

NFC3

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Recovery of Strategic High-Value Fission Products from Spent Nuclear Fuel during Reprocessing

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The Net Zero transition and increasing living standards around the world are placing exponentially increasing demands on scarce natural materials essential for decarbonisation and modern, high-technology applications [1]. As nuclear power has been identified as a key, low-carbon energy source in grid decarbonisation by many nations, expanded use of the technology will inevitably push up demand for the finite natural uranium and thorium reserves [2]. Combined with the high construction costs and long build times for reactors and their supporting infrastructure, a substantial rethink of the nuclear fuel cycle (NFC) to a more holistic, and sustainable approach is needed, incorporating comprehensive resource utilisation and advanced waste management [3].

The bulk of the 7-11 kilotons of spent nuclear fuel (SNF) produced annually is not reprocessed primarily due to limited capacity brought about by high costs, proliferation concerns, and negative image – most SNF is viewed as a waste rather than a resource [3]. Despite this, reprocessing and responsible management of SNF as a resource will be the key to the long-term sustainability of the NFC. SNF is not just rich in U and Pu for further energy generation, many fission products (FPs) are valuable resources in their own right, either as the elements or isotopes [1,3]. For example, SNF contains the resources such as the platinum group metals (PGMs) Ru, Rh, and Pd, and rare earth elements (REEs) Y, and La to Dy at concentrations ($\text{kg}/\text{t}_{\text{SNF}}$) far higher than in most natural ores ($\text{g}/\text{T}_{\text{ore}}$) [4]. Thus, SNF represents an untapped resource of these high-value strategic materials whose recovery would simultaneously offset the high costs of reprocessing and reduce waste volumes while implementing circular economic principles [3]. Other potential resources such as the noble gases (He, Kr, and Xe) and a range of isotopes useful for medical, sensing, and power generation applications are also present in significant quantities [3,4].

Although the concept of recovery of FP resources from SNF during reprocessing is not new [4], it has received more attention in recent years and is receiving timely attention in light of recent geopolitical, technological, and climate shifts [3,5]. This presentation will highlight the potential FP resources present in SNF and their value, the likely separation, recovery, and purification routes [5], and the probable effects on the NFC should this concept be implemented and will be discussed in the context of current and likely future NFC implementations. The necessity for decay storage and the end-use applications for these materials is also examined [1,3,5].

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- [1] S. Bourg and C. Poinssot, *Prog. Nucl. Ener.*, **2017**, 94, 222.
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A new approach for monitoring radionuclides in hydrometallurgical separation processes based on Raman spectroscopy

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The reprocessing of nuclear fuel offers unique advantages regarding both, the best use of the resource and the minimization of the radioactive wastes, and for the success of this challenge, the partitioning of radionuclides contained is essential. Nowadays, the most advanced technology is focused on the hydrometallurgical separation concept, based on liquid-liquid extraction methods. This approach, built on the use of selective extractants, is well-established for U and Pu separation, by the industrial process PUREX (Plutonium Uranium Reduction Extraction). The current international research efforts are addressed to the recovering of minor actinide elements, for which, different strategies are being demonstrated at different Technology Readiness Level (TRL).

In this work, we propose the use of the fluorescence of key radionuclides measured by Raman spectroscopy (RS) as a tool to monitor processes performance of at laboratory scale. It should be noted that this tool is envisioned for in situ analysis, allowing it to be used for online monitoring of radionuclides, in the stream solutions of the reprocessing plants for safety purposes.

As proof-of-concept we show in this work how Eu and Nd can be successfully monitored in an *i*-SANEX (*Innovative-Selective ActiNide Extraction*)-like process by using the RS. For this aim we follow these radionuclides in three steps: i) extraction of Nd and Eu from an aqueous nitric acid solution (3 M) with *N,N,N',N'*-tetraoctyl-diglycolamide, TODGA (0.2 M in OK), ii) stripping actinides with 2,6-bis[1-(propan-1-ol)-1,2,3-triazol-4-yl]pyridine, PTD (0.04 M in 2.1 M HNO₃) and iii) stripping lanthanides with 0.01 M HNO₃.

A new unsymmetrical diglycolamide for selective americium partitioning

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For the last two decades, diglycolamides such as TODGA (*N,N,N',N'*-tetraoctyldiglycolamide), have been at the forefront of solvent extraction systems for actinide partitioning. Their extraction properties, and their compliance with the CHON principle, have led to the synthesis and study of a large number of diglycolamides.^[1] To date, TODGA remains the most promising of the diglycolamides studied. However, previous research has mainly focused on symmetrical diglycolamides. Only a limited number of diglycolamides with different alkyl chains have been investigated for their extraction capabilities, and even fewer have been tested in americium-curium separation systems.^[2]

In this work, the extraction properties of a new diglycolamide, *N,N*-diisopropyl-*N',N'*-didodecyldiglycolamide (iPDdDGA) was investigated using batch-scale solvent extractions. The Americium Selective Extraction (AmSel) process was chosen as a reference system.^[3] In this two-step extraction process, americium, curium, and the lanthanides are first coextracted with TODGA from a HAR solution, then in a second step, americium is selectively stripped with the water-soluble SO₃-Ph-BTBP (3,3',3'',3'''-([2,2'-bipyridine]-6,6'-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate). In the new system studied in this work, TODGA has been replaced by iPDdDGA. For the loading step, the kinetics, thermodynamics, the influence of the nitric acid concentration and the influence of the ligand concentration were investigated. In the stripping step, the kinetics and the influence of the complexing agent concentration were investigated. Particular attention was paid to the americium/curium separation factors obtained with iPDdDGA, and these were compared with those reported for TODGA.

The extractions quickly showed performant extraction properties for iPDdDGA, with distribution ratios obtained that are approximately two orders of magnitude higher than for TODGA. Therefore, decreased iPDdDGA concentrations of 0.005 M were used in loading experiments, while 0.1 M was maintained as the iPDdDGA concentration for stripping tests. Fast kinetics were observed both during studied loading and stripping of the actinides and light lanthanides. During stripping, improved separation was observed between americium and curium, with separation factors around 3. This is a small but significant improvement compared to the TODGA-based AmSel process which typically shows separation factors around 2.5. This demonstrates the potential of diglycolamides with different alkyl chains to improve existing actinide partitioning systems.

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Population balance solution in the context of the actinides oxalic precipitation

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Oxalic precipitation is a crucial step on the actinides recycling process since it defines the morphology and the physical characteristics of the raw materials to the MOX fuel fabrication process. One of the narrowest constraints concerns the size of the particles produced since it determines the proper operation of the entire solid treatment chain. The population balance equation (PBE) is a well-known statement used to predict crystal size distribution in precipitation processes. Nowadays a considerable quantity of PBE numerical solution strategies is reported in the literature. However, there is no a general methodology leading to the solution of the PBE in any context.

A deep understanding of the industrial actinides separation process requires the solution of the steady state PBE. In addition, the study of actinides precipitation is highly constrained by safety and criticality issues. For these reasons, the modelling approach includes the development of experimental and numerical methods based on harmless species. In this concern, previous works focused on the development of a numerical methodology able to simulate the precipitation of neodymium oxalate [1].

This work focuses on:

- The arrangement of the numerical methodology to the specific context of the uranium precipitation. The treatment of the size-dependent agglomeration induces an additional numerical difficulty due to the dependency of both, PBE and agglomeration kernel on the particle size.
- The detailed comparison between the neodymium and uranium precipitation systems in terms of: systems of equations, numerical analysis, crystallisation phenomena and sensibility analysis.

As result, an accelerated fixed point algorithm based on the crossed secant method [2] is adapted to overcome the difficulty and accurately solving the uranium agglomeration PBE. A detailed comparison of the crystallisation phenomena taking place in the precipitation of neodymium and uranium is performed. Finally, a general framework to model the loose agglomeration is stated and can be applied to the simulation of the actinides precipitation in general. Future works aim the inclusion of the size dependent agglomeration on a multicompartmental model.

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Preliminary extraction and characterization studies of water-soluble BTP-(COOH)₈ for the separation of trivalent actinides

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Separation of An and Ln is an important part in the recycling of nuclear fuel. Therefore, many ligands have been tested over the years and several separation processes have successfully been demonstrated on the laboratory scale (e.g., SANEX, DIAMEX). Current research aims at the development of new ligands which are built only with carbon, hydrogen, oxygen, and nitrogen (CHON), because they can be incinerated completely without secondary waste production.

We tested the new water-soluble ligand 2,6-bis [5,6-di(3,4-dicarboxyphenyl)-1,2,4-triazin-3-yl] pyridine (BTP-octa-COOH, Figure 1) for the selective separation of Am(III) and Cm(III) from trivalent Ln. This ligand has the characteristic of having eight carboxylic acid groups in the outer periphery and a pyridine in the central core, where the metal ion complexation occurs. The ligand might act as CHON alternative to the sulphonated aqueous ligands used in the i-SANEX¹ (SO₃-Ph-BTP) and AmSel² systems (SO₃-Ph-BTBP). We present results of extraction studies using BTP-octa-COOH, which showed good Eu/Am separation factors at low HNO₃ concentration in combination with TODGA as extractant (Figure 1). The stoichiometry of metal ion complexation was studied by solvent extraction slope analysis and time resolved laser-induced spectroscopy (TRLFS) in HClO₄ and HNO₃. The formation of 1:1 and 1:2 complexes was found, and conditional stability constants of each formed species were determined. This study gives a better understanding of the coordination with An(III) and Ln(III) with BTP-octa-COOH.

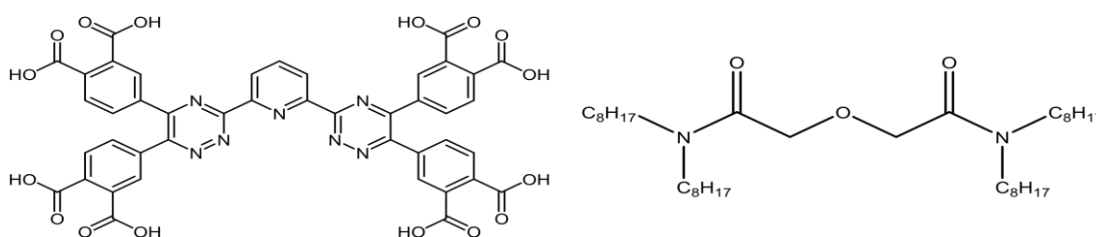


Figure 1. Left: BTP-(COOH)₈ structure. Right: TODGA structure

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From Water-Soluble Peroxo Complexes of Plutonium(IV) to Solid State Plutonium peroxide

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Since the Manhattan project, it is known that the addition of hydrogen peroxide on acidic solutions of plutonium leads to the formation of coloured complexes, transitioning from the brown to the red as the concentration of H_2O_2 increases.[1] The addition of H_2O_2 in large excess involves the formation of green precipitates which have been used as precursors for the preparation of PuO_2 or in waste management processes.[2] Nevertheless, the structures of these compounds remain unclear and the only reported structure for a Pu peroxo compound in the literature involves a dimeric peroxo carbonato compound of Pu(IV) showing bridging $\mu^2, \eta^2\text{-O}_2$ ligands.[3] In the current study, we synthesized and characterized a new peroxo based complex of Pu(IV) of green colour offering a strong stability in solution. The complex displays original absorption spectra in solution. Raman, FT-IR and X-ray absorption spectroscopies evidenced a polymeric peroxide bridged structure. Solid-state diffuse reflectance spectroscopy analyses showed analogous solution and solid structures (Fig.1). Intriguingly, XRD further demonstrated that the precipitate shows a similar crystalline structure with the one of the old-reported green PuO_2 precipitate precursor. Therefore, we believe that the synthesis and spectroscopic characterization of this new compound sheds light on the structure of the an historical Pu solid compound which remains undetermined to date.

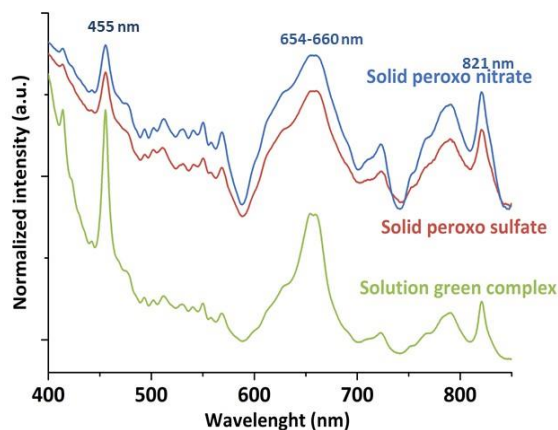


Figure 1: Vis-NIR absorption spectrum of the green peroxo complex observed in aqueous nitric solution or at the solid state by diffuse reflectance spectroscopy.

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Crystallization of Tri- and Tetravalent Plutonium Diglycolamides

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Used nuclear fuel (UNF) creates a significant obstacle when it comes to the widespread adoption of nuclear power. Over time, transuranic and lanthanide fission products accumulate, the latter of which are neutron poisons that reduce the efficiency of nuclear fuel. From here, the UNF must be recycled/reprocessed to remove these problematic isotopes. Of particular interest is the separation of minor actinides (Am, Cm, & Np) from the UNF as they are very long lived and responsible for the majority of the heat and radiotoxic burden of UNF.

Many proposed strategies for separating the minor actinides employ liquid-liquid extraction methods that utilize chelating ligands to preferentially complex the minor actinides over the lanthanides. One such proposed class of chelating ligands are the diglycolamides (DGA). These ligands have shown great promise due to their high affinity towards the trivalent transuranic elements, particularly that of americium and curium. Additionally, DGAs fall under the CHON doctrine, where the ligand only consists of carbon, hydrogen, oxygen, and nitrogen, thereby reducing the level of waste generated as compared to methods utilizing phosphorus and sulphur-based extractants.¹ However, these separation processes are subject to intense, multicomponent radiation fields which results radiolytic reactions in these environments to produce transient tetravalent actinide species. Understanding the interactions between these transient species and DGAs is vital.

In this study², plutonium was crystallized with the hydrophilic tetramethyl diglycolamide (TMDGA) and characterized by single-crystal X-ray crystallography. Homoleptic crystalline products were produced containing plutonium(III) and plutonium(IV), providing an opportunity to study subtle differences across oxidation states in the same compound. Geometry calculations were also performed on the coordinating oxygen atoms and the solid-state absorption spectra were analysed and compared to similar plutonium structures.

Acknowledgements: This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DESC0021372.

[1] Ansari, S.A., *et al.*, *Chem. Rev.* **2012**, 112 (3), 1751–1772.

[2] Rotermund, B.R., *et al.*, *Inorg. Chem.* **2023**, 62 (32), 12905–12912.

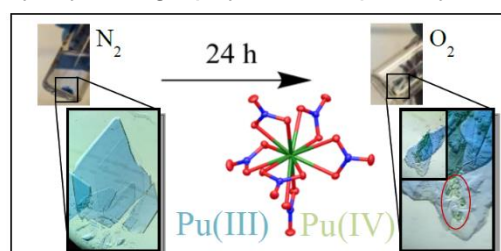


Figure 1 : Crystal samples of plutonium(III) TMDGA oxidizing and recrystallizing to form the corresponding plutonium(IV) compound. Both structures maintained the same coordination environment across both oxidation states.

Reactivity of actinides mono-cations with NH₃ in the gas phase

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Over the last decades, reactions between actinides mono-cations and small molecules in the gas phase have attracted a great interest. Gas phase reactivity is a simple approach (no matrix effect) to better interpret and understand the role of actinide's electronic structure and contribution of 5f electrons to their reactivity. In addition, from an analytical point of view, the differences in actinide reactivity can help resolve isobaric and polyatomic interferences that complicate the analysis of some isotopes in Inductively Coupled Plasma Mass Spectrometry (ICP-MS) such as ²³⁸U/²³⁸Pu, ²³⁸U¹H/²³⁹Pu or ^{242m}Am/²⁴²Cm.

Experimental studies using different mass spectrometry techniques have revealed differences in actinide reactivity with several gaseous molecules (NH₃, O₂, CO₂, CH₄, C₂H₄ ...). An experimental correlation between actinides reactivity and their electronic promotion energies has been established. [1] The lower the energy, the better the reactivity. For instance, with NH₃, U⁺, Np⁺ and Cm⁺, whose electronic promotion energies are less than 0.5 eV, react completely to form AnNH⁺ whereas Pu⁺ and Am⁺, whose energies are greater than 1 eV, do not react.

Quantum chemical computations were performed to characterize reaction mechanisms between actinides mono-cations and small gas molecules. The geometries of the transition states and the thermodynamic properties were determined using Density Functional Theory (DFT). Firstly, reactions of several actinides mono-cations (Ac⁺, Th⁺, Pa⁺, U⁺, Np⁺, Pu⁺, Am⁺ and Cm⁺) with NH₃ were investigated. In the case of Ac⁺, Th⁺, Pa⁺, U⁺, Np⁺ and Cm⁺, after formation of the An⁺-NH₃ complex, actinide mono-cation inserts itself in N-H bond until H₂ is eliminated via two transition states and intermediate species HAnNH₂⁺. Figure 1 shows the reaction scheme for Cm⁺ with NH₃. The other elements have a similar mechanism. For Pu⁺ and Am⁺, a limiting step occurs with the formation of the first transition state, as shown in Figure 1. The theoretical results confirm the experimental results reported in the literature. This prove the need for actinide mono-cations to have a reactive electronic configuration with two non-f electrons. The higher the electron promotion energy, the more difficult it is to achieve a reactive configuration. The bonding evolution along the reaction pathway was studied using different tools such as natural bond order (NBO) and electron localization function (ELF). These analysis confirms reaction pathways and revealed differences in orbital participation in bond formation, which could also influence the reactivity of actinides.

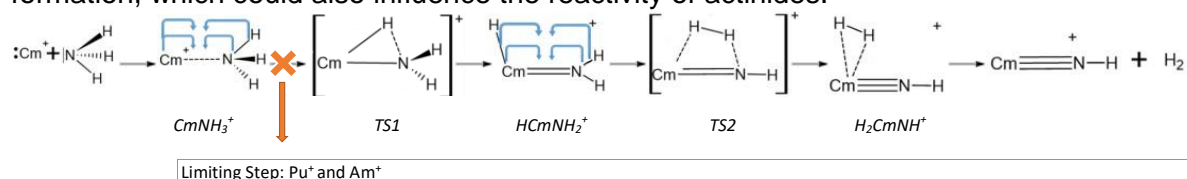


Figure 1: Reaction scheme for Cm + NH₃ determined from DFT.

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Synthesis and Solid-state NMR of actinide Halides

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The thermal and electrochemical properties of molten salts make them attractive for use in metal electrorefining, concentrated solar power, and next-generation nuclear reactors, such as molten salt reactors. A full examination of the physical properties of candidate salt is necessary for industrial implementation, but access to pure, anhydrous materials for these studies is hindered by dangerous and thermally complex synthetic methods. Here, we also describe preliminary static solid-state NMR studies of UCl_3 and related materials and discuss potential applications of this technique for the characterization of unknown samples.

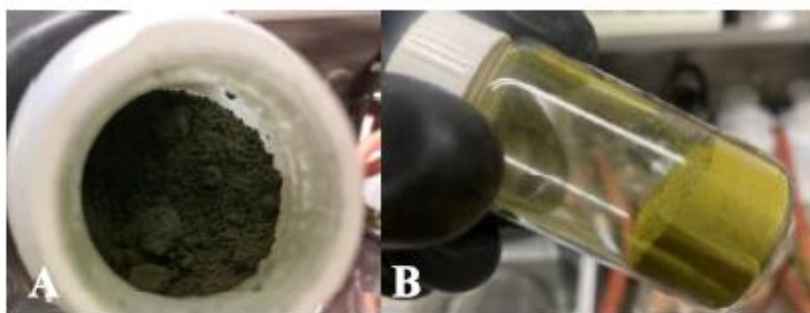


Figure 1a : UCl_3py_2 before thermal ligand elimination.

Figure 2a : Anhydrous UCl_3 prepared from UCl_3py_2

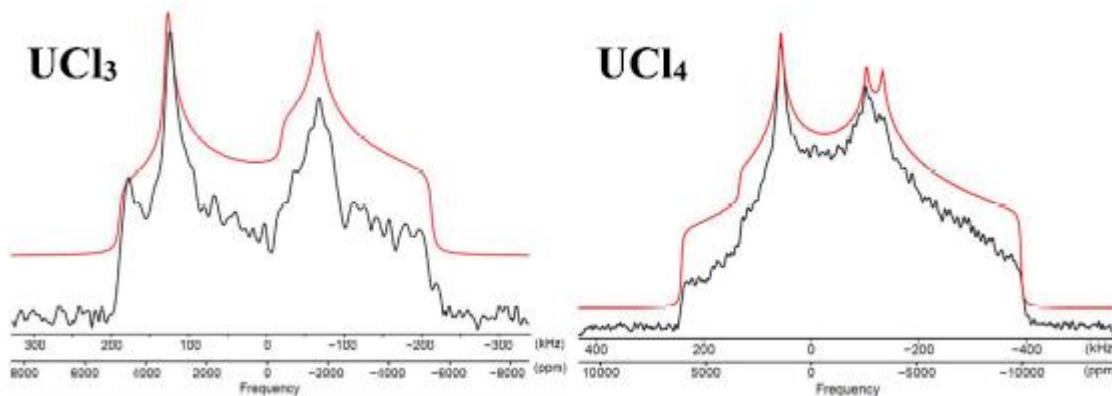


Figure 2: Experimental (black) and simulated (red) ^{35}Cl static SSNMR of anhydrous UCl_3 et UCl_4 .

[1] Erickson, K. A, S. S ; Scott, B.L. ; Monreal, M.J. « thermal Elimination of Pyridine from a Uranium Trichloride Precursor. »

[2] Altenhof, A.R. ; Erickson, K.A. ; Fetrow, T.V. ; Monreal ; M.J. ; Mason, H.E. $^{35/37}\text{Cl}$ SSNMR as a Probe for Paramagnetism in lanthanide and actinide materials »

Volatile fission products in actinide oxides: A first-principles study

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Volatile fission products such as iodine, caesium and tellurium can chemically react with one another to form corrosive compounds for the cladding of LWR fuels UO_2 and $(\text{U,Pu})\text{O}_2$. To avoid this phenomenon, which may favour stress corrosion cracking under transient power conditions, one must understand the complex chemistry of I, Cs and Te in actinide oxides and its influence on these volatile species behaviour within the fuel.

Using the Hubbard-corrected density functional theory (DFT+U), we determined and compared trapping and mobility properties of I, Cs and Te in UO_2 and $(\text{U,Pu})\text{O}_2$. We showed that the oxidation state of each fission product depends on the type and charge of its incorporation site. As illustrated in figure 1, we also computed the XANES spectra of I, I_2 and Cs, for each considered trap, in UO_2 and $(\text{U,Pu})\text{O}_2$, using the FDMNES code [1] and the DFT+U atomic configurations. The comparison of the calculated spectra with the experimental ones contributes to the identification of the chemical forms and trapping sites of iodine and caesium in UO_2 .

The use of a Hubbard term allows us to account for the strong correlations of actinides 5f electrons. To avoid the metastable states inherent to this method, we used a dedicated procedure [2], which also allows us to monitor the valence of each species in the simulation.

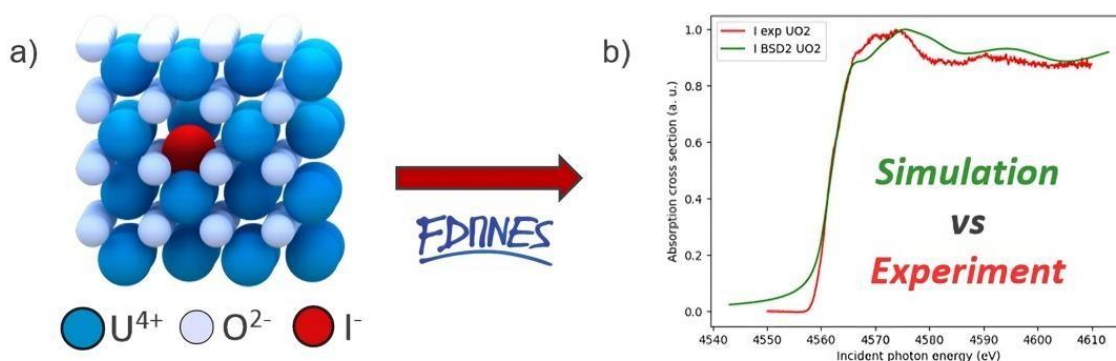


Figure 1: a) DFT+U calculated atomic structure of an iodine atom in a defect of UO_2 . b) Comparison of the corresponding computed XANES spectrum of iodine L_3 edge with the experiment, measured on an iodine-implanted virgin UO_2 sample [3].

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Moving from diglycolamide to monoglycolamide-a better extractant for treatment of high-level waste

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N,N,N',N'-Tetraoctyldiglycolamide (TODGA) has been identified as the promising extractant for group separation of trivalent actinides from high-level waste solutions. Despite the excellent extraction properties of TODGA, extensive aggregation of TODGA molecules in non-polar diluents such as *n*-dodecane resulted in undesirable third phase effects. A modified diluent having 5 vol.% 1-octanol in *n*-dodecane was recommended for TODGA solvents so as to overcome the third phase effects, though un-modified non-polar diluents are recommended for solvent extraction processes involving nuclear materials[1]. The simple monoglycolamide derivative of TODGA, namely *N,N*-di-octyl-2-hydroxyacetamide (DOHyA, Figure 1) was found to have extraction properties similar to that of TODGA during our studies [2]. The aggregation of DOHyA was minimal due to the less number of polar groups, thereby effectively preventing the third phase formation, without a phase modifier. Figure 2 compares the aggregate size distribution plots for TODGA and DOHyA in *n*-dodecane after equilibration with 4 M nitric acid.

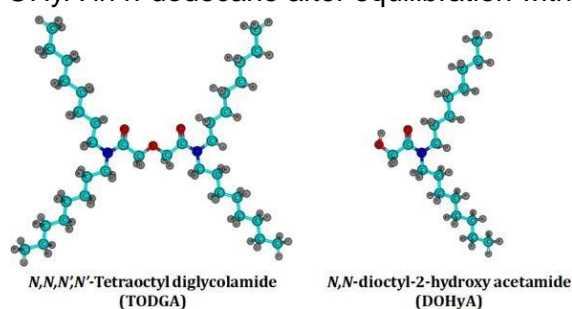


Figure 1: Structure of TODGA and DOHyA

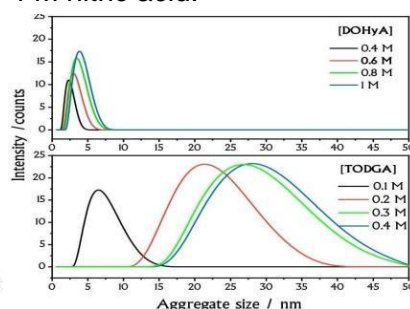


Figure 2: Comparison of aggregate distribution

Extraction stoichiometry studies using Am(II) and Eu(III) revealed the formation of 1:5 (Metal:DOHyA) complexes during extraction from 4 M nitric acid medium. A comparison of UV-VIS spectra of Nd(III) complexes of TODGA and DOHyA revealed a better hydrophilic environment in DOHyA extracted phases. The structural features of DOHyA enabled significant co-extraction of water during metal ion extraction yielding a hydrophilic environment for metal ions thereby stabilizing the polar metal-ligand aggregates. For TODGA solvents, an additional phase modifier such as 1-octanol was essential for a similar stabilizing effect. FT-IR studies showed that the hydroxyl group of DOHyA was not involved during co-ordination with metal ions. The availability of hydroxyl groups for hydrogen bonding with water molecules was found to play a key role in the extraction properties of DOHyA. When the hydrogen of hydroxyl group in DOHyA was replaced by alkyl groups, the new ligands were found to have no extraction of trivalent metal ions. The results of our studies have revealed the promising nature of this monoglycolamide ligand for partitioning of trivalent metal ions from high-level waste, and a comparison of TODGA and DOHyA solvents shall be discussed in detail.

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Development of automated microfluidic system for actinide separation and analysis

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Advancement in analytical device miniaturisation through microfluidic technology offers an alternative approach towards radiochemical analysis. When compared to traditional macroscale analytical process, microfluidics devices manipulate and process fluid samples typically in the microlitre range, which provides benefits in terms of more efficient mixing and precise conditions control that are not feasible in macroscopic systems while reducing waste generation.

Microfluidic extraction devices are fabricated using poly (methyl methacrylate). Recovery and separation of uranium from trace elements relevant to the nuclear fuel cycle are demonstrated using UTEVA® chromatographic resins packed within the microdevice in concentrated nitric acid media. enabling analysis of nuclear materials with a drastic volume reduction to ≤ 0.1 ml per analysis. A novel online analytical system was also developed in parallel. Where flows from the microfluidic separation system are redirected towards a coupled ICP-MS system, enabling online analysis of trace elements and actinide as it is separated within the microdevice with minimal operator - sample interaction. Such an online microdevice – ICP-MS system enables automated separation-detection of radioactive samples within 1 hours of sample uptake while generates less radioactive waste, satisfying the As Low As Reasonably Achievable (ALARA) principle.

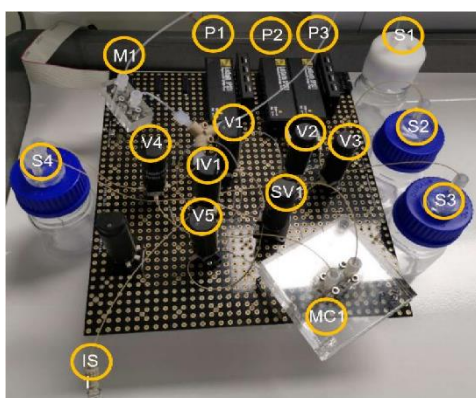


Figure 1: ICP-MS integrated microfluidic actinide separation – analysis system.

Molecular prediction of lanthanide cation transfer for liquid-liquid extraction

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Liquid-liquid extraction is a key hydrometallurgical process used to selectively separate the lanthanide cations, such as in the SANEX process (Selective ActiNide EXtraction) [1] developed by CEA for the recycling of spent nuclear fuels. In this process, the lanthanide cations are transferred from an acid-enriched aqueous phase to an organic phase containing malonamide extractants, like DMDOHEMA, diluted in a mixture of alkanes. This ion transfer between the two phases is governed by the Gibbs energy of transfer ΔG_{tr} which is measured experimentally by the distribution coefficients of the ions [2].

This work deals with the prediction of the Gibbs energies of transfer of lanthanide cations using Steered Molecular Dynamics (SMD), an out-of-equilibrium simulation technique for Molecular Dynamics. The SMD methodology uses a moving biasing harmonic potential to steer the lanthanide cations from the aqueous phase to the organic phase, allowing for accurate sampling of the free energy landscape of the interface [3,4].

We simulated water octanol interfaces as a model system for liquid-liquid extraction. In nuclear hydrometallurgy, octanol (octan-1-ol) is used as a phase modifier to prevent the formation of a heavy organic third phase associated with criticality risks. Calculating the molecular orientation revealed that the octanol molecules at the interface organize themselves in a rigid bilayer structure, as previously observed [5] (Fig. 1), preventing the water transfer toward octanol. SMD simulations will be used to determine the Gibbs energy barrier of this interface, allowing the calculation of the water solubility in octanol.

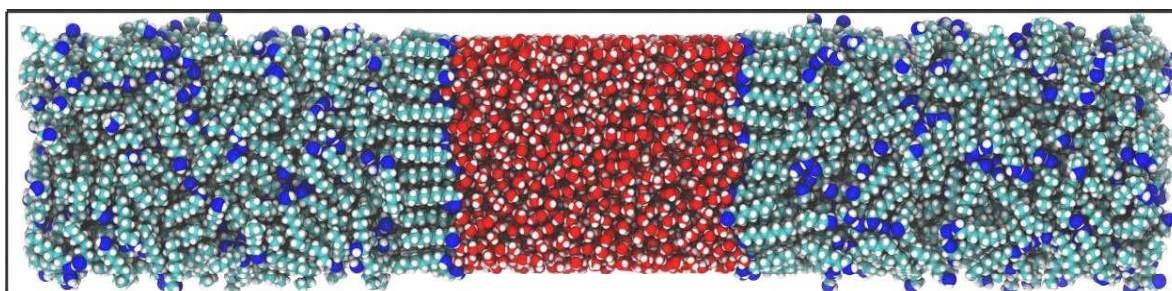


Figure 1: Snapshot of the water-octanol interface. To emphasize the interface, the oxygen atoms of octanol molecules are represented in dark blue.

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Impacts of Lanthanide Ion Complexation on the Radiation Robustness of Diglycolamide Extractants

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Nuclear power reactors represent a clean and reliable source of baseload energy. However, nuclear reactors produce used nuclear fuel (UNF), which, if not recycled/reprocessed, must be disposed of as high-level radioactive waste, necessitating long-term storage options. UNF contains approximately a third of the periodic table, including the radioactive minor actinides (MA) americium and curium. Removal of these MA from UNF would greatly reduce the radiotoxic burden, volume, and cost of a storage facility or geological repository. Thus, a significant global effort has been devoted to the design of reprocessing strategies for the clean separation of the MA from UNF. As MA separations are difficult, due to the presence of lanthanide elements in UNF and their remarkably similar chemical properties, many extractants have been studied. The diglycolamide (DGA) class of extractants are promising for this separation as they exhibit high distribution coefficients for the MAs, high metal loading capacities, and are robust in highly acidic radiation environments.¹

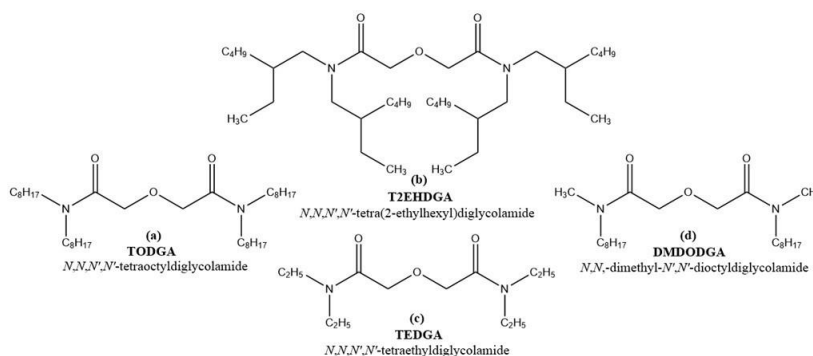


Figure 1: DGA structures investigated by this work.

Although radiation-induced degradation studies have been completed for a variety of DGA architectures, the majority of these have been performed in the absence of metal ion complexation. This is problematic, as recent irradiation studies of TODGA (Figure 1) demonstrated that metal ion complexation can have drastic impacts on chemical reactivity, the rate of degradation, and degradation product distribution,^{2,3} all of which can impact the performance of a MA separation process. Here, we investigate the impacts of metal ion complexation and molecular structure (Figure 1) on the radiation robustness (≤ 500 kGy) of DGAs using cobalt-60 gamma irradiation and quantitative gas chromatography techniques.

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SO₃-Ph-BTBP stability studies under AmSel process conditions

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With the view to achieving the Advanced Nuclear Fuel Cycle, many efforts are set in the aim of separating Am, as one of the most relevant minor actinides, from fission products such as lanthanides and other actinides such as Cm, to produce new fuel or transmutation blankets for advanced nuclear reactors [1]. In that sense, one of the major challenges the scientific community is dealing with is the separation of Am from Cm due to their similar chemical behaviour, reason why several strategies are being developed to this end. This is the case of the AmSel (*Americium Selective extraction*) process, based on liquid-liquid extraction methods, the most mature technologies towards the proper management of nuclear waste currently [2].

The AmSel process involves a first step (co-extraction step) in which the Ln(III) and An(III) are co-extracted from the PUREX (*Plutonium Uranium Reduction EXtraction*) raffinate [2] using an organic phase containing a TODGA (*N,N,N',N'*-tetraoctyl diglycolamide) based solvent. Subsequently, a selective stripping of Am(III) using a watersoluble SO₃-Ph-BTBP (6,6'-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine) separates Am(III) from Cm(III) and the Ln(III), thanks to the inverse selectivity of SO₃-PhBTBP and TODGA towards Am and Cm [2]. One of the limiting points for the development of this kind of processes is that, due to the highly radioactive field and nitric acid concentration, solvents are prone to degradation, which could cause undesirable effects such as loss of selectivity, third phase formation, etc. Therefore, it is important to carefully study the stability and resistance of the chosen ligands and systems prior to their industrial application.

In recent years, TODGA's stability has been extensively studied [3-5], while only a few studies have been performed to SO₃-Ph-BTBP [6]. This work evaluate the stability of SO₃-Ph-BTBP under the AmSel process conditions using Quantitative Raman Spectroscopy to have a better understanding on how the gamma irradiation conditions can affect it. These studies range from simple scenarios (providing fundamental information) to more complex and representative ones, involving contacting phases and the presence of metals during the irradiation.

Fundamental results indicate that, when the aqueous phase is irradiated in contact with the organic phase, the stability of the SO₃-Ph-BTBP is higher, what could be related to a protective effect over the SO₃-Ph-BTBP by the organic phase during irradiation. On the contrary, its complexation with metals does not have a significant effect. Additionally, more realistic experiments were carried out with both factors simultaneously, acting synergistically and resulting in an almost negligible degradation.

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Conversion of U(VI) and Pu(IV) by peroxide precipitation and hydrothermal treatment

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With the development of Fast Neutron Reactor (FNR), new adjustments of the nuclear fuel cycle are needed. Particularly, the current Mixed Oxide (MOx) fuel synthesis has to be reconsidered as the oxide properties will have to fit different specifications. Indeed, the homogeneity of the cations distribution has to be improved to allow the use of higher Pu content, then further reprocessing of spent MOx fuel.

In this context, we study the synthesis of actinides oxides (UO_2 , PuO_2 and mixed $(\text{U,Pu})\text{O}_2$) by hydrothermal conversion with hydrogen peroxide as precipitant agent. The first step of the process consist in the direct and simultaneous precipitation of both uranium (VI) and plutonium (IV) in nitric acid by hydrogen peroxide (at their most stable oxidation state in this media) as uranium (VI) peroxide and plutonium (IV) peroxonitrate [1][2]. Then, the decomposition of actinides peroxides will be achieved by soft hydrothermal conditions (temperature ranged from 100 to 250°C and pressure from 1 to 50 bars) instead of classical thermal treatment [3]. This step allow to safely managing the peroxide decomposition reaction by not handling powder material and potentially control the final oxide morphology [4]. Moreover, the oxides obtained exhibit a very low carbon content, due to the carbon free reagent used.

Our project focusses on both the actinide peroxide precipitation and the hydrothermal conversion of these peroxo-phases to form the corresponding oxide. On the one hand, the precipitation study evidenced that U and Pu can be precipitated under compatible conditions. The conditions chosen have a significant impact on the crystal structure of the plutonium peroxide. Additionally, it has been evidenced that the uranium peroxide morphology can be controlled based on the solution initial over saturation. On the other hand, regarding the hydrothermal treatment, plutonium dioxide (PuO_2) has been obtained by this method for the first time. Uranium peroxide hydrothermal treatment in the same conditions led to the formation of a solid uranium hydroxide, $(\text{UO}_2(\text{OH})_2)$ which could potentially be converted into oxide by a pre thermal treatment or sintering.

These first results pave the way to the potential preparation of actinide mixture by peroxide precipitation pathway and the preparation of MOx fuel thanks to hydrothermal synthesis, which will be studied in the near future.

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Electrochemical Investigation of Uranium Redox Diamond Behavior in Molten Chloride Salts Using Boron-Doped

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The liquid salt fuel system and fast reactor technology of Generation IV Molten Salt Reactors (MSRs) simultaneously address concerns over waste, safety, and nonproliferation. However, work is still needed to understand the impacts of the harsh fuel salt systems and their subsequent containment corrosion. Electroanalytical chemistry methods can probe several fundamental aspects of complex high-temperature actinide molten salt chemistry so long as the electrodes can withstand the molten salt environment for prolonged periods. Boron-doped diamond (BDD) is expected to be resilient against harsh environments, given its primarily sp^3 -carbon structure. As such, BDD could be used to characterize dynamic molten salt fuel matrices and *in situ* corrosion control and monitoring within the core containment vessels. However, the corrosion and performance of BDD as an electrode material in molten salts are not yet fully understood. In this study, we investigated the corrosion resistance of BDD by soaking the material in chloride and molten fluoride salts (LiCl-KCl, NaCl-KCl, LiF-KF, and FLiNaK) between 500-700 °C for over 250 hours in air. Scanning electron microscopy was used to identify topographical changes in diamond crystal structures. Little, if any, corrosion or change to the BDD was observed. As a result, we pursued the use of free-standing BDD for electrochemical measurements in harsh molten salt analytes. The Eu(II/III) and U(III/IV) redox couples were studied in LiCl-KCl and $MgCl_2NaCl$ solvent salts. Comparisons were also made between the two solvent systems to study the impact of cation size on oxidation state stabilization. Techniques like cyclic voltammetry provided valuable insight regarding the lanthanide and actinide species with improved resolution of redox peaks that metal electrodes often struggle to capture fully, given the complex f-block redox behavior occurring in MSR fuels. This work advances the understanding of both MSR fuel chemistry and fundamental actinide chemistry by probing f-block oxidation states within molten salts. Additionally, this work is proof-of-concept for the feasibility of BDD as electrode material for harsh environments and as a potential candidate for *in-situ* MSR fuel characterization. Future studies include soak-testing inside an inert environment, comparisons to other chloride and fluoride solvent salt systems, and analytical electrochemical investigations of other actinide redox couples like Pu(III/IV).

Structural Investigation of Th in Uranium Oxides for Development of Age-Dating Reference Microparticles in Nuclear Safeguards

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In order to verify the compliance with the Treaty of Non-Proliferation of the member states, the International Atomic Energy Agency (IAEA) sends safeguards inspectors to nuclear facilities. During the in-field verification activities, the inspector, *inter alia*, takes swipe samples, which contain U-bearing microparticles. These microparticles are analyzed in their isotopic compositions, especially the isotope ratios $n(^{236}\text{U})/n(^{238}\text{U})$ and $n(^{235}\text{U})/n(^{238}\text{U})$, which evaluate the absence of undeclared nuclear materials and activities by mass spectrometric analytic methods such as Large Geometry - Secondary Ion Mass Spectrometry [1]. To support the IAEA in its sustainably robust Quality Assurance and Control system for analytical measurements on nuclear safeguards samples and to maintain the credibility of the IAEA with its member states, a physical aerosol-based process has been implemented in the laboratories of Forschungszentrum Jülich to produce well-defined uranium oxide microparticulate reference materials for the verification of isotopic measurements [2]. Therefore, these microparticulate uranium-oxide reference materials must have a welldefined elemental and isotopic composition, size, morphology, and certain shelf-life [3]. To enhance the mass spectrometric analytical measurements for the detection of even small amounts of fission products and other isotope ratios such as $n(^{230}\text{Th})/n(^{234}\text{U})$, which is of interest for the age-dating of U-bearing materials in general and for the IAEA in particular, the uranium oxide reference materials need to be further developed towards composite (Ulanthanides and U-Th) reference materials in microparticulate form. To produce such composite microparticles and draw conclusions about their stability and shelf-life, the incorporation behaviour of the dopants into the uranium-oxide structure and consequently the stability of the materials must be investigated. However, this is an analytical challenge, since the quantities of microparticulate material produced with the aerosol-based set-up at Jülich are limited to the μg range. Therefore, a synthesis route was adapted to produce ammonium diuranate doped with various lanthanides [4], [5] and Th as a kind of "internal reference materials" which serve as a bulky model system for comparison. These "internal reference materials" were investigated by TG-DSC to determine the temperature range of the phase transition from UO_3 to U_3O_8 of the doped uranium-containing materials and then calcined at defined temperatures. To investigate the structural incorporation of the dopants into the uranium-oxide structure, the calcined materials were further characterized by structural investigations using XRD, Raman, and IR spectroscopy. This presentation will present results on the incorporation of Th into the uranium oxide structures and attempt to transfer these findings to the microparticulate system.

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Atomistic modeling of sodium borosilicate glasses containing uranium

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Safe and effective management of high-level nuclear waste (HLW) is of considerable interest to ensure the sustainable utilization of nuclear energy. One method of long-term storage and disposal involves the processing and transformation of the spent fuel into a glass, a technique known as *vitrification*. Sodium borosilicate glasses are generally accepted as a proper HLW isolating media. Understanding the microstructure and migration of heavy cations in these glasses provide insights in mechanisms of delocalization of actinides from the radioactive wastes during long-term storage. To fully exploit these glasses for applications, fundamental insights about the atomic structure is needed. The x-ray and neutron diffraction experiments have provided the average structure of these glasses, but these methods alone are insufficient to determine the atomic structure, which are comprised of several atomic pair distributions overlapping with each other. I will briefly describe a method to obtain realistic computer models of these glasses containing uranium by jointly exploiting the experimental information (diffraction data) and the density functional theory approach. I will then discuss on the atomic structure of these glasses for varying glass-former concentrations.

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Study of dissolution kinetics and mechanisms of the phases formed during the oxidation of (U,Pu)O₂ in concentrated nitric acid

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The use of MOx (mixed oxide of uranium and plutonium) (U,Pu)O₂ fuels in nuclear reactors has gained increasing attention as a way to stabilize the plutonium inventory in France through the multi-recycling of plutonium. However, the plutonium multi-recycling practice requires the optimization of the existing reprocessing plant capabilities to process spent MOx fuels. One of the challenges is to extract the latter from its cladding before the dissolution step. One promising solution is the oxidation of MOx spent fuels through thermal treatment [1-3], leading to phase transformations, which can facilitate the fuel-cladding separation. Nevertheless, it is important to ensure that the resulting phases are highly soluble in nitric acid. To this date, there is limited data available on the behavior of hyperstoichiometric (U,Pu)O_{2+x} phases [4,5] during dissolution, making it difficult to optimize the reprocessing of spent MOx fuels.

The aim of this work is to fill this gap by studying the kinetics and mechanisms governing the dissolution of the different phases observed during the oxidation of (U,Pu)O₂: U₃O₈, (U,Pu)O_{2+x}, (U,Pu)₃O₈ and (U,Pu)₄O₉. These mechanisms will be crucial in determining the physicochemical conditions that maximize the plutonium dissolution yield, helping to optimize the reprocessing of spent MOx fuels and improve the efficiency of the multirecycling of plutonium.

During this conference, we will present the experimental set-up which allows us to carry out dissolution experiments while continuously monitoring the release of U and Pu via in situ UV-Vis spectrophotometry. Special attention will also be paid to ex situ solid-state characterizations (BET, XRD, SEM, Raman spectroscopy etc.) to follow the composition and structure of the solid samples before, during, and at the end of dissolution experiments. The dissolution behaviors of the phases studied will be compared and the differences observed will be discussed in terms of the reaction mechanisms involved.

Acknowledgements:

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About NFC3

The conference intends to provide a unique platform dedicated to discussions on the latest chemistry research progress and breakthroughs within the nuclear fuel cycle community. **NFC3** is a virtual event and aims to give the opportunity for young scientists to exchange and present chemistry advances related to all aspects of the nuclear fuel cycles.

The **NFC3** conference was first organized in 2021 with more than 260 participants registered from 93 research institutes and 27 different countries.

Organizing committee:

The **NFC3** conference is organized jointly by the French Alternative Energies and Atomic Energy Commission (CEA), the University of Montpellier (UM) and the French National Centre for Scientific Research (CNRS).

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