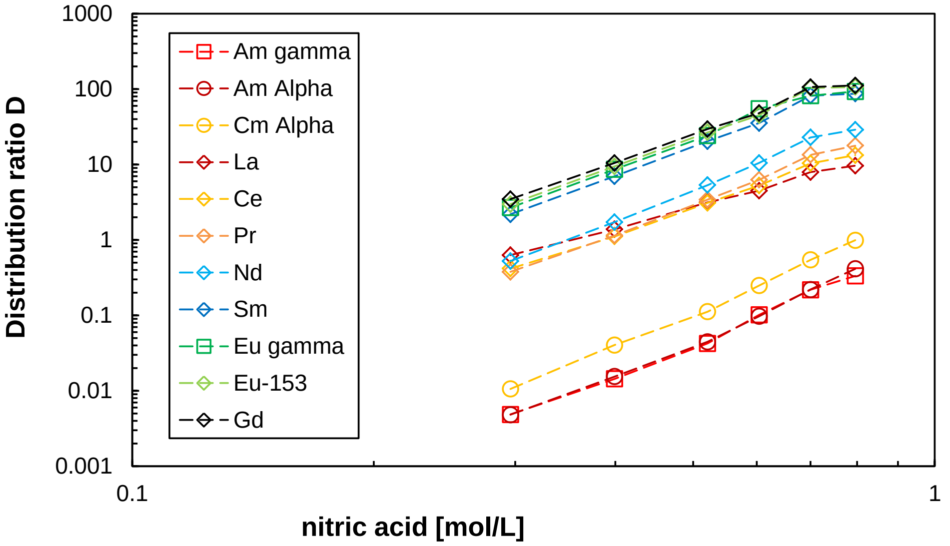


Figure 1. Distribution ratios of metal ions in the AMSEL system for different TODGA batches and comparison to literature data taken from Wagner et al. Org: 0.2 mol L^{-1} TODGA (Description of batches in the text) + 5 vol.-% 1-octanol in kerosene (JUELICH = TPH, Lit. = Exxsol D80); aq.: 0.8 mol L^{-1} HNO_3 + SO_3-Ph-BTBP (JUELICH = 0.01 mol L^{-1}, Lit. = 0.02 mol L^{-1}).



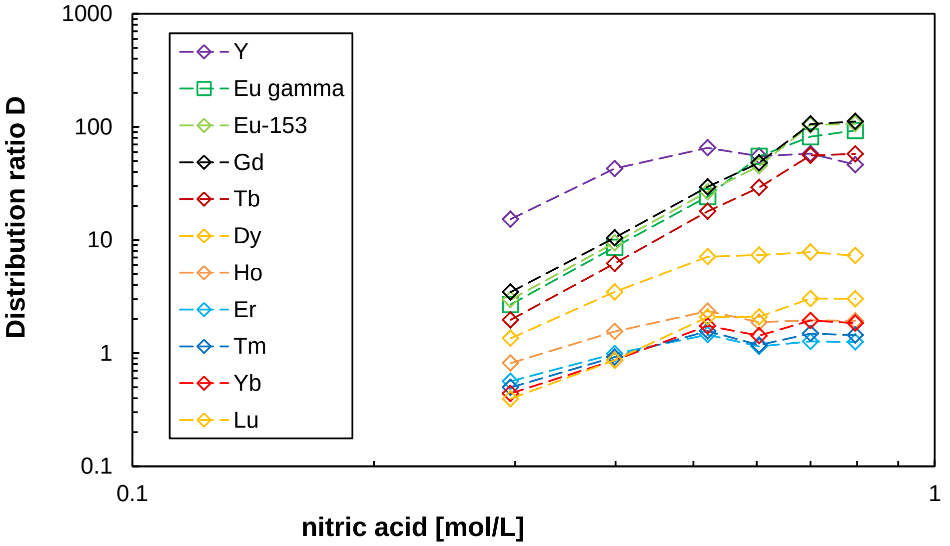


Figure 2. Distribution ratios of metal ions in the AMSEL system as a function of the HNO_3 concentration. Org: 0.2 mol L^{-1} TODGA (TechnoComm older batch) + 5 vol.-% 1-octanol in TPH; aq.: HNO_3 + 0.01 mol L^{-1} SO_3-Ph-BTBP.

ACTION PLAN

An AmSel process flow-sheet will be developed in collaboration with KIT, based on the results of single centrifugal contactor tests. The flow-sheet will be tested in the JUELICH centrifugal contactor battery.

LIST OF PUBLICATIONS

1. Wilden, A. et al. Unique Difference and Unprecedented Inversion of Selectivity in the Complexation of Trivalent Actinides and Lanthanides by Different Diastereomers of Me2-TODGA. J. Am. Chem. Soc. 2018, submitted.
2. Halleröd, J., Ekberg, C., Authen, T., Bertolo, L., Lin, M., Grüner, B., Svehla, J., Geist, A., Panak, P., Wagner, C. and Aneheim, E.: On the basic extraction properties of a phenyl trifluoromethyl sulfone based GANEX system containing CyMe4-BTBP and TBP. Published, Solvent extraction and Ion Exchange.

3. Rikard Malmbeck, Daniel Magnusson, Michael Carrott, Andreas Geist, Xavier Hérès, Manuel Miguirditchian, Giuseppe Modolo, Udo Müllich, Christian Sorel, Robin Taylor, Andreas Wilden, Homogenous Recycling of Transuranium Elements from Irradiated Fast Reactor Fuel by the EURO-GANEX Solvent Extraction Process, submitted to Radiochimica Acta.
4. Eros Mossini, Elena Macerata, Andreas Wilden, Peter Kaufholz, Giuseppe Modolo, Nicolò Iotti, Alessandro Casnati, Andreas Geist, Mario Mariani, Optimisation and single-stage centrifugal contactor experiments with the novel hydrophilic complexant PyTri-Diol for the i-SANEX process, Solvent Extraction and Ion Exchange, 36(4), pp. 373-386.
5. Ossola, A.; Macerata, E.; Mossini, E.; Giola, M.; Gullo, M. C.; Arduini, A.; Casnati, A.; Mariani, M., 2,6-Bis(1-alkyl-1H-1,2,3-triazol-4-yl)-pyridines: selective lipophilic chelating ligands for minor actinides, Journal of Radioanalytical and Nuclear Chemistry2018, Volume 318, Issue 3, pp 2013–2022

CONCLUSIONS

The work package concerns flowsheet development of key processes for homogeneous and heterogeneous recycling so it is expected that most studies will commence later in the project. No significant delays or causes for concern were raised by the partners in the HYPARs.

Manpower on the WP has increased in semester 3, particularly in task 1. In the last semester good progress has been made on both the CHALMEX and AMSEL flowsheet development. An important step was the EURO-GANEX workshop at which the forward plans for optimisation of the process were agreed. This plan will be followed from the next semester onwards.

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 Task 7.4 on characterization of MABB precursors. This semester major progresses were achieve in Task 7.1 with establishment of a model to describe the effect of the Pu content in the dissolution rates of $U_{1-x}Pu_xO_{2\pm\text{⍰}}$, preliminary results on the absence of effect of residual organic presence on Th oxalate solubility and in Task 7.3 with $U_{0.9}Am_{0.1}O_{2-\text{⍰}}$ dense pellet fabrication from microsphere precursors reducing dust generation⍰ For Task 7.4, Concept flowsheets for (U,Pu) and MA co-conversion processes have been designed in EXCEL (for an Advanced PUREX process coupled to a i-SANEX process) and (U,Pu) co-precipitation studies have been prepared.

MAIN RESULTS

TASK 7.1

MANPOWER

Expected effort for the period 2 men.month

Actual effort spent during the period 2 men.month

MAIN PROGRESSES

In the previous semesters eighteen samples of (U,Pu)O2 were synthetized and characterized with a Pu amount ranging from 0 to 100 % and with different morphologies in order to be able to collect data on dissolution kinetics on single phases depending on the dissolution parameters on one hand and on the solid parameters (Pu amount, morphology parameters: crystallite size, SSA,…) on the other hand.
This semester was dedicated to the dissolution of $(U,Pu)O_2$ samples with different Pu content made last year.
As exposed in [1] (*see references page 40*) the stoichiometry of oxides used in this study was determined by TIMS analyses performed on total dissolution aliquots. Table 4 summaries the structural parameters of the oxides studied during this semester and already given in [1].

Table 4 : Structural parameters for each powders of (U,Pu)O2 synthetized by sol-gel route and calcined at different temperature.

Compound	Calcination temperature (°C)	Lattice parameter (Ă)	Average crystallite sizes (nm)	Specific surface area (m²/g)
$U_{0,64}Pu_{0,36}O_2$	1500	5.4419 (1)	185 (5)	0.4 ± 0.3
$U_{0,43}Pu_{0,57}O_2$	850	5.4276 (1)	49 (1)	0.4 ± 0.3
$U_{0,39}Pu_{0,61}O_2$	850 a	5.4321 (1)	43 (1)	1 ± 0.1
	850 b	5.4228 (1)	33 (1)	1.5 ± 0.3
	1000 c	5.4241 (1)	69 (2)	0.9 ± 0.2
$U_{0,24}Pu_{0,76}O_2$	850	5.4131 (1)	56 (2)	2.2 ± 0.2
PuO_2	850	5.3980 (1)	17 (1)	6.3 ± 0.5

The lattice parameters vary with the plutonium content according to the Vegard's law. This law was plotted in Figure 3 from the values presented by Young *et al.* [2] for UO_2 and Freeman *et al.* [3] for PuO_2. The experimental lattice parameters are nearly perfectly aligned with this law, indicating that they correspond to the theoretical lattice parameters calculated from the TIMS characterization. In the case of $U_{0,39}Pu_{0,61}O_2$ 850 a, there is a slight deviation from the line corresponding to a slight sub-stoichiometry of the compound. Also on Table 4, the oxides resulting from the same calcination temperature presents similar average crystallite sizes. Furthermore, the average crystallite sizes seem increase while the calcination temperature increases, that is coherent with data from the literature describing crystal growth during the sintering process [4].
The specific surface areas obtained are all of the same order of magnitude and rather small, but in accordance with the values already obtained in the literature for actinide oxides [5]. Specific surface area of the oxides appears to be lower when the calcination temperature applied to obtain the oxide is high.

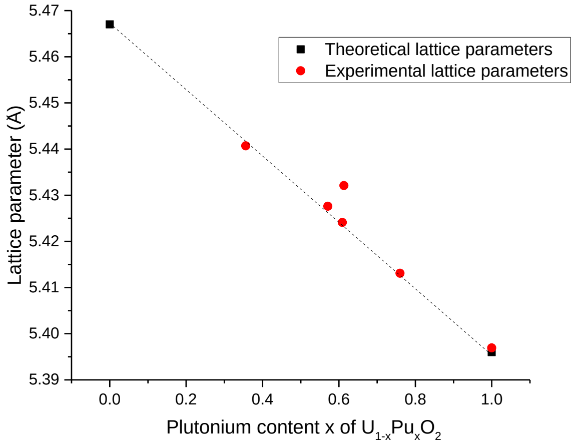


Figure 3 : Evolution of the lattice parameter with Pu content in (U,Pu)O_2 solid solution, measured by XRD and compared with Vegard's law.

Each dissolution test was conducted in a dissolution reactor of 60mL with 15 mL of nitric acid and 300 mg of oxide powder (Figure 4). The lid of the reactor was equipped with a cooling column allowing potential nitrous vapors to condense. For safety issues the top of this cooling column was connected to a gas cleaner composed of soda 2M to ensure no nitrous emission inside the globe box. The solution was heated using a hot plate; temperature was followed using a thermometer. The solution was homogenized using a magnetic stirrer at 300rpm. Once the solution at the right temperature, the oxide powder was introduced inside the reactor at t=0. Then, aliquots of the dissolution liquor were sampled using a syringe and analyzed by alpha counting to follow the dissolution kinetics; the error bar applied to the experimental measurement is equal to 10% from pre-establish standards. The congruence of uranium and plutonium was verified and the mixed powders dissolve homogeneously.

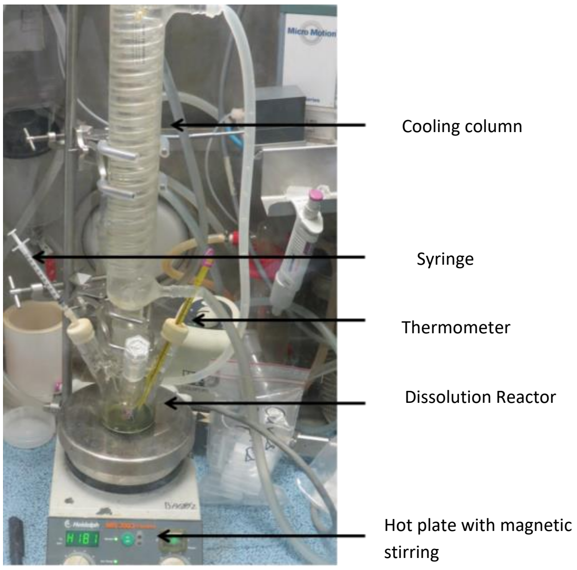


Figure 4: Dissolution apparatus set up in glove box

Last semester, the powder morphology effect on dissolution was reported for different PuO_2 samples [6] defining a model only based on crystallite size and specific surface area. To perfectly describe the effect of the Pu content, it is essential to validate that the model describing effect of the morphology induced on dissolution is also valid for (U,Pu)O2. Thus, three $U_{0.39}Pu_{0.61}O_2$ oxide powders were synthesized with different crystallite sizes and specific surface areas (Table 4). These oxides were dissolved under the same experimental conditions and the kinetics rates of dissolution are shown in Figure 5. The figure shows that for a same plutonium content, the dissolution rate can vary by a factor of 4 only due to morphological differences.

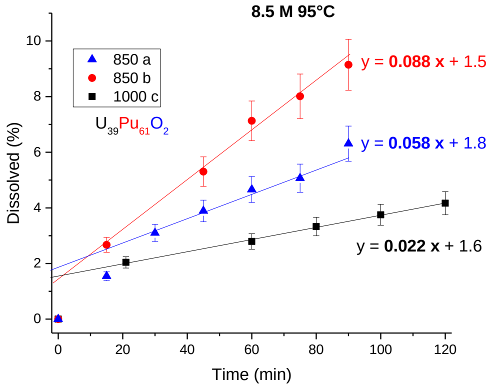


Figure 5 : Dissolution of three$U_{0.39}Pu_{0.61}O_2$ powders, in 8.5 $mol.L^{-1}$ nitric acid at 95°C.

Keeping the same partial orders for the crystallite size and the specific surface area than determined in PuO_2 model (ie -1 and 0.33 respectively), the resolution of the system of three equations with an unknown leads to the empirical law Eq. 1. The correlation coefficient of this law is 0.99. This coefficient expresses the possibility to describe satisfactorily the kinetics of dissolution from the morphological characteristics of the powders. This extrapolation is applied to all mixed oxides and makes it possible to dissociate, under same experimental conditions, the effects of the plutonium content and the morphological effects.

$$y = 10^{0,35} * Tc^{\,-1} * S_{spé}{}^{0,33} \qquad \text{Eq.1}$$

With Tc the crystallite size in nm and Sspé the specific surface area in $m^2.g^{-1}$.

The experimental conditions of dissolution of all samples of this study were kept constant (i.e. $[HNO_3]$ = 8.5M at 95°C, stirring rate of 300 rpm), in order to look at the specific effect of the plutonium content on dissolution of $(U,Pu)O_2$. The determination of the concentration of plutonium in solution allows reaching the mass of dissolved oxide and thus the percentage of powder dissolved at each instant. All these percentages lead to a line and by a linear regression, the slope of the line corresponds to the dissolution kinetics rate. The dissolutions of the compound presented different plutonium content are illustrated in Figure 6. In the same way that has already been found in the scientific literature, increasing the plutonium content leads to a decrease in kinetics. A factor close to one thousand is observed between the dissolution kinetics of $U_{0.64}Pu_{0.36}O_2$ and PuO_2. However, as it can be seen, the dissolution rate of the PuO_2 sample is faster than the dissolution rate of the $U_{0.24}Pu_{0.76}O_2$, this can be explained by morphological parameters making this PuO_2 powder more favorable to dissolution than the $U_{0.24}Pu_{0.76}O_2$ sample (lower crystallite size and higher specific surface area). It has to be noticed that the dissolution kinetic rate of the $U_{0.64}Pu_{0.36}O_2$ powder is obtained only from two experimental points, because of a high reactivity of this powder. The Table 4 presented morphologies refractory to dissolution in nitric medium, so there is here a consequent effect of the plutonium content on the dissolution kinetics. Some tests were carried out under similar experimental conditions on powders with lower plutonium content and the dissolution rates were too fast to be measured experimentally.

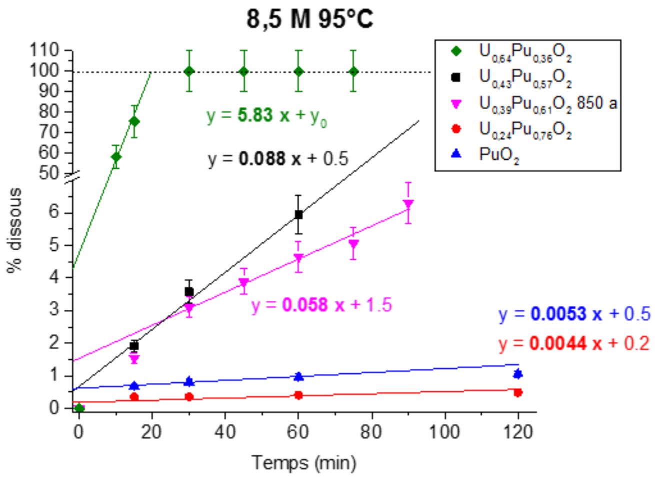


Figure 6 : Dissolution of (U,Pu)O_2 powders with different plutonium content and different morphologies in the same experimental conditions ([HNO_3]=8.5mol.L^{-1} at 95°C).

Considering Eq.1 to be $= k * Tc^{-1} * S_{spé}{}^{0,33}$, under same experimental conditions the constant k depends only on the Pu content of the mixed oxide. By plotting the logarithmic functions of the constant k according to the plutonium content, a line is obtained (Figure 7) defining by the regression presented in Eq. 2.

To conclude, the effect of the plutonium content on the dissolution kinetics is defined by a power function.

$$k = \%Pu^{-9.5} * 10^{-17.3} \qquad \text{Eq.2}$$

With %Pu the plutonium content of the oxide powder in percent.

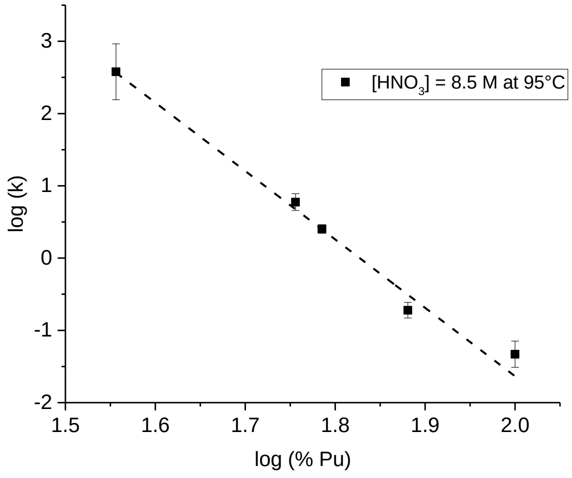


Figure 7: Relation between the kinetic rate constant and the plutonium content of the oxide for dissolution in 8.5 mol.L^{-1}nitric acid at 95°C.

ACTION PLAN

Delivery report has to be written.

TASK 7.2

MANPOWER

Expected effort for the period 2.8 men.month

Actual effort spent during the period 2.81 men.month

MAIN PROGRESSES

Introduction

Complexing ligands are increasingly being used in the separation processes proposed for actinide recycling. However, there is concern regarding how they will affect the downstream conversion process if they are carried over from the partitioning process as part of the advanced reprocessing flowsheet. A key issue is whether complexing agents or their degradation products (such as acetic acid) will enhance the solubilities of actinide ions and reduce the efficiency of the oxalate co-precipitation process. This will lead to decisions on whether an organic destruction stage is needed before oxalate co-precipitation or after (before the oxalate mother liquor is recycled into the process). The effects on the downstream oxalate precipitation process in the presence of acetic acid (AA) and acetohydroxamic acid (AHA) is thus being investigated. The initial stage is to validate methods using thorium nitrate and determine the solubility of the thorium in the oxalate mother liquor (OML).

Experimental Method

The solubility of thorium in the OML was measured to determine the effect of varying acidity and in the presence of AHA and AA. The experimental conditions investigated are presented in Table 1.

Experiment No	HNO3 (M)	Oxalic Acid (M)	Thorium Nitrate (M)	Ligand (M)
1	0.2	0.2	0.00228	0
2	0.3	0.03	0.00228	0
3	3	0.3	0.00228	0
4	3	0.03	0.00228	0
5	0.1	0.3	0.00228	0.05
6	0.2	0.2	0.00228	0.05
7	0.2	0.1	0.00228	0.05
8	0.3	0.03	0.00228	0.05
9	1	0.15	0.00228	0.05
10	1	0.1	0.00228	0.05
11	3	0.25	0.00228	0.05
12	3	0.15	0.00228	0.05
13	3	0.03	0.00228	0.05
14	3	0.01	0.00228	0.05

The molarity of the thorium was kept constant and, if a ligand was present, this was also added at consistent concentration. Similarly to previous experiments in our lab, a Radley Carousel reaction station was used to carry out the precipitation experiments and was maintained at a constant temperature of 25°C. For each experiment 1 mL of thorium nitrate stock was added to each reaction vessel followed by the desired quantities of nitric acid, ligand (if required) and ultra pure water. A magnetic stirrer was added to each experiment and the stirrer plate was set to 500 rpm. Once the temperature had stabilised, the required amount of oxalic acid was added and left to stir. At 4 and 6 hours, the stirrer was switched off and the precipitate was left to settle. Aliquots of the supernate were taken and diluted in order to carry out ICP-MS analysis to determine the concentration of thorium.

Results and Discussion

Previous work carried out by NNL measured the solubility of thorium in the OML with no ligand present. In order to confirm these results, a small selection of experiments (1-4 from Table 1) were conducted which were directly comparable to tests carried out previously. A comparison of the results from 2016 and the data collected in 2018 show a very close correlation and are presented in Figure 1. This validation provided confidence to move forward with the experiments in the presence of AHA and AA.

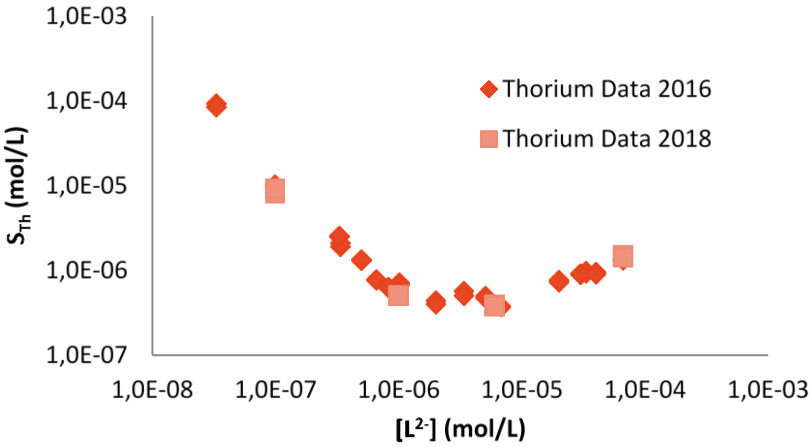


Figure 8. Thorium Oxalate solubility data comparison between results collected in 2016 and 2018.

As detailed above, ten different experiments at varying acidities were conducted for each of the two ligands. As the few thorium data points obtained replicated the previous results, it was considered reasonable to compare the experiments containing AA and AHA to the original data set, shown in Figure 2.

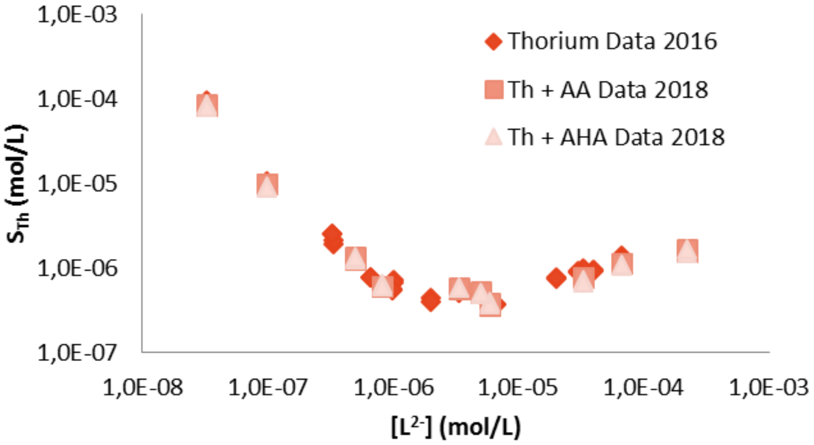


Figure 9. Thorium oxalate solubility data comparison in the presence of two different complexants (Acetic Acid and AcetoHydroxamic Acid).

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.

The results demonstrate that the presence of the two different ligands do not affect the solubility of the thorium in the OML, as they follow the same trend as the initial thorium experiments where no complexant was present.

ACTION PLAN

- Complete Pu(oxalate) solubility experiments
- Start electrochemical ligand decomposition studies

TASK 7.3

MANPOWER

Expected effort for the period 3 men.month

Actual effort spent during the period 3 men.month

MAIN PROGRESSES

1. Introduction

During the previous semester [6],mixed oxide microspheres $U_{0.90}Am_{0.10}O_{2\pm}$ were fabricated by thermal treatments of ion exchange resin loaded with Am^{3+} and UO_2^{2+} cations. The degradation of the polymeric skeleton under air followed by reducing heat treatment led to the synthesis of spherical precursors with diameter comprised between 325 µm and 425 µm and apparent density of (24 ± 1)% TD. A solid solution was formed during the reducing heat treatment and ensured a homogeneous distribution of uranium and americium atoms in the solid. Fabrication of a pellet using this precursor was then attempted during this semester.

2. Green and sintered pellets

A mass of approximately 600 mg of oxide precursors was pressed into pellet. The green pellet obtained was sintered in a dilatometer under Ar/H_2 (4 vol.%) and the axial linear shrinkage was recorded as a function of temperature (Figure 10). Table 5 summarized the green and sintered pellet characteristics.

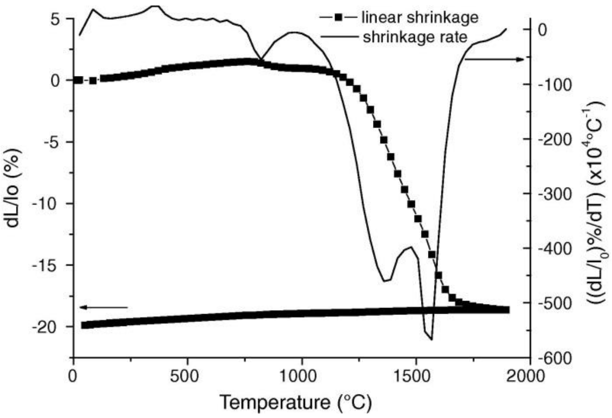


Figure 10 : Dilatometric analysis of U0.9Am0.1O2 green pellet: axial shrinkage and shrinkage rate curves in function of temperature under a reducing atmosphere of Ar/H2 (4 vol.%).

Table 5 : Green and sintered $U_{0.9}Am_{0.1}O_2$ pellet characteristics.

Pellet	Mass (g)	Height (mm) ±0.01	Diameter (mm) ±0.01	Density (g.cm^{-3}) ±0.05	Density (%TD) ±0.05	Porosity (%) ±0.5	Axial shrinkage ±0.5 (%)	Diametral shrinkage ±0.2 (%)	Mass loss (%)
Green	578	4.54	5.44	5.47	49.4	50.6	19.6	20.4	2.2
Sintered	565	3.65	4.33	10.51	94.9	5.1			

2.1. Dilatometric analysis

Several phenomena are observed during sintering. The plots of the dilatometric curve and shrinkage rate show that a slight contraction of the pellet is first recorded at around 800°C marking the beginning of sintering. Densification slows down from 850°C till 1000°C. This phenomenon could be related to crystallization mechanisms (coherent domain growth) or to carbon removal in the form of hydrogenated carbon compounds. Linear shrinkage of the pellet accelerates again at 1000°C and the highest shrinkage rate is observed at 1570°C. This temperature is significantly lower than that observed with the UMACS process, but in the same order of magnitude as that of samples prepared from a coconverted oxalate [1]. Shrinkage drops off from 1750°C which indicates that higher temperature should not be necessary to reach high densities if a plateau is applied. Furthermore, axial and diametral shrinkages calculated from geometrical measurements on green and sintered pellets are respectively 19.6 ± 0.7% and 20.4 ± 0.7%, revealing an isotropic shrinkage.

2.2. Carbon content

The carbon content of the sintered pellet was measured from a pellet fragment by TGA–µGC under air and was assessed to be 100 ± 10 ppm. A large decrease of carbon content (close to 93%), initially present in the oxide precursor, was achieved during sintering. This observation proves that the carbon content of the pellet can be simply managed by heating at a higher temperature than that specified for oxide precursor synthesis and can be evacuated without any dedicated treatment.

2.3. Density and microstructure

The apparent density of the sintered pellet is 94.9 ± 0.5% TD. This measurement is in accordance with FEG-SEM micrographs recorded on a fractured pellet (Figure 11) which reveals a dense and homogeneous microstructure composed of grains of 5–15 µm. No traces of microsphere are evidenced which would prove that the microspheres were finely crushed and mixed during compaction, thus avoiding the penalizing ‘‘blackberry’’ effect [7]. A few submicronic pores are homogeneously dispersed throughout the pellet and are mainly located at grain boundaries. In comparison to initial precursor microstructure characteristics, grain growth is confirmed. Those observations indicate that the last stage of sintering has been reached which is consistent with the value of the sintered density [8].

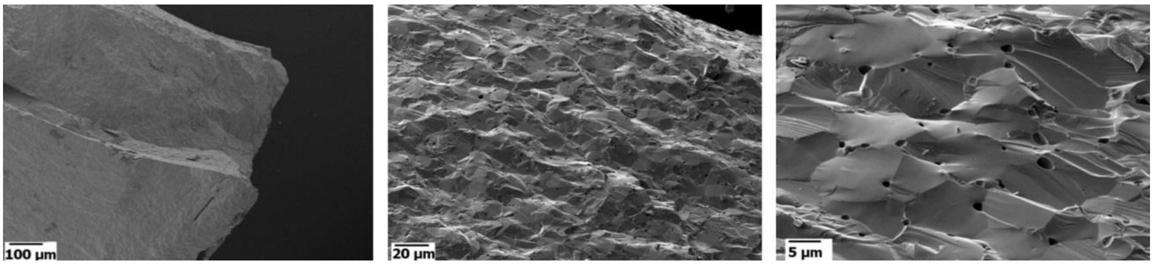


Figure 11 : FEG-SEM micrographs of U0.9Am0.10O2 sintered pellet with a tilted SEM sample holder.

2.4. Structural aspects: XRD analysis

Based on XRD pattern of a milled fragment of the sintered pellet, the oxide still exhibits a single fluorite-type structure. Refined lattice parameter is 5.4658(2)Å. This value is much higher than the lattice parameter measured on the oxide precursor (5.4511(2)Å). The most probable explanation for such a difference would be a variation of oxygen/metal ratio and, more precisely, a decrease during the sintering. This would mean that the so-called ‘‘reduced’’ microsphere were incompletely reduced compared to a pellet after sintering at 1750°C under Ar–H_2 (4 vol.%). Two reasons could explain it:

– the relatively low temperature used during the reduction thermal treatment, considering the significant reduction required (i.e., from U_3O_8 to UO_2);

– the high reactivity of the ‘‘reduced’’ microspheres after synthesis, favouring the re-oxidation of the sample during the time between the reducing heat treatment and the XRD sample preparation. A recent XRD study showed that uranium–americium mixed oxides are easily oxidized under ambient conditions [9].

4. Conclusion

Oxide microspheres obtained using the WAR process exposed in HYPAR2 were suitable for pressing and a pellet with a high density of 94.9 ± 0.5% of TD was achieved after dynamic sintering under a reducing atmosphere up to 1800°C. This pellet meets the required specifications for dense pellet envisaged for Am transmutation in fast breeder reactors and proves the technical feasibility of the CRMP process for MABB application. In comparison to other fabrication process implying powder metallurgy like UMACS or co-converted route, CRMP technology presents the advantage of being a dust-free process with easily transferable materials. The green pellet obtained showed a good reactivity during sintering which would allow decreasing the common required sintering temperature (1750°C).

ACTION PLAN

After this success in the production of dense (U,Am)O_2 pellet with less dust generation than conventional routes, using oxalic co-converted precursors, work will now be focused on another synthesis route avoiding powder precursor generation.

TASK 7.4 CHARACTERIZATIONS

MANPOWER

Expected effort for the period 2.9 men.month

Actual effort spent during the period 2.88 men.month

MAIN PROGRESSES

(U,Pu) co-precipitation studies have been prepared

ACTION PLAN

- Complete (U,Pu) co-precipitation studies
- Extend to mixed actinides

REFERENCES

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[5] Y.B. Rao, R.B. Yadav, R.N. Swamy, B. Gopalan, S. Syamsundar, Determination of specific surface area of uranium oxide powders using differential thermal analysis technique, Journal of thermal analysis vol 44, pages 1439-1448, 1995.

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[8] S.-J.L. KangSintering Densification, Grain Growth, and Microstructure Elsevier Butterworth-Heinemann, Amsterdam; Boston; London (2005)

[9] D. Horlait, F. Lebreton, P. Roussel, T. Delahaye Inorg. Chem., 52 (2013), p. 14196

LIST OF PUBLICATIONS

J. Holt, M. Sarsfield, D. Whittaker, R. Orr, R. Taylor, Uranium and thorium mixed oxide characterisation studies, Fifteenth Information Exchange Meeting, Manchester, United Kingdom 30 September-3 October 2018, Programme and Book of Abstracts (2018), p.124.

CONCLUSIONS

Work progress for Tasks 7.1 and 7.3 are OK to be able to write the associated deliverables. Work on Task 7.2 have started with first solubility determinations on Th oxalate prior moving to Pu oxalate. Electrochemical ligand decomposition studies will start soon. Characterization work on actinide oxalate precipitates started with U,Th oxalate samples and will moved on (U,Pu) oxalate.

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

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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

MANPOWER

Total: NNL 3.5pm

MAIN PROGRESSES

The design pack incorporates a flowsheet which provides mass balance data of species through the process. As part of the design process, a gPROMs model of the plant was constructed. FISPIN modelling data was used to generate a representative spent fuel inventory which acted as an input to the gPROMs model. The model output has been included as an appendix to this report.

The outcome of this report will provide a baseline for the Euro-GANEX process and will allow for safety evaluations and studies, after which further phases of design can commence. The baseline can also be utilised by the Sim-Plant tool, currently under development at NNL, which will allow for the comparison of the benefits of different reprocessing flowsheets.

Progress: finished and delivered on time.

DIFFICULTIES

2 weeks delay in submission.

ACTION PLAN

D8.1 “Process description report of concept Euro-GANEX plant” was submitted - delivered on M12.

TASK 8.2

MANPOWER

Total: KIT 2.9pm

MAIN PROGRESSES

This deliverable discusses and compares some of the more advanced separation concepts for heterogeneous recycling options developed in Europe. These are processes separating trivalent minor actinides (with a focus on americium) from the raffinate solution originating from processes such as

PUREX, where U and Pu are managed separately, or an evolution of PUREX, allowing a co-recovery and a co-management of U and Pu.

Six process schemes are presented, each consisting of one, two or three solvent extraction cycles. The choices for the various solvent extraction processes are briefly introduced. Next, the most suitable choices are selected, and then, the six process schemes are compared to one another. The simplest schemes (with the lower steps, etc.) were found to be the most viable ones. Finally, some further directions for future R&D are proposed.

Progress: finished and delivered on time.

ACTION PLAN

D8.2 "Report on the comparison of SX processes for heterogeneous recycling" - delivered on M12.

TASK 8.3

MANPOWER

Total: LGI 3.9pm

MAIN PROGRESSES

This task proposes a mapping of the different status and alternatives for each ESNII concept waste treatment process. The study undertakes a comparative assessment of the different recycling needs and options considered and identifies the facilities that could integrate the reprocessing options at EU level. Building on links with existing gen IV concepts (ASTRID, ALFRED and MYRRHA), three spent fuel recycling scenarios have been studied considering the spent fuel treatments associated and reactor and fuel cycle options proposed. Some parameters have been considered as comparative indicators when information was available: the evolution of the radiotoxicity, the final waste surface disposal and the needs and evolution of existing waste treatment facilities.

A 1-day workshop was organised by LGI with ORANO, EDF and CEA partners in order to discuss the focus on the deliverable and the expected results.

ORANO (1pm) and EDF (1.5pm) have participated in this task and deliverable as experts, through interviews, workshops and review of the deliverable.

Progress: finished and delivered on time.

DIFFICULTIES

Difficulties finding information of the real state of development of ASTRID and ALFRED.

ACTION PLAN

D8.3 "Mapping of the different status and alternatives for each ESNII concept" - delivered on M18.

TASK 8.4

MANPOWER

Total: NNL 6.5pm

MAIN PROGRESSES

Develop a “SimPlant” model to illustrate how changes to a baseline could affect the size of the reprocessing and associated plants with which it has close interactions, e.g. waste treatment and vitrification plants. This will allow comparison of the holistic effect of chemical process changes on nuclear plants and site footprints.

Progress: Flowsheet build of EURO-GANEX process from fuel receipt to powder finishing has begun.

ACTION PLAN

Report to be delivered M48

TASK 8.5

MANPOWER

Total: LGI 3.9pm

MAIN PROGRESSES

The last task of WP8 will assess the impact of implementing a closed cycle across the full nuclear fuel cycle, from mining and fuel fabrication to spent fuel conditioning. The task will use the results from previous tasks and will organise a set of face-to-face semi structured interviews to identify the main changes, main issues, blocking points and impact on the actors involved (some will disappear; some new actors will appear from opportunities in the cycle). The stakeholders will encompass actors from industry, nuclear associations, policy makers, research centres, etc.

Progress: no progress has been reported in this period.

ACTION PLAN

Report to be delivered M36

AREVA (1pm) and EDF (1.5pm) participate in the whole WP as expert, participating to interviews and reviews of the deliverables.

WP9

INTRODUCTION

A key challenge in industrialisation of any process is proving that it is safe to operate. This is especially true of nuclear installations, which can be societally controversial, and as such, are subject to intense scrutiny by a variety of regulators.

Work Pack 9 will produce safety studies into advanced reprocessing flowsheets to allow foresight of potential safety issues and direct future research and engineering efforts to tackle these issues for resolution.

By resolving issues at an early stage, plants are safer and can also be built more quickly and cheaply as hazards have been eliminated or mitigated from a very early stage. The increased safety and reduced cost of these plants will go some way to mitigating societal concern with nuclear.

MAIN RESULTS

TASK 9.1

MANPOWER

Expected – 2.80pm

Actual – 2.79pm

MAIN PROGRESSES

A consortium safety review on the entire EURO-GANEX process – Head-Eng, Chemical Separations and Finishing – was held as a Learning Session at the GENIORS Winter meeting in Antwerp in October 2018. This supplemented and added to an internal NNL review conducted by Subject Matter Experts in September 2018. The Concept Design produced by NNL in WP8 was utilised as the basis for these reviews.

DIFFICULTIES

None encountered

ACTION PLAN

The findings of both the internal NNL and consortium-wide reviews will be combined and a list of Research and Development recommendations will be made to direct research to investigate safety issues at an early stage with a view to elimination or mitigation of the issue.

TASK 9.2

MANPOWER

Expected – 2.00pm

Actual – 1.95pm

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 15/06/2018) were sent on to the IRSN in August 2018.

Work done: Internal documents/data collection, first thoughts and pre-evaluation to initiate the IRSN' safety review of the Euro-Ganex reprocessing plant design and flowsheet focused on criticality safety

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

Step 1: Depletion calculations for MOX fuel in fast reactors have been gathered and are under analysis. The configurations calculated are based on a 600 MWe ASTRID-V1 like concept considered as iso-generator. This low void effect sodium fast reactor (SFR) has an heterogeneous design with an internal core that alternate fissile and fertile fuels (4 different zones) and an external core composed of a fissile and a fertile fuels (2 different zones). The fuel depletion of this reactor is strongly impacted by its heterogeneity and also depends on the initial fresh fuels composition. The fresh fuel changes depending on the recycled fuel to make it. Indeed the isotopic composition of Pu may be not always the same in function of its history and by consequence the Pu content necessary to be critical and achieve the target burnup (100 GW.d/tons) also. So, to evaluate large possible fresh and used fuels compositions, 1000 fuel depletion calculations were performed with the VESTA code. Large but credible ranges of initial isotopic composition (Pu, Am) and Pu content were considered (e.g. 15% to 40% of Pu) in each core. The set of the simulation forms a databank composed of the depletion up to 100 GW.d/tons of the 1000 different fresh fuels. The purpose is using these databanks to estimate the isotopic compositions of Am, Cm, Pu and searched penalized cases. Depending on the first results of this analysis, additional calculations could be performed (such as a burner configuration for the reactor).

The analysis of the SFR fuel depletion calculations results is in progress.

Task 9.2-b: Criticality studies (verification of the bounding nature of water moderation with regard to new extractants and diluents)

Subtask 1: Collect density of fissile species in GANEX solvents and write a methodology to establish a density law for NCS evaluations, including the need in terms of data and chemical measurements

Deliverable D9.3: Report on the methodology to establish a density law including the need in terms of data and chemical measurements depending of the range of applicability (Month 25)

The drafting of the methodology report has been finished. Approval of the report is in progress (see Annex for the content of the report)

DIFFICULTIES

IRSN needs information quickly on Euro-GANEX solvents chemical data.

ACTION PLAN

N/A

TASK 9.3

MANPOWER

Expected – 0pm

Actual – 0pm

MAIN PROGRESSES

The objectives of this task are:

- To perform corrosion assessments for stainless steels SS304L & S316L in the presence of as many of the GANEX inventory permutations as resource permits.
- To perform long term corrosion studies in relevant inventory permutations.
- To conduct corrosion and plant material compatibility tests for extraction and stripping stream compositions proposed for the EXAm process.

ULANC's GENIORS-funded work on this WP is currently not due to start until 1st Jan 2019 and then run for a period of 18 months. However, as described in GENIORS HYPARS 1 & 2, we have already made significant progress towards the WP objectives – even though the GENIORS-funded period of work has yet to begin. The manpower effort expended on this non-GENIORS funded work, and the associated results, can therefore be considered as match to the main GENIORS grant.

However, due to the PDRA in question having to work temporarily on another contract, no further matching effort has been expended this half-year – although they will be back at work on GENIORS related research come Jan 2019. Consequently, for this HYPAR, we have nothing to report for WP3.9.

DIFFICULTIES

N/A

ACTION PLAN

Corrosion studies of Trans-1,2-diaminocyclohexane-N,N,N',N'-tetraaceticacid (CDTA) and hydrazine in HNO3 concentrations up to 7.5 mol dm-3

LIST OF PUBLICATIONS

None.

CONCLUSIONS

Work Pack 9 is currently on schedule (with the exception of aspects of Task 9.3 – D9.6).

Task 93 deliver D9.6 will be delayed from Month 24 to Month 48. During the delay, Lancaster University will be performing ligand corrosion work funded by another source. This work will be reported through GENIORS channels, and as such, represents additional gearing for the GENIORS programme.

This task is self-contained and its delay will have no impact on the rest of the GENIORS programme.

WP12

INTRODUCTION

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

MAIN RESULTS

TASK 12.1

MANPOWER

ULEEDS: 0.25 pm

MAIN PROGRESS

To date there have been 5 awards - three secondments and two travel bursaries - with a total value of €8,762. There is a further award to CIEMAT, pending.

ACTION PLAN

Send out reminder for applications to the fund.

TASK 12.2

MANPOWER

ULEEDS: inc in above

MAIN PROGRESS

D12.2 Organisation of the think-tank event was completed and the event was run on the 23rd/24th October 2018. A report covering the organisation of the event was issued. The Think Tank was be divided into two sessions:

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- Session 1 (day 1) had the aim to identify the main hazards and technical issues associated with the Euro-Ganex process. The output from the session was a register of issues, prioritise as to their importance or degree of effect. The hazards were then evaluated against a set of criteria normally used for industrial safety assessments.
- Session 2 (day 2) used the output from session 2 and evaluated how the issues could be addressed and what R&D may be required. The output from the session was a list of R&D/design tasks and their expected impact on the issues.

Outputs from both sessions will be summarised and issued in a report on the whole event for M20.

ACTION PLAN

Output from the Think Tank will be a joint UnivLeeds/NNL report

TASK 12.3

MANPOWER

ULEEDS: inc in above

MAIN PROGRESS

An example syllabus has been developed with the following proposed structure: Four segments, with an approximate participation time of 45-60mins each. At the end of each segment there will be a short assessment to ensure assimilation of the content, before the next segment is opened for access.

Learning outcomes for the package will be:

- Understand what principles of solvent extraction when applied to nuclear operations
- Understand reprocessing and the type of technology used in current facilities
- Be able to identify the key chemistry and compounds used in the Purex, i-Sanex and Ganex flowsheets
- Be able to compare the advantages and disadvantages of the Purex, i-Sanex and Ganex flowsheets

A detailed script for the 4 packages is being developed by the ULEEDS Digital Education Service. This will be completed and presented at the 2nd annual meeting. Also, it is planned to have a draft version of Part 1: Understanding the principles of solvent extraction, ready for demonstration at the meeting.

TASK 12.4

MANPOWER

Chalmers

MAIN PROGRESS

Main tasks complete – no further progress to report.

CONCLUSIONS

The project is continuing, with no serious delays. Progress is as expected and the main focus for the next semester will be completing the next stage of Task 423 in WP12.

WP13

INTRODUCTION

WP13 aims to engage with stakeholders and raise awareness on GENIORS and its achievements through specific communication actions. It will also ensure the dissemination of knowledge acquired towards the scientific community and other relevant stakeholders, including publications in scientific journals and participation in conferences.

MAIN RESULTS

TASK 13.1 – COMMUNICATION TOOLKIT

MANPOWER

LGI was the only contributor to this task during this reporting period: 0.3 PM

MAIN PROGRESSES

The second elements of the communication toolkit were designed and distributed to all GENIORS partners to promote the project: this included the project flyer and the project roll-up.

ACTION PLAN

The project roll-up and flyers had been used for the 2nd Project Meeting, taking place in Würzburg (Germany), from 16-18 April 2018. Moreover, they will be used for other upcoming events in order to increase the project's visibility: some flyers had been distributed to partners who will attend events, conference and/or workshops.

TASK 13.2 – COMMUNICATION & DISSEMINATION PLAN

MANPOWER

LGI was the only contributor to this task during this reporting period: 0 PM

MAIN PROGRESSES

The Communication and Dissemination Action Plan deliverable D13.2 was submitted. It includes:

- Communication strategy: definition of audiences and key messages
- A detailed planning of all communication actions over the project duration according to the defined target audiences, including press releases
- An event and publications management plan

Task 13.2 will also disseminate the results of the GENIORS project to the scientific community and stakeholders by:

- Coordinating scientific publications, including open access journals, free (online) journals, and online repositories.
- Coordinating the participation of partners in conferences to disseminate knowledge and results.

As we are early in the project, no results have yet been disseminated.

ACTION PLAN

The action plan will be implemented and monitored during the course of the project in order to identify areas of improvement and measure its success.

TASK 13.3 – ANNUAL NEWSLETTERS

MANPOWER

LGI was the only contributor to this task during this reporting period: 0.2 PM

MAIN PROGRESSES

The first electronic project newsletter was designed (and distributed in July 2018) to inform stakeholders of the project’s progress. It included:

- An interview of the project coordinator
- A recap on the 2nd project meeting in Würzburg
- Social media recap: reminder to follow GENIORS on Twitter (@Geniors_H2020) + the public website (www.geniors.eu)
- A short blurb on the GENIORS flyer available to download
- Past events attended by the GENIORS partners (Juelich contribution)
- Relevant news and highlights per WP (KIT and CIEMAT contributions)

The newsletter is available here: www.geniors.eu/resources

ACTION PLAN

Attracting more people to subscribe to receive the future GENIORS newsletters via Twitter and the project website.

TASK 13.4 – PROJECT WEBSITE

MANPOWER

LGI was the only contributor to this task during this reporting period: 0.5 PM

MAIN PROGRESSES

A website was designed and released in September 2017. It is regularly maintained and updated (deliverables for download, news and upcoming events…). In addition, the online audience is monthly measured through Google Analytics.

DIFFICULTIES

Traffic to the website is still limited. It is important to have news/updates from the various work packages shared with WP13 in order to update the website and make it a lively platform.

ACTION PLAN

The website will be maintained and continuously updated.

LIST OF PUBLICATIONS

Publications :

6. Colin R. Gregson, Gregory P. Horne, Robin M. Orr, Simon M. Pimblott, Howard E. Sims, Robin J. Taylor, Kevin J. Webb, *Molecular Hydrogen Yields from the Self-Radiolysis of Plutonium or Americium Irradiated Nitrate Solutions*, J. Phys. Chem. B, 122 (9), pp 2627–2634 (2018).
7. Wilden, Andreas, Mincher, Bruce J., Mezyk, Stephen P., Twight, Liam, Rosciolo-Johnson, Kristyn M., Zarzana, Christopher A., Case, Mary E., Hupert, Michelle, Stärk, Andrea, Modolo, Giuseppe. *Radiolytic and Hydrolytic Degradation of the Hydrophilic Diglycolamides*, Solvent Extr. Ion Exch., submitted.
8. J. Halleröd, Ch. Ekberg, T. Authen, L. Bertolo, Mu Lin, B. Grüner, J. Švehla, Ch. Wagner, A. Geist, P. Panak, and E. Aneheim. *On the basic extraction properties of a phenyl trifluoromethyl sulfone based GANEX system containing CyMe4-BTBP and TBP*. Solv. Extr. , Ion Exch., submitted.
9. J. Narbutt, I. Herdzik-Koniecko, M. Rejnis-Strzelak, "The use of synergistic effects of lipophilic modifiers of TODGA-containing organic phase for improving separation of americium(III) from the early lanthanides in the process of stripping the metals with hydrophilic ligands. A novel concept for solving the problem" (in Polish), Raport IChTJ, Seria B nr 2/2017, Warszawa 2017, 14 pp.
10. Daniel Whittaker, Andreas Geist, Giuseppe Modolo, Robin Taylor, Mark Sarsfield, Andreas Wilden, Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA, accepted, Solv. Extr. Ion Exch. (2018).

Publication submitted:

11. *Mossini, E. et al. Optimization and single-stage centrifugal contactor experiments with the novel hydrophilic complexant PyTri-Diol for the i-SANEX process, Solvent Extr. Ion Exch., submitted*
12. **Synthesis of size-controlled UO_2 microspheres from the hydrothermal conversion of U(IV) aspartate,** J. Maynadié, V. Trillaud, J. Manaud, J. Hidalgo, D. Meyer, R. Podor, N. Dacheux, N. Clavier**,** *Cryst Eng. Com.*, 2018 / *Submitted - Under Review*.

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13. R. Malmbeck et al., J. Radioanal. Nucl. Chem, Modified diglycolamides for grouped actinide separation, 2017, in press.
14. Halleröd, J., Ekberg, C., Authen, T., Bertolo, L., Lin, M., Grüner, B., Svehla, J., Geist, A., Panak, P., Wagner, C. and Aneheim, E.: On the basic extraction properties of a phenyl trifluoromethyl sulfone based GANEX system containing CyMe4-BTBP and TBP. Submitted to Solvent extraction and Ion exchange.
15. Eros Mossini, Elena Macerata, Andreas Wilden, Peter Kaufholz, Giuseppe Modolo, Nicolò Iotti, Alessandro Casnati, Andreas Geist, Mario Mariani, Optimisation and single-stage centrifugal contactor experiments with the novel hydrophilic complexant PyTri-Diol for the i-SANEX process, submitted to Solvent Extraction and Ion Exchange.

Oral communications:

4. A. Wilden, et al. *Radiolytic Degradation of the Hydrophilic Diglycolamides*, 11th International Conference on Methods and Applications of Radioanalytical Chemistry (MARC XI), April 8-13, 2018, Kailua-Kona, Hawaii, USA.
5. A. Kimberlin, "*Investigation of TODGA radiolysis by combining experimental and computational approaches*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
6. L. Berthon "*Investigation of Pu(IV) – N,N-dialkylamide complexes in solution under ionizing radiation*" Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
7. M.C. Charbonnel, "*Importance of stability studies in the development of a new solvent extraction process for the multi-recycling of uranium and plutonium from spent nuclear fuels*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
8. A. Wilden, "*Radiolytic Degradation of the Hydrophilic Diglycolamides*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
9. E. Macerata, "*A review of ageing, hydrolysis and radiolysis effects on PyTri-based stripping solvents for i-SANEX/GANEX processes*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
10. D. Whittaker, "*Tracking hydrogen formation in static vessels containing solutions relevant to the i-SANEX process under gamma irradiation*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
11. Robin Orr, "*Modelling the long-term radiation chemistry of nitrate and nitric acid solutions*". Second edition of Radical Behaviour workshop (RB2018), 19-20 April 2018, Würzburg, Germany.
12. **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*.
13. **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*.
14. **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 / *Accepted.*
15. **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 / *Accepted.*

CONCLUSIONS

In WP1, since the start of the GENIORS project only little R&D related to the fission product chemistry was carried out. It is expected that the planned work will gain momentum in the next semester. CEA and JUELICH are planning to speed up their planned work.

After first year of GENIORS project it can be reported a more than optimal development of WP2 activities. Particularly, during this second semester 27.58 pm has been reported over the 13.4 pm estimated average, mainly due to the effort dedicated to Task1 Radiolysis & degradation products (19.58 pm). Activities regarding gas generation and modelling (Task 3 and 4 respectively) continue as expected and activities related to destruction of organics (Task 2) has recently started (2.5 pm).

In WP3, Some small difficulties, which can be overcome have been identified but most of the actions in this workpackage have started as planned. After one year, 35.85 pm have been realized within WP3, corresponding to 24.4 % of the 147.1 pm planned for the complete project.

In WP4, several ways of preparation of precursors are now under progress. They will allow to provide a large variety of materials, with various compositions and microstructures. This will allow to developed multiparametric dissolution experiments on the prepared samples (planned to begin soon). Only few difficulties encountered by the partners for both tasks: T4.1 and T4.2.

In WP5, A round ruby study of the different irradiation facilities was started. Data has been collected and subsequent meetings are to be held at the 2018 GENIORS autumn meeting.

In WP6, The work package concerns flowsheet development of key processes for homogeneous and heterogeneous recycling so it is expected that most studies will commence later in the project. No significant delays or causes for concern were raised by the partners in the HYPARs.

In fact, despite the low levels of manpower dedicated to WP6 in semester 1-2 there has been already one significant development – the promising results obtained by JRC on the modified DGA ligand that may be a candidate to replace the TODGA+DMDOHEMA combination in the EURO-GANEX process. A journal paper is already published on this subject. In the last semester good progress has been made on both the CHALMEX and AMSEL flowsheet development.

In WP7, as planned, the first dissolution data on model compounds were obtained during this semester. For the conversion work, dust free MABB precursors were synthetized using WAR process. Concerning the characterization work, as a pre-cursor to studies with plutonium and minor actinides, a range of (U,Th) mixed oxalate precipitates were calcined to mixed oxides under air and inert atmospheres. Raman and powder X-ray diffraction analysis are ongoing.

In WP8, The deliverable D8.3 is well advanced in terms of methodology, main sections and content. Firstly, the work focuses on the state of the art of ASTRID, ALFRED and MYRRHA. It is followed by a description of the system's cycles, possible waste treatment strategies and the proposition and description of three waste treatment scenarios. There have been several interactions with partners and external experts to validate the work and provide relevant information. A meeting with the partners from CEA, ORANO and EDF was held on June at LGI offices in Paris. The objective of the meeting was to agree on the focus of the deliverable, content and structure to follow. A follow-up meeting was planned in August to inform the partners about the advancement of the deliverable.

In WP9, the presence of DEHiBA in the organic phase is found to have no effect on the corrosion rate of SS304L and SS316L in Exxsol D80. The presence of DEHiBA in the organic phase when that phase is contacted with nitric acid is found to reduce the rate of SS316L in HNO_3, but has no effect on SS304L.

Design and prototyping of a suitable experimental setup for long term corrosion studies has also been carried out.

Four steel types have been acquired for testing (SS316L, SS304L, NAG 18/10 and SS310), characterised and turned into rotating disk electrodes. A double junction arrangement suitable for long term corrosion testing has been developed with the aid of the National Nuclear Laboratory (NNL) and a prototype setup is under construction.

Based on work carried out in SACSESS, SO_3-Ph-BTP and AHA in HNO_3 has been identified as the most suitable corrosion system to initially be studied long term. Rotating disk and rotating cylinder electrodes will be manufactured and used for these tests, to provide similar conditions to those expected in storage tanks, process pipework and centrifugal contactors.

In WP10, no activity in period 2. A cluster meeting is planned on period 3

In WP12, Two awards for travel bursaries have been made totaling €1,982. This brings the total awarded to date to €8,762 leaving €11,238 in the fund. The operational process for the Think Tank has been developed and agreed. There has been an initial meeting to identify existing examples of online training packages. Delivery platform options have been identified.

WP13 is on track. However, the challenges that lie ahead are mainly the creation of content in order to populate the website, the GENIORS Twitter account and the future project newsletters. It is important for work package leaders to share updates in their WPs with the communications team in order to have information on which to communicate.

ANNEXES

DOMAIN	1	WP	1	WP Leader	G. Modolo
Manpower dedicated to this WP on the period			9.5		

Contribution to Deliverables (number and title of each deliverable)

D1.1 : Report on the speciation and extraction of key fission products [due month 36]
D1.2 : Identification of optimized conditions for effecter fission product masking/scrubbing [24], postponed to month 30 (Min 11.6 – ExCom4 Minutes Antwerpen – 23/10/2018)

Contribution to Milestones (number and title of each milestone)

MS1 : provide information on WP activity for the Work-Package Activity Summary Report 1 (month 7)
MS2 : provide information on WP activity for the Work-Package Activity Summary Report 2 (done)

Main achievements - Progress

Task 11 Problematic fission products - extraction chemistry

CEA: The ruthenium extraction properties were studied for 2 monoamides (DEHiBA & MOEHA) as a function of the nitric acid concentration in the initial aqueous phase.Speciation was then studied in both aqueous and organic phase for MOEHA using RAMAN, FTIR and XAS. Monoamides behaviour contrast for lower acidic conditions compared to TBP: with monoamides, no hydrolysed complexes of ruthenium are extracted.

ICHTJ: Reduction of TcO_4– by AHA in HNO_3 solutions to technetium(II), with formation of the hydrophilic $[Tc^{II}(NO)(AHA)_2H_2O]^+$ complex has been confirmed. The conditions were determined for the TODGA / HNO_3 extraction system studied, when the distribution ratio of trace amounts of the reduced technetium is lower than one.

FZJ: The Fe extraction of TODGA was studied for different TODGA and HNO_3 concentrations.

Main difficulties - Delays

CEA: DEHiBA (used in the GANEX 1st cycle) poorly extract Ru which limit the speciation analysis by FTIR and XAS. Further effort may be done to enhance Ru extraction in DEHiBA to probe its speciation and validate MOEHA as a good representative of the monoamide extractants.

FZJ: Work to be planned in Task1.1 and 1.2 is delayed, since the ICP-MS was broken. A new machine was bought and installed. It is ready for operation and it is expected that the planned work will be carried out as scheduled.

Scientific publications, patents (beneficiary name and type of publication)

Journal:
Int. Conference Oral:
Int. Conference Poster:
Proceedings:
Patent:

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.

DOMAIN	1	WP	2	WP Leader	Hitos Galán
Manpower dedicated to this WP on the period				30.01	

Contribution to Deliverables (number and title of each deliverable)

D2.1 Stability and safety studies of hold extraction systems (1 for each CyMe4BTBP, HidroBTBP, TODGA & PTD) (due m39, IIC).
D2.2 Stability studies of stripping agents (due m24, UNIPR).
D2.3 Destruction of organic (due m30, CEA).
D2.4 Impacts on process safety of gas generation (due m32, POLIMI).
D2.5 Molecular modelling of particular degradation mechanism of extracting and complexing agents (due m36, CTU).

Contribution to Milestones (number and title of each milestone)

MS2: provide information on WP activity for the Work-Package Activity Summary Report 1. CEA (due m13)

Main achievements - Progress

Task 2.1 Radiolysis & degradation products (19.35 mp)

- Study about differences between in-situ alpha (provided by the decay of ^{241}Am) and external gamma radiolysis (by a ^{60}Co source) on organic TODGA and aqueous PTD solutions. For both ligands, main degradation products and Am complexes were identified after radiolysis by internal alpha radiolysis. Bond Dissociation Energies were calculated for TODGA and Fukui functions were calculated for PTD ligand. (CEA, 8 pm).
- Stability study of aqueous phases: irradiation of CDTA and EDTA solutions under more realistic conditions (0-50 kGy and concentrated HAR solutions (CIEMAT, 0.75 pm). TODGA structural degradation studies: It has been identified the structures of new possible TODGA DCs formed only when air-sparging is used.
- Procedure for new radiation stability testing of hydrophobic (CyMe$_4$-BTBP and CyMe$_4$-BTPhen) and hydrophilic (Sulfonated BTPhen) extraction systems. (CTU, 0.8 pm).
- More concentrated samples of CyMe4- BTBP (in FS-13, FS-13+TBP and octanol+TBP) was prepared at Chalmers Univ. and irradiated by γ-source in contact with 4M HNO$_3$. Analysis by HPLC and conditions set up for semi-preparaive separations have been carried out by IIC to attempts NMR characterization of degradation products (IIC, 2.1 pm).
- The radiolysis of mTDDGA and TPDGA was studied in collaboration with Bruce Mincher and Gregory Horne (INL, USA), Steve Mezyk (California State University Long Beach, USA), and SCK-CEN (Mol). TPDGA was synthesized by TWENTE. (Julich, 0.7 pm).
- Americium and plutonium loading experiments with aged and irradiated PTD solutions have been performed within the collaboration with CEA. Hydrolytic stability of PTD in nitric acid has been continued. According to the decision of the Consortium to include the new lipophilic derivative PTEH stability towards radiolysis, hydrolysis and ageing has been studied (POLIMI, 5 pm).
- A new batch of PyTriDiol was produced to feed the studies carried out by partner. A sample was sent to POLIMI and another to CEA (UNIPR, 2 pm-synthesis).

Task 2.2 Destruction of organics (3.0 mp)

- Experiments have been started to evaluate the reactive thermal reactions between extractants (TODGA and TEHDGA) and nitric acid (CEA, 3.0 pm).

Task 2.3 Gas generation (4.66 mp)

- Establishing gas generation during irradiation of i-SANEX and GANEX solvents with He$_2$+ ions with an energy of 5.5MeV using beam currents. Data has been analysed and a paper drafted. Iván Sanchez-Garcia (from CIEMAT) training process to allow to participate in basic fundamental loading experiments with plutonium (related to solvent degradation, gas generation and the EURO-GANEX process development) at NNL. (NNL, 4.16 ppm).
- On-going gamma irradiation experiments on the PTD-TODGA extracting system under different experimental conditions. (POLIMI, 0.5 pm).

Task 2.4 Radiolysis modelling (3.0 mp)

- DFT calculations of bond dissociation energies of the C-O$_{Ether}$ bonds in diglycolamides to explain experiment observed (Julich, 1.0 ppm).

The theoretical work on CyMe$_4$-BTBP was further deepened and presented in several forms. Further, ground state properties of TMDGA and TEDGA modifications were analyzed by DFT. (CTU, 2.0 mp).

Main difficulties - Delays

No major difficulties have been reported. Although there was some delays due to:

- No CyMe$_4$-BTBP or CyMe$_4$-BTPhen available for experiments during this period. No degradation products/adducts of CyMe$_4$-BTBP and CyMe$_4$-BTPhen synthesized yet (CTU).
- Problems in the measurement of H_2 generation due to viscosity of solvents. Work planned in WP 2 by NNL delayed to fit NNL-CIEMAT scheduling (NNL).
- Sample to be supplied to IIC from CTU delayed. Besides, one member of IIC team had to be replaced (IIC).
- Significant differences in comparative irradiation experiments where observed (Julich).

Scientific publications, patents (beneficiary name and type of publication)

Journal: 4 accepted and 1 submitted (1 CTU, 1 Julich and 1 IIC, 1 POLIMI/UNIPR and 1 submitted by CTU).
Conference paper: 3 CTU.
Int. Conference Oral: 3 (1 Julich and 2 POLIMI/UNIPR).
Corresponding list is given at the end of the document.

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
CEA			■											■					■					
CHALMERS							■																	
CIEMAT													■		■									
CNRS																								
CTU							■			■											■			
ICHTJ																								
IIC		■			■																			
IRSN																								
JRC-ITU																								
JUELICH					■										■	■								
KIT																								
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NNL			■															■						
POLIMI	■																		■					
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UEDIN																								
UNIMAN																								
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UREAD				■																				
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EDF																								
AREVA																								

DOMAIN	1	WP	3	WP Leader	P. Guilbaud
Manpower dedicated to this WP on the period			40.63		

Contribution to Deliverables (number and title of each deliverable)

D3.1 : Status on the PyTri-Diol properties [due m36]
D3.2 : Status on Distribution data and chemical modelling [due m40]
D3.3 : Status on TODGA organic phase loading [due m36]
D3.4 : Status on solvent clean-up & recycling [due m40]

Contribution to Milestones (number and title of each milestone)

MS1 : provide information on WP activity for the Work-Package Activity Summary Report 1 (done)
MS2 : provide information on WP activity for the Work-Package Activity Summary Report 2 (done)
MS3 : provide information on WP activity for the Work-Package Activity Summary Report 3 (done)

Main achievements - Progress

Task 3.1 Optimisation of systems

- Microcalorimetry measurements by isothermal titrations have been started in order to determine the stability constants and the associated thermodynamic parameters of PTD complexes with Ln(III) and Am(III).
- Further experiments were performed on the metal to ligand complex formation by means of ESI-MS.
- The lipophilic PTD derivative (PTEH) was studied in order to check its relevance in r- and 1c-SANEX processes.
- Heteroleptic complexes of Am^{3+} and of Eu^{3+} ions with both T-DGA and SO_3-Ph-BTP^{4-} ligands were characterized.
- Further lipophilic modifiers of the TODGA-containing organic phase were studied.
- The possibility of using aromatic diluents for a TODGA based GANEX system was assessed. Cm(III) and Eu(III) complexes were identified in an aromatic TODGA solvent.
- The extractant mTDDGA was studied as a potential candidate to be used in a new GANEX process.
- Extraction kinetics of radioactive ^{152}Eu(III) and ^{241}Am(III) by the extractant $CyMe_4$-BTBP (+ TODGA) in 1-octanol have been studied using the rotating membrane cell (RMC) technique.

Task 3.2 Distribution data and chemical modelling

- Extraction of HNO_3, An(III) and Ln(III) into a TODGA-diisopropyl benzene (DIPB) solvent was studied (distribution ratios as function of HNO_3 and TODGA concentrations).

Task 3.3 Physico-chemical & loading

- The loading capability of PTD-based stripping solutions has been studied.
- A TODGA-diisopropyl benzene solvent was loaded with La(III).
- Studies coupling experiments with MD simulations for the characterization of the species formed in TODGA, TODGA+octanol and TODGA+DMDOHEMA organic phases have been continued.

Task 3.4 Solvent clean-up & recycle

- The technical feasibility of the cleanup and recycling of used PTD solutions has been evaluated considering the related advantages and positive effects on the whole separation process.
- TODGA solvent clean-up: Studies about the influence of detrimental degradation compound V (diglycolamic acid, DODGAA) on the extraction process: solubility limits in OK and first clean-up experiments.
- Radiation dose study started – looking at effects of dose from future spent fuels on solvents used in EURO-GANEX processes and implications for solvent degradation, clean up and recycling.

Transverse to Tasks 3.1, 3.2 & 3.3

- Synthesis of a new PTD batch was produced to feed the studies carried out by other partners.

Main difficulties – Delays

Task 3.1 Optimisation of systems

- Extraction kinetics studies: ordering of radioactive Ce(III) was delayed (waiting for safety agency authorisation).

Task 3.4 Solvent clean-up & recycle

- Not enough amount of degradation products XII and XIII to perform parallel experiments.
- Experimental work delayed at NNL due to delays in secondment of Ivan Sanchez from CIEMAT (see WP1.2 for more details).

Scientific publications, patents (beneficiary name and type of publication)
Journal: 3 published, 1 accepted + 1 submitted Int. Conference Oral: 3 Int. Conference Poster: 0 Proceedings: 0 Patent: 0 The corresponding list is given at the end of this document.

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	**CIEMAT**	**CNRS**	CTU	**ICHTJ**	IIC	IRSN	JRC-ITU	**JUELICH**	**KIT**	LGI	**NNL**	**POLIMI**	SCK-CEN	**TWENTE**	UEDIN	UNIMAN	**UNIPR**	UNIVLEEDS	**UREAD**	ULANC	EDF	AREVA
CEA	■													■		■			■					
CHALMERS																								
CIEMAT			■								■		■											
CNRS				■															■					
CTU																								
ICHTJ																■								
IIC																								
IRSN																								
JRC-ITU																								
JUELICH										■	■		■			■			■					
KIT			■							■	■		■	■										
LGI																								
NNL			■							■	■		■					■						
POLIMI	■										■								■					
SCK-CEN																								
TWENTE	■					■				■						■								
UEDIN																								
UNIMAN													■											
UNIPR	■			■						■				■					■					
UNIVLEEDS																								
UREAD																					■			
ULANC																								
EDF																								
AREVA																								

DOMAIN	1	WP	4	WP Leader	CNRS
Manpower dedicated to this WP on the period					

Contribution to Deliverables (number and title of each deliverable)

No deliverable during the period.
4 deliverables in WP4:
D4.1 Understanding the evolution of an interface during dissolution of actinide oxide materials by macro/microscopic approaches combination [**month 40**] – **CNRS**
D4.2 Innovative dissolution routes for highly plutonium doped $(U,Pu)O_2$ and $(U,Pu,MA)O_2$ samples [**month 45**] – **CEA**
D4.3 Studies of non-powder routes for the synthesis of MOX fuels materials, potentially bearing minor actinides and blanket fuel materials [**month 36**] – **SCK.CEN**
D4.4 Impact of the precursor “history” (nature, structural, microstructural and morphological parameters) during the conversion and sintering to actinide based dioxide materials [**month 45**] – **CNRS**

Contribution to Milestones (number and title of each milestone)

MS3 : provide information on WP activity for the Work-Package Activity summary Report 3 [19]

Main achievements - Progress

T41 Study of the solid/liquid interfaces during dissolution [1-48] – Task Leader : CNRS

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 has begun in month 6. The impact of the cerium mole loading on the chemical durability of $U_{1-x}Ce_xO_2$ solid solutions was examined.
Uranium and cerium releases were the same during dissolution tests, showing a two-stage evolution. The first was associated to uncatalysed dissolution mechanisms (control by surface driving reactions) while the second was associated to catalyzed mechanisms (fast release of the cations in the solution).
For uranium enriched materials, the dissolution seemed to have the same behavior than UO_2 ; the oxidation of uranium controlling the overall dissolution kinetics. In addition, the release of uranium and cerium in solution seemed to be faster when increasing the uranium mole loading in the samples.

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

The study of the solid/liquid interfaces during dissolution has begun through the synthesis of CeO_2 and $Ce_{0.8}Gd_{0.2}O_{1.9}$ samples using oxalic route and calcined at different temperatures to obtain samples exhibiting different levels of crystal defects and morphological parameters. The set-up of the Netzsch microserie grinder has been done to study the milling/dissolution couplings. Ceria samples heated at 1200°C were ground then characterized before and after the grinding step. The dissolution of raw and ground samples of CeO_2 were performed. The grinding step increased significantly the mass of dissolved material for given time and dissolution conditions. This effect was not only limited to the increase of specific surface area.

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) models, beginning with CeO_2 as UO_2 surrogate and containing either Pd ε-particles or fission products (Nd) or both, using polymer assisted deposition (PAD) and subsequent low-temperature calcination has been developed. The method was derived from a layer-by-layer (LbL) method based on the work of Liu *et al*. for the synthesis of Ln-doped $LaPO_4$ and $CePO_4$. Structural characterization and leaching/dissolution studies are under way on CeO_2 model system. Studies into the effect of γ irradiation (up to 100 kGy) on the structure and leaching/dissolution of these films have been initiated.

T42 Study of the solid/liquid interface during conversion [1-48] – Task leader : SCK.CEN

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

The synthesis of Ce-doped particles using Ce(IV) as precursor was tested. Spherical particles were obtained for molar Ce metal fraction up to 10 %. XRD analyses of the dried particles were carried out and the thermal behaviour was studied via TG-DSC. The gelled spheres were thermally treated and the products were analysed using powder XRD. A linearly decrease of lattice parameter with increasing Ce content up to 20% was 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. The structure of $U(C_2O_4)_2.2H_2O$ was observed below 180°C whereas $UO_{2+x}.nH_2O$ was prepared above this temperature with the loss of the classical square platelet shape of the oxalate. The residual carbon contents were significantly lower than that usually obtained through thermal conversion. Additionally, controlling of the pH allowed to optimize the uranium precipitation yield and to orientate the morphology towards agglomerated microspheres. Crystalline $UO_{2+x}.nH_2O$ samples were obtained after only 1 hour of heat treatment at 250°C. Finally, first results concerning the preparation of $(U,Ce)O_2$ mixed oxides were obtained and showed that the quantitative recovery of both uranium and cerium could be obtained through a heat treatment of 24 hours at 250°C and for pH = 4. Further studies are now devoted to sintering of the samples prepared as well as to the $(U,Ln)O_2$ systems.

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

$UO_2.nH_2O$ microspheres were obtained through hydrolysis of uranium(IV) in the presence of aspartic acid under hydrothermal conditions (160°C). A multiparametric 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 size of the particles produced (200 – 1200 nm range). For all the conditions tested, the characterization of the powders showed the formation of fluorite type $UO_2.nH_2O$ 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 microspheres. Complementary FIB experiments further confirmed the absence of porosity within these particles. Finally, preliminary tests concerning the shaping of the UO_2 microspheres into pellets were undertaken and revealed that green densities up to about 45 %TD can be obtained at 400-600 MPa without any crushing of the particles. First dilatometric studies are now under progress to evaluate the sintering capability of the compacts.

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. Preliminary studies on the conversion of uranyl nitrate into uranium oxide were done. Uranyl nitrate solution was heated to dryness on a hot plate in order to obtain uranyl nitrate crystals, which were dissolved in distilled water and mixed with a quantity of fuel necessary to obtain a ratio fuel/$UO_2(NO_3)_2$ equal to 1 and 1.7. The heating rate was 10°C/min up to 300°C in air, leading to the formation of uranium oxide. The ignition temperature was in the range of 180-210°C. The process conditions impacted the nature of the phases obtained, the compound UO_{2+x} was obtained for the ratio (glycine/$UO_2(NO_3)_2$) equal to 1.7 whereas a mixture of UO_{2+x} and U_3O_8 was observed for a ratio of 1.

Main difficulties - Delays

Dissolution and leaching investigations on CeO_2 and UO_2 – UNIMAN

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 have been 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.

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

The gelation parameter found to be suitable for the production of Ce doped particles using Ce(III) as precursor do not lead to satisfying products with Ce(IV) as starting material.

Scientific publications, patents (beneficiary name and type of publication)
<u>Journal: Yes</u> **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). <u>Int. Conference Oral: Yes</u> **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*. **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* **Thermal decomposition and structural changes of lanthanide-doped uranium dioxide particles prepared by internal gelation**, C. Schreinemachers, G. Leinders, G. Modolo, M. Verwerft, K. Binnemans , T. Cardinaels; RadChem 2018 - 18th Radiochemical Conference, Marianske Lazne (Czech Republic), 13-18 May 2018 / *Given*

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
CEA	**X**			**X**																				
CHALMERS																								
CIEMAT																								
CNRS	**X**			**X**											**P**									
CTU																								
ICHTJ																								
IIC																								
IRSN																								
JRC-ITU																								
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SCK-CEN				**P**											**X**									
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DOMAIN	2	WP	5	WP Leader	
Manpower dedicated to this WP on the period					

Contribution to Deliverables (number and title of each deliverable)

D5.1 Experimental and modelling studies of transfer kinetics in the reference separation processes (Juelich, ULANC, CNRS, CEA)
D5.2 Impacts of solvent degradation and recycle on the EURO-GANEX process (CIEMAT, CEA)
D5.3 Performances on microelectrode for online monitoring of relevant parameters (UEDIN)
D5.4 contribution of computational multi-disciplinary approaches to the design of solvent extraction devices (ULEEDS)
D5.5 Status of flowsheet calculations made for WP22 process testing (Juelich, KIT, NNL, CEA)

Contribution to Milestones (number and title of each milestone)

Main achievements - Progress

CIEMAT:

- Progress has been made on the irradiation loop design at Nàvade
    - radiolytic stability of solvent
    - material stability at high nitric acid concentrations
- Simulations are being performed investigating the process stability

ULEEDS:

- New design of operational (boundary) conditions of PSEC multiphase CFD model resulting in description of a cyclic steady-state system under flooding limitations and a dispersed flow regime.
    - Upper disengagement (settling) section is included in the model
    - A comparative study has been performed using a different modelling method
    - Another comparative study with reference modelling work resulting in a conference paper under review

ULANC:

- The extraction kinetics of fission products and lanthanides have been studied, concluding in the limiting reaction rate was that of TODGA with Ce(III)
- Suppression by nitric acid at low concentrations was also studied, and it was found that this effect is diminished below concentrations of 0.7 mol dm^{-3}.

UEDIN:

- New electrodes have been designed and produced: Pt arrays with and without ion exchange membrane, which has also been tested for its suitability. The behavior of exemplar species have also been tested.

NNL:

- An article has been submitted for publication in Solvent Extraction and Ion Exchange
- Initial modelling studies on minor actinides and lanthanides completed.

Main difficulties - Delays

In general, the major difficulty of the different partners has been availability of equipment, due to various reasons. The work in this WP has been in general delayed with many partners not yet started their work half way into the project.

Scientific publications, patents (beneficiary name and type of publication)

Effective collaboration between Beneficiaries (put crosses in boxes)																								
	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
CEA																								
CHALMERS																								
CIEMAT													x											
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JUELICH																								
KIT																								
LGI																								
NNL										x	x							x				x		
POLIMI																								
SCK-CEN																								
TWENTE																								
UEDIN																					x			
UNIMAN																								
UNIPR																								
UNIVLEEDS																								
UREAD																								
ULANC											x		x			x								
EDF																								
AREVA																								

DOMAIN	2	WP	6	WP Leader	Robin Taylor
Manpower dedicated to this WP on the period			10.55		

Contribution to Deliverables (number and title of each deliverable)

D6.1: Assessment of applications of PTD in i-SANEX and EUROGANEX processes

- Contributions from POLIMI, UNIPR

D6.2: Optimized flowsheets for homogeneous recycling of advanced MOX fuel in GEN IV reactors

- Contributions from CHALMERS, KIT

D6.3: Optimized flowsheets for heterogeneous recycling of advanced MOX fuel in GEN IV reactors

- Contributions from JUELICH, POLIMI

Contribution to Milestones (number and title of each milestone)

MS1: provide information on WP activity for the Work-Package Activity Summary Report 1

- Completed via this WPASR report

MS2: provide information on WP activity for the Work-Package Activity Summary Report 2

- Completed via this WPASR report

MS3: provide information on WP activity for the Work-Package Activity Summary Report 3

- Completed via this WPASR report

MS4: provide information on WP activity for the Work-Package Activity Summary Report 4
MS5: provide information on WP activity for the Work-Package Activity Summary Report 5
MS6: provide information on WP activity for the Work-Package Activity Summary Report 6
MS7: provide information on WP activity for the Work-Package Activity Summary Report 7
MS9: EURO-GANEX trial complete and TRU nitrate product ready for conversion studies

Main achievements - Progress

A general highlight was the meeting held in Antwerp, in conjuction with the half year meeting, to discuss the way forward for the development of the EURO-GANEX process. Minutes have been prepared and circulated to the interested partners. A programme of work, distributed between the partners, was formulated. It was decided to focus on proving the basic science that will underpin the use of m-TDDDGA and PTD in the optimised EURO-GANEX process. Flowsheet testing will be postponed until later phases of GENIORS or a follow-on project.

JUELICH have prepared a paper on the fundamental extraction properties of methylated DGA molecules that has been submitted to the prestigious Journal of American Society.

KIT have led the preparation and submission of a paper to Radiochimica Acta that reports the hot test of the EURO-GANEX process. Although this was work done under ACSEPT, it is the benchmark demonstration test of the EURO-GANEX process that has defined the scope of work in GENIORS. Full publication in a peer reviewed journal will be a major landmark.

JUELICH – Key highlight:

- The extraction behaviour of trivalent lanthanides in the AmSel system was studied.

POLIMI – Key highlight:

- During this semester POLIMI finalized the revision of the paper concerning the single-stage centrifugal contactor experiments with the TODGA-PTD system submitted to Solvent Extraction and Ion Exchange journal. The paper has been published.

CHALMERS – Key highlight :

- It has been found that the highest uranium concentration the system can handle is 50 g U/L, with 10 g Pu/L, 1g (inactive) Eu/L and trace amounts of Am and Np
- A virtual meeting was held to discuss the way forward for CHALMEX process development.

KIT – Key highlight :

- A batch of mTDDGA (cis:trans ≈ 50:50) was synthesised and Am(III) + Ln(III) extraction into a mTDDGA/kerosene solvent was studied.

UNIPR

- A new lipophilic ligand based on the Pyridine Triazole unit was synthesized and tested, showing interesting properties for the EURO-GANEX process. Samples were sent to POLIMI & KIT.

No progress this semester at: CEA, CIEMAT, ICHTJ, JRC, NNL, TWENTE

Main difficulties - Delays

The work package concerns flowsheet development of key processes for homogeneous and heterogeneous recycling so it is expected that most studies will commence later in the project. No significant delays or causes for major concern were raised by the partners in the HYPARs. NNL noted that studies in WP6 depended on the outcomes of the EURO-GANEX workshop held in Antwerp.

Scientific publications, patents (beneficiary name and type of publication)

Journal:

1. Wilden, A. et al. Unique Difference and Unprecedented Inversion of Selectivity in the Complexation of Trivalent Actinides and Lanthanides by Different Diastereomers of Me2-TODGA. J. Am. Chem. Soc. 2018, submitted.
2. Halleröd, J., Ekberg, C., Authen, T., Bertolo, L., Lin, M., Grüner, B., Svehla, J., Geist, A., Panak, P., Wagner, C. and Aneheim, E.: On the basic extraction properties of a phenyl trifluoromethyl sulfone based GANEX system containing CyMe4-BTBP and TBP. Published, Solvent extraction and Ion Exchange.
3. Rikard Malmbeck, Daniel Magnusson, Michael Carrott, Andreas Geist, Xavier Hérès, Manuel Miguirditchian, Giuseppe Modolo, Udo Müllich, Christian Sorel, Robin Taylor, Andreas Wilden, Homogenous Recycling of Transuranium Elements from Irradiated Fast Reactor Fuel by the EURO-GANEX Solvent Extraction Process, submitted to Radiochimica Acta.
4. Eros Mossini, Elena Macerata, Andreas Wilden, Peter Kaufholz, Giuseppe Modolo, Nicolò Iotti, Alessandro Casnati, Andreas Geist, Mario Mariani, Optimisation and single-stage centrifugal contactor experiments with the novel hydrophilic complexant PyTri-Diol for the i-SANEX process, Solvent Extraction and Ion Exchange, 36(4), pp. 373-386.
5. Ossola, A.; Macerata, E.; Mossini, E.; Giola, M.; Gullo, M. C.; Arduini, A.; Casnati, A.; Mariani, M., 2,6-Bis(1-alkyl-1H-1,2,3-triazol-4-yl)-pyridines: selective lipophilic chelating ligands for minor actinides, Journal of Radioanalytical and Nuclear Chemistry2018, Volume 318, Issue 3, pp 2013–2022

Int. Conference Oral:

Modolo, G. et al. Actinide-Lanthanide separation - the crucial point during the recycling of minor actinides from used nuclear fuel. 10th International Conference on f-Elements (ICFE-10), Lausanne, Switzerland, 3-6 September 2018.

Int. Conference Poster:

Authen, T. L., Halleröd, J., Aneheim, E., Ekberg, C. : CHALMEX: on the possibility of a 1-cycle GANEX process. October 2018.

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
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DOMAIN	2	WP	7	WP Leader	Leturcq (CEA)
Manpower dedicated to this WP on the period			10.69		

Contribution to Deliverables (number and title of each deliverable)

D7.1 Report on dissolution model development [month 36] (**CEA**)
D7.2 Report on efficiency of the electrochemical decomposition of ligands from SX processes and on its inputs on MABB precursor properties
D7.3 Report on the development of the different MABB precursor synthesis routes and their contribution on MA homogenity, dust reduction, lowering sintering temperature [month 45] (**CEA**)
D7.4 Product quality, characterization and testing (**NNL**)

Contribution to Milestones (number and title of each milestone)

M7.1 “availability of model compounds” **achieved.**

Main achievements - Progress

T71 Dissolution of model compounds

CEA: Dissolution of the different (U,Pu)O_2 samples and study of the effect Pu content on dissolution rates.

T72 Interface between SX and Conversion

NNL: New studies of Th(oxalate) precipitation have been completed to measure residual solubilities after the precipitation, to validate methods prior to Pu-active experiments.

T73 Uranium/minor actinide based oxide conversion dedicated to transmutation

CEA: Fabrication of dense $U_{0.9}Am_{0.1}O_2$ pellet from microsphere precursors.

T7.4: Characterizations

NNL: Calcination and characterization of (U,Th) oxalate simulants has been completed.
Concept flowsheets for (U,Pu) and MA co-conversion processes have been designed in EXCEL (for an Advanced PUREX process coupled to a i-SANEX process). (U,Pu) co-precipitation studies have been prepared

Main difficulties - Delays

NNL : Moving to mixed actinide solutions (containing MA from i-SANEX or EURO-GANEX processes) requires validation of methods with Th, U and single component solutions first.

Scientific publications, patents (beneficiary name and type of publication)

Journal:
Int. Conference Oral:
Int. Conference Poster:
Proceedings: 1. J. Holt, M. Sarsfield, D. Whittaker, R. Orr, R. Taylor, Uranium and thorium mixed oxide characterisation studies, Fifteenth Information Exchange Meeting, Manchester, United Kingdom 30 September-3 October 2018, Programme and Book of Abstracts (2018), p.124.
Patent:

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
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DOMAIN	3	WP	8	WP Leader	LGI

Manpower dedicated to this WP on the period	1 (NNL) + 1 (LGI) + 2 (KIT)

Contribution to Deliverables (number and title of each deliverable)

D8.1 “Process description report of concept Euro-GANEX plant” (M12)
D8.2 “Report on the comparison of SX processes for heterogeneous recycling” (M12)
D8.3 “Mapping of the different status and alternatives for each ESNII concept” (due in M18)
D8.4 “SimPlant” – Engineering simulation of integrated plants (due in M48)

Contribution to Milestones (number and title of each milestone)

MS2: provide information on WP activity for the Work-Package Activity Summary Report 2 (M13)

Main achievements - Progress

D8.1 and D8.2 were successfully delivered on M12.

D8.3 Mapping of the different status and alternatives for each ESNII concept

The deliverable was finished and submitted on the scheduled time (M18).

Firstly, the work is focused on the state of the art of ASTRID, ALFRED and MYRRHA. It is followed by a description of the system’s cycles, possible waste treatment strategies and the proposition and description of three waste treatment scenarios. There have been several interactions with partners and external experts to validate the work and provide relevant information. A meeting with the partners from CEA, ORANO and EDF was held on June at LGI’s office in Paris. The objective of the meeting was to agree on the focus of the deliverable, content and structure to follow. A follow-up meeting was planned in August to inform the partners about the advancement of the deliverable.

D8.4 – Report on “Sim-Plant” Methodology and flowsheet comparison

Flowsheet build of EURO-GANEX process from fuel receipt to powder finishing is ongoing (due in M48). It should be noted that this also contributes to T8.1.

Main difficulties - Delays

D8.1 has two-week submission delay.
D8.3 LGI faced some difficulties concerning the state of development of ASTRID and ALFRED.

Scientific publications, patents (beneficiary name and type of publication)

None

Effective collaboration between Beneficiaries (put crosses in boxes)

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
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DOMAIN	3	WP	9	WP Leader	NNL
Manpower dedicated to this WP on the period				ULanc – 0 but work to date funded by Lloyd's Register Foundation IRSN – 1.95pm NNL – 2.79pm	

Contribution to Deliverables (number and title of each deliverable)

D9.1: Safety Review minutes

D9.2: Report on major hazard analysis for the Euro-GANEX process focusing on criticality aspects

D9.3: Report on the methodology to establish a density law

D9.6 : Assessment of the corrosion vulnerability of common plant materials in the presence of key process streams

Contribution to Milestones (number and title of each milestone)

MS1: provide information on WP activity for the Work-Package Activity Summary Report

Main achievements - Progress

Task 9.1: Safety Review of a Euro-GANEX plant
The Concept Design for the EURO-GANEX plant has been complete under WP8.
An internal review was held with NNL Subject Matter Experts on the Head-End and Finishing processes within the plant.
A consortium review was held as a learning session at the GENIORS Antwerp meeting. Deliverable on track for Month 24.

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 15/06/2018) sent on to the IRSN in August 2018.**
Work done: Internal documents/data collection, first thoughts and pre-evaluation to initiate the IRSN' safety review of the Euro-Ganex reprocessing plant design and flowsheet focused on criticality safety
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
Step 1: Depletion calculations for MOX fuel in fast reactors have been gathered and are under analysis. The configurations calculated are based on a 600 MWe ASTRID-V1 like concept considered as iso-generator. This low void effect sodium fast reactor (SFR) has an heterogeneous design with an internal core that alternate fissile and fertile fuels (4 different zones) and an external core composed of a fissile and a fertile fuels (2 different zones). The fuel depletion of this reactor is strongly impacted by its heterogeneity and also depends on the initial fresh fuels composition. The fresh fuel changes depending on the recycled fuel to make it. Indeed the isotopic composition of Pu may be not always the same in function of its history and by consequence the Pu content necessary to be critical and achieve the target burnup (100 GW.d/tons) also. So, to evaluate large possible fresh and used fuels compositions, 1000 fuel depletion calculations were performed with the VESTA code. Large but credible ranges of initial isotopic composition (Pu, Am) and Pu content were considered (e.g. 15% to 40% of Pu) in each core. The set of the simulation forms a databank composed of the depletion up to 100 GW.d/tons of the 1000 different fresh fuels. The purpose is using these databanks to estimate the isotopic compositions of Am, Cm, Pu and searched penalized cases. Depending on the first results of this analysis, additional calculations could be performed (such as a burner configuration for the reactor) → **The analysis of the SFR fuel depletion calculations results is in progress.**
Task 9.2-b*:* Criticality studies (verification of the bounding nature of water moderation with regard to new extractants and diluents)
Subtask 1: Collect density of fissile species in GANEX solvents and write a methodology to establish a density law for NCS evaluations, including the need in terms of data and chemical measurements
Deliverable D9.3: Report on the methodology to establish a density law including the need in terms of data and chemical measurements depending of the range of applicability (Month 25) → **The drafting of the methodology report has been finished. Approval of the report is in progress (see below the content of the report)**

Task 9.3

The objectives of this task are:

- To perform corrosion assessments for stainless steels SS304L & S316L in the presence of as many of the GANEX inventory permutations as resource permits.
- To perform long term corrosion studies in relevant inventory permutations.
- To conduct corrosion and plant material compatibility tests for extraction and stripping stream compositions proposed for the EXAm process.

ULANC's GENIORS-funded work on this WP is currently not due to start until 1st Jan 2019 and then run for a period of 18 months. However, as described in GENIORS HYPARS 1 & 2, we have already made significant progress towards the WP objectives – even though the GENIORS-funded period of work has yet to begin. The manpower effort expended on this non-GENIORS funded work, and the associated results, can therefore be considered as match to the main GENIORS grant.
However, due to the PDRA in question having to work temporarily on another contract, no further matching effort has been expended this half-year – although they will be back at work on GENIORS related research come Jan 2019. Therefore, no further progress has been made for this WPASR.

Main difficulties - Delays

T9.1 – None
T9.2 – IRSN needs information quickly on Euro-GANEX solvents chemical data.
T9.3 – None

Scientific publications, patents (beneficiary name and type of publication)

Not applicable.

Effective collaboration between Beneficiaries (put crosses in boxes)

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DOMAIN	4	WP	12	WP Leader	Bruce Hanson
Manpower dedicated to this WP on the period				0.25 (UNIVLEEDS only)	
Contribution to Deliverables (number and title of each deliverable)					
D12.1 Report on travel bursary and secondment grant attribution (ULEEDS, R, PU, M45) D12.2 Organisation of the think-tank event (ULEEDS, R, PU, M20) - ***COMPLETE*** D12.3 Deliverable report on specification for on line packages (ULEEDS, R, PU, M13) - ***COMPLETE*** D12.4 Draft Purex package ready for testing (ULEEDS, R, PU, M31) D12.5 Draft iSanex/Ganex package ready for testing (ULEEDS, R, PU, M45) D12.6 Packages tested and released (ULEEDS, R, PU, M48) D427 Knowledge and Data Management Plan (CHALMERS) - ***COMPLETE***					
Contribution to Milestones (number and title of each milestone)					
MS14 Attribution of travel bursaries and/or secondment grants MS17 Convene development group from project partners and agree roles for online training courses MS18 Draft specification for on line packages for consultation					
Main achievements - Progress					
T121 Travel bursaries and secondment grants - Task leader: ULEEDS We have received 1 further application for a travel bursary during the current reporting period. To date there have been 5 awards - three secondments and two travel bursaries - with a total value of €8,762. We will continue to encourage applications to the travel bursary and secondment fund and allocate grants as appropriate. T122 Think-Tank - Task leader: ULEEDS The operational process for the Think Tank has been run and an output report will be produced M20. T123 On line training packages - Task leader: ULEEDS ULEEDS Digital Education Team have been engaged and have start work on a detailed “script” of the 4 packages. The aim is to present this and a draft version of Part 1 at the next meeting.					
Effective collaboration between Beneficiaries (put crosses in boxes)					

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
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DOMAIN	4	WP	13	WP Leader	LGI
Manpower dedicated to this WP on the period			1PM		
Contribution to Deliverables (number and title of each deliverable)					
Contribution to Milestones (number and title of each milestone)					
Main achievements - Progress					
• Editorial preparation of the first project newsletter (content, design, social media recap…). • Promoting the 2nd Project Meeting in Würzburg (Germany) followed by the 2nd edition of the Radical Behaviour workshop (RB2018). • Design of a flyer and a roll-up to promote GENIORS at different upcoming events. • Monthly reports of online audience through Google Analytics. • Social media: daily management of the GENIORS Twitter account + monitor the online audience (followers, retweets…). • Updates of the project website (deliverables for download, news and upcoming events…).					
Main difficulties - Delays					
• Engaging partners in following the GENIORS Twitter account. • Attracting audience to the project website and to subscribe to receive the future project newsletters.					
Scientific publications, patents (beneficiary name and type of publication)					
Journal: Int. Conference Oral: Int. Conference Poster: Proceedings: Patent:					
Effective collaboration between Beneficiaries (put crosses in boxes)					

	CEA	CHALMERS	CIEMAT	CNRS	CTU	ICHTJ	IIC	IRSN	JRC-ITU	JUELICH	KIT	LGI	NNL	POLIMI	SCK-CEN	TWENTE	UEDIN	UNIMAN	UNIPR	UNIVLEEDS	UREAD	ULANC	EDF	AREVA
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[i] Malmbeck, R.; Magnusson, D.; Geist, A. Modified diglycolamides for grouped actinide separation. J. Radioanal. Nucl. Chem. 2017, 314, 3, 2531-2538. DOI:10.1007/s10967-017-5614-2.

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[iii] M. Sypula , A. Wilden , C. Schreinemachers , R. Malmbeck , A. Geist , R. Taylor & G. Modolo Solv Extr Ion Exch 30, 7, 748-764.

[iv] Wilden A, Mincher BJ, Mezyk SP, Twight L, Rosciolo-Johnson KM, Zarzana CA, Case ME, Hupert M, Stärk A, Modolo G (2018) Radiolytic and hydrolytic degradation of the hydrophilic diglycolamides. Solv Extr Ion Exch 36(4):347–359.

[v] Kimberlin, A.; Berthon, L.; Saint-Louis, G.; Camès, B.; Guillaumont, D.; Paquet, A.; Guilbaud, P. Investigation of TODGA Radiolysis by Combining Experimental and Computational Approaches, 2nd Radical Behavior Workshop, Würzburg, Germany, 19-20 April, 2018.

[vi] Galán, H.; Zarzana, C. A.; Wilden, A.; Núñez, A.; Schmidt, H.; Egberink, R. J. M.; Leoncini, A.; Cobos, J.; Verboom, W.; Modolo, G.; Groenewold, G. S.; Mincher, B. J. Gamma-radiolytic stability of new methylated TODGA derivatives for minor actinide recycling. Dalton Trans. 2015, 44, 41, 18049-18056. DOI:10.1039/c5dt02484f

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