GENIORS

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WPASR 4

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Summary

WPASR4

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CONTENT

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WP1

INTRODUCTION

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

The total man power (pm) dedicated in WP1 to semester 1-4 is summarized in Table 1.

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

Table 1: Manpower (in pm) devoted to WP1

MAIN RESULTS

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Task by task, highlight the main progresses, delays, difficulties with analysis comments, action plan if needed. Give information and short analysis on manpower (expected, realized, explanation on discrepancies)

TASK 1.1

MANPOWER

9 pm was realized this semester by CEA, ICHTJ, JUELICH, KIT and TWENTE. After 4 semester 61.1 % of efforts planned for the complete project (Task 1: 37.2 pm) were realized. Obviously the men power of UREAD (700h) was allocated wrong in this task of WP1. The synthesis of degradation products should be assigned to WP2.

MAIN PROGRESSES

<u>Ruthenium speciation in GANEX 1st Cycle (Comparison of solvent extraction systems) CEA</u>

In solvent extraction experiments, Fletcher et al. (1) as well as Lefebvre et al. (2,3) excluded the presence of TBP in the inner coordination sphere of RuNO complexes in the PUREX process for both solvent extraction performed from 1 and 4 M nitric acid. We previously demonstrated that the five exchangeable ligands, nitrate, nitrite hydroxide or water molecules can be identified in both aqueous and organic phases thanks to spectroscopic tool such as FTIR, RAMAN and EXAFS. Thanks to those spectroscopic measurements, CEA demonstrated the analogous ruthenium behavior in amide ligand (MOEHA and DEHiBA) solvent extraction and in the TBP solvent extractions. The same type of analysis was extended to the TODGA solvent extraction process. It allows the comparison of ruthenium extraction properties for TODGA 0.2M in TPH/5% octanol with TBP and monoamide systems

Under higher acidic condition ([HNO_3] aq > 3 M), the behaviour is similar to the one observed previously with TBP or monoamide extractants: formation of trinitrate ruthenium nitrosyl complex with two coordinating water molecules. The interaction with the solvent occurs through an outer sphere hydrogen bond with coordinated water molecules. Nevertheless, TODGA and TBP contrast with monoamides for lower acidic conditions under which hydrolysed complexes of ruthenium are observed.Further efforts are made to introduce nitrite ligand in the system. The first results in the aqueous phase show a strong affinity between ruthenium and nitrite that easily substitute nitrate and hydroxo ligands in the ruthenium coordination sphere.

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(1) J. M. Fletcher, C. E. Lyon and A. G. Wain, Journal of Inorganic & Nuclear Chemistry, 1965, 27, 1841..

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

(3) 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.

The results obtained show that 4 M acetohydroxamic acid present in 1 M HNO_3 aqueous solution heated to 95 °C, quickly reduces weight amounts of Tc(VII) to Tc(II). Subsequent solvent extraction by 0.2 M TODGA in kerosene + 5 vol% octanol at room temperature effectively removes Am(III) from this aqueous phase, while the reduced technetium(II) quantitatively remains in the aqueous phase in the form of the complex with AHA, resulting in very high separation factor, $SF_{Am/Tc} = 1.1 \cdot 10^5$. However, further research is required to complete the study. The applied concentration of 4 M AHA is much higher than 1 M suggested for the reduction of plutonium and neptunium in the EURO-GANEX process, although higher concentrations of AHA (up to 3 M) have also been studied [2]. In the further work we plan to study the effect of the AHA concentration on the efficiency of Tc(VII) reduction and of the Am/Tc separation, as well as the effect of temperature on the kinetics of the processes. The results would show whether the efficient quantitative separation of americium (and other actinides) from significant amounts of technetium fission product will be possible in the EURO-GANEX process.

(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.

(2) M. Carrott, A. Geist, X. Hérès, S. Lange, R. Malmbeck, M. Miguirditchian, G. Modolo, A. Wilden, R. Taylor (2015). Distribution of plutonium, americium and interfering fission products between nitric acid and a mixed organic phase of TODGA and DMDOHEMA in kerosene, and implications for the design of the "EURO-GANEX" process. Hydrometallurgy, 152, 139-148.

Extraction of key fission products into mTDDGA TODGA (FZJ)

The speciation of ruthenium and palladium in aqueous and organic systems is often difficult to analyse. Uni Hannover offers the possibility to study these systems using ESI-MS techniques. The possibility for collaboration with Uni. Hannover was evaluated during a bilateral meeting in Hannover. Representative samples will be measured.

Extraction data of key fission products with the mTDDGA system (new EURO-GANEX system) were collected .

Different diastereomers of the extractant mTDDGA were studied to be used in a new GANEX process. As known from the scoping study published by Malmbeck et al.,[1] we expected significant extraction only at higher nitric acid concentrations. Therefore, we used aqueous phases composed of nitric acid of different concentration between 1-6 mol/L HNO3 containing trace amounts of inactive metals (10^{-5} mol/L each) and spiked with radioactive tracers. Most metal ions show the same trends in nitric acid concentration (increasing distribution ratios with increasing nitric acid concentration) and order of diastereomers (cis > mixture > trans). The Ln extraction pattern shows a maximum for the extraction of Er, which is comparable to Me2-TODGA (TWE-14)[2]. Ru and Sr distribution ratios were low under all conditions.

Tc extraction doesn't follow the trend in nitric acid concentration, which could be explained by its extraction as anion. It follows the order of diastereomers (cis > mixture > trans).

Fe, Pd, and Mo extraction don't follow the trends. Their distribution ratios are nearly independent of the HNO_3 concentration, and they follow a different order of diastereomers: trans > cis > mixture. Even though it could be possible that the trans isomer extracts these metal ions better, the order of diastereomers doesn't make much sense, as the mixture of diastereomers should show an intermediate behavior in any case. Therefore, the Fe, Pd, and Mo extraction is currently not understood and further experiments are needed to understand their behavior.

(1) 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.

(2) Wilden, A.; Kowalski, P. M.; Klaß, L.; Kraus, B.; Kreft, F.; Modolo, G.; Li, Y.; Rothe, J.; Dardenne, K.; Geist, A.; Leoncini, A.; Huskens, J.; Verboom, W. Unprecedented Inversion of Selectivity and Extraordinary Difference in the Complexation of Trivalent f-Elements by Diastereomers of a Methylated Diglycolamide. Chem. Eur. J. 2019, 25, 21, 5507-5513. DOI:10.1002/chem.201806161.

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

Sr(II) is less extracted with the DIPB-based solvent compared to the TPH/octanol based solvent; distribution ratios for non-loading conditions are lower by a factor of approximately 9. However, at an initial Sr(II) concentration of 1 mol/L almost the same distribution ratios are found, $D_{Sr(II)} \approx 0.02$, with organic phase Sr(II) concentrations of ≈ 0.02 mol/L. For both solvents, Am(III) and Eu(III) distribution ratios remain constant up to initial Sr(II) concentrations lower than 0.025 mol/L. With the TPH/octanol diluent, Am(III) and Eu(III) distribution ratios slightly decrease beyond 0.025 mol/L Sr(II) due to partial loading of the solvent. With DIPB, distribution ratios slightly increase. This could be due to the higher nitrate concentration in the system due to addition of $Sr(NO_3)_2$. The separation factor $SF_{Eu/Am}$ is constant and independent of the used solvent or initial Sr(II) concentration.

DIFFICULTIES

CEA: The ruthenium speciation and consequently its extraction properties depend on very slow kinetics that affect the measured extraction equilibria. We currently use systematic sample preparation procedures to avoid unconsitency in extraction values but this kinetic aspect may affect long-term behaviour in both aqueous and organic solutions.

ACTION PLAN

CEA: Publication to include the first results of this work is submitted. Nitrite ligands influence on extraction properties and speciation. Back extraction experiments.

ICHTJ: Studies on the effect of the AHA concentration on the efficiency of Tc(VII) reduction, and the effect of temperature on the kinetics of the process. Further studies on the details of solvent extraction separation of technetium (in weight amounts) from americium in the TODGA / HNO3 extraction system. Preparation and submission of publication.

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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. Obviously the men power of UREAD (700h) was allocated wrong in this task 2 of WP1. The synthesis of degradation products should be assigned to WP2.

LIST OF PUBLICATIONS

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

Wilden, A. et al. Thermodynamic and structural aspects of actinide and lanthanide extraction and complexation with diglycolamides. Oral presentation at the Institute seminar, Gottfried Wilhelm Leibniz University Hannover, Institute for radioecology und radiation protection (IRS), Hannover, Germany, 24 January 2019.

CONCLUSIONS

Since the start of the GENIORS project already 61.1 % of the planned actions related to the fission product chemistry (Task 1.1) were carried out. It is expected that the planned work on the optimization of scrubbing steps (3 pm for FZJ) within Task 1.2 will start 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 understand and improve the degradation of the ligands as well as of the extraction systems is the main goal. Solvent degradation may lead to many undesirable effects, for that, the identification of loses of efficiency, the behaviour troublesome degradation products or any mal operation situation due to degradation are the key issues. Work is divided in four task: T21 Radiolysis & degradation products; T22 Destruction of organics; T23 Gas generation and T24 Radiolysis modelling.

MAIN RESULTS

TASK 2.1 RADIOLYSIS & DEGRADATION PRODUCTS (TASK LEADER: JULICH)

MANPOWER

12.75 mp (1 pm CEA, 1.8 pm CTU, 2.45 pm IIC, 1.5 pm CIEMAT, 1 pm Julich, 3.5 pm POLIMI, 2.5 pm-synthesis UNIPR) and 10 pm-synthesis (UREAD) were reported this semester.

MAIN PROGRESSES

Studies of BTBP and BTPhen:

During this forth semester, it has been continued the stability studies CyMe$_4$-BTBP and CyMe$_4$-BTPhen in fluorinated diluent.

CyMe$_4$-BTBP and CyMe$_4$-BTPhen in fluorinated diluent BK-1 were tested by CTU for its radiation stability against gamma radiation. Up to 300 kGy, the following extraction systems were irradiated: organic phase containing 1 mmol/L CyMe$_4$-BTBP in BK1, organic phase containing 1 mmol/L CyMe$_4$-BTPhen in BK1, organic phase containing 1 mmol/L CyMe$_4$-BTBP in BK1 in contact with 1 mol/L HNO_3, and organic phase containing 1 mmol/L CyMe$_4$-BTPhen in BK1 in contact with 1 mol/L HNO_3. The results showed that when the organic phase is irradiated alone, the CyMe$_4$-BTBP and CyMe$_4$- BTPhen are not able to extract the tested metals (Am, Eu, Cm) even after irradiation by a low dose like 50 kGy. The presence of nitric acid containing aqueous phase during the irradiation decreases significantly the degradation of tested extracting compounds, a higher stability against radiolysis was observed. In that sense, BK-1 behaves in a similar way as the cyclohexanone-based diluents, however, this trend dramatically differs from the behaviour of the system with another fluorinated diluent like FS-13.

IIC has continued with the analysis by HPLC and MS of degradation products from the irradiated samples of CyMe$_4$-BTBP at Chalmers facilities. The large and more concentrated (50 mM) samples that were irradiated at Chalmers Univ. during last semester by γ-source in Ganex solvent (70% FS-13, 30% TBP, 1200 kGy) and octanol+TBP (dose 300 kGy) were used. Despite the degree of degradation remained relatively low, pre-separation of the degradation products by semi-preparative liquid chromatography led to removal of most of the solvent and afforded fractions enriched by one or several degradation products. MS and $^{1}H/^{13}C$ NMR spectra of all collected fractions were measured. NMR shifts of individual degradation products could be identified and assigned, though still on tentative basis. Complete assignments would be possible after final separation of current fractions by HPLC.

Studies of lipophilic PTEH:

POLIMI has continued the study of the degradation of the PTEH system (0.2 mol/L PTEH in OK + 10 vol% 1-octanol) by means of extraction tests and HPLC-MS (ESI) analyses that enabled to identify some of the PTEH degradation products and their overall impact on the extracting performances.

No remarkable alterations of the extraction efficiency were highlighted for solutions subjected to ageing, hydrolysis and irradiation up to 300 kGy.

Five possible degradation compounds have been identified and followed as function of the dose. According with the literature, the weakest part of the molecules seems to be the lateral branches; therefore, in all the hypothesized by-products structures the complexing site is preserved. These results explain why the affinity towards MA of aged and irradiated samples is almost invariable. Moreover, the lipophilicity of by- products seems to be not compromised and it is not expected they migrate to the aqueous phase.

Stability studies of diglycolamides:

- *TODGA-based systems:*

To go further in the understanding of the most relevant process-conditions and to simulate radiation by basic tests, CIEMAT activities about the influence of experimental conditions have continued as part as part of a more global study that has been included in WP5.

Validation of dosimeters (Perspex, ceric/cerous, Fricke and alanine) in the irradiation facilities at SCK•CEN was conducted using TODGA samples. Dose constants were not significantly differing from the values found by Zarzana *et al*. [1]

- *mTDDGA :*

The radiolytic stability study of mTDDGA has been continued this semester as part of Juelich-SCK•CEN collaboration. It has been identified 11 degradation compounds (10 radiolytic and hydrolytic), which are generally analogue to identified degradation compounds of TODGA and its methylated derivates [2-3]. Degradation compounds due to the breaking of the ether and C-N bonds were the most clearly observed.

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- *Hydrophilic DGAs (TEDGA, Me-TEDGA, Me2-TEDGA and TPDGA)*

Hydrophilic DGAs has been investigated by Juelich under neutral pH and concentrated aqueous nitrate solution, with a combination of steady-state gamma and time-resolved pulsed electron irradiation experiments supported by analytical techniques and multi-scale modelling calculations. The radiolysis of hydrophilic DGAs in 5.0 M nitrate solutions undergo first-order decay and significantly slower and less structurally sensitive than under pure water conditions, but similar to their lipophilic analogues. These findings are promising for the deployment of hydrophilic DGAs as actinide aqueous phase stripping and hold-back agents, due to the presence of nitrate in envisioned large-scale process conditions.

The degradation products observed in this study were generally identical to those observed in previous DGA radiolysis studies although in different proportions [4,5,6,7]. Overall, similar product distributions were observed for the radiation- induced degradation of the hydrophilic DGAs in 5.0 M $NaNO_3$ (aq) compared to pure water conditions, indicating similar radiolytic pathways. However, in $NaNO_3$ (aq) solutions reaction products with radiolytic NOx species are observed, the efficacy of which may have more significant impact upon process performance than those degradation products formed under pure water conditions alone. These NOx adducts need to be isolated and their respective chemistries elucidated.

Stability studies of stripping or masking agents:

Preparation of deliverable D2.2 *Stability studies of stripping agents*. Currently, under revision.

- *SO_3PhBTP:*

On-going activities about relevant-process conditions to simulate the degradation in a real process have been carried out in WP5. The analysis of a full Euro-GANEX system submitted to radiation (TODGA-DMDOHEMA / AHA- SO_3-Ph-BTP) has been carried out.

- *CDTA :*

Previous semester a series of irradiation experiments of CDTA and EDTA had 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). However, EDTA samples had showed solubility problems in no-diluted simulated HAR solution in 4 mol/L HNO_3.

This semester, the extraction behavior of these irradiated samples (Ln, An and FP distribution ratios) has been analyzed. D_{Eu} and D_{Am} by Euro-GANEX solvent from irradiated CDTA samples were almost invariable; therefore, it can be said that CDTA degradation is neither affecting to Ln and An extraction under these more realistic conditions. However, the decrease of D_{Eu} and D_{Am} by Euro-GANEX solvent from irradiated EDTA samples (just 10 kGy) and the initial solubility problems in nondiluted simulated HAR solution, it excludes EDTA from being an alternative to CDTA as masking agent of FP. Regarding FPs, even at low irradiation doses it has been corroborated problems to keep

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Zr and Pd in the aqueous phase and small third phase formations containing those metals, probably due to CDTA DCs.

DIFFICULTIES

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

- No degradation products/adducts of CyMe$_4$-BTBP and CyMe$_4$-BTPhen synthesized yet (CTU).
- No availability of ^{60}Co-sources at Náyade facility.
- Quantification of mTDDGA in irradiated solvents after validation of the dosimetry was unsuccessful and the whole experiment has to be repeated (Juelich).
- Purification of TODGA and problems to carried out coupling reactions with Br-BTPhen (UREAD).

ACTION PLAN

CIEMAT: On-going activities of SO_3PhBTP analysis and CDTA stability studies.

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

IIC: separation of DCs of irradiated CyMe4-BTBP and CyMe4-BTPhen samples, in BK-1 solvent, characterization by NMR methods- this is already under progress. Analysis of stability will be continued.

JUELICH: Further radiolysis data will be evaluated with mTDDGA and TPDGA.

POLIMI: The hypothetic PTD DCs that have been synthesised will be compared with PTD degraded samples by HPLC to confirm the structure of PTD DCs and their extraction properties.

UNIPR: Synthesis of PTD.

UREAD: Analysis with NMR, LC, and MS of irradiated samples from Prague. Synthesis of degradation compounds of CyMe$_4$-BTBP.

TASK 2.2 DESTRUCTION OF ORGANIC (TASK LEADER: CEA)

MANPOWER

1.5 pm realized this semester (1.0 pm CEA, 0.5 pm UNIPR).

MAIN PROGRESSES

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Thermal decomposition of neat TODGA in contact with nitric acid has been studied by CEA at high temperature in order to evaluate the behaviour of the molecule in case of accidental introduction of organic phase in an evaporator during the concentration operations of the fission products or recovery of nitric acid in nuclear fuel reprocessing plants. The influence of different parameters as the acidity, the amount of TODGA and radiation dose on the thermokinetics data of the reaction (T_{onset}, DT/dt, DP/dt, DH, Ea and pre-exponential A) have been analysed. The evolution of the temperature and the pressure for the acidity of 2.5 M (slowest reaction) indicates that the decomposition of the TODGA is a complex process, with several reactions until the complete transformation of the organic phase in CO and CO_2. In conditions of HNO_3 11.5 M, the reactivity of TODGA is much higher than that of TBP, probably due to the higher number of carbon in the TODGA molecule.

Differential Scanning Calorimetry experiments were driven by UNIPR on PTD, pyTriTetraol (PTT), PyTriEtHex and some of their precursors in order to study their stability upon heating or hazard for its synthesis, associated with the handling of azides. Azide precursors are rather volatile or not decomposed even at >250°C; PTD, PTT and PTEtHex data suggest that triazoles are rather stable to heating.

DIFFICULTIES

No difficulties reported.

ACTION PLAN

CEA: Influence of other important parameters will be studied: the ratio V_{org}/V_{aq}, the filling ratio of the cell and the presence of radiolysis degradation products.

All pm charged by UREAD to this task have been reallocated in task 1.

TASK 2.3 GAS GENERATION (TASK LEADER: POLIMI)

MANPOWER

0.15 pm were realized this semester by NNL.

MAIN PROGRESSES

Gas generation of TODGA based systems:

NNL Gas Generation Studies (from TODGA Processes) under Work Package 2 had been completed in HYPAR3. In an attempt to understand some of the findings of that work, experiments have been undertaken by both NNL and GENIORS's American partners. The experiments aim to understand different pathways that H_2 is formed during γ-irradiation. Specifically we are aiming to provide an answer as to why GH_2 values for GANEX and *i*-SANEX solvents are similar despite the vast difference in functional group and n-dodecane concentration. This work will form part of a future collaborative publication.

DIFFICULTIES

No major difficulties have been reported, although there were some delays affecting to task2:

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

ACTION PLAN

NNL work will form part of a future collaborative publication.

TASK 2.4 RADIOLYSIS MODELLING (TASK LEADER: CTU)

MANPOWER

pm realized this semester (1.6 pm CTU and 1 pm Juelich).

MAIN PROGRESSES

Modelling studies of water soluble diglycolamides:

The ground state properties of TEDGA, TMDGA, Me-TEDGA and Me_2-TEDGA ligands were analysed at CTU by the quantum mechanical methods (DFT). The role of HNO_3 in degradation processes was incorporated in the model. The obtained results support the previously observed trends and indicate that HNO_3 enhances the radiolytic stability of the ligands in concern. Moreover, molecular dynamics simulations were performed dealing with a detail conformation analysis of TEDGA, TMDGA, Me-TEDGA and Me_2-TEDGA molecules in aqueous environment. Remarkable correlation is found between the intramolecular bonds torsion dynamics and the experimentally observed chemical stability of the tested molecules in pure water and in water / nitric acid environments.

DFT calculations (PBE) were also conducted for TODGA, methylated TEDGAs and mTDDGA in vacuum by Juelich with the following observations:

a) Similar sensitation of the hydrogen atoms on the ether backbone as reported by Koubsky *et al*. [8] was found.
b) Methylation causes a decrease in BDE of the ether bond for both diastereomers, although these calculations don't take steric effects into account.
c) If the chain length increases, a lower energy is needed to dissociate the C-N bond, in agreement with the higher dose constant found for TMDGA compared to TEDGA [9].

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DIFFICULTIES

No difficulties reported.

ACTION PLAN

CTU: Further detailed DFT simulations of degradation reaction pathways will be performed on the models where acidic affects were implemented. The conformations analysis of DGA ligands in water and water / nitric acid mixtures by MD will continue.

LIST OF PUBLICATIONS

Publications :

1. L. Celbová: Computer simulations of extraction solutions. Diploma thesis, FNSPE CTU in Prague, Prague 2019 supervisor: L. Kalvoda.
2. Horne, G. P.; Wilden, A.; et al. Radiolysis of Hydrophilic Diglycolamides in Aqueous Nitrate Solution; NTRD-MRWFD-2019- M3FT-19IN030102018; Idaho National Laboratory, Center for Radiation Chemistry Research, Idaho Falls, ID, USA: 2019.
3. Afsar, P. Distler, L. M Harwood, J. John, J. S. Babra, Z. Selfe, and J. Westwood, Heterocycles, 2019. –published pre-press.
4. Afsar, J. S. Babra, P. Distler, L. M. Harwood, I. Hopkins, J. John, J. Westwood, Z. Y. Selfe, Heterocycles, 2019, Submitted.

Conferences:

Oral communications:

1. J. John et al.: The 1,2,4-Triazine Ligands – from Irradiated Nuclear Fuel Reprocessing to Chromatography Resins, Invited Plenary talk, RANC 2019 conference, May 5–10, 2019, Budapest, Hungary.
2. Verlinden, B. et al. Effect of Ionizing Radiation on a New Modified Diglycolamide for Grouped Actinide Extraction. 14th TIHANY Symposium on Radiation Chemistry, Siófok, Hungary, 25-30 May 2019.
3. E. Mossini, E. Macerata, W. Panzeri, L. Brambilla, A. Mele, C. Castiglioni, A. Casnati,
4. M. Mariani, Radiolytic degradation of hydrophilic PyTri ligands for minor actinide recycling, oral presentation at RANC 2019, 5-9 May 2019, Budapest, Hungary.

Poster communications:

1. FISA 2019 and EURADWASTE ´19 Conferences, Pitesti, Romania, 4 – 7 June 2019. “Stability studies of GANEX system under different irradiation conditions.” Iván Sánchez-García, Hitos Galán, Jose Manuel Perlado and Joaquín Cobos. Paper under preparation.

CONCLUSIONS

After 24 months of GENIORS project work it has been reached almost 90% of the effort dedicated to WP2 and in general it can be reported a more than optimal development of WP2 activities.

This semester has been reported 17 pm plus 10 pm related to synthesis. UREAD has charged 5 pm to task 2 that have been reallocated in task 1. Most of efforts have been dedicated to task 1, which has reached around of 99% of dedicated pm.

Deliverable D.2.2 has been written and it is under revision. However, deliverables D2.3 *Destruction of organics* and D2.4 *Gas generation* should be prepared in the following 2 semesters, although ~30% of pm of this tasks are not reported yet.

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WP3

INTRODUCTION

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

MAIN RESULTS

TASK 3.1 OPTIMISATION OF SYSTEMS (TASK LEADER: POLIMI)

MANPOWER

10.2 pm realized this semester (CEA, CNRS, KIT, JUELICH, POLIMI).

58.55 pm realized since the beginning of the project, corresponding to 75.1 % of the 78 pm planned for the complete project.

MAIN PROGRESSES

- The study of the extracting behaviour of both PTD and PTEH ligands as a function of the temperature was conducted. In addition the speciation studies on PTEH solutions by TRLFS, ESI-MS and NMR investigations and the relative data analysis was launched.
- In order to determine the stability constants and the associated thermodynamic parameters of PTD complexes with Ln(III) and Am(III) cations, microcalorimetry measurements by isothermal titrations have been started with La, Gd, Sm, Ce, Y, Eu, Nd and Pr. Experiments were performed under the conditions of the process at 0.45M HNO_3. The protonation constant was first determined by micro-calorimetry, confirming the previously obtained data by POLIMI using NMR. The protonation constant will allow for the accurate determination of multiple equilibria in the system
- The recently developed modified tetradecyldiglycolamide (mTDDGA) was further studied on its extraction properties. All experiments were conducted with the ligand in a diasteriomeric ratio (trans:cis) of 1:3.5. Samples of previous extraction experiments were measured by ICP-MS. These form a valuable addition to the already available data of radio-analytics. Further research in the speciation behaviour of neptunium and plutonium is necessary.

This project has received funding from the EURATOM research and training programme 2014-2018 under grant agreement No 755171.

- The extraction of Am(III) and Eu(III) from nitric acid into TODGA in TPH/octanol mixtures was studied. Obviously, the octanol content has no significant effect on distribution ratios for 5–50 vol.% octanol. Distribution ratios are slightly larger for 100% octanol. Interestingly, the absence of octanol has a pronounced effect: distribution ratios are smaller by approximately one order of magnitude for low to intermediate nitric acid concentrations. For initial nitric acid concentration of 1 mol/L and beyond, distribution ratios are similar to those measured with the TPH/octanol diluents. The same effect is observed with Eu(III), except that distribution ratios are greater by a factor of approximately 7–8, as also observed elsewhere
- Studies have been performed for the comparison of kinetics of Eu(III) by TODGA (+ 5% octanol) by extraction and back-extraction:
    - Effect of the concentration of TODGA and of the rotation speed of the cell on the kinetics.
    - Effect of Eu(III) (macro)-concentration in the extraction by CyMe$_4$-BTBP.
    - Effect of PTD on the extraction rate of Eu(III) by TODGA.
    - Extraction kinetics of HNO_3 from 3 M HNO_3 solution by 0.2 M TODGA.
    - Interfacial tension measurements with TODGA.

DIFFICULTIES

- Extraction kinetics studies: ordering of radioactive Ce(III) was delayed (waiting for safety agency authorisation)
- High heat of dilution (endothermic) with weak heat of complexation (exothermic) lead to difficult analyse of the calorimetry data. The decay heat of americium require to work with lower concentrations and to adapt the experimental parameters.

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

MANPOWER

8.75 pm realized (KIT, ICHTJ, UNIPR)

14.75 pm realized since the beginning of the project, corresponding to 108.5 % of the 13.6 pm planned for the complete project.

MAIN PROGRESSES

- Solvent extraction of Am(III) and Eu(III) was studied in the system containing two ligands that compete for the metal cation: a lipophilic extractant T-DGA in 1-octanol solution and a hydrophilic stripping agent SO_3-Ph-BTP in aqueous phase: 0.3 M HNO_3 + 0.7 M $NaNO_3$. Dependences were studied of the distribution ratios on the concentrations: (i) of the extractant (0.012 to 0.08 M) in the absence of the stripping agent, and (ii) of the stripping agent (5·10–6 to 4·10–2 M) at 0.02 and 0.04 M T-DGA. A difference between the current and previous experimental results has been found and the cause was tried to explain.

- Am(III), Cm(III) and Ln(III) distribution data for the AmSel system (TODGA/SO3-Ph-BTBP) were determined for varied temperatures (10–50°C).
- The complexation of An(III) and Ln(III) with 2,6-bis(1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl)-pyridine (PTEH) was studied using time-resolved laser fluorescence spectroscopy and NMR

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

MANPOWER

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

23.95 pm realized since the beginning of the project, corresponding to 70.4 % of the 34 pm planned for the complete project.

MAIN PROGRESSES

Loading of TODGA organic phases studies:

- The La(III) loading (solvent: 0.1 mol/L TODGA in diisopropylbenzene (DIPB), was extended to initial La(III) concentration of almost 2 mol/L to investigate the existence of a 1:2 complex in the organic phase.
- 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.

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

MANPOWER

4.14 pm realized (CIEMAT NNL, POLIMI)

8.52 pm realized since the beginning of the project, corresponding to 39.6 % of the 21.5 pm planned for the complete project.

MAIN PROGRESSES

- Ongoing activities about the influence and clean-up of detrimental degradation compound V (diglycolamic acid, DODGAA) on the extraction process
- Development of calculations for estimating the dose to new organic solvents such as TODGA during the reprocessing of future spent fuels. This was shared with GENIORS partners at the radiation chemistry sub-meeting in Marcoule. The model is now being used to evaluate consequences for solvent clean up processes.
- The decontamination feasibility of fresh, aged and irradiated PTEH solvents was demonstrated.

DIFFICULTIES

- DCs XII (1.1 gr), XIII (1.6 gr) and XXI (2.0 gr) have been supplied by University of Twente to continue with the studies within WP3. However, it was not possible to start these yet (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:

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2. J. Narbutt, “Solvent Extraction for Nuclear Power”, Chapter 24 (invited) in: Handbooks of Separation Science: Liquid-Phase Extraction, C.F. Poole, editor. Elsevier, **2019**. Approved
3. Wilden, A. et al. Unprecedented Inversion of Selectivity and Extraordinary Difference in the Complexation of Trivalent *f*-Elements by Diastereomers of a Methylated Diglycolamide. Chem. Eur. J., **2019**, *25* (21), 5507-5513**,** DOI:10.1002/chem.201806161.

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1. Wilden, A. et al. Application of Methylated Diglycolamides in the EURO-GANEX Process. 43rd Actinide Separations Conference 2019, Kingsport, TN, USA, 20.-23.05.2019.

CONCLUSIONS

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

After 24 months, 105.77 pm have been realized within WP3, corresponding to 71.9 % of the 147.1 pm planned for the complete project.

WP4

INTRODUCTION

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

Partner	Total planned	WPASR 1	WPASR 2	WPASR 3	WPASR 4
CNRS/ICSM	38.5	1.6	2.2	7.7	8.4
CEA	15.4	0.0	3.0	3.0	1.0
SCK.CEN	20.0	2.5	2.5	2.5	2.5
UNIMAN	11.0	0.0	0.0	6.0	6.0
Total	**84.9**	**4.1**	**7.7**	**19.2**	**17.9**

MAIN RESULTS

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

MANPOWER

4.3 pm (CNRS) – 1 pm (CEA) – 6 pm (UNIMAN) ⇒ Total : 11.3 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 panel of defined uranium-lanthanide solid solutions has begun in 2018.

In order to study the impact of the lanthanide mole loading on the chemical durability of $U_{1-x}Nd_xO_{2-y}$, $U_{1-x}Gd_xO_{2-y}$ and $U_{1-x}Ce_xO_2$, several dissolution tests were performed in static conditions. Around 100 mg of powder heated at 1000°C were put in contact with 20 mL of 2 M HNO_3 at room temperature (or at 60°C) for few days in high-density polytetrafluroethylene (PTFE) vessels. During this time, aliquots of

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300 µL were regularly taken off and replaced by the same volume of fresh nitric acid solution to maintain a constant volume of solution.

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

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

Due to the breakdown of the grinding device, the study of the impact of the grinding energy on the generation of defects and their consequences on the dissolution kinetics did not progress during this semester.

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. Four kinds of samples have been prepared : CeO_2, CeO_2 + 2% Nd, CeO_2 + 1% Pd and CeO_2 + 2% Nd + 1% Pd. Bulk ceramics were prepared for comparison with powders.

Structural characterization and leaching/dissolution studies have been completed in water on virgin CeO_2 model system and after γ irradiation (up to 100 kGy). The samples were characterized by XRD, SEM, TRLFS and XAFS/XANES. The most apparent physical effect of γ irradiation on the films was the production of visible cracks within their structure. Upon irradiation, the XRD patterns of the films underlined the formation of M_2O_3 in several doped samples, suggesting reduction has occurred. The reduction of Ce^{4+} to Ce^{3+} seems to be particularly strong in the presence of the Pd ε-particles.

The leaching tests in deionized water showed that saturation conditions were reached in solution within 24 hours (Pd concentrations being too low to be analysed).

Note that complementary dissolution tests are required in nitric acid to approach the reprocessing conditions (as it was discussed during the fourth project meeting, Madrid, June, 17-19th, 2019). Some discussions in this sense will be conducted in the next semester

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, reproducibly preparation of high-quality films of desired phase was reached, with a thickness of approximately 5 microns. 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. This has now been addressed. Active works have begun. Some challenges have been encountered in the availability of XPS, XANES and XAFS techniques due to the movement of analytical equipment within the university.

Concerning the studies developed at CEA, the study of the impact of the grinding energy on the generation of defects and the impact on dissolution did not progress during this semester due to the breakdown of the grinding device.

ACTION PLAN

CNRS/ICSM: Dissolution tests were developed on various $U_{1-x}Nd_xO_{2-y}$, $U_{1-x}Gd_xO_{2-y}$ and $U_{1-x}Ce_xO_2$ solid solutions in 2M HNO_3 at room temperature and 60°C. They will be completed during the next semester on sintered samples. Complementary multiparametric dissolution tests will be performed on the uranium-lanthanide 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 continued.

UNIMAN: Leaching/dissolution studies of both films and bulk samples are being investigated under simulated SNF storage conditions. They should be completed by experiments in conditions more representative for reprocessing conditions.

The effect of α - irradiation on the structure and on the leaching kinetics of CeO_2 samples will be continued 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"). Accelerator usage is scheduled by 30-31 May, 2019.

The PAD method developed for the preparation of CeO_2 films is under testing on UO_2 system. Due to different chemical behaviours of Ce^{4+} and U^{4+} (oxidizing vs. reducing), reducing or inert atmosphere will be required for the 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 will be undertaken, followed by leaching/dissolution studies including effect of irradiation. Moreover, the results obtained on CeO_2 are being written up for imminent publication.

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

MANPOWER

4.1 pm (CNRS/ICSM) + 2.5 pm (SCK.CEN) ⇒ Total : 6.6 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 hydrolysis of uranyl, Ce^{3+} and Ce^{4+} ions by thermal decomposition of urea, as well as the hydrolysis of various mixtures was investigated. Experiments were performed at 90°C and 100°C. After reaching the desired temperature, urea was added to the solution containing the metals in a given mole ratio compared to the metal content, R(urea). The hydrolysis reaction was monitored by pH experiments. The most suitable conditions to track the reaction were a temperature of 90°C and an urea content of R(urea) = 25. Such conditions were appled for U-Ce mixtures. After hydrolysis, the final obtained precipitates were characterized by PXRD and UV-Visible spectroscopy. Their thermal decomposition will be investigated by TG-DSC analysis coupled with EGA-MS measurements. After conversion, the final samples will be characterized by PXRD and SEM.

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

The direct precipitation of uranium oxides has been undertaken under hydrothermal conditions through the *in situ* conversion of uranium oxalate. Below 180°C, $U(C_2O_4)_2.nH_2O$ was formed whereas $UO_{2+x}.nH_2O$ was prepared above this temperature. SEM observations revealed the loss of the classical square platelet shape of the oxalate, while the evaluation of the residual carbon and water contents led to values significantly lower than that usually obtained through direct thermal conversion. Additionally, the pH control allowed to optimize the uranium precipitation yield and to orientate the morphology towards agglomerated microspheres. From the multiparametric study of the hydrothermal conversion, crystalline $UO_{2+x}.nH_2O$ samples were obtained after only 1 hour of heat treatment at 250°C (5 hours being necessary to improve the crystallinity of the powders). Rietveld refinement also revealed that the unit cell parameter no longer evolved between 5 and 48 hours, meaning that the O/M ratio remained constant in the prepared samples. Finally, first results concerning the preparation of $U_{1-x}Ce_xO_2$ mixed oxides were obtained and showed that the recovery of uranium was quantitative through a heat treatment of 24 hours at 250°C and pH = 5 whereas cerium recovery depended on the cerium content in the starting mixtures. Studies are now devoted to the study of the sintering capability of the prepared samples.

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

$UO_2.nH_2O$ microspheres were obtained through the hydrolysis of uranium(IV) in the presence of aspartic acid under hydrothermal conditions (160°C). A multi-parametric study involving time, temperature, concentration of the reactants was then undertaken. It showed that a 50% excess in aspartic acid led to monodisperse powders. The addition of mechanical stirring during the hydrothermal process allowed to accurately control the average diameter of the particles produced (400 – 2500 nm range). For all the conditions tested, the characterization of the powders showed the formation of fluorite type $UO_2.nH_2O$ 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. They revealed that green densities up to about 45 %TD can be obtained when pressing 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. In a first stage, this reaction was employed with an actinide surrogate element. The conversion of $Gd(NO_3)_3$ to Gd_2O_3 was obtained with glycine and citric acid as fuel, for a heating temperature of 300°C. Under these conditions, for a fuel / $Gd(NO_3)_3$ stoichiometric ratio, the monoclinic phase Gd_2O_3 was obtained with a high specific surface area (10-20 m^2/g), a small amount of residual carbon and a good crystallinity. The ignition of the precursors leading to the conversion nitrate / oxide was observed at a temperature of about 210°C.

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

ACTION PLAN

SCK.CEN: During the next semester, the investigation of the thermal decomposition of the precipitates formed within the hydrolysis experiments as well as the characterization of the samples resulting from the thermal treatment will be continued.

CNRS/ICSM: During the next semester, the direct precipitation of uranium oxides under hydrothermal conditions will be extended to $U_{1-x}Ln_xO_{2-y}$ 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 uranyl nitrate to uranium dioxide and of gadolinium nitrate to gadolinium oxide by Solution Combustion studies will be completed/extended for uranium-cerium bearing solid solutions..

LIST OF PUBLICATIONS

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

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

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

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

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

CONCLUSIONS

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

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 17.3 person-months has been reported split into 11.3 person-months for Task 1 (KIT, CHALMERS, NNL), and 6 person-months for Task 2 (JUELICH, KIT, CEA, POLIMI). This represents an increase on semester 3 which reported 10.6 person-months.

	task 1		task 2	
	expected	achieved	expected	achieved
JRC				
JUELICH	0	0	1	4.5
KIT	1.8	5	0.4	0.5
CHALMERS	5	5	0	0
CEA	0	0	0	0.5
NNL	2.5	1.3	0	0
CIEMAT	0	0	0	0
POLIMI	0	0	0.3	0.5
ICHTJ	0	0	0	0
UNIPR	0	0	0	0
total	9.3	11.3	1.7	6

MAIN PROGRESSES

INITIAL FISSION PRODUCT STUDIES (@CHALMERS)

Cadmium extraction was investigated over a range of acid concentrations from 2M to 6M HNO_3, and analysed using ICP-MS. In all studies, the remaining cadmium in the aqueous phase was below the detection limit of the instrument, suggesting that cadmium is completely extracted by the solvent. Extraction equilibrium is reached within 20 minutes of contacting of solvent with aqueous phase. Increasing acid molarity also increased the extraction overall.

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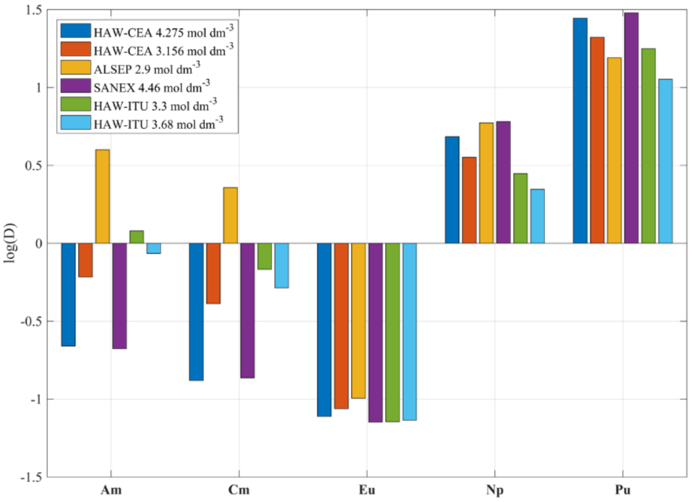
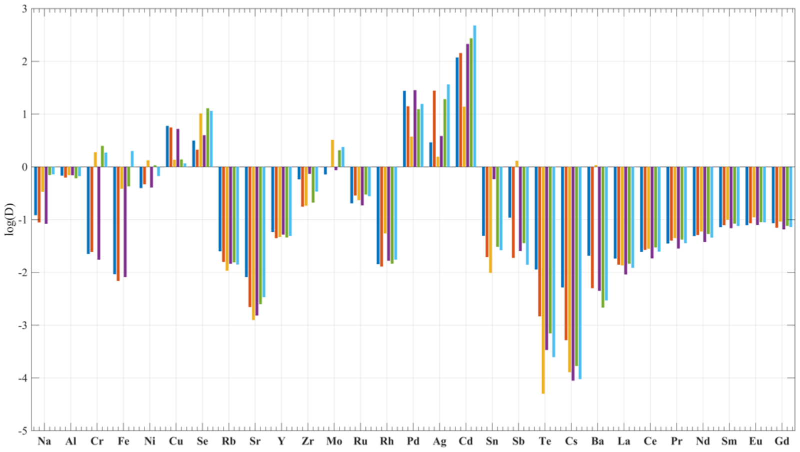
Palladium extraction was also proven to be significant, with D>10 for 4M nitric acid. As previously seen, extraction increased with increased molarity of nitric acid, and extraction equilibrium was achieved after 20 minutes of contacting time.

PERFORMANCE OF SOLVENT ON SIMULATED HAR SOLUTIONS (@JÜLICH)

A research stay was done at Jülich, Germany, to evaluate the performance of the CHALMEX solvent on simulated HAR solutions, of varying compositions and molarities. As can be seen from simple batch tests done, the americium extraction is well below necessary levels for good separation from the lanthanides. Surprisingly, the neptunium extraction is maintained at similar levels as in isolated tests with only neptunium. Plutonium is also, unsurprisingly maintained at acceptable levels.



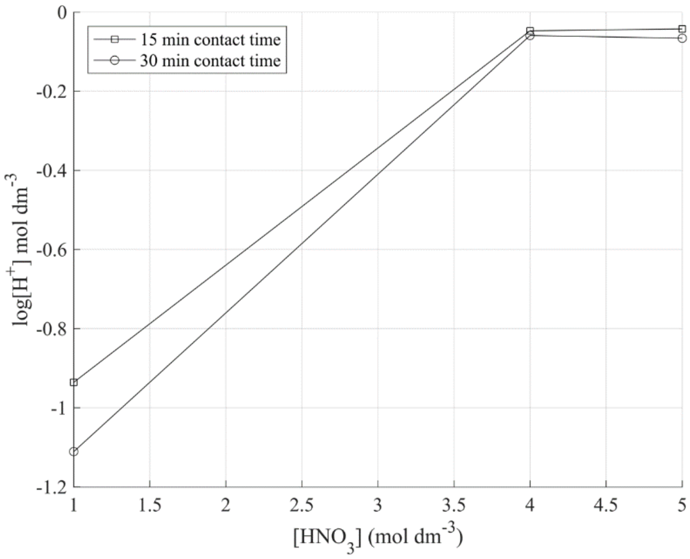
When inspecting the extraction of fission-, corrosion- and activation products, it becomes clear that some elements are preferentially extracted. In order of decreasing distribution ratios, the elements of most concern when considering the graph below is Cd>Pd>Ag>Se>Cu>Mo, and to a lesser extent Cr, all of which display distribution ratios>1. However, Cd is present in comparatively low concentrations in both the CEA, ITU and SANEX raffinates (~14-17 mg/L) compared to palladium for example (87-193 mg/L respectively).

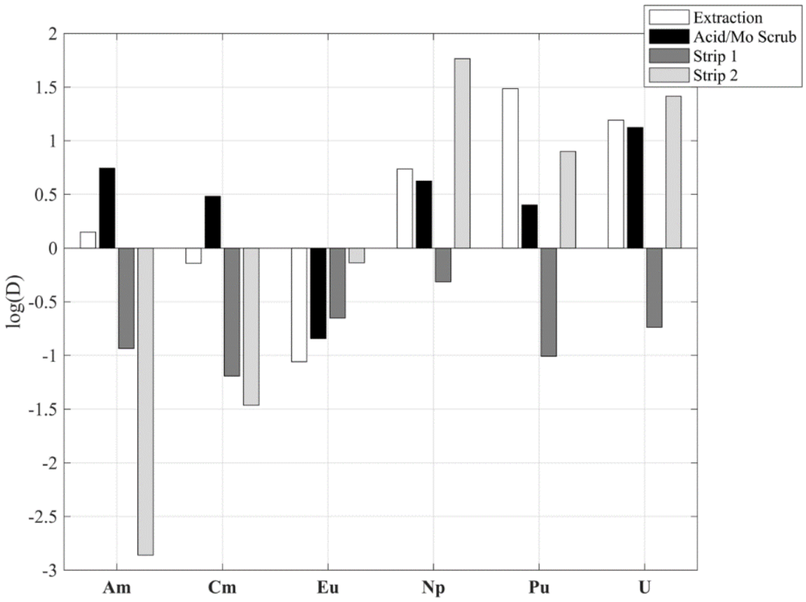


Kinetics studies were subsequently performed on both the CEA raffinates to investigate the extraction kinetics of the fission products and actinides under these conditions. It was found that cadmium reaches extraction equilibrium at around 10 minutes of contacting (Am reaches equilibrium after around 20 minutes of contacting), while the other elements of concern all reach extraction equilibrium within 5 minutes of contacting.

ACID EXTRACTION

Acid extraction of the solvent have been determined, and the results can be seen in the figure below. Acid concentrations of 1-5M was tested, at both 15 minutes and 30 minutes contact time. Both the aqueous and the organic phase was titrated with 0.1M NaOH. As can be seen, a significant amount of acid is extracted into the organic phase, showing the need for an acid scrub step.





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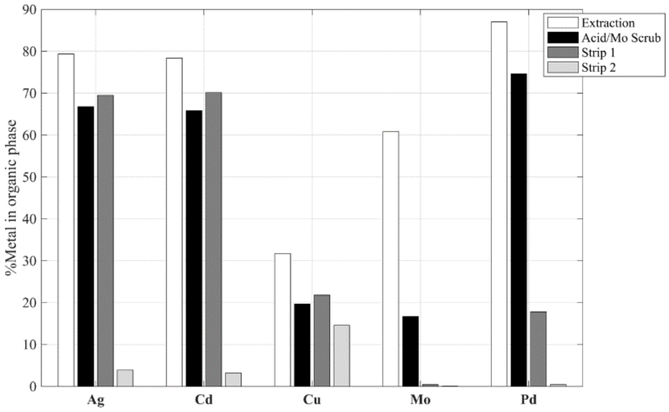
LARGE SCALE BATCH TESTING OF PROPOSED SIMPLIFIED PROCESS FLOW DIAGRAM (@JÜLICH)

A simplified flow diagram including one acid/Mo scrub step and two strip steps post extraction was tested on larger scale for batch extraction. The initial volumes were 5 mL solvent and 5 mL HAR raffinate. The raffinate tested was HAW-ITU (3.3M HNO_3), due to its lower metal content (in particular Fe) compared to the CEA-raffinates. The acid/Mo scrub was 0.6M glucono-lactone and 0.99M $NaNO_3$ in 0.01M HNO_3, as previously shown an effective scrubbing solution. The strip solution was 0.5M glycolic acid with pH adjusted to 4 using NaOH. The figure below shows the fission products of main concern during the extraction, scrub and strip, that are present in the HAW-ITU solution.

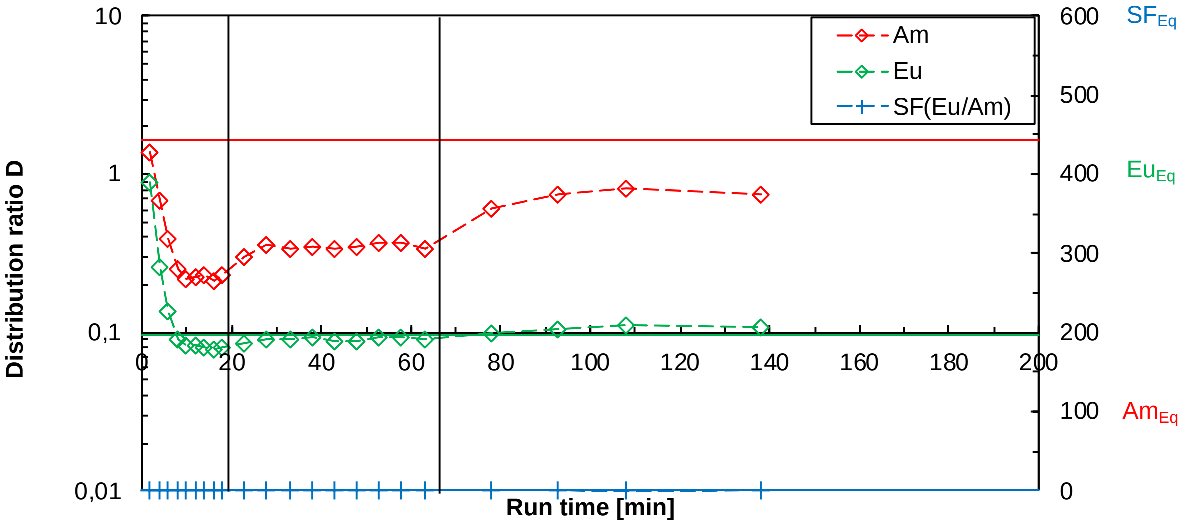


As can be seen in the figure above, the scrubbing step had good effect on especially Mo, but it also to some extent proved efficient in removing Pa, especially in the first stripping stage. From the figure below one can see that despite the initial low extraction of Am, at least it is kept in the organic phase during the scrubbing step and is easily stripped in the consecutive stripping stages.

Some issues were experienced during the large scale batch tests: after the first step, third phase formation was observed at the interface between the organic and aqueous phases. The third phase was removed from the vial before the experiments were continued as planned. These results established the need for investigating third phase inhibitors in the next term.

SINGLE CENTRIFUGAL CONTACTOR TEST (@JÜLICH)

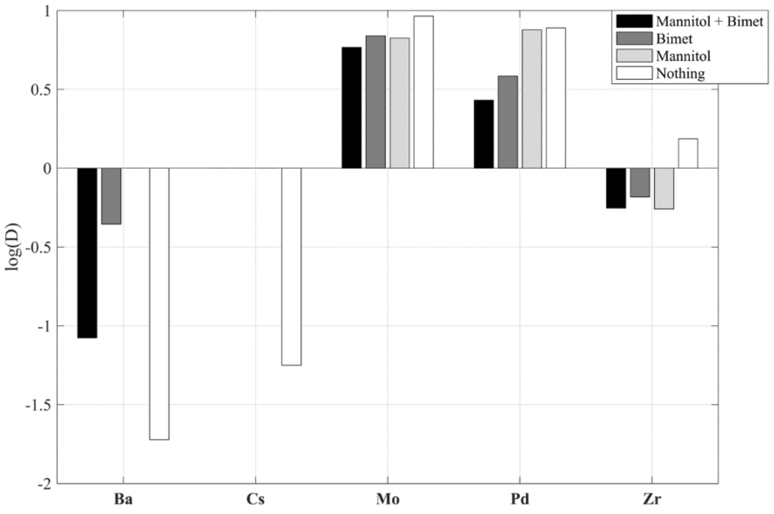
A single centrifugal contactor test was run on the CHALMEX solvent and simulated HAR (HAR-ITU 3.3M), at 3 different flow rates: 60 mL/hr, 30 mL/hr and 10 mL/hr. The figure below shows the respective distribution ratios for Am and Eu for the test as a whole. The various flow rates are indicated by the vertical lines in the diagram, with higher to lower flow rates going from left to right.



For 60 mL/hr, the phase separation appeared to be good, but some phase entrainment became apparent post sampling and centrifugation. Ag, Cd and Pd all showed high distribution ratios throughout the test, at all flow rates. More surprisingly, the Mo distribution ratios were <1 during the whole test. Cu was not detected in the organic phase. For the lowest flow rate, 10 mL/hr, phase entrainment was visually identified, even prior to centrifugation. The highest stage efficiency was achieved for the highest flow rate (60 mL/hr), at 7.8%.

SCRUBBING AND SUPPRESSION OF TROUBLESOME FISSION PRODUCTS (@CHALMERS)

Scrubbing and suppression studies have been initiated in the last part of this period, using agents previously shown effective in the CHALMEX process: mannitol and bimet. The extractions were performed under non-loading conditions, and the results achieved to date can be seen below. The remaining fission product experiments are still pending. As can be seen, mannitol and bimet together shows a good ability to well over half the Pd extraction. Where bars are missing, no extraction was detected.



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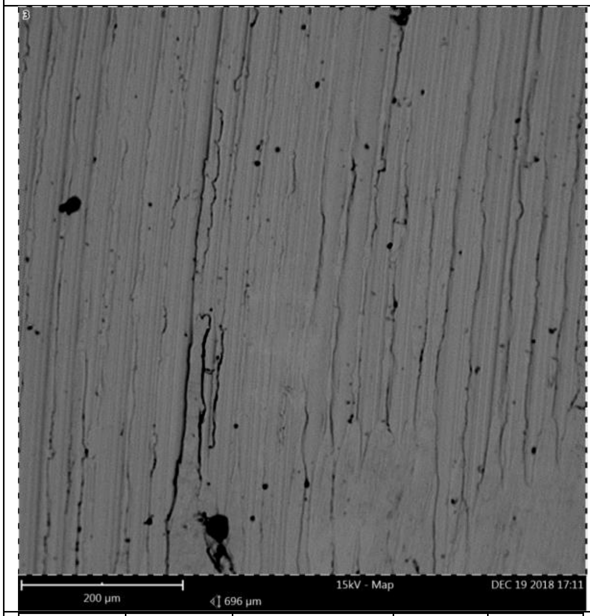
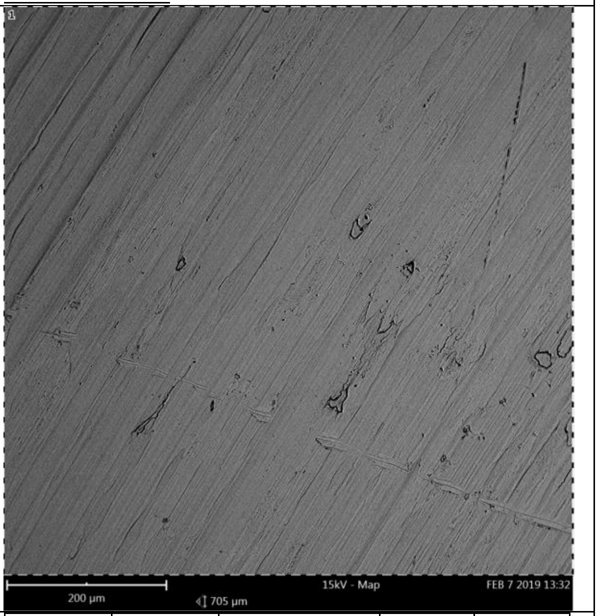
Selective stripping of Cd experiments have also been performed, thought the results are pending.

CORROSION STUDIES

Pieces of 316L SS and 310 SS were submerged in various solvents to investigate possible corrosion effects on the steel. The 316L SS was submerged in HNO_3, 100% FS-13 and the CHALMEX solvent respectively. The steel submerged in 100% FS-13 showed little to no signs of corrosion (analysed by SEM-EDX)

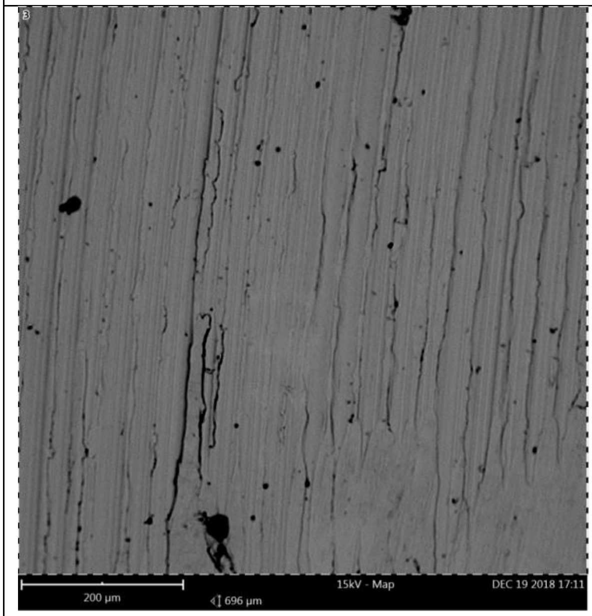
<table>
<tr><td colspan="2">100% FS-13</td></tr>
<tr><td>Pre-irradiation</td><td>Post-irradiation</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><td>
<table>
<tr><th>Element Number</th><th>Element Symbol</th><th>Element Name</th><th>Atomic Conc.</th><th>Weight Conc.</th></tr>
<tr><td>26</td><td>Fe</td><td>Iron</td><td>68.19</td><td>68.48</td></tr>
<tr><td>24</td><td>Cr</td><td>Chromium</td><td>17.52</td><td>16.38</td></tr>
<tr><td>28</td><td>Ni</td><td>Nickel</td><td>8.24</td><td>8.70</td></tr>
<tr><td>14</td><td>Si</td><td>Silicon</td><td>2.13</td><td>1.07</td></tr>
<tr><td>42</td><td>Mo</td><td>Molybdenum</td><td>1.62</td><td>2.80</td></tr>
</table>
</td><td>
<table>
<tr><th>Element Number</th><th>Element Symbol</th><th>Element Name</th><th>Atomic Conc.</th><th>Weight Conc.</th></tr>
<tr><td>26</td><td>Fe</td><td>Iron</td><td>69.75</td><td>70.12</td></tr>
<tr><td>24</td><td>Cr</td><td>Chromium</td><td>17.46</td><td>16.35</td></tr>
<tr><td>28</td><td>Ni</td><td>Nickel</td><td>9.47</td><td>10.00</td></tr>
<tr><td>14</td><td>Si</td><td>Silicon</td><td>1.80</td><td>0.91</td></tr>
<tr><td>42</td><td>Mo</td><td>Molybdenum</td><td>1.51</td><td>2.62</td></tr>
</table>
</td></tr>
</table>

The steel samples submerged in the CHALMEX solvent however, showed significant corrosion.

To determine if the corrosion was a result of the TBP or the ligand, further studies were initiated by submerging 310 SS in 100% FS-13, the CHALMEX solvent, the PUREX solvent and $CyMe_4$-BTBP in 100% TBP and irradiated to high doses (~2300 kGy). Only one of the solvents was shown to cause pitting corrosion. However, the high doses melted the labels off the vials, and identification of the solvents are underway. Using FTIR, it was identified that the solvent did not contain TBP and so it is likely that the corrosion is cause by the ligand. NMR studies are scheduled for late May 2019 to definitely identify the solvent.

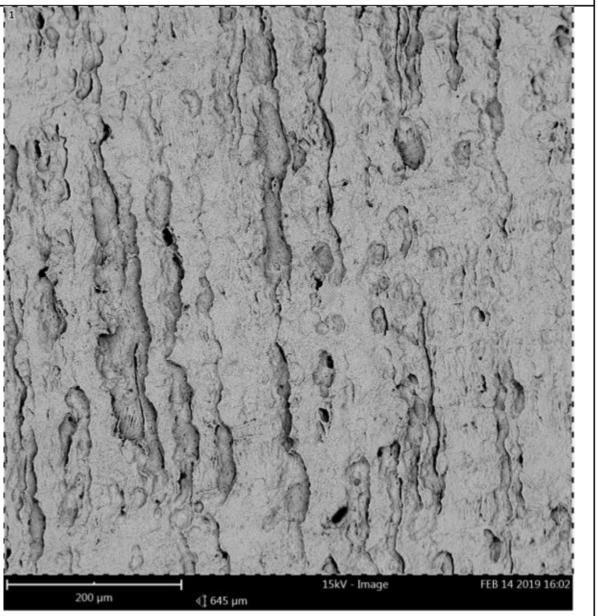
10 mM CyMe$_4$-BTBP in 70%$_{vol}$ FS-13 and 30%$_{vol}$ TBP

Pre-irradiation



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
26	Fe	Iron	68.19	68.48
24	Cr	Chromium	17.52	16.38
28	Ni	Nickel	8.24	8.70
14	Si	Silicon	2.13	1.07
25	Mn	Manganese	1.87	1.85
42	Mo	Molybdenum	1.62	2.80

Post-irradiation



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
26	Fe	Iron	69.98	72.15
24	Cr	Chromium	17.26	16.56
28	Ni	Nickel	8.03	8.70
14	Si	Silicon	2.93	1.52
16	S	Sulfur	1.81	1.07

PREPARATION OF A PU(IV) STOCK SOLUTION

Intended for use in mTDDGa EURO-GANEX loading studies, a Pu(IV) stock solution with a Pu(IV) concentration of ≥ 50 g/L was prepared.

1.5 g PuO_2 were dissolved in concentrated HNO_3 and refluxed for 10 h, resulting in complete dissolution. The volume of the solution was reduced to 5 mL. 13 mL of 1 mol/L HNO_3 were added to set the acid concentration to approximately 5 mol/L. UV/Vis spectroscopy in 5 mol/L HNO_3 showed that the solution was ≈ 75 % Pu(IV) and ≈ 25% Pu(VI) (Figure 1 left, black line). Pu(VI) was reduced to Pu(IV) by addition of H_2O_2. The solution was then heated to 70°C to destroy excess H_2O_2.

UV/Vis spectroscopy revealed pure Pu(IV) (Figure 1 left, green line). The solution was analysed by ICP-MS, alpha and gamma spectroscopy, LSC and acid-base titration.

The final solution is 68 g/L of Pu(IV)-239 dissolved in 5.9 mol/L HNO_3 (Figure 1 right). The solution furthermore contains 0.1 g/L U-235, 0.6 g/L Pu-240, 1.5 mg/L Pu-241 and 9 mg/L Am-241.

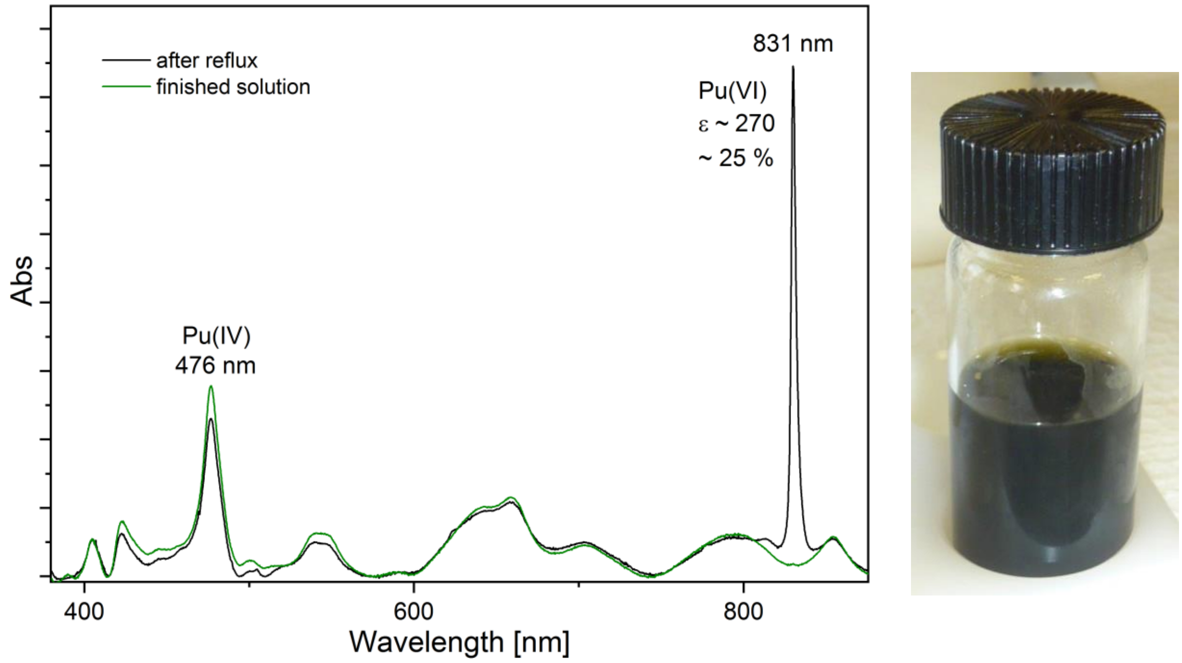


Figure 1. Left, absorption spectra of the Pu dissolution solution after dissolution (black line) and after reduction (green line). Right, final Pu(IV) stock solution: 68 g/L Pu(IV) in 5.9 mol/L HNO_3.

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.

TASK 1.2: HETEROGENEOUS RECYCLING

MANPOWER

A total of 17.3 person-months has been reported split into 11.3 person-months for Task 1 (KIT, CHALMERS, NNL), and 6 person-months for Task 2 (JUELICH, KIT, CEA, POLIMI). This represents an increase on semester 3 which reported 10.6 person-months.

	task 1		task 2	
	expected	achieved	expected	achieved
JRC				
JUELICH	0	0	1	4.5

KIT	1.8	5	0.4	0.5
CHALMERS	5	5	0	0
CEA	0	0	0	0.5
NNL	2.5	1.3	0	0
CIEMAT	0	0	0	0
POLIMI	0	0	0.3	0.5
ICHTJ	0	0	0	0
UNIPR	0	0	0	0
total	9.3	11.3	1.7	6

MAIN PROGRESSES

DIFFICULTIES

TPAEN is considered unsuitable for development of americium alone separations in heterogeneous recycle. Efforts should focus on alternative processes.

ACTION PLAN

Focus on AMSEL process.

LIST OF PUBLICATIONS

Journal:

1. Wilden, A., Kowalski, P.M., Klaß, L., Kraus, B., Kreft, F., Modolo, G., Li, Y., Rothe, J., Dardenne, K., Geist, A., Leoncini, A., Huskens, J., Verboom, W., Unprecedented Inversion of Selectivity and Extraordinary Difference in the Complexation of Trivalent f Elements by Diastereomers of a Methylated Diglycolamide, (2019) Chemistry - A European Journal, 25 (21), pp. 5507-5513
2. 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, Solv. Extr. Ion Exch. 36, 223-256 (2018).
3. 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. Solvent extraction and Ion Exchange, 36(4), pp. 360-372 (2018).
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 (2018).
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 Chemistry (2018), Volume 318, Issue 3, pp 2013–2022

6. 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, in press, Radiochimica Acta DOI:10.1515/ract-2018-3089 (2019).

Int. Conference Oral:

1. 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.
2. Robin Taylor, Developing options for future recycling of spent nuclear fuel in the UK, invited presentation at Safe & Sustainable Back end of the fuel cycle conference, Prague, 2019.

Int. Conference Poster:

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

CONCLUSIONS

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

Manpower on the WP has increased in semester 4. In the last semester good progress has been made on the CHALMEX process (although corrosion studies may be better placed in Domain 3 rather than this work package).

However, progress needs to be accelerated on EURO-GANEX and AMSEL process development in semesters 5-6.

WP8

INTRODUCTION

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

MAIN RESULTS

TASK 8.1

Already finished and delivered on time.

TASK 8.2

Already finished and delivered on time.

TASK 8.3

MANPOWER

0.8 PM during this period.

MAIN PROGRESSES

Delivered on time.

DIFFICULTIES

- Understanding the real status of ASTRID, ALFRED and MYRRHA was challenging,
- There is no enough information in order to obtain overall view of the advancements in the waste management field.

ACTION PLAN

None

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TASK 8.4

The works related to the development of SimPlant for plant footprint and plant sizing are on progress and funded by the UK leverage.

TASK 8.5

MANPOWER

None of LGI's 3.9pm has been used yet.

MAIN PROGRESSES

The task assessing the impact of implementing a closed cycle on nuclear fuel cycle has been initiated.

ACTION PLAN

- Interview questions will be prepared. Then, the meeting will be organised by experts from Orano (1pm) and EDF (1.5pm). They will participate in the whole WP as expert, participating to interviews and reviews of the deliverables.
- Final report will be submitted in M36.

LIST OF PUBLICATIONS

None

CONCLUSIONS

None

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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 SAFETY REVIEW OF A EURO-GANEX PLANT

MANPOWER

Expected – 2.80pm Actual – 2.79pm

MAIN PROGRESSES

The final deliverable – a report detailing the outcomes and research recommendations from internal and consortium reviews – has been completed and submitted to the ECCP. A summary of the recommendations is included in the Appendices. Please see full report for further detail.

TASK 9.2

MANPOWER

Expected – 2.00pm Actual – 1.95pm

MAIN PROGRESSES

Task 9.2-a: Preliminary hazard analysis focusing on criticality safety

<u>Subtask 1</u>: 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).

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This preliminary safety review has been started, taking into consideration the conclusion of the previous safety reviews carried out by NNL and IRSN in the framework of the SACSESS project. This review will be based upon IRSN's knowledge and experience of reprocessing of FR MOX fuels in Marcoule and La Hague plants and will be mainly focused on criticality safety. Besides criticality, areas/hazards for consideration will be also radiation protection, materials selection/corrosion, flammability and explosion, chemical compatibility, thermal stability/reactivity, radiolysis, radioactive decay heat and management of liquid and gaseous effluents. This work will be about the operations from head-end section to co-conversion unit (different process options or alternatives might be also compared) and will consider the interface between each process step (mechanical preparation, voloxidation, dissolution, separation, conversion, storage/fuel fabrication, effluent management). Concerning criticality safety, the review will confirm the control methods propose by NNL in D8.1 report or propose other control methods based on the IRSN's knowledge of the French reprocessing facilities. Moreover, a depletion calculation for a realistic initial composition of MOX fuel and an Astrid reactor will be performed. This depletion calculation will allow IRSN to compare the amount of U, Pu, Am and Cm of this calculation to the NNL Euro-GANEX flowsheet and process data. Based on the results on this depletion calculation (in particular the isotopic composition of U, Pu, Cm and Am), simple criticality calculations will be performed in order to estimate minimal critical dimensions/properties (for example: cylinder diameter, plate thickness, amount of water, concentration) of different fissile media and to confirm the proposed control methods for the different part of the Euro-GANEX process. These calculations might take into consideration incidental situations in the chemical separations unit considering, in particular, the separation of actinides (for example, Cm from Am if chemically or physically feasible). The depletion calculation have been performed. The criticality review and the simple criticality calculations have to be done.

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

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

Deliverable D9.2: Report on major hazard analysis for the Euro-GANEX process focusing on criticality aspects covering subtasks 1 and 2 (issue Month 48) ⍰⍰Writing up not yet begun

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

<u>Subtask 1</u>: 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 (issue Month 25)

The report is already finished and has been uploaded on the GENIORS platform in January 2019 (awaiting NNL's approval). In this report, the expected data are specified as well as their extent with regards to the operation field of the process.

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

IRSN is therefore waiting for data to allow establishing a density law in the concentration ranges of the Euro- GANEX process and compare criticality values with the ones obtained for water as a solvent. Data partially covering the operation field of the Euro-GANEX process could be provided by some partners. Additional data could then be given by others, the objective being to have an optimized coverage of the process concentration ranges. In case no data would be available, density laws with other types of solvent for which similar data would be available might be investigated. Besides, density law for TBP/TPH could be established as reference also allowing testing the methodology.

Deliverable D9.4: Report with collected data on the Euro-GANEX solvents and the density laws built (issue Month 36) → Writing up not yet begun, pending collection of data

Subtask 3: Perform some critical calculations to compare standard critical values (fissile mass, cylinder diameter, slab thickness, volume…) obtained with established density laws (subtask 2) and those obtained with density law by water

The end result will be included in Deliverable D9.2 (issue Month 48).

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 for NNL, no work has been performed this half-year and we would now like to request a postponement of the start date for our GENIORS funded work until 1st December 2019. The funded work would then run through until the end of the GENIORS project itself in May 2021.

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

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.

WP10

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

MAIN RESULTS

TASK 10.1 CLUSTERING EVENTS

MANPOWER

Globally on track (less man power realized this period but more was realized last period).

MAIN PROGRESSES

Deliverable 10.1 issued.

Clustering Event 2 realized (GENIORS participation/contribution to INSPYRE summer school).

ACTION PLAN

Write deliverable D10.2 (CEA)

TASK 10.2 STAKEHOLDERS EVENTS

MANPOWER

Globally on track (less man power realized this period but more was realized last period).

MAIN PROGRESSES

No progress this period.

CONCLUSIONS

Progress of organizing Clustering/Stakholders Events is on track (2 Clustering Events and 1 Stakeholders Event organized; 2 Clustering Events and 1 Stakeholders Event still to be organized).

WP12

INTRODUCTION

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

MAIN RESULTS

TASK 421

MANPOWER

ULEEDS: 0.03pm

MAIN PROGRESSES

One secondment award of €1,780 has been made.

ACTION PLAN

Continue to encourage applications to the fund.

TASK 422

This task is complete.

TASK 423

MANPOWER

ULEEDS: 0.10 pm

MAIN PROGRESSES

The course outline has been created and the script/content is being developed with Leeds DES.

Course Structure

Four lessons

Lesson 1: Introduction to solvent extraction and the PUREX process

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- Principles and history of solvent extraction applied to nuclear operations.
- Starting with the Hanford B through to Thorp/Cap la Hague UP2/3.
- This package will include the extraction chemistry associated with U/Pu into TBP.
- PUREX basic principles
- Principles of solvent extraction

Lesson 2: The application of the PUREX process

- The Purex process as applied to Thorp – overall step through the plant
- A description of the main process steps using the UK's Thorp reprocessing plant as the reference – main focus on separation

Lesson 3: Enhancements to PUREX

- A description of newer forms of Purex, such as COEX and NUEX and also add-on flowsheets such as i-Sanex.
- This package will include the extraction chemistry associated with Np/Am/Cm extraction.

Lesson 4: Advanced recycle options

- Alternatives to Purex.
- GANEX family of flowsheets, including the extraction chemistry associated with U, Pu, Am and Cm.

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

ACTION PLAN

1. Continue with advertising availability of the bursary scheme
2. Complete the development of the on-line courses, with a finished outline document and then scripts. The next project date is for D424 Draft Purex package ready for testing (ULEEDS, R, PU, M31). This will be hit.

TASK 424

No progress to report this period. No milestones or deliverables were connected with this task.

No milestones or deliverables are connected with this task.

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CONCLUSIONS

T421 will continue to be advertised for new applications.

T422 is complete and has been reported through Task 321 Safety Review of a Euro-GANEX plant (NNL).

T423: Work is ongoing for each of the 4 packages. The content is being worked up in detail with Leeds DES.

T424 is ongoing.