NFC3 - 2026

Nuclear Fuel Cycle: A Chemistry Conference – 2026

BOOK OF ABSTRACTS

Monday, February 2, 2026

13:45	Introduction to NFC3	

Material Chemistry
Chairs : Eleanor L. BRIGHT (ESRF - HZDR) & Matthieu VIROT (ICSM)

14:00	Hydrothermal reduction conversion of uranium (VI) to UO_2 using carboxylic acids	Dorian LAFFONT ICSM
14:20	Impact of microstructural properties on the dissolution kinetics of MOx $(U,Pu)O_2$ fuel	Vincent BOSQUE GUARDIA CEA
14:40	The oxidation of Ln-doped UN spent fuel materials: structural and thermodynamic considerations	Pascal UHLEMANN FZJ
15:00	Multi-colloidal self-assembly route for the preparation of Mixed Oxide nuclear fuels	Hélène BARBIER ICSM
15:20	Cerium Speciation in Molten Salt Environments	Sheridon KELLY LLNL, LANL
16:00	**KEYNOTE #1: Crystallographic relationships and intermediate oxides in the oxidation of UO_2**	**Eleanor L. BRIGHT ESRF-Rossendorf & HZDR**
16:40	Understanding the sintering of MOX nuclear fuels: challenges associated with the characterization of a multiphasic microstructure	Evan MOREL CEA
17:00	Alternative deconversion pathway for UF_6 and uranium recovery	Renee OLNEY U. Nevada, Las Vegas
17:20	Impact of hydroxide precipitation on the Sintering and Chemical Durability of $U_{1-x}Th_xO_2$ solid solutions	Lorenzo CALLEJON ICSM
17:40	Impact of fission products on the thermophysical properties of $(U,Pu)O_{2-x}$ fuels using a SIMMOx approach	Matthias ROUCAYROL CEA

Tuesday, February 3, 2026

Separation Chemistry
Chairs : Elena MACERATA (POLIMI) & Jessica JACKSON (Colorado S. of Mines)

14:00	Actinide precipitation in complex organic media	Mathéo HENRY ICSM
14:20	Hydrophobic CMPO-based low-melting mixtures for sustainable Spent Nuclear Fuel recycling	Massimiliano F. S. TENTORIO Politecnico di Milano
14:40	Molecular Dynamics Study of Uranium Extraction from TBP/Heptane Solutions Using Amidoxime-Grafted Silica	Emília V. F. DE ARAGÃO CEA

15:00	Impact of Accumulated TODGA Degradation Compounds on a CHON-Compliant AmSel Process	Pablo VACAS-ARQUERO CIEMAT
15:20	Use of diglycolamide derivatives for rhodium recovery	Vairani Amaru, CEA
16:00	**KEYNOTE #2: f-Element Separations with a Focus on Uranium Recycling**	**Santa JANSONE POPOVA** **ORNL**
16:40	Oxidant-free oxidative separation of Bk(IV)/Cf(III) and Ce(IV)/Ln(III) using 3,4,3-LI-(1,2-HOPO) and Design of Experiments	Elise ENG U. California Berkeley, LBNL
17:00	Self-assembly of grafted surfactants for actinides extraction under cloud point conditions	Morvan GAUDIN CEA
17:20	Kinetic Studies of U(IV) and Pu(IV) in Aqueous Nitric and TBP/Dodecane Solutions	Matthew COMINS PNNL
17:40	Controlling Viscosity and Interfacial Properties in Monoamide Solvents: Roles of Nitric Acid, Uranium, and Phase Modifiers	Anh DANG Colorado School of Mines

Wednesday, February 4, 2026

Solution Chemistry
Chairs : Koichiro TAKAO (Institute of Science Tokyo) & Melody MALOUBIER (IJCLab)

14:00	Ruthenium speciation during acidification of alkaline solution using a UV-Visible fast detector and an in situ probe	Mathis LEBLANC CEA
14:20	Inactive studies into the effect of insoluble fission products on the generation of Ag2+ for the dissolution of MOx fuel	Nicholas BRAMAH Lancaster University
14:40	Experimental and Quantum Chemical Insights into the Coordination Chemistry of Protactinium(V) in Chloride Media	Tamara SHAABAN PhLAM, UMR 8523
15:00	Destabilization pathway of the $[Pu_6O_4(OH)_4]^{12+}$ cluster in acetate medium	Maëva MUNOZ CEA
15:40	**KEYNOTE #3: Actinide Colloidal Phases and their Impact on Nuclear Waste Management**	**Julia NEUMANN** **Argonne National Laboratory**

Conditioning and Repository
Chairs : Thierry MENECKART (SCK-CEN) & Nicolas DACHEUX (ICSM)

16:20	Aging and Oxidation Processes of UO2 Nanoparticle Materials Under Ambient Conditions Relevant to Interim Storage of Spent Fuel	Kevin D. STUKE FZJ
16:40	Synthesis, Formation and Characterization of Chukanovite (Fe2(OH)2CO3) and Its Role in the Dissolution of MOX Fuel under Reducing Conditions	Mustapha G. SALEH Chalmers
17:00	Investigations Into the Spectroscopic Changes of Actinyls Based on Hydroxide and Nitrate Ligation	Castro LESLIE U. California Berkeley, LBNL
17:20	Towards an Understanding of the Behaviour of Ruthenium in the Vitrification of Highly Active Waste: A Study of the Volatilisation of RuO2	Bibi SHEHRBANO Lancaster University

Hydrothermal reduction conversion of uranium (VI) to UO_2 using carboxylic acids

D. Laffont [1], S. Benarib [2], P. Estevenon [2], N. Dacheux [1], N. Clavier [1]
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The development of advanced nuclear reactors requires innovative methods for producing mixed oxide (MOx) fuels, particularly $(U,Pu)O_{2\pm\delta}$. The current MELOX process results in a heterogeneous microstructure with uneven U and Pu distribution, which might be inadequate for future scenarios like multi-recycling of plutonium in Fast Neutron Reactors (FNRs) [1]. Traditional wet chemistry processes, such as oxalic precipitation, often induce unsuitable morphologies and can introduce carbon impurities, impacting shaping and sintering steps. Hence, hydrothermal conversion of oxalate compounds into oxides has recently emerged as a promising method, eliminating carbon impurities and improving powder morphology. This process involves precipitating actinide cations in oxalic acid, followed by hydrothermal treatment at 180-250°C for 24-72 hours, yielding actinide oxides with good cationic homogeneity. If these works mainly focused on An (III) and An(IV), insights from geochemistry suggest that the reduction of uranyl ions can be achieved under hydrothermal conditions, particularly through interactions with organic compounds, such as carboxylic acids [2].

Our study then investigated the possible conversion of a mixture of uranyl and oxalate ions into uranium (IV) oxide, through a multi-parametric study (time, pH, U/oxalate molar ratio). pH was found to be the most crucial condition. At 250°C and pH 1.2, pure UO_2 was obtained. However, higher pH values resulted in a mixture of UO_2, α-U_3O_8, and meta- schoepite. Optimal hydrothermal conversion conditions leading to UO_{2+x} with a precipitation yield of 97% were achieved after 24 hours at an initial pH of 1. In parallel, in situ XANES analyses were performed on the FAME beamline at ESRF and revealed an almost complete reduction of uranium (VI) in solution and changes in uranium complexation due to oxalate decomposition [3]. A preliminary mechanism for the reductive hydrothermal conversion of uranium (VI) to UO2+x was proposed. Future research will focus on extending investigations to mixed systems incorporating thorium, as a surrogate for Pu (IV).

In a parallel study, we investigated the hydrothermal conversion of uranyl (U(VI)) solutions into uranium dioxide (U(IV)) in the presence of various carboxylic acids such as glycolic, and formic acids. To this end, a multiparametric study, taking into account reaction time, pH, and the uranium/carbon molar ratio, was conducted to identify the conditions leading to quantitative conversion of uranium (VI). The solid phases obtained were then characterized by X-ray diffraction and SEM.

[1] Haas et al., Prog. Nucl. Energ., 49 (2007) 574-582
[2] S. Nakashima et al., Geochim. Cosmochim. Acta, 48 (1984) 2321- 2329
[3] S. Benarib et al., Dalton Trans., 53 (2024) 13982- 13995

Impact of microstructural properties on the dissolution kinetics of MOx (U,Pu)O2 fuel

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The development of more sustainable nuclear energy requires the closure of the nuclear fuel cycle. The recovered plutonium from spent UOx fuel via the PUREX process [1] is recycled in France to produce mixed $(U,Pu)O_2$ oxide fuels (MOx). However, spent MOx fuel is not yet reprocessed.

The dissolution kinetics of plutonium rich-dioxide in nitric acid are slow. This behaviour results in the accumulation of solid residues rich in plutonium during the dissolution, first step of the reprocessing process. Besides the plutonium content, the amount of solid residues and the fuel dissolution rate are likely to be influenced by microstructural properties of the fuel pellets [2-4] such as grain size, density, porosity, actinide spatial distribution and cation oxidation states. Although some studies have provided insight into the relationships between these microstructural properties and MOx fuel dissolution, they are rarely multi-parametric [5]. Experimental evidence that only one parameter under investigation varies is lacking in most of these papers.

The present study aims to address this issue by carrying out a systematic investigation of fresh MOx fuel dissolution. To this end, a multi-parametric approach is carried out, integrating fabrication of MOx pellets with controlled microstructural properties, advanced characterization techniques and operando monitoring of dissolution experiments. Different batches of MOx pellets with a mass ratio Pu/(U+Pu) = 11% were prepared under various conditions. Their microstructural properties were characterized using a multi-scale approach. This enabled us to check that the targeted properties (density, grain size, homogeneity and oxygen stoichiometry) required for our multi-parametric investigation were achieved for each pellet. Dissolution experiments in nitric acid were carried out to discriminate the effects of each parameter variation on the dissolution behavior. In addition to regular dissolution experiments, operando monitoring of the dissolutions [6] involving SEM observations at different dissolution stages of a given pellet were also carried out for the first time on MOx $(U,Pu)O_2$ materials, allowing the observation of the microstructural changes during dissolution progress.

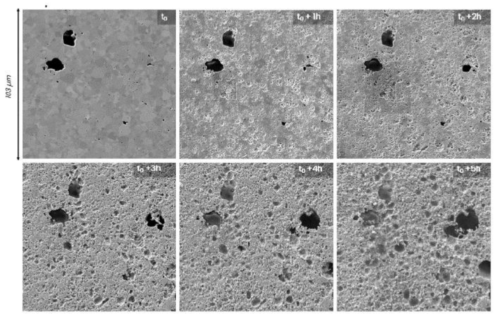

Figure 1: Evolution of the local surface during the dissolution of a homogeneous MOx pellet in HNO_3 3.2M at 65°C for 5 hours.

[1] R.S. Herbst et al., Woodhead Publishing, p.141-175, 2011.
[2] R. F. Taylor et al. Journal of Applied Chemistry, vol. 13, no 1, p. 32-40, 1963.
[3] A. L. Uriarte and R. H. Rainey, Technical Report, Oak Ridge National Laboratory, 1965.
[4] N. Desigan et al., JNM, vol. 554, 2021.
[5] T. Barral et al., Corrosion Science, vol. 222, 2023.
[6] R. Podor, Materials Characterization, vol. 150, p.220-228, 2019.

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The oxidation of Ln-doped UN spent fuel materials: structural and thermodynamic considerations

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Uranium nitride (UN) is among the primary fuel types considered for the next-generation nuclear fuel, intended for use in Generation IV fast reactors and advanced small modular reactors (SMRs) [1]. However, UN is susceptible to oxidation by atmospheric oxygen and water, posing enhanced safety risks for handling, disposal and accident scenarios [2]. This chemical risk becomes unpredictable, when fission products in the fuel matrix alter the material properties. Simulations have predicted the behaviour of the fission products in the fuel matrix [3], while the knowledge about their impact on material properties remains limited. A strategic method to gain more insight in the properties of spent nuclear fuel (SNF) based materials is the model system approach, which utilise high resolution experimental methods to target key single effects occurring in SNF. In the present work, LnN and UN materials have been synthesised and their structures, in addition to oxidation and thermodynamic stability, have been examined. A key point of this work has been to examine the potential transferable phenomena seen in UO_2-based SNF, where Ln-inclusion leads to increased oxidation resistance. To explore this phenomenon a combination of thermogravimetric measurements and high-temperature oxide melt calorimetry measurements have been used, which were supported by X-ray diffraction analysis to determine associated structural phases. In addition, high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XANES) and extended X-ray absorption fine structure (EXAFS) measurements have been performed to determine local structure changes during the oxidation. The results of this investigation will be discussed in relation to the fundamental actinide chemistry of Ln-U-N phases in addition to their occurrence and stability as SNF.

[1] F. Dehlin, E. Pallarès Abril, J. Wallenius, Annals of Nuclear Energy 2025, 212, 110861.

[2] K. Watkins, A. Gonzales, A. R. Wagner, E. S. Sooby, B. J. Jaques, Journal of Nuclear Materials 2021, 553, 153048.

[3] Degueldre, C., D. Goddard, G. Berhane, A. Simpson, C. Boxall, Journal of Nuclear Materials 2024, 592, 154900.

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Multi-colloidal self-assembly route for the preparation of Mixed Oxide nuclear fuels

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The MOX nuclear fuel (mixing of uranium and plutonium oxides) used in some of the French Pressurized Water Reactors (PWRs) is prepared by powder metallurgy. In the frame of the development of next generation Sodium-cooled Fast-neutron Reactors (SFRs), innovative soft preparation methods are today investigated to improve the material homogeneity at a nanometric scale preventing the formation of plutonium clusters and for safety reason, to limit powder use during fabrication process. Recently, the colloid self-assembly route has been identified as an interesting method to prepare from aqueous sols, an actinide oxide material made of a loose packing of nanoparticles with an ordered distribution without generating dust until the shaping stage.[1] Controlling the pH of An-containing solution and using a complexing agent to limit hydrolysis and condensation reactions led to control the size of the colloids around a few nanometers.

Based on the same method, we prepared during this work multi-colloidal sols by mixing Th and Ce nitrate salts with 6-aminocaproic acid as complexing agent and fixing the pH between 3 and 6. These sols were compared to sols prepared by mixing mono-colloidal sols of Th and Ce. The sols obtained were studied by Small-Angle X-ray Scattering (SAXS) to determine the size, nature, shape and colloidal fraction of Th and Ce in colloids as a function of the experimental conditions. After the sol freeze drying and a thermal treatment, high resolution transmission electron microscopy (HRTEM) and elemental analysis have highlighted final materials consisting of assemblies of monodisperse nanoparticles presenting a homogenous distribution of Th and Ce at a nanometric scale.

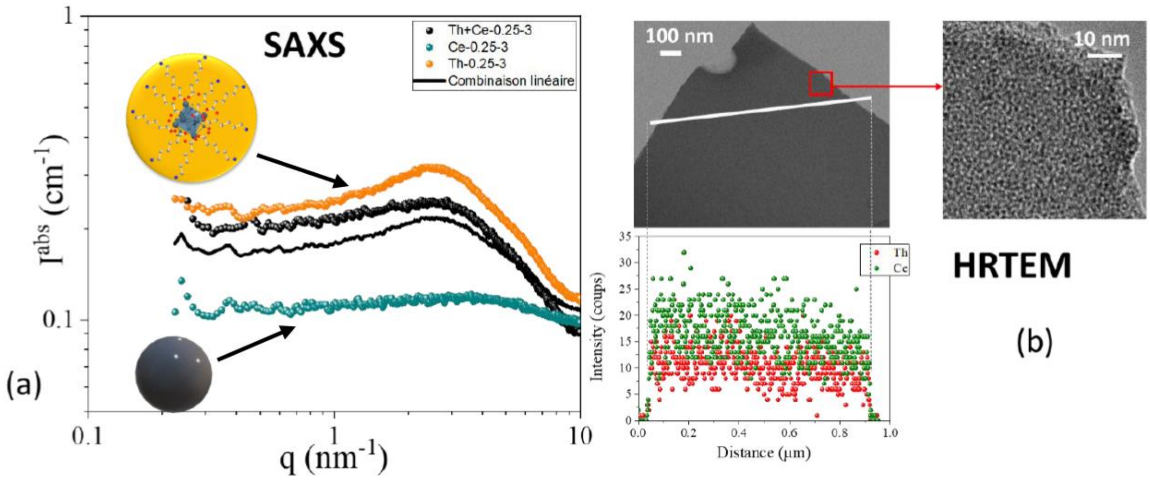

Figure 1: (a) SAXS patterns of the mono, multi-colloidal sol and linear combinations of the SAXS patterns of the mono-colloidal sol at pH 3 and (Th+Ce)/ACA = 0.25. (b) HRTEM images and elemental analysis of the obtained mixed oxide material.

[1] Z. Lu, et al., ACS Appl. Mater. Interfaces, 2022, 14, 53165-53173.

Cerium Speciation in Molten Salt Environments

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Understanding of actinide and fission product chemistry and properties in molten salt environments is in ever-growing demand, with applications in pyroprocessing of spent nuclear fuel, allowing for closure of the nuclear fuel cycle, and in the development of molten salt reactors (MSRs). One major gap in this area of research is the understanding of the chemical speciation of relevant actinides in molten salts. Attempts to characterize analytes at molten temperatures have been hindered by the complexity of developing in- line spectroscopy tools that are compatible with high temperature and air- and water-free environments necessary for such research. Post-mortem samples (i.e.: analyzed after heating and cooling) can give some idea of changes created by the heating process, but do not give insight into the intermediate species that would be present at high temperatures.

Despite these challenges, a complete picture of chemical speciation in molten salts would allow for better-informed decisions on the steps to pyroprocessing: what species need to be oxidized or reduced to isolate the desired actinide? How much reductant or what voltage needs to be applied given this information? What other species are present that need to be mitigated? Additionally, assessing chemical speciation will aid in understanding upcoming molten salt reactors, as properties such as melting point, thermal stability, etc., can be assessed in relation to the species present in the fuel.

In this work, we focus on the chemical speciation of cerium (Ce) in $CaCl_2$, where cerium is used as a surrogate for the relevant radioactive actinides: uranium (U) and plutonium (Pu). Although Ce is not universally an ideal surrogate for actinides, in this system it provides a valid approximation due to its similar ionic radius, access to the +3 and +4 oxidation states, and comparable reduction potentials, offering meaningful insight into actinide speciation as we develop analytical techniques to assess both in-situ and post-mortem samples. Speciation as a function of temperature and as a function of Ce concentration were studied. Analysis of PXRD data from post-mortem samples indicates conversion of CeO_2 starting material to CeOCl at higher temperatures, while SEM images reveal morphological evolution from small, round particles to larger sheets as temperature increases. Infrared and Raman spectroscopy studies further support the speciation of Ce in the salt environment and provide insight into the Ce-O and Ce-Cl bonding. Post-mortem samples have been studied, and in-situ techniques are being developed in order to determine what intermediate species might be present when the salts are at molten temperatures.

Prepared by LLNL under Contract DE-AC52-07NA27344.

Crystallographic relationships and intermediate oxides in the oxidation of UO_2

E. Lawrence Bright [1,2], L. M. Harding [3], R. S. Springell [3], L. Amidani [1,2], G. H. Lander[3]
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The oxidation of uranium dioxide, UO_2, is of major interest to the nuclear industry. As UO_2 is oxidised to U_4O_9, U_3O_7, and U_3O_8, often during short- or long-term storage, the physical and chemical properties of the fuel are altered. The crystal structure of these higher oxide phases is somewhat uncertain. Crystallographic relations during an oxidation process can have significant effects on the rate, mechanism, and properties of the product. Allen and Holmes theorized a transformation of (111) UO_2 into (100), however, recent lab-based work has shown that the UO_2 (001) surfaces oxidise to form U_3O_8 (130) in a topotactic transformation [2].

We present work from experiments at the ID11 and ROBL (BM20) beamlines at ESRF, where x-ray diffraction and HERFD-XANES data was obtained during in-situ oxidation of a (001) UO_2 thin film as it topotactically oxidised to U_3O_8. With this data, we show new insight into the mechanisms of this topotactic transformation, revealing that the intermediate oxide phases (UO_{2+x}, β-U_4O_9, U_3O_7) form during this process. This provides a novel route for obtaining single crystal (multi-domain) samples of these intermediate oxides, allowing single crystal x-ray diffraction analysis of their crystallographic structures, which we will compare with published structures. Furthermore, investigation of diffuse scattering in the UO_{2+x}, β-U_4O_9 range, along with the coupling of these results to XANES spectra gives unprecedented insight into the relationship between oxidation states and structural ordering in the UO_{2+x} phase range.

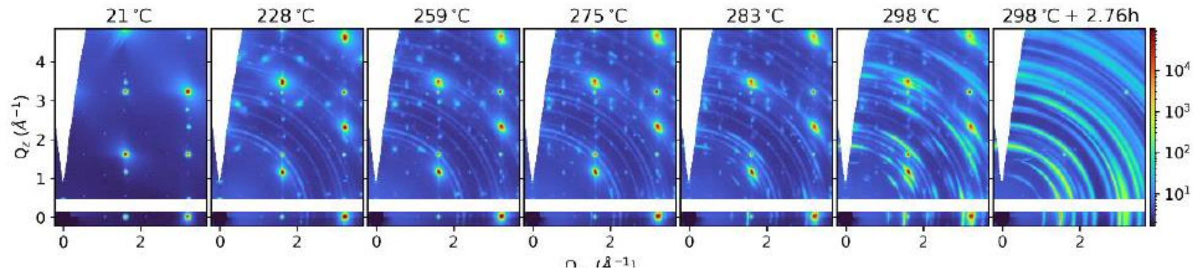

Figure 1: Reciprocal space maps taken from a single crystal UO_2 thin film at exposed to air at increasing temperatures (given above each plot) showing the formation of U_4O_9, U_3O_7, and finally U_3O_8.

[1] G. C. Allen, N. R. Holmes, J. Nucl. Mater. 231-237, 223 (1995).
[2] J. M. Wasik (2009) "Oxidation of Uranium Dioxide" (Doctoral thesis, University of Bristol, Bristol, UK)

Understanding the sintering of MOX nuclear fuels: challenges associated with the characterization of a multiphasic microstructure

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Mixed oxides (MOX) nuclear fuels are high-performance ceramics used worldwide in Light Water Reactor (LWR) to produce decarbonized energy; leveraging recovered plutonium from spent nuclear fuel to close the nuclear fuel cycle and reduce waste. Industrially, MOX cylindrical pellets are manufactured through the Melox process by Orano Melox. This powder metallurgy process revolves around two main consecutive steps. A master blend is prepared by co-grinding PuO_2 and UO_2 powders, with a Pu/(U+Pu) content around 28 wt%. This master blend is diluted using raw UO_2 to reach the target Pu/(U+Pu) content (typically < 11 wt%). Shape forming of the green body is achieved through uniaxial pressing and the pellets are sintered at high temperature (1700°C) under a controlled reductive atmosphere. This process leads to a microstructure presenting a distinctive plutonium distribution: master blend agglomerates (20-100 µm) exhibiting a higher plutonium content are dispersed in a matrix constituted of uranium dioxide agglomerates. A third pseudo-phase (coating) with an intermediate plutonium content is also located at the interfaces between the two other phases. This process also leads to porosities (about 5 vol%) presenting specific morphologies depending on their location in the microstructure.

As the non-uniformity in plutonium spatial distribution impacts fuel properties and behaviour during irradiation, recent works reported the development of joint characterization of both grain size and their plutonium content. This approach however requires heavy logistical means (both electron probe micro analysis and scanning electron microscopy, alignment of datasets and image treatment) limiting the number of samples that can be studied that way. To overcome such challenges regarding the total characterization of LWR MOX complex microstructure, we have developed new experimental procedures coupling experimental results and image analysis. Characterization of pore morphology is achieved through unsupervised learning. Correlative phase-based grain size measurement is achieved in a very straightforward manner, using a single equipment, improving acquisition time and with no need for datasets alignment.

These new insights will feed simulations and models to predict MOX sintering behavior, reducing reliance on nuclear material experiments. This tandem of experimental and computational approaches advances the understanding of MOX process/microstructure/property relation and paves the way for future fabrication- characterization work.

Alternative deconversion pathway for UF6 and uranium recovery

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The current stockpile of depleted uranium hexafluoride (UF_6), 1.2 million tons worldwide, necessitates the deconversion of UF_6 to a more chemically stable form of uranium. The corrosive and volatile nature of UF_6 causes it to be potentially hazardous for continued long-term storage. The conventional method of deconversion, combining UF_6 with water vapor, produces a water-soluble form of uranium, uranyl fluoride. This requires further treatment, which typically ends with U_3O_8 for storage. However, recent studies have demonstrated that UF_6 can be chemically stabilized with room temperature ionic liquid through a redox reaction[1]. This work builds on that by exploring the recovery of UF_4 from the inert UF_6-IL solution, using water. Water added to the UF_6-IL solution induces the precipitation of a uranium-containing green solid. We examined the precipitate following the addition of two different volumes of water. We also compare various mixing methods: high agitation, light agitation, and non-agitation to observe the effects on the product yield and morphology. The uranium solid was characterized through thermogravimetric analysis, powder X-ray diffraction, and scanning electron microscopy (SEM). The chemical composition of the precipitate was investigated by energy-dispersive spectroscopy in the SEM. The precipitate was found to be UF_4 mixed with other uranium fluoride species. While anhydrous UF_4 displays spherical morphology, needle-like morphology has been reported for hydrated UF_4[2]. In our samples, we found needles among other morphologies, as referenced in Figure 1. In the non-agitation and light agitation treatments, the needles appear to have a nucleation point, which was confirmed via in-situ optical microscopy. This work provides a direct pathway from UF_6 to stable uranium fluoride solids.

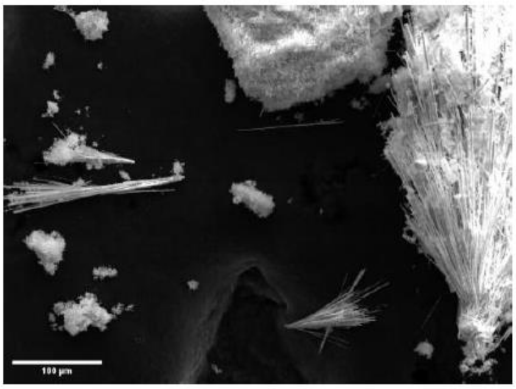

Figure 1: SEM micrograph of precipitate obtained through light agitation with 50% v/v water (1 mL) added; various morphologies are observed

[1] Higgins, C. J., et al. "Direct dissolution and spectroscopic characterization of uranium hexafluoride in ionic liquid." Journal of Radioanalytical and Nuclear Chemistry 331, no. 12 (2022): 5205-5213.

Impact of hydroxide precipitation on the Sintering and Chemical Durability of $U_{1-x}Th_xO_2$ solid solutions

L. Callejon [1] , M. Fulchiron [1], L. Claparede [1], J. Lautru [1] , N. Clavier [1] , R. Podor [1] , S. Szenknect [1] , N. Dacheux [1]
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During their stay in the reactor core, mixed oxide (MOx) fuels undergo significant elemental and microstructural changes. Then, irradiated fuels exhibit significant cationic heterogeneity, with areas enriched in plutonium resulting from the manufacturing process. These areas are resistant to dissolution when plutonium content is greater than 35 wt.% [1]. Additionally, irradiation leads to the formation of fission products (FPs) in gaseous, metallic, and oxide forms, as well as within the fluorite structure [2]. These complex chemical and microstructural changes cause changes in the dissolution kinetics of the fuel during reprocessing, which can lead to the formation of insoluble residues. Although little information exists in the literature regarding the dissolution of irradiated heterogeneous fuels, a recent study examined the dissolution of heterogeneous model compounds based on $(U,Th)O_2$ with varying degrees of heterogeneity, using thorium as a plutonium surrogate [3]. As part of this study, the hydroxide precipitation synthesis route [4] was optimized to investigate the impact of different modifications on the behavior of sintered materials under dissolution conditions. The influence of the order of addition of the reagents was studied with respect to its effect on the microstructure, the cationic homogeneity and finally the dissolution kinetics of the final compounds resulting from the two synthesis routes considered: Direct Droplet Adding (DDA) and Indirect Droplet Adding (IDA). Once the synthesis method was optimized, lanthanide and/or metallic elements were introduced directly during the synthesis to finally obtain well densified sintered pellets. Dissolution experiments were performed on all prepared samples.

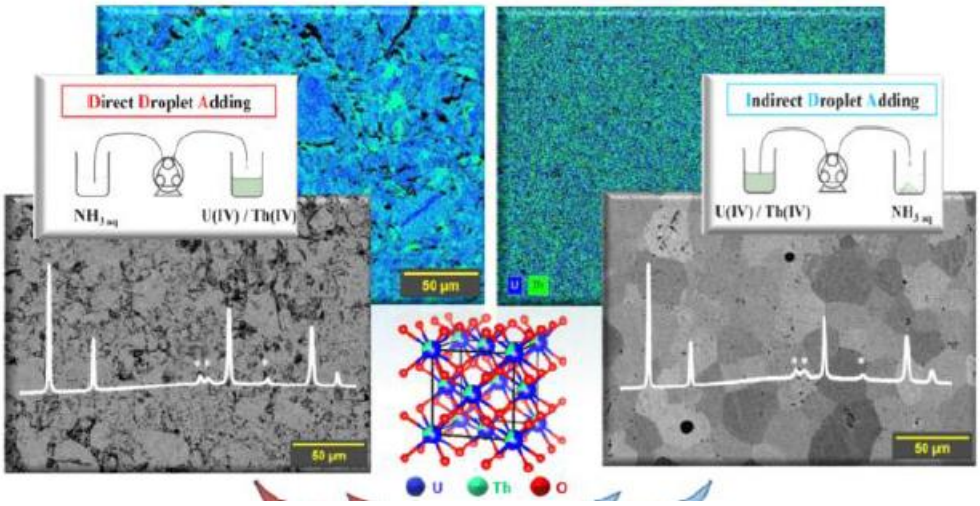

Figure 1: Summary of the two chemical routes (DDA and IDA methods) of $U_{1-x}Th_xO_2$ solid solutions.

[1] D. Vollath, H. Wedemeyer, H. Elbel, E. Günther, Nuclear Technology, 71 (1985) 240–245.
[2] H. Kleykamp, Journal of Nuclear Materials, 131 (1985) 221–246.
[3] C. Hours, L. Claparede, N. Reynier-Tronche, I. Viallard, R. Podor, N. Dacheux, Journal of Nuclear Materials, 586 (2023) 154658.
[4] J. Martinez, N. Clavier, A. Mesbah, F. Audubert, X.F. Le Goff, N. Vigier, N. Dacheux, Journal of Nuclear Materials, 462 (2015) 173–181.

Impact of fission products on the thermophysical properties of $(U,Pu)O_{2-x}$ fuels using a SIMMOx approach

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Uranium-plutonium mixed oxides, $(U,Pu)O_{2-x}$ (MOx), containing between 20% and 35% Pu and an oxygen stoichiometry in the range of $1.94 \leq O/M < 2.00$ (with M = U + Pu), are the reference fuels for future French Sodium-cooled Fast Reactors (SFRs). During irradiation, plutonium fission continuously generates more than 30 fission products (FPs), which progressively modify the fuel composition. The high thermal gradient leads to microstructural evolution, as well as Pu and oxygen redistribution along the pellet radius. To develop SFRs, a safety criterion must be respected which is the margin to the fuel melting, defined as the difference between the temperature of MOx fuel during irradiation in-reactor (~2470 K at high burnup) and its melting temperature (~3000 K), and set as 200 K. To better assess this safety margin, an in-depth understanding of the impact of FPs on the thermophysical properties (αth, λth, Cp and Tmelting) of MOx is required. Due to the very high radiotoxicity of irradiated MOx, direct measurements of its thermophysical properties are extremely challenging, leading to a lack of data. Furthermore, the accumulation of irradiation effects (microstructure, O/M, Pu content, FPs) makes it impossible to study the impact of each parameter individually, including the specific impact of FPs on fuel properties.

To overcome this difficulty, a separate-effects strategy was developed using SIMMOx materials [1,2], which are fresh $(U,Pu)O_{2-x}$ fuels doped with representative non-radioactive FPs. Thermal diffusivity and melting point were measured on 26% Pu SIMMOx samples incorporating up to 11 FPs, using laser flash (LAF) and continuous-wave laser heating (CLASH) techniques. Various batches of SIMMOx were studied, including samples containing FPs soluble in the $(U,Pu)O_{2-x}$ matrix, as well as samples also containing secondary phases, such as metallic FPs inclusions and perovskite-like oxide precipitates. The results demonstrate a significant impact of FPs on both thermal diffusivity and melting behaviour. The thermal diffusivity values obtained on SIMMOx materials are consistent with those measured on irradiated MOx they are designed to simulate, validating the SIMMOx approach. In contrast, unirradiated MOx exhibits higher diffusivity values, highlighting that such properties cannot be directly investigated on unirradiated MOx fuel. The melting temperature of unirradiated MOx (~3050 K) decreases with incorporation of soluble FPs, and this decrease is even more pronounced when metallic FPs are added. Furthermore, perovskite-like oxide precipitates also decrease the melting temperature but modify the melting behaviour. These results will be further detailed during the conference.

[1] R. Caprani, et al., Journal of Nuclear Materials, 585, 154607, 2023.
[2] R. Caprani, PhD Thesis, University of Montpellier, 2023.

Actinide precipitation in complex organic media

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The reprocessing steps of uranium oxide (UOx) in the French nuclear fuel cycle consist in two consecutive processes, PUREX (Plutonium Uranium Reduction Extraction) and MIMAS (Micronized MASter blend). While these processes come up with good purity and yields, they also present several drawbacks [1], e.g. the high number of steps, the management of primary and secondary effluents, the risk of plutonium proliferation or even the use of toxic compounds such as hydrazine. In this regard, several reprocessing alternatives are being considered [1, 2]. The chemical co-precipitation of U, Pu or their analogues has been widely investigated [3]. However, very few studies report the direct co-precipitation from the extraction solvent. This study focuses on the development of a selective actinide precipitation (U and Th) from a loaded organic phase (Extractant= TBP). This work is therefore devoted to the synthesis of various actinide-coordination polymer (An-CP) and the subsequent annealing step in order to form suitable actinide oxide precursors.

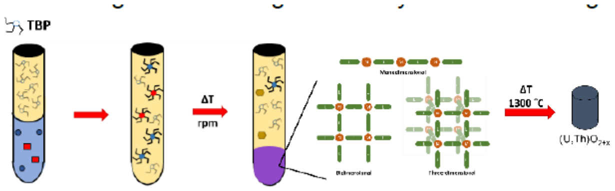

Figure 1: Schematic diagram of experimental method

Three systems were investigated: two single-metal systems containing either uranium or thorium, and one mixed-metal system combining both uranium and thorium. Notable differences were observed between the two single-metal systems (U and Th). In the mixed systems, a selective competitive behavior was observed, with precipitation preferentially favoring thorium based on yield measurements. Finally, heat treatments resulted in the formation of uranium oxide and thorium oxide from the single-metal systems. Mixed oxides were also obtained, and under certain conditions, the formation of actinide phosphate oxide phases was observed.

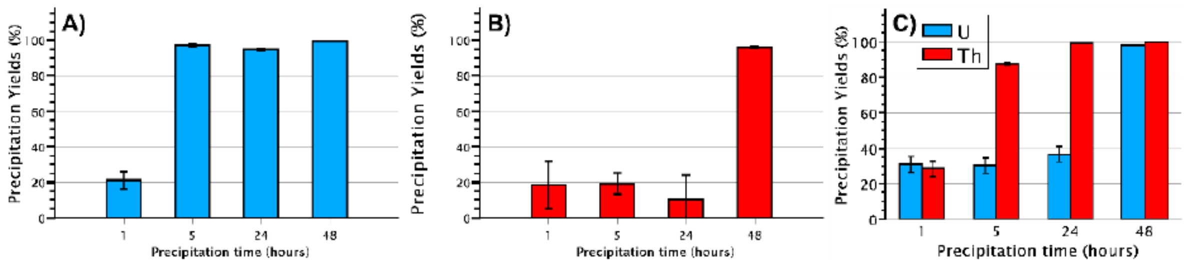

Figure 2: Precipitation yields of A) uranium-based systems B) thorium-based systems C) uranium-thorium-based systems precipitated at different time

[1] Status and Trends in Spent Fuel Reprocessing; TECDOC Series; INTERNATIONAL ATOMIC ENERGY AGENCY: Vienna, 1999.
[2] Colledge, H. et al. A Review of Alternative Finishing Options for Uranium/Plutonium and Minor Actinide Nitrate Products from Thermal and Fast Reactor Fuels Reprocessing. Progress in Nuclear Energy, 2023, 165, 104903. DOI: doi.org/10.1016/j.pnucene.2023.104903.
[3] Collins, E. D. et al. Evaluation of Co-Precipitation Processes for the Synthesis of Mixed-Oxide Fuel Feedstock Materials; ORNL/TM-2011/164, 1024695; 2011; p ORNL/TM-2011/164, 1024695.

Hydrophobic CMPO-based low-melting mixtures for sustainable Spent Nuclear Fuel recycling

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The recycling of spent nuclear fuel plays a crucial role in reducing radioactive waste burden, optimizing resource utilization and ensuring the sustainability of the nuclear energy cycle. Traditional solvent extraction processes, however, often rely on organic phases composed of environmentally hazardous compounds. In recent years, increasing attention has been devoted to the development of greener and more efficient extraction media capable of maintaining or improving separation performance while minimizing environmental impact.

Within this framework, Deep Eutectic Solvents (DES) may emerge as a promising alternative to conventional organic solvents. DES are mixtures typically composed of a hydrogen bond donor and a hydrogen bond acceptor, which together form a eutectic system with unique physicochemical properties and higher concentrations of the ligands, making them attractive candidates for advanced SNF recycling processes. [1]

Novel hydrophobic low-melting mixtures were designed using Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), a ligand used for An and Ln extraction. [2] The ligand powder was mixed with various hydrogen bond donors, including decanoic acid, oleic acid, menthol and thymol, forming binary and ternary mixtures. The so-obtained low-melting mixtures were evaluated over time in contact with nitric acid and used as organic phase in solvent extraction experiments. Among the tested formulations, significant differences were observed. The CMPO–decanoic acid system exhibited remarkable extraction performances toward americium and europium, with distribution ratios even in the order of several hundreds. The formulation containing menthol also showed excellent extraction properties. However, the presence of menthol induced a distinct behaviour of the organic phase, making the extraction efficiency largely independent of the nitric acid concentration in the aqueous phase. In addition, the CMPO- based low-melting mixtures were tested for their radiolytic stability up to doses of 200 kGy, showing remarkable resistance to radiation damage and to prolonged contact with concentrated acidic media.

The organic phases developed thus exhibit properties of high interest for advanced nuclear fuel recycling, combining excellent extraction efficiency with remarkable radiolytic stability and overcoming solubility issues. These findings highlight the potential of such DES-like systems as promising candidates for the development of greener and more sustainable approaches to nuclear fuel reprocessing.

[1] Schaeffer, N. et al. Green Chem. 22, 2810-2820, 2020. DOI: 10.1039/d0gc00793e,

[2] Mathur, J. N. et al. Waste Management, 13, 317-325, 1993. DOI: 10.1016/0956-053X(93)90060-A

Molecular Dynamics Study of Uranium Extraction from TBP/Heptane Solutions Using Amidoxime-Grafted Silica

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The production of energy from nuclear sources generates a variety of radioactive wastes, and in particular Radioactive Liquid Organic Waste (RLOW). RLOW contains a wide range of organic molecules and radioactive species along with halogens, heavy metals, nitrates, carbonates, sulfates and other components. To be compatible with existing waste management systems, RLOW must undergo pre-treatment. Current treatment methods of RLOW consists in incineration-vitrification and hydrothermal oxidation, and complementary methods are being researched in order to selectively remove the radioactive species from the liquids.

Recent studies have demonstrated that functionalized silica materials exhibit strong potential for uranium extraction from acidic sulfate solutions via liquid-solid extraction [1,2]. Molecular dynamics simulations have contributed to giving insights on phenomena surrounding the speciation of uranium by ligands grafted onto mesoporous silica at the aqueous phase/solid interface [3].

Extending our study to organic-phase systems, we simulate a TBP/heptane solution of uranyl nitrate in contact with amidoxime-grafted silica. The objective is to examine the speciation behavior of uranyl cations at the organic-phase/solid interface and to assess the influence of water and other components in the solvent phase. A key challenge lies in developing a simplified yet realistic surface model while incorporating polarization effects in classical molecular dynamics simulations. With our results we intend to offer insight into uranium coordination and extraction mechanisms in organic medium relevant to RLOW treatment.

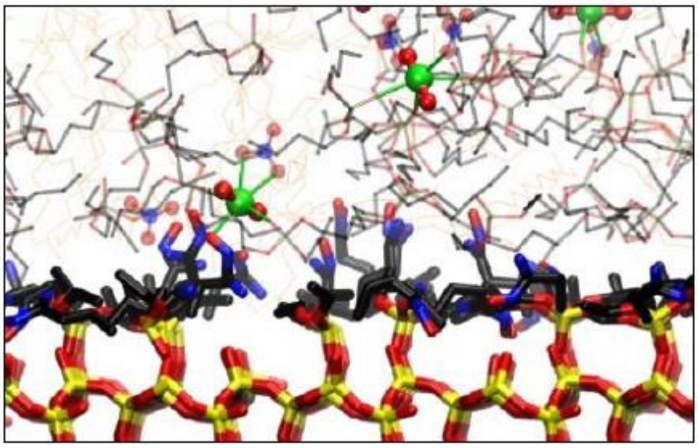

Figure 1: Molecular representation of the organic-phase/solid interface in the simulation. Silicon, oxygen, carbon, nitrogen and uranium atoms are represented in yellow, red, black, blue and green, respectively. Hydrogen atoms have been omitted.

[1] A. Dressler, A. Leydier, A. Grandjean, Molecules, 2022, 27(14), 4342.
[2] A. Dressler, T. Le Nedelec, A. Leydier, F. Cuer, T. Dumas, A. Grandjean, Chem. Eng. J. Adv., 2022, 9, 100225.
[3] D. M. Martinez, Etude par dynamique moléculaire de la séparation de l'uranium (VI) sur support solide, Diss. Montpellier, Ecole nationale supérieure de chimie, 2022.

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Impact of Accumulated TODGA Degradation Compounds on a CHON-Compliant AmSel Process

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The Advanced Nuclear Fuel Cycle is regarded as one of the most sustainable approaches for the management of nuclear waste, as it involves the selective separation of minor actinides (MAs: Np, Am, and Cm) from fission products such as lanthanides (Ln). This strategy also enables the production of new fuels or transmutation targets [1].

Interest in the selective separation of Am has increased along last decades. However, given the close chemical similarities between Am and Cm, achieving an efficient separation remains a challenge. Consequently, novel separation strategies have been developed, including the AmSel (Americium Selective Extraction) process [2]. The AmSel process is based on liquid-liquid extraction techniques, designed to operate in a continuous mode (recycling the organic phase on each cycle) and to be implemented following the PUREX process. The separation of Am(III) from Cm(III) is enabled by the inverse selectivity of two ligands: TODGA, in the organic phase, exhibits a higher affinity for Cm(III); and hydrophilic Am(III) selective like PrOH-BPTD in the aqueous phase. The latter one is a CHON-compliant alternative to the original AmSel reference aqueous ligand, the SO3-Ph-BTBP [3].

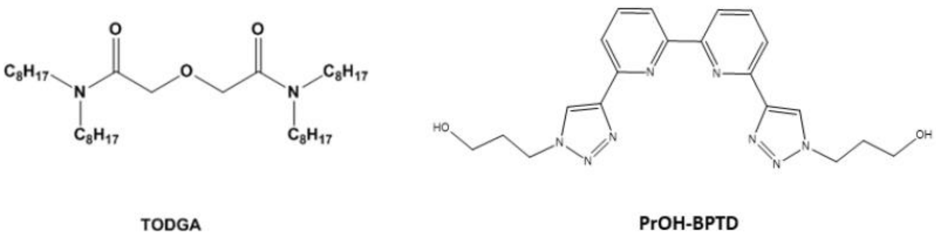

Figure 1: CHON-compliant AmSel process molecules: TODGA (left), PrOH-BPTD (right).

A critical aspect in the development of this process is the chemical stability of the ligands, as they are exposed to extreme operational conditions, which have been shown to promote their degradation. It is well-studied that the degradation of TODGA produces a range of degradation compounds [4-6]. The accumulation of these degradation compounds when the organic phase is recycled have been proved to affect the selectivity of the AmSel process when SO_3-Ph-BTBP is used as the reference aqueous ligand [7].

This work explores and compares the impact of the accumulation of TODGA degradation compounds on the selectivity of a CHON-compliant AmSel process using the novel aqueous ligand, the PrOH-BPTD.

[1] Baron, P. et al., Progress in Nuclear Energy 117, 103091 (2019).
[2] Wagner, C. et al., Solvent Extraction and Ion Exchange 34, 2, 103-113 (2016).
[3] Weßling, P. et al., Inorganic Chemistry 61, 44, 17719–17729 (2022).
[4] Sugo, Y. et al., Radiochimica Acta 90, 3, 161-165 (2002).
[5] Galán, H. et al., Procedia Chemistry 195 – 201 (2012).
[6] Sánchez-García, I. et al., EPJ Nuclear Sciences & Technologies 5, 19 (2019).
[7] Vacas-Arquero, P. et al., Progress in Nuclear Energy 183, 105677 (2025).

Use of diglycolamide derivatives for rhodium recovery

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Rhodium is a platinum-group metal (PGM) widely used in catalysis, particularly in the automotive industry. Due to its rarity (1 ppb in earth's crust), its high industrial demand, and its exceptionally elevated market price, reaching 240 000 €/kg in October 2025, rhodium is considered a critical metal [1]. Interestingly, Spent Nuclear Fuel (SNF) could represent a valuable secondary source, as it contains significant amount of platinum-group metals including rhodium, that remain currently unexploited. Approximately 700 kg of rhodium per year (~ 700 ppm) accumulate in SNF, almost entirely as the stable isotope,103Rh [2]. However, the selective recovery of Rh from SNF remains a challenge, due to the complex chemical composition of the spent fuel, which contains a wide range of elements from across the periodic table, and the chemical properties of rhodium species formed in nitric acid media. Moreover, according to the Hard and Soft Acids and Bases (HSAB) principle, rhodium is classified as neither a soft nor a hard acid [3].

To address this challenge, liquid–liquid extraction was selected as the strategy for rhodium recovery, aiming to extract rhodium under highly acidic conditions and subsequent strip it by decreasing the acidity. To this end, several neutral extractants incorporating both hard (oxygen) and soft (nitrogen or sulfur) donor atoms were designed and synthesized, drawing inspiration from the diglycolamide (DGA) structural framework.

The influence of the donor atom, its number, and position, as well as the presence of branching and the distribution of alkyl chains on the structure of the molecule were investigated. The extraction behavior of Rh will be compare to that of other elements present in the raffinate, such as platinum group metals (Pd and Ru), a lanthanide (Nd) and a minor actinide (Am), in order to evaluate the selectivity new extractants.

[1] Rhodium price | Umicore Precious Metals Management https://pmm.umicore.com/en/prices/rhodium/ (accessed Oct 12, 2025).
[2] Hodgson, B. J.; Turner, J. R.; Holdsworth, A. F. A Review of Opportunities and Methods for Recovery of Rhodium from Spent Nuclear Fuel during Reprocessing. JNE, 2023, 4 (3), 484–534. https://doi.org/10.3390/jne4030034.
[3] Ho, T.-L. Hard Soft Acids Bases (HSAB) Principle and Organic Chemistry. Chem. Rev., 1975, 75 (1), 1–20. https://doi.org/10.1021/cr60293a001.

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f-Element Separations with a Focus on Uranium Recycling

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Over the past eight decades, uranium recovery, purification, reprocessing, and recycling technologies have evolved to meet the changing demands of the nuclear fuel cycle. Solvent extraction remains a cornerstone of these operations, employing tailored organic extractants and ion-exchange reagents. This presentation will provide a high-level overview of persistent challenges in uranium separations, including extractant stability under process-relevant conditions, phase behavior and hydrodynamics, and selectivity in complex chemical matrices. Emphasis will be placed on emerging solvating extractants for U(VI) recovery and on how molecular design choices can translate into improved process performance.

Oxidant-free oxidative separation of Bk(IV)/Cf(III) and Ce(IV)/Ln(III) using 3,4,3-LI-(1,2-HOPO) and Design of Experiments

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Oxidation methods have been employed for the separation of Bk-249 from its Cf-249 daughter, using HDEHP and an oxidant to access Bk(IV), enabling facile separation from Cf(III) and Cm(III). This was first proposed by Peppard1 in 1957, whose process is now known as BERKEX, but improvements have largely focused on the use of either more effective or milder oxidants. In this study, we present a method of ligand-based oxidative separation without the need for additional oxidants, systematically optimized via design of experiments. We employed a ligand from the class of hydroxypyridinones, which are hard O-donors widely used in preservatives, radiopharmaceuticals, and separations.2,3 The 1,2- hydroxypyridinone (1,2-HOPO) moiety can be attached to a spermine backbone to yield 3,4,3-LI-(1,2-HOPO), an octadentate chelator with high binding affinity toward trivalent and tetravalent f-elements. Critically, it can stabilize tetravalent Bk as well as tetravalent Ce without the need for an additional oxidant, according to the proposed process shown in Figure 1. Here, we utilized design of experiments (DoE) to systematically optimize the extraction of Ce(IV) along three process parameters. Effect of these parameters were also investigated for Bk(IV)/Cf(III) separations and separation factors were achieved on the order of 103. This provides a method of ligand-stabilized oxidative separation without the need for an additional oxidant, establishing a framework that can be expanded to other actinides with accessible tetravalent states.

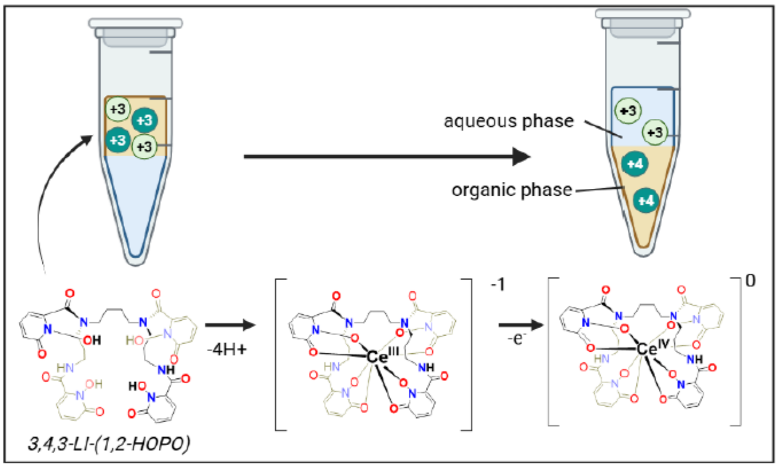

Figure 1: Liquid-liquid separation of 4+ and 3+ metals using 3,4,3-LI-(1,2-HOPO)

(1) Peppard, D. F.; Moline, S. W.; Mason, G. W. J. Inorg. Nucl. Chem. 1957, 4 (5–6), 344–348.
(2) Zhu, Y.-Z.; Chen, K.; Chen, Y.-L.; Zhang, C.; Xie, Y.-Y.; Hider, R. C.; Zhou, T. Food Chem. 2022, 385, 132730.
(3) Cusnir, R.; Imberti, C.; Hider, R. C.; Blower, P. J.; Ma, M. T. Int. J. Mol. Sci. 2017, 18 (1).

Self-assembly of grafted surfactants for actinides extraction under cloud point conditions

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To enhance the safety of nuclear fuel reprocessing, solvent-free extraction methods based on water-soluble molecules with molecular recognition capabilities are being explored. Among them, cloud point extraction (CPE) exploits thermo-responsive nonionic surfactants whose solubility changes with temperature, inducing phase separation in aqueous media. While CPE is well suited for metal ion extraction, it typically requires the addition of hydrophobic complexing agents[1]. However, the need for large amounts of surfactant remains a major limitation in terms of molecular efficiency.To overcome this drawback, our project investigates the covalent grafting of complexing groups onto surfactant molecules[2], leading to bifunctional architectures that combine thermo-reversible solubility and metal ion complexation within a single molecule. A related system (C8E10 functionalized with an acetyl-lysine methyl ester, 80 mM) was previously studied[3] in $LiNO_3$ medium. Here, we extend this approach to uranyl ion (UO_2^{2+}) extraction under nitric conditions (4 M HNO_3) relevant to spent nuclear fuel reprocessing. The surfactant design incorporates a malonamide moiety, known for its chelating affinity toward actinides (IV) and (VI)4,5, grafted onto polyethylene glycol alkyl ether chains.

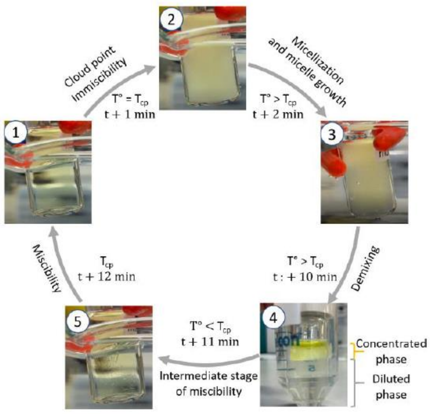

Figure 1: Stages of extraction of 0.1 M of uranyl nitrate in 4 M nitric acid by cloud point in a thermostatic bath with a C12E5L 0.3 M L being N,N,N',N'-tetramethylmalonamide

Preliminary results demonstrate the feasibility of uranyl extraction through the successive stages of a cloud point process (Figure 1). In this work, I will present a comprehensive molecular and supramolecular analysis, together with a quantitative characterization of the phase behavior, for both grafted and non-grafted systems, while systematically varying the position of the chelating moiety along the CiEj surfactant structure.

[1] Pytlakowska et al. (2013), 10.1016/j.talanta.2013.02.037 ;
[2] Coulombeau et al. (2004), 10.1021/la049832r ;
[3] Larpent. (2007), 10.1039/b707016k;
[4] Makombé (2022) 10.1016/j.molliq.2022.120701
[5] Nigond (1994) 10.1080/07366299408918212

This work is funded as part of France 2030 through the ESOP (Extraction Par SOlvant Pur) project of the Programme d'Investissement d'Avenir (PIA).

Kinetic Studies of U(IV) and Pu(IV) in Aqueous Nitric and TBP/Dodecane Solutions

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The reduction of Pu(IV) to Pu(III) is a critical step in the Plutonium Uranium Redox Extraction (PUREX) process wherein greater than 99% back-extraction of Pu into the aqueous phase can be achievable, contingent upon the choice of reductant. Common reducing agents include hydroxylamine nitrate (HAN), ferrous sulfamate, and uranous nitrate. Unlike HAN and ferrous sulfamate, U(IV) is extracted to the organic phase, and thus reduction of Pu(IV) may occur at the interface, in the aqueous phase, or in the organic phase. Kinetic studies of U(IV)-Pu(IV) reactions, unfortunately, have been largely confined to aqueous phase systems. Comprehensive data on Pu(IV) reduction kinetics in homogeneous aqueous and organic phases are necessary to accurately model and simulate this reaction within solvent extraction environments. To address this gap, we have determined the kinetics of Pu(IV) reduction by U(IV) in both aqueous nitric acid solutions and 30% TBP/dodecane solutions. These reactions were monitored in situ by UV-Vis spectrophotometry across a range of nitric acid and metal ion concentrations. Standard reference spectra for U(IV), Pu(III), and Pu(IV) in aqueous and organic phase systems were acquired, including Pu(III) in TBP/dodecane (Figure 1), which was achieved by addition of ascorbic acid to a Pu(IV) solution (already extracted into 30% TBP/dodecane). The overlapping UV-Vis spectra of the metal ions were deconvoluted using these reference spectra with an in-house Python script, enabling concentration profiles of each species as a function of time. The experimentally derived rate laws and rate constants for both aqueous and organic systems will be presented and will subsequently be applied to refine predictive models for the PUREX process.

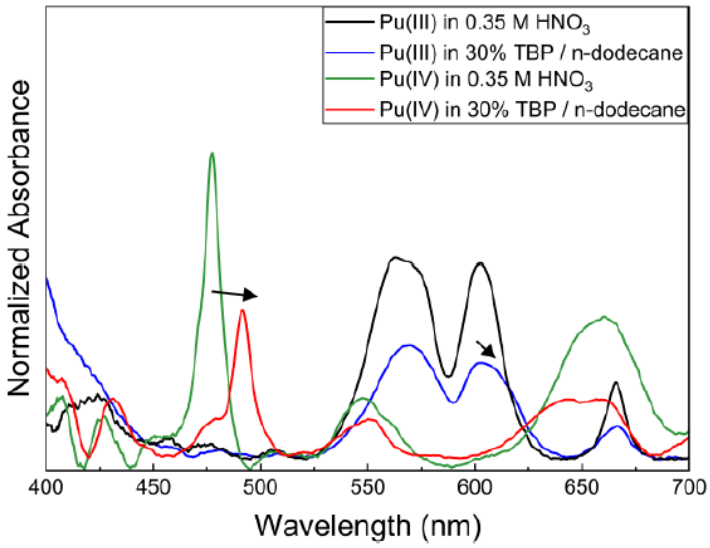

Figure 1: Normalized absorbance of Pu(III) and Pu(IV) spectra in 0.35 M HNO3 or 30% TBP/n- dodecane, with arrows indicating changes in characteristic peaks between phases.

Controlling Viscosity and Interfacial Properties in Monoamide Solvents: Roles of Nitric Acid, Uranium, and Phase Modifiers

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N,N-dialkylamides offer an efficient and cost-effective alternative to tributyl phosphate (TBP) in nuclear fuel reprocessing as they follow the CHON principle and can be structurally tuned by varying the alkyl substituents. These substitutions influence not only actinide selectivity and third-phase formation but also key physicochemical properties, such as density, viscosity, and interfacial tension (IFT), that are critical for the design and operation of solvent contactor equipment.

This study investigates how alkyl substituents, nitric acid concentration, uranium loading and phase modifiers affect viscosity and IFT in three monoamide systems: N,N-di(2-ethylhexyl)butyramide (DEHBA), N,N-di(2-ethylhexyl)isobutyramide (DEHiBA), and N,N-dihexylbutyramide (DHBA). Increasing aqueous HNO3 concentration (0.1 – 6 M) raised viscosity and lowered IFT, correlating with greater acid uptake into the organic phase. Upon uranium loading, viscosity increased sharply due to aggregate formation of U– ligand complexes, while IFT remained nearly constant.

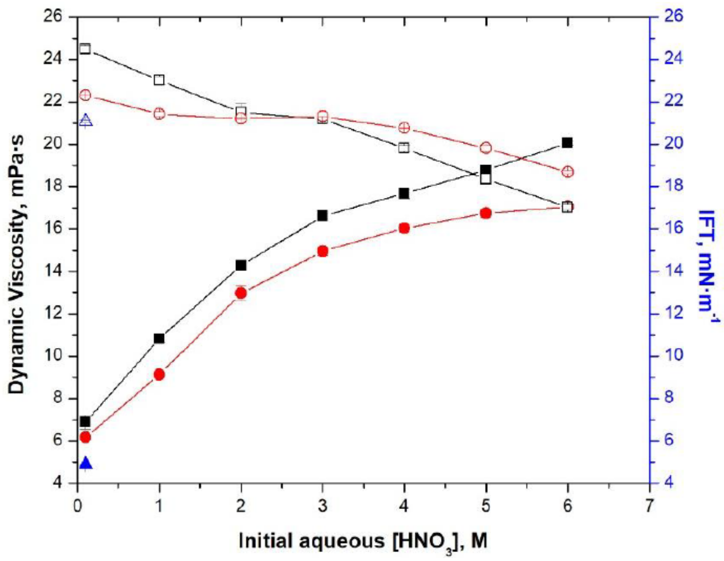

Figure 1. Dynamic viscosity (closed symbols) and interfacial tension (open symbols) of 1.5 M DEHBA (■), DEHiBA (●), and DHBA (▲) as a function of initial aqueous HNO3 concentration. The diluent was n-dodecane, and the ligand solutions were contacted with 100 g/L U at the specified acid concentrations. DHBA formed third phase at all concentrations above 0.1 M HNO3 after U contact.

Among the phase modifiers, 1-octanol acted as a co-surfactant, increasing viscosity and reducing uranium extraction, whereas m-xylene served as an effective co-solvent, suppressing third-phase formation and lowering viscosity without significantly changing IFT. FTIR and Raman spectra showed hydrogen bonding between 1-octanol and the ligand carbonyl group, weakening U–Oyl coordination, while m-xylene enhanced U–ligand interactions. Overall, m-xylene was identified as the optimal modifier for improving both chemical and physical performance of monoamide-based extraction systems.

Ruthenium speciation during acidification of alkaline solution using a UV-Visible fast detector and an in-situ probe

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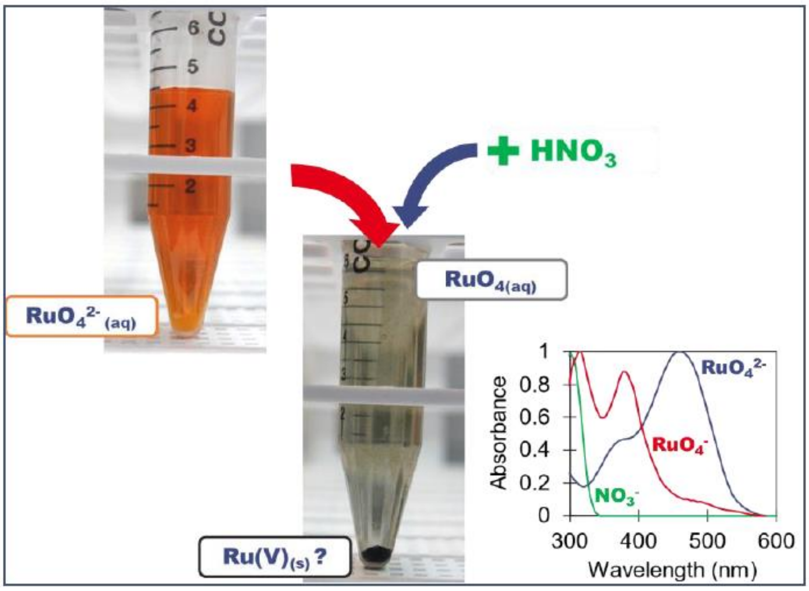
Ruthenium is a highly radioactive and volatile fission product of interest in the context of nuclear fuel reprocessing R&D studies. Its radioactivity also benefits the nuclear medicine field. Taking into account its tendency to volatilize in oxidizing media, alkaline traps are often used to capture Ru vapors. An acidification of the samples or an alkalization of the standards is required to analyze an element by ICP-MS or ICP-OES of these alkaline solutions. However, this step leads to the precipitation of most of the Ru in solution, resulting in an incorrect quantification. This study aims to identify and quantify the acidification by-products and understand their formation mechanisms. A UV-Visible fast detector coupled to an in-situ probe monitors the existing Ru species at a millisecond scale. Thousands of spectra with large Ru-bands are obtained and then deconvoluted using a Multivariate Curve Resolution algorithm. Results indicate a two-steps reaction: the first one involving ruthenate (RuO_4^{2-}) and leading to perruthenate (RuO_4^-) and a Ru(V) precipitate; the second one involving the perruthenate and leading to the release of the same Ru(V) precipitate and the highly volatile ruthenium tetroxide (RuO_4). These analyses help to estimate the formation and kinetic constants of these reactions.



Inactive studies into the effect of insoluble fission products on the generation of Ag2+ for the dissolution of MOx fuel

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Mixed oxide fuels (MOx) containing mixtures of uranium and plutonium oxides (UO_2 and PuO_2, respectively), are widely used in Europe. Currently about 40 reactors in Europe (Belgium, Switzerland, Netherlands and France) are licensed to use MOX, and over 30 are doing so. However, spent MOx fuels containing high percentages of PuO_2 prove challenging to reprocess via methods based on the dissolution of spent uranium oxide (UOx) based fuels in aqueous HNO_3, such as the plutonium uranium redox extraction (PUREX) method. This is because PuO_2 is difficult to dissolve in the HNO_3 media used for fuel dissolution at the process headend. This can lead to PuO_2-rich insoluble residues remaining undissolved after HNO_3 dissolution, both causing a challenge to manage criticality hazard due to accumulation and to control PuO_2 to prevent it from entering downstream reprocessing pathway.

One means to obviate this issue is the use of Advanced Oxidation Process (AOP)- based dissolution method. One such AOP method uses an electro-generated Ag^{2+} mediator to promote the oxidative dissolution of SNFs. An aspect of irradiated MOx dissolution requiring further investigation is the effect of insoluble fission products (IFPs) on the efficacy of Ag^{2+} electro-generation and thus subsequent SNF dissolution. IFPs occur mostly as metallic particles, termed "ε-particles", consisting of noble metals Mo, Pd, Rh, Tc and Ru. These "ε-particles" can catalyze water oxidation by AOP reagents such as Ag^{2+}, thereby promoting side-reaction and impacting the capacity of Ag^{2+} to dissolve PuO_2 rich particles. The IFPs vary in composition depending on fission yield, oxygen potential, temperature gradient and fuel burnup.

Herein, we present the results of our experiments exploring the efficacy of electro- generation of Ag^{2+} for fuel dissolution in the absence and presence of IFPs. In this context, electrochemical study of the Ag^{2+}/Ag^{+} system under conditions relevant to fuel dissolution plants shows the electro-generation of Ag^{2+} from Ag^{+} to be an EC′ process, i.e. an electrochemical step E which generates Ag^{2+}, followed by a chemical step, C′, that regenerates the reactant Ag^{+} for the electrochemical step, the latter of which may be catalyzed by IFPs.

Through voltametric measurements and the use of extant analytical models of EC′ systems, kinetic rate parameters for both steps have been determined on commonly used Pt rotating disk electrodes (RDEs) and Boron-Doped Diamond (BDD) electrodes to study the impact of both catalytic activity of the working electrode (WE) material and applied convection to this electrochemical system. Experiments were conducted in MOx dissolution relevant HNO_3 concentrations, both in the absence and presence of IFP nanoparticles, allowing for quantitative assessment of the effect of acidity and the presence of ε-nanoparticles on Ag^{2+} generation. These studies demonstrated the rate parameter for the C′ step increases with increasing amounts of Pd, Ru, and Rh as IFP

Experimental and Quantum Chemical Insights into the Coordination Chemistry of Protactinium(V) in Chloride Media

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Protactinium(V) shows unusual chemistry among actinides because it does not form the typical actinyl (AnO +) unit. Instead, it features a mono-oxo bond whose stability varies strongly with the ligand environment. This bond, observed in oxalate and sulfate media, can weaken or disappear upon complexation, as shown for fluoride systems [1]. Theory also indicates that the Pa(V) mono-oxo bond is far more sensitive to coordination than the uranyl di-oxo bond [2].

A major issue in Pa(V) chemistry is the discrepancy between experimental Pa-O distances (~1.75 Å) and theoretical predictions (~1.85 Å) in oxalate and sulfate complexes [3]. Experimental work is further complicated by Pa(V)'s strong hydrolysis, scarcity, and radiological constraints.

Here, we investigate Pa(V) complexes in chloride media using XANES/EXAFS supported by quantum-chemical calculations. Since chloride is a weak ligand, the mono-oxo bond is expected to persist [4], yet no structural data existed for Pa(V)-chloride systems [5]. Our EXAFS analysis of 3 M and 12 M HCl samples reveals two coordination environments and a Pa-O distance of ~1.83 Å, in excellent agreement with theory. This shows that the mono- oxo bond remains stable even under highly acidic conditions. The XANES spectra also display a unique shoulder above the edge, which FEFF simulations associate with the oxo group.

These findings reconcile theory with experiment and provide the first direct structural evidence for Pa(V)-chloride complexes, offering new insight into the coordination chemistry of this challenging actinide [6].

1. M. Mendes, et al. Inorg. Chem. 2010, 49, 9962–9971.
2. T. Shaaban, et al. Chem. Eur. J. 2024, 30 (15), e202304068.
3. H. Oher, et al. Phys. Chem. Chem. Phys. 2023, 25 (14), 10033–10041.
4. T. Shaaban, et al. Chem.l Comm. 2024, 60 (97), 14376–14379.
5. R. Muxart, et al.(1974) Compléments au nouveau traité de chimie minérale. Masson
6. M. Maloubier, T. Shaaban, et al., Angew. Chem. Int. Ed. 2025, accepted.

Destabilization pathway of the $[Pu_6O_4(OH)_4]^{12+}$ cluster in acetate medium

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Understanding the aqueous chemistry of actinides remains a major challenge in both fundamental and applied nuclear science. Actinides speciation controls their solubility, transport, and reactivity, directly impacting key fields such as nuclear fuel reprocessing, long-term waste management, and environmental migration. Under certain chemical conditions, hydrolysis and condensation reactions lead to the formation of well-defined oxo-hydroxo polynuclear species.[1,2] These molecular entities, located at the interface between monomeric complexes and colloidal nanoparticles,[3,4] are essential to describe the early steps of actinide polymerization and the mechanisms governing their transformation into solid or colloidal phases.

Among the structural motifs identified for tetravalent actinides, the hexanuclear $[Pu_6O_4(OH)_4]^{12+}$ cluster is one of the most recurrent. [1, 2, 4–6] This species has been thoroughly characterized and was observed in several ligand environments, notably in the presence of carboxylate donors such as acetate, glycine or DOTA. While numerous spectroscopic studies have reported its formation, the stability and persistence of this molecular species remain uncertain.[2,5,6] A central question is whether this cluster corresponds to a thermodynamically stable entity or to a transient intermediate along the pathway leading to PuO_2 nanoparticles. Resolving this issue is crucial to better understand plutonium behavior under both industrial and environmental conditions.

In this work, we investigate the temporal evolution of the $[Pu_6O_4(OH)_4]^{12+}$ cluster in acetate medium using a multi-technique experimental approach. UV–Vis–NIR spectroscopy and X- ray Absorption Spectroscopy (XAS) allowed to monitor molecular species in solution, while Small-Angle X-ray Scattering (SAXS) measurements provided insights into their size and morphology. Complementary experiments under α-radiolytic conditions were performed to assess the influence of radiolysis on the cluster stability over time.

[1] Knope, K. E. Chem. Rev., 2013, 113 (2), 944–994.
[2] Tamain, C. Chem. – Eur. J., 2017, 23 (28), 6864–6875.
[3] Cot-Auriol, M. Chem. Commun., 2022, 58 (94), 13147–13150.
[4] Sigmon, G. E. Chem. – Eur. J., 2019, 25 (10), 2463–2466.
[5] Chupin, G. Inorg. Chem., 2022, 61 (12), 4806–4817.
[6] McCusker, T. L. CrystEngComm, 2025, 27 (4), 507–515.

Actinide Colloidal Phases and their Impact on Nuclear Waste Management

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Actinide behavior in nuclear waste systems is commonly framed in terms of solubility limits and equilibrium speciation. However, a growing body of evidence demonstrates that actinides, particularly plutonium, readily form persistent colloidal phases under a wide range of chemical conditions relevant to both nuclear waste processing and long-term disposal. These colloidal phases occupy a critical length scale between dissolved species and bulk solids, strongly impacting their chemical reactivity.

This presentation examines the origins and stability of actinide colloidal phases, with a focus on plutonium as a paradigmatic example. After introducing the fundamental pathways of actinide hydrolysis, oligomerization, and nanophase formation, the talk highlights recent observations of plutonium colloid chemistry related to ongoing cleanup efforts in the high- level waste (HLW) tanks at the Hanford site, a former plutonium production site in the US. Under highly alkaline, radiolytic, and chemically complex conditions, plutonium persists in nanoparticulate and colloidal forms [1] that challenge traditional assumptions about the solubility of Pu species directly influencing waste treatment, separations efficiency, and safety considerations.

The discussion then extends to environmental transport at legacy nuclear sites and geological repositories, where evolving geochemical conditions promote the formation of both intrinsic actinide colloids and actinide association with mineral and organic colloids [2]. In these systems, colloid-facilitated transport can decouple actinide mobility from solubility constraints, complicating performance assessment and long-term risk predictions. By linking near-field tank waste behavior with far-field repository processes, this presentation emphasizes that actinide colloids are not system-specific anomalies but a fundamental manifestation of actinide chemistry that needs to be recognized and incorporated into waste management strategies that rely on robust and chemically informed models across the nuclear waste lifecycle.

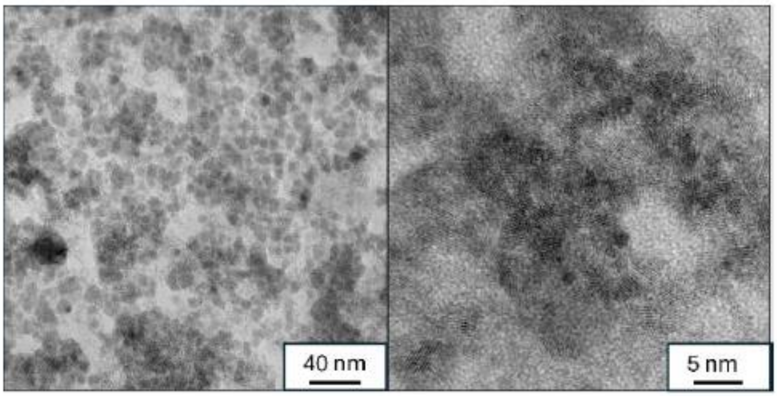

Figure 1: Hydrolytically synthesized PuO_2 Nanoparticles in Solution of NaOH at pH 10, representing similar chemical conditions that are encountered in HLW storage tanks at the Hanford Site.

[1] Delegard, C. H. et al., Chemical Disposition of Plutonium in Hanford Site Tank Wastes; Richland, Washington, PNNL-23468, Rev.1, 2015.
[2] Walther, C. and Denecke M.A. Actinide Colloids and Particles of Environmental Concern. Chemical Reviews 2013, 113.2, 995–1015.

Aging and Oxidation Processes of UO_2 Nanoparticle Materials Under Ambient Conditions Relevant to Interim Storage of Spent Fuel

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Mixed Oxide (MOX) nuclear fuel is a topical nuclear fuel that consists of a mixture of UO_2 and PuO_2 and is used currently to fuel many nations' nuclear energy programs. After extended burnup, the fuel undergoes heterogenization forming what is known as the high burn-up structure (HBS). HBS regions of the fuel exhibit increased porosity compared to UO_2 and occur as nanomaterials. A detailed investigation of these materials regarding their formation and thermal stability is necessary to support use of nuclear fuel and further for its eventual disposal within a final geological nuclear repository.[1] The complexity of spent nuclear fuel (SNF) challenges its direct investigation. Therefore, simplified model systems are prepared and studied to examine single effects in complex systems.

Following this line of investigation UO2 based nanomaterial compounds were synthesized as model materials for HBS SNF, using an adapted hydrothermal method and subsequently investigated in the context of their chemistry in relation to the HBS of SNF.[2] Characterization of the synthesized materials were conducted on fresh materials as well as on samples aged over month in air to investigate the oxidation and aging processes by using powder X-ray diffraction and scanning electron microscopy to respectively determine the material structure and morphology of these nanoparticle materials. High Energy Resolution Fluorescence Detected X-ray absorption near-edge structure (HERFD-XANES) measurements were performed at BM20 at the European Synchrotron Radiation Facility (ESRF), to determine the local structure and redox changes to the nanoparticles. Measurements performed on the U-M4 edge revealed surprising diversity in the U redox states where U^{+4}, U^{+5} and U^{+6} were identified, although the compounds occur as single-phase structure from PXRD measurements. The origin of this unexpected behavior is reckoned to the unique nanostructure of the materials and their ability to form oxidized layers upon air exposure with subsequent chemical transport of U cations. These hypotheses were subsequently tested using extended X-ray absorption near edge structure measurements. The results of this work will be discussed in relation to the chemistry of UO_2 nanomaterials vs. micromaterials in addition to their relevance to HBS nuclear fuel chemistry.

[1] V. V. Rondinella, T. Wiss, Materials Today, Volume 13, Issue 12, Pages 24-32, 2010.

[2] R. Zhao, L. Wang, Royal Society of Chemistry, Volume 16, 2645-2651, 2014.

Synthesis, Formation and Characterization of Chukanovite ($Fe_2(OH)_2CO_3$) and Its Role in the Dissolution of MOX Fuel under Reducing Conditions

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Spent nuclear fuel (SNF), primarily composed of $UO_{2(s)}$, is a major source of concern in the context of geological disposal. Upon canister breach, $UO_{2(s)}$ can undergoes oxidative dissolution, leading to the release of radio nuclides into the surrounding groundwater [1]. The dissolution behavior of $UO_{2(s)}$, is strongly influenced by the redox conditions of the surrounding environment. In reducing environments, the solubility of UO_2 is generally low [2], limiting the mobility of uranium and other actinides. In a deep geological disposal system such as the Swedish KBS-3 concept, each canister intended for spent nuclear fuel contains roughly 14 tonnes of iron, highlighting the critical role of iron in the repository design [3].

Chukanovite ($Fe_2(OH)_2CO_3$), an Fe(II) hydroxy-carbonate mineral, is an important corrosion product formed under anoxic, carbonate-containing conditions relevant to deep geological nuclear waste repositories. Its formation at the waste canister–groundwater interface may influence redox conditions and thereby affect radionuclide mobility. In this study, chukanovite was synthesized under strictly reducing conditions using two precipitation routes. The synthesized material was characterized using different analytical techniques such as XRD,FT-IR spectroscopy, Raman spectroscopy, XPS, SEM-EDX, ICP-OES and chemical analysis.

The results confirmed the formation of pure, crystalline chukanovite in both cases with structural features consistent with the Fe(II) bearing minerals. Distinct vibrational bands corresponding to hydroxyl and carbonate groups were observed in FTIR and Raman spectra, while XPS analysis verified Fe(II) as the dominant oxidation state. SEM-EDX revealed a compact microstructure composed of aggregated solid samples. Thermodynamic evaluation yielded a Gibbs free energy of formation ($\Delta G^o f$) in close agreement with literature values (-1169 to -1174 $kJ \cdot mol^{-1}$), indicating strong stability under reducing, carbonate-rich conditions.

The stability of chukanovite has important implications for long-term repository performance. Its formation can maintain low redox potentials through continuous Fe(II) buffering, thereby limiting the dissolution of spent nuclear fuel (UO_2) and the mobility of actinides such as uranium and plutonium. Future work will investigate the dissolution behavior of unirradiated MOX fuel in the presence of chukanovite to understand the interactions between these phases and important radionuclides under repository-relevant conditions.

[1] D.W. Shoesmith, J. Nucl. Mater. 282 (2000) 1-31.
[2] I. Grenthe, X. Gaona, A. Plyasunov, L. Rao, W.H. Runde, B. Grambow, R.J.M Konings, A.L Smith, E.E Moore, OECD Nuclear Energy Agency Data Bank Eds., OECD publications, Paris, France (2020
[3] Nuclear fuel and waste management Co. (SKB). Technical Report TR-21-02, Svensk Kärnbränslehantering AB (2022).

Investigations Into the Spectroscopic Changes of Actinyls Based on Hydroxide and Nitrate Ligation.

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As nuclear energy mitigates the increase in global energy demands, processing spent nuclear fuel (SNF) efficiently is increasingly more crucial.1,2 Especially relevant when considering waste from nuclear activities such as that stored at U.S. DOE sites, actinide speciation is important and guides the selectivity of the extraction process.3 While on-line and real-time monitoring techniques such as Raman spectroscopy are being prepared for implementation in tank waste processing, complementary techniques such as luminescence spectroscopy for actinyl species, which are important in the nuclear fuel cycle, could add supporting evidence with additional spectroscopic signatures that harness their optical properties.4,5 Herein, the goal of this work is to investigate the changes in luminescence of actinyls based on changes in ligand coordination, nitrate to hydroxide, in the solid-state. By measuring the emission of both ligand to metal and f-f transitions of these species, advancement to fundamental photophysical knowledge as well as application in monitoring and nuclear forensics through completed benchmark studies would be added.5 The far-reaching, scientific motivation of these luminescence studies is to understand actinyl speciation in alkaline conditions as reprocessing SNF in alkaline media could improve the possibility of its reuse in nuclear fuel production.3,6-8 With a rise in pH and increase in hydroxide concentration in tanks, such as those at the U.S. DOE Hanford Site, understanding both actinyl nitrate to hydroxide species is important.7 Using single-crystal X-ray diffraction and measured emission via microspectrophotometer, metal complex structures can be directly compared to their emission spectra. Using ^{238}U, an emission spectrum of a single crystal of $(C_{16}H_{36}N)_2[U_2(NO_3)_4(OH)_2O_4]$ excited at 420 nm shows features associated with typical vibronic progression corresponding to the S11 → S00 and S10 → S0ν (ν = 0-4) electronic transitions (Figure 1).9-10 As the four main maxima 500, 521, 545, and 571 nm show a bathochromic shift when compared to uranyl (VI) nitrate hexahydrate, realizing more benchmark studies can help with fundamental speciation as well as help with interpretation of species in alkaline waste.

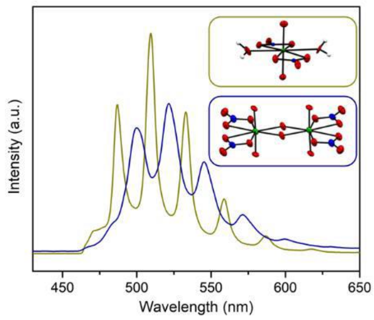

Figure 1: Emission spectra

[1] Nighoskar, A. et. al. Nucl. Eng. Technol. 2025, 57 (1), 103144. / [2] Clayton, R et. al. Clean Techn. Environ. Policy 2025, 27 (2), 665. / [3] Boyarintsev, A. V. et. al. Nucl. Eng. Technol. 2023, 55 (2), 391. / [4] Woodall, S et. a. Chem. Commun. 2015, 51 (25), 5402. / [5] Lines A.M. et. al. 2021. Richland, WA: Pacific Northwest National Laboratory. / [6] Tse, P. et. al. Anal. Chim. Acta 2020, 1107, 1. / [7] Peterson, R. A. et. al. Environ. Sci. Technol. 2018, 52 (2), 381. / [8] Clark, D. L. et. al. Inorg. Chem. 1999, 38 (7), 1456. / [9] Autillo, M.; Wilson, R. E. Inorg. Chem. 2019, 58 (5), 3203. / [10] Brachmann, A. et. al. Radiochim. Acta 2002, 90 (3), 147.

Towards an Understanding of the Behaviour of Ruthenium in the Vitrification of Highly Active Waste: A Study of the Volatilisation of RuO2

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The recycling of spent nuclear fuel is essential for closing the nuclear fuel cycle, allowing recovery of actinides such as uranium and plutonium. However, these processes generate highly active (HA) liquid waste streams that require careful treatment and immobilisation to ensure long-term safety. Among the fission products, ruthenium is of particular concern due to its radioactive isotope ^{106}Ru and its tendency to form volatile species under process-relevant conditions. This volatility, especially during high-temperature steps such as vitrification, poses challenges for containment and environmental protection, demanding a deeper understanding of ruthenium's thermal behaviour and chemical transformations (1, 2).

This study investigates ruthenium dioxide (RuO_2), the predominant and thermodynamically stable form of ruthenium under oxidising conditions, and a key species during HA waste vitrification. Thermogravimetric analysis (TGA) was performed on commercial RuO_2 under nitrogen, oxygen, and air to assess mass loss associated with thermal decomposition, dehydration, and volatilisation. An initial mass loss corresponding to dehydration was observed across all atmospheres, followed by additional mass loss under oxidising conditions, suggesting partial volatilisation through the formation of volatile oxides such as RuO_4.

Post-treatment characterisation using scanning electron microscopy (SEM) and X-ray diffraction (XRD) revealed pronounced recrystallisation and grain growth of RuO_2 upon heating, particularly under inert and air atmospheres. These findings provide insight into the thermal stability and transformation pathways of RuO_2, emphasising the role of atmosphere and temperature in influencing its volatility. Such understanding is crucial for improving vitrification strategies and mitigating ruthenium release during the management of high-level radioactive waste (3).

1. Mun C, Cantrel L, Madic C. Review of Literature on Ruthenium Behaviour in Nuclear Power Plant Severe Accidents. Nuclear technology. 2006;156(3):332-46.
2. Harrison MT. Vitrification of High Level Waste in the UK. Procedia Materials Science. 2014;7:10-5.
3. Shehrbano B, Boxall C, Turner J, Wilbraham R. Towards an understanding of the behaviour of ruthenium during vitrification of highly active waste: A study of the volatilisation of RuO2. MRS Advances. 2025.