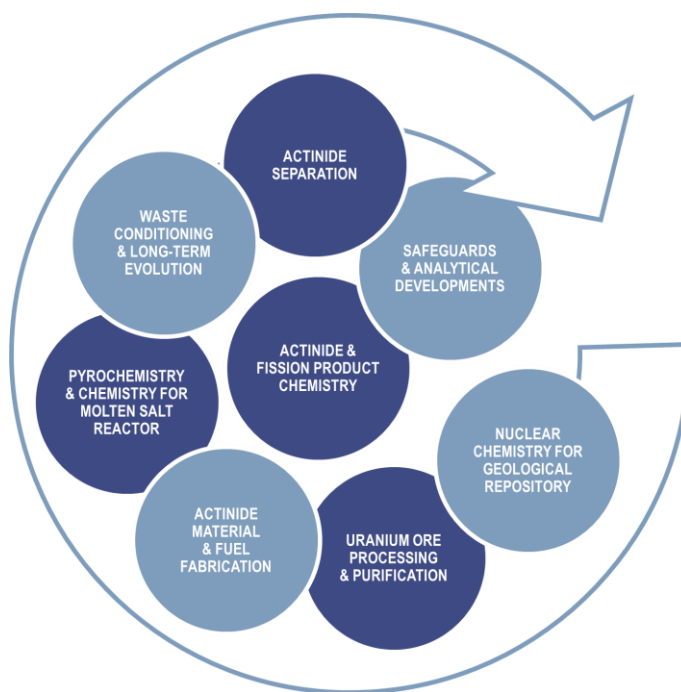


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ACTINIDE AND FISSION PRODUCTS SEPARATION

SEP P01 – Conception, Synthesis and Evaluation of New Extractants Systems for Rhodium Valuation

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Rhodium is widely used in catalysis and particularly in automotive industry. Its rarity (1 ppb in earth's crust), its industrial demand and its high cost reaching 140000 €/kg^a at the end of 2023 makes it a critical metal. Spent Nuclear Fuel (SNF) contains valuable resources that remain currently unexploited. Throughout the irradiation of nuclear fuel, the fission of uranium (²³⁵U) and plutonium (²³⁹Pu and ²⁴¹Pu) yields elements of significant interest, such as platinoids and includes rhodium. Among these elements, approximately 500 kg/year of rhodium are generated in SNF almost entirely as its stable isotope (¹⁰³Rh). Despite being currently considered as a nuclear waste, the rhodium accumulated in SNF could become a valuable resource. Because of the presence of a large part of elements from the periodic table in SNF and the chemical properties of rhodium in nitric acid media, its selective recovery from SNF remains a challenge. This project aims to propose a selective recovery process of rhodium by either solvent extraction or solid phase extraction processes. Numerous classes of extractants have been reported in the literature^b, such as phosphonic acids, sulfurs or ammoniums compounds as shown in Figure 1.

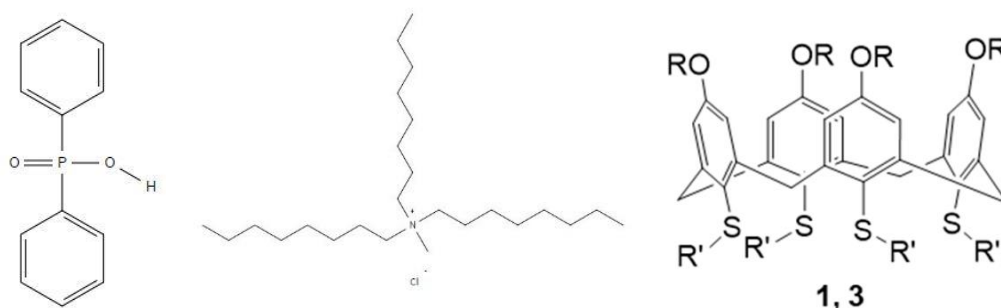


Figure 1 : Examples of various classes of extractants for the Rh extraction (left: diphenylphosphinic acid DPPA, middle: Aliquat 336, right: calix(n)arenethioethers)

Figure 1 presents three extractants used in solvent extraction, arranged in ascending order of performance, from the least effective on the right to most effective on the left. Firstly, Phosphonic acids such as DPPA do not extract rhodium whatever the conditions. Secondly, ammonium salt like Aliquat 336 displays good extraction performances with the recovery of almost all the rhodium. However, the extraction must be carried out at low temperature to be optimal (9°C). Lastly, calix(n)arenethioethers exhibits the best performance. However, this extractant has drawbacks such as: its slow kinetics of extraction, its difficult synthesis, and the difficulty in optimizing desirable extraction conditions. Differences in rhodium extraction performance of these molecules can be explained by the HSAB principle. Indeed, rhodium is neither a soft nor a hard acid making it difficult to extract. DPPA (phosphonic acid) and Aliquat 336 (quaternary ammonium) are hard bases whereas calix(n)arenethioethers (sulfur and ether) are mixed hard and soft bases. Thus, it could be interesting to design new extractants combining a mix of HSAB hard and soft bases either for solvent or solid phase extraction processes. The challenge lies in ensuring the compatibility of these molecules with industrial processes (nitric acid media, acidity, rhodium concentration, temperature...). This research is part of the PREPAC project (recovery of platinoids in SNF) and aims to synthesize new extractants for the selective recovery of rhodium and to compare the extraction results acquired by either

^a « Rhodium price | Umicore Precious Metals Management ». Accessed on 01/12/24

^b Hodgson, Turner, et Holdsworth, « A Review of Opportunities and Methods for Recovery of Rhodium from Spent Nuclear Fuel during Reprocessing ».

solvent extraction or solid-phase extraction. Additionally, it will present various experimental conditions for rhodium extraction.

SEP P02 – The CoXTL Concept: an Alternative Solution to Nuclear Fuel Recycling through Hexavalent Actinide Co-Crystallization

Jeffrey D. Einkauf¹, Jennifer M. Pyles², Luke R. Sadergaski³, Laetitia H. Delmau³,
Bruce A. Moyer¹, and Jonathan D. Burns²

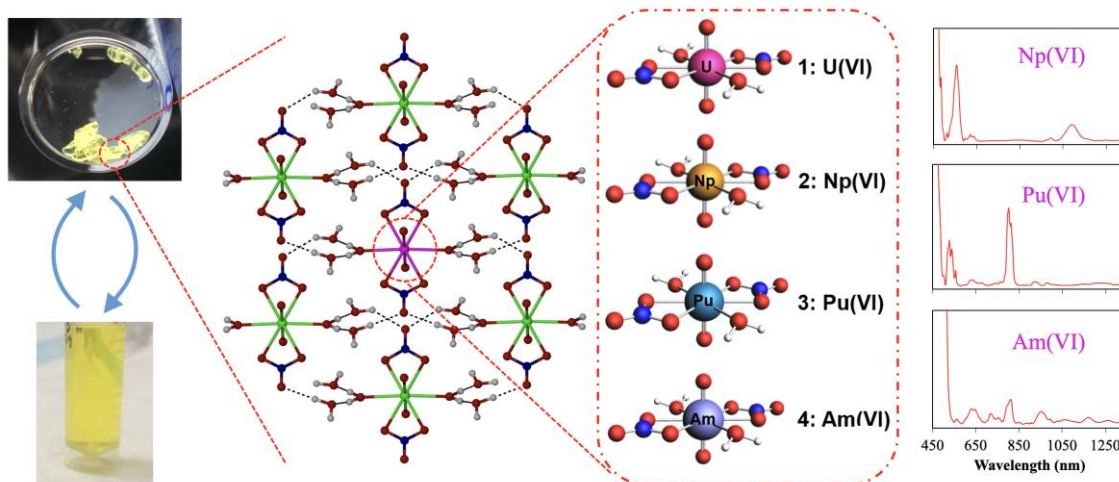
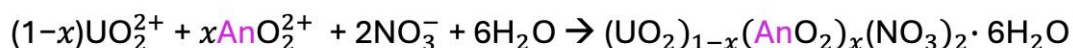
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An alternative approach to nuclear fuel recycling appears possible using crystallization. To enable sustainable nuclear power, several challenges need to be addressed. One of the main challenges is developing a separation/recycling scheme for used nuclear fuel that enhances the recovery of the U, Pu, and other actinide (An) species. Sequentially, the ideal separation process should minimize the impact of waste bound for a geological repository, maintain nonproliferation standards, and have the ability to scale the process for a diverse fleet of reactor fuels.

The CoXTL concept aims to develop a single-step separation technology for the recovery of actinides ranging from U to Am as a group using a co-crystallization method with uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Recent studies have shown the transuranic species in their hexavalent state—Np(VI), Pu(VI), or Am(VI), which exist as the dioxo actinyl molecular ions, AnO_2^{2+} —have near proportional removal from solution to that of U(VI). The co-crystallization approach has extremely high selectivity for the An(VI) species while completely discriminating against fission products, including problematic species such as Zr, Mo, Tc, and Ru. Aspects of the separation of the hexavalent actinides from fission products will be discussed, including the scale-up of this process to the 100 g scale. These experiments will be analyzed by ultraviolet-visible spectroscopy and inductively coupled plasma mass spectrometry to determine the separation of each element.



SEP P03 – Influence of Pu(IV) and Pu(VI) on the Extraction Properties Of Anion Exchange Resins

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Anion exchange in nitric acid is a process used to purify plutonium from metallic impurities. The process is based on the selective extraction of the anionic hexanitrate complex $[\text{Pu}(\text{NO}_3)_6]^{2-}$ formed at high concentrations of nitric acid.

The principle of this anion exchange method is based on the fact that plutonium forms anionic species at high nitric acid concentrations, whereas the other elements, such as americium, do not form such anionic complexes. However, Pu(VI) can be present in the feed solution. This oxidation state may perturb the purification process, as Pu(VI) species cannot be fixed by the resin.

In the present study, lab scale investigations were carried out to qualify the purification of an aged Pu nitrate solution in the frame of facility dismantling preparation operations. Pu(VI) was observed by spectrophotometry in the solution before (a) and after (b) ion exchange for Am/Pu separation (figure 1).

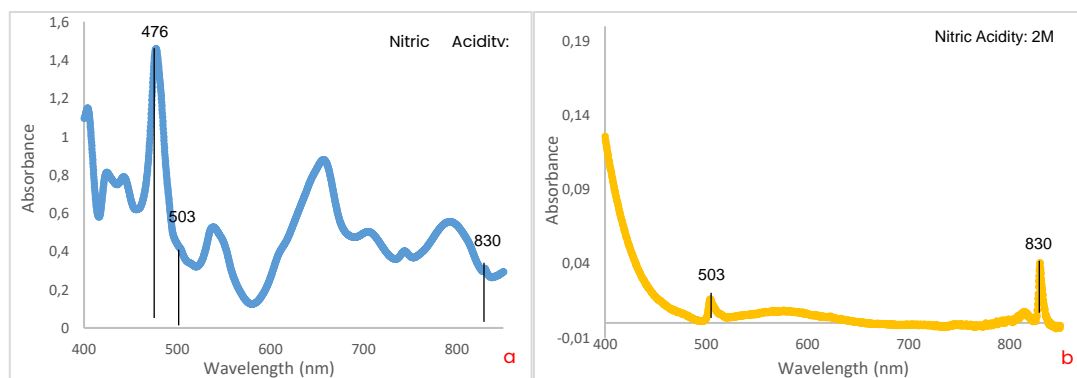


Figure 2 : Absorption spectra of a solution before Am/Pu separation (a) and effluent generated by separation process with anionic resins (b) (Wavelength: 476 nm: Pu(IV), 503 nm: Am, 830 nm: Pu(VI))

These results confirmed that presence of plutonium within the effluents was mainly due to Pu(VI). Consequently, hydrogen peroxide was added to the solution to reduce Pu(VI) to Pu(IV). Finally, this oxidation state adjustment restored the anion exchange separation selectivity leading to a considerable reduction of the plutonium concentration within the effluents.

SEP P04 – Extraction and Speciation Study Of Plutonium(IV) And Technetium(VII) Coextraction with N,N-Dialkyl Amide

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In the objective to multicycle the plutonium contained in spent fuel, it is necessary to design new recovery and separation processes. In this framework, new liquid-liquid extraction processes are under investigation to separate and recover uranium and plutonium from irradiated MOX. N,N-dialkylamides are considered as alternatives to tributylphosphate (TBP) due to their ability to extract uranium from nitric acid, their tunable selectivity for uranium(VI) versus plutonium(IV) and fission products by modifying their alkyl chain, their complete incinerability (only composed of CHON elements) and the nature of their radiolysis and hydrolysis products with acceptable robustness.[1,2]

Among the fission products generated by irradiation of nuclear fuel, the technetium is a long-lived radioelement. ⁹⁹Tc is the major isotope with a lifetime around 2.1×10^5 years. During the dissolution process of irradiated fuel in nitric acid, technetium is produced at the oxidation degree +VII. The Tc(VII) is in its anionic form, the pertechnetate TcO_4^- , which can enter into the composition of organic complexes with highly extracted elements.

Previous works demonstrated that technetium(VII) is coextracted with uranium(VI) by TBP or N,N-dialkylamides.[3,4]. The increase of the distribution ratio in presence of Tc(VII) was explained considering the formation of mixed uranium-technetium species with a general formula $\text{UO}_2(\text{TcO}_4)(\text{NO}_3)_x$ in which pertechnetate anion coordinate the uranyl cation in the inner coordination sphere. To deepen the understanding of technetium behavior in presence of plutonium, and establish thermodynamic models for simulating the extraction properties, it is important to investigate the technetium speciation in the presence of plutonium.

The goal of this work is to study the extraction of technetium in presence of plutonium in nitric acid medium by N,N -dialkyl amide. First, distribution ratio measurements for technetium were performed under various Pu/Tc molar ratios and nitric acid concentrations. The results showed a link between the extraction of technetium and the plutonium concentration as shown in (Figure 1(A)).

Then, organic phases after contact with aqueous phases containing Pu(IV), Tc(VII) or a Pu(IV)+Tc(VII) were characterized by various spectroscopic techniques and mass spectrometry. The speciation of complexes highlights specific interactions between Pu^{4+} and TcO_4^- as shown for example in the NMR spectra presented Figure 1 (B).

By combining molecular speciation and extraction data, the stoichiometry of organic complexes involved in the extraction equilibria was proposed. These data allowed the establishment of a thermodynamic model for the extraction of Tc(VII) in the presence of Pu(IV), simulating the extraction properties.

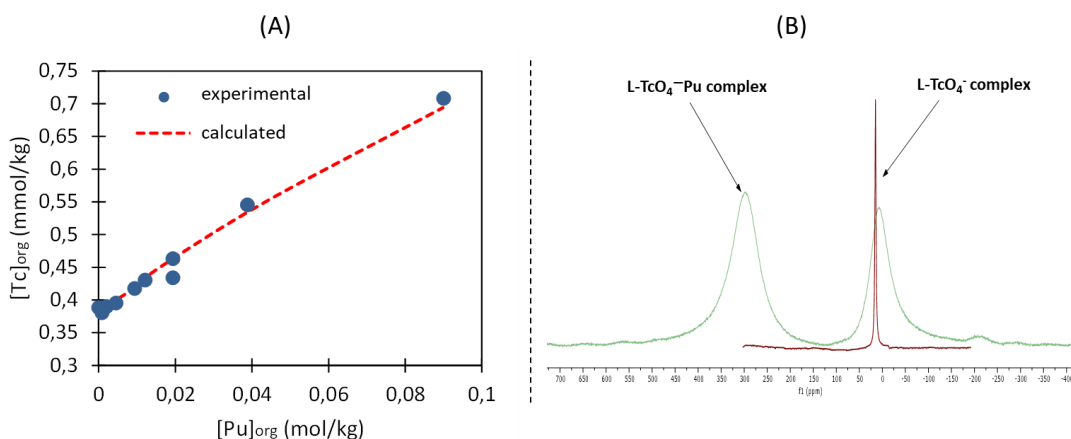


Figure 3: (A) NMR ^{99}Tc spectra for an organic phase containing only Tc(VII) (red spectrum) and Tc(VII)+Pu(IV) (B) experimental and calculated $[Tc]$ (mmol/kg) vs. $[Pu]$ (mol/kg) in organic phases obtained by extraction experiments from aqueous solution with various Pu/Tc molar ratios.

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SEP P05 – Exploration of Alkaline Processing of Spent Nuclear Fuel

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The notion of processing spent nuclear fuel (SNF) in alkaline media has been investigated in several different countries over the last three decades.¹⁻⁵ This interest stems from the potential advantages in avoiding the hot nitric acid dissolution step and the complications associated with it; e.g., equipment corrosion, complicated off-gas treatment, etc. The previously proposed alkaline processing schemes for SNF rely on the dissolution of the fuel in carbonate/hydrogen peroxide media. One of the limitations is the relatively low solubility of uranium under such conditions, compared to what can be achieved by dissolution in nitric acid. Processing of such dilute solutions—typically less than 0.25 M U—would require larger processing equipment or reduced throughput compared to traditional acid-based SNF processing; both of which would adversely impact the economic viability. For this reason, we focused our initial explorations of this subject on the alkaline dissolution step itself, with the aim of producing more concentrated alkaline uranium solutions.

We also assumed in our study that the SNF might be pretreated *via* voloxidation to remove tritium and potentially iodine prior to dissolution. Thus, starting uranium oxide materials included UO_2 , $\alpha\text{-U}_3\text{O}_8$, and UO_3 (both γ and ϵ polymorphs). A systematic scoping study was conducted to identify the nature and concentration of a carbonate solution matrix most promising for the dissolution of SNF. The following characteristics were considered: (1) the relative rate of dissolution, (2) capacity of the dissolver solution for uranium, (3) stability of the solution against precipitation, (4) kinetics of conversion to the uranium(VI) *tris*-carbonato complex upon decomposition of peroxide, and (5) precipitation of uranium(VI) *tris*-carbonate complex with time.

Four systems were initially compared: (i) $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2$, (ii) $(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2$, (iii) $(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2 + \text{urea}$, and (iv) $(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2 + \text{guanidine carbonate (GC)}$. In comparing these four systems, the following variables were kept constant: (a) the uranium source was UO_2 , (b) the UO_2 -to-solution ratio set to yield 0.3 M U upon complete dissolution, and (c) the initial H_2O_2 concentration was 1.6 M. The $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2$ system was found to have favorable dissolution kinetics with 98% of the uranium dissolved after 4 h with 1.0 or 1.25 M Na_2CO_3 . The solutions were found to be very stable with respect to precipitation, with no precipitate observed after standing for 20 days. However, the addition of sodium to the system and the persistence of uranium(VI) peroxy and peroxocarbonate species were viewed as potential disadvantages of the $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2$ system. The sodium addition would ultimately become a waste issue, whereas the persistent uranium(VI) peroxy and peroxocarbonate species could potentially complicate subsequent separation steps.

$(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2$ was less effective than $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}_2$ in dissolving UO_2 , and this system was plagued by formation of gel-like precipitates. The addition of 1 M urea to the $(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2$ solutions did not remedy the precipitate formation, with a dense foam formed in all cases. On the other hand, addition of 0.5 M GC to the $(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_2$ system yielded a favorable dissolution medium. Essentially quantitative dissolution of UO_2 was achieved within 4 h with 1.25 or 1.5 M $(\text{NH}_4)_2\text{CO}_3 + 1.6 \text{ M } \text{H}_2\text{O}_2 + 0.5 \text{ M GC}$. The uranium(VI) peroxy and peroxocarbonate species were unstable in the latter system, with ultimate conversion to $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. The $(\text{NH}_4)_2\text{CO}_3/\text{H}_2\text{O}_2/\text{GC}$ system was chosen for further development.

A series of experiments was performed in which UO_2 was dissolved in $(\text{NH}_4)_2\text{CO}_3/\text{H}_2\text{O}_2/\text{GC}$ with varying concentrations of $(\text{NH}_4)_2\text{CO}_3$ and GC. The initial H_2O_2 concentration was set at 2.0 M in these experiments and the target uranium concentration was 0.5 M. Results from these experiments indicated solutions with 1.25 to 1.5 M $(\text{NH}_4)_2\text{CO}_3$ and 0.75 to 1.0 M GC were effective at dissolving UO_2 with complete dissolution achieved within 3 h. The resulting solutions were stable towards precipitation. In contrast, it was found that dissolution of $\alpha\text{-U}_3\text{O}_8$ in the $(\text{NH}_4)_2\text{CO}_3/\text{H}_2\text{O}_2/\text{GC}$ system was much less effective with only about 50% being dissolved over a two-day period.



Figure 4. Solutions prepared by dissolution of UO_2 in 0.75 – 1.5 M $(\text{NH}_4)_2\text{CO}_3$, 1 M $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ and 1.6 M H_2O_2 [increasing in $(\text{NH}_4)_2\text{CO}_3$ concentration from left to right]; photographs taken at 22 h after preparation.

Dissolution experiments were performed for $\gamma\text{-UO}_3$ with and without H_2O_2 present. It was hypothesized that because the uranium is already present in the +6 oxidation state in UO_3 , the H_2O_2 oxidant is unnecessary in this case. However, poor dissolution in 1.5 M $(\text{NH}_4)_2\text{CO}_3$ + 1.0 M GC was achieved without H_2O_2 present. Addition of 2 M H_2O_2 dramatically improved the dissolution of $\gamma\text{-UO}_3$. Similar behavior was observed with $\varepsilon\text{-UO}_3$, with and without doping with non-radioactive fission product elements.

In summary, an alkaline dissolving medium consisting of ammonium carbonate, hydrogen peroxide, and guanidine carbonate has been developed for dissolving uranium oxide phases. Effective dissolution of UO_2 and UO_3 in this medium has been demonstrated, however U_3O_8 is only partly dissolved. Uranium concentrations double that normally achievable in carbonate/hydrogen peroxide systems can be achieved.

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SEP P06 – Controlled Precipitation of Actinides in a Complex Organic Phase

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The reprocessing steps of uranium oxide (UO_x) 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, 4]. However, very few studies report the co-precipitation directly in the organic phase. This study focuses on the development of a selective actinide precipitation (U and Th) from a loaded organic phase (Extractant = TBP or mono-amide). This work is devoted to obtaining various porous organic/inorganic hybrid materials (Metal organic Frameworks, MOF) with well-defined structures by varying the organic linker (**Erreur ! Source du renvoi introuvable.**). These linkers possess the advantage of being composed of only CHON atoms. Thereby, all of the linker elements can be released by the annealing step except for carbon. However, even though contributing to the structure contamination, its quantity remains relatively low. The MOF's morphology can be preserved^[5] upon thermal conversion to the actinide oxide form. This represents an advantage in nuclear fuel precursor design. In the end, this study has focused on the direct precipitation of actinides in the organic phase, enabling a one-step gain over the PUREX process.

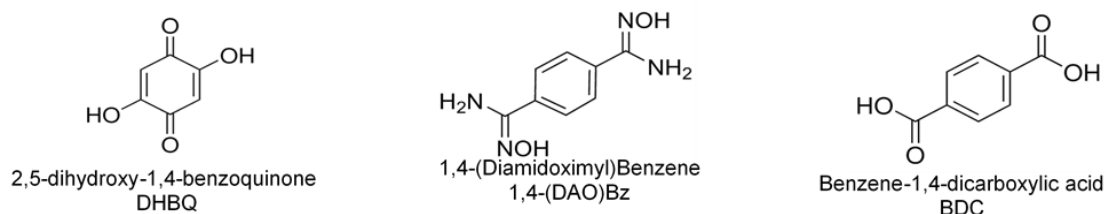


Figure 1: Organic linkers used

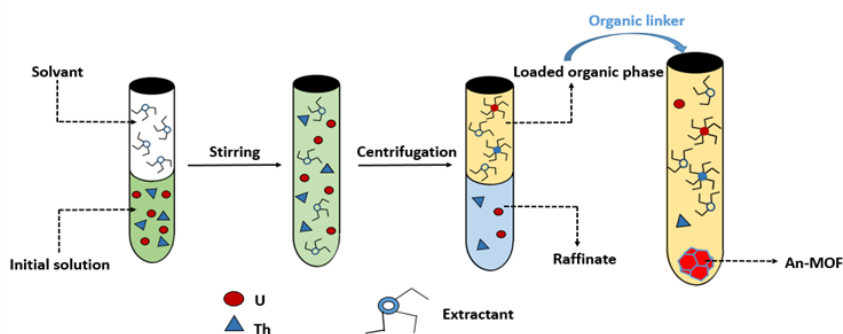


Figure 5: Schematic diagram of experimental method

The entire experimental procedure was carried out for separate U(VI) and Th(IV) systems, but also for mixed uranium and thorium system. Aqueous solutions and organic solutions were firstly mixed. In the former, the solutions were composed of

uranium and/or thorium dissolved in HNO_3 . In the latter, the organic solutions were composed of pre-equilibrated TBP/*n*-dodecane or mono-amide. The raffinate solutions were analysed using ICP-OES in order to determine U (VI) and Th(IV) concentrations in the loaded phase. In this way, different quantities of linkers can be introduced, enabling different molar ratios with the actinides (1:1 – 1,5:1 – 2:1) (**Erreur ! Source du renvoi introuvable.**). The resulting precipitates (An-MOF) (**Erreur ! Source du renvoi introuvable.**) underwent chemical, morphological and structural analyses before and after the thermal conversion and sintering steps.

Preliminary results, on the direct uranium precipitation in the organic phase by DHBQ linker revealed interesting structures and morphologies. In fact, depending on the experimental conditions, different morphologies can be observed (**Erreur ! Source du renvoi introuvable.**).

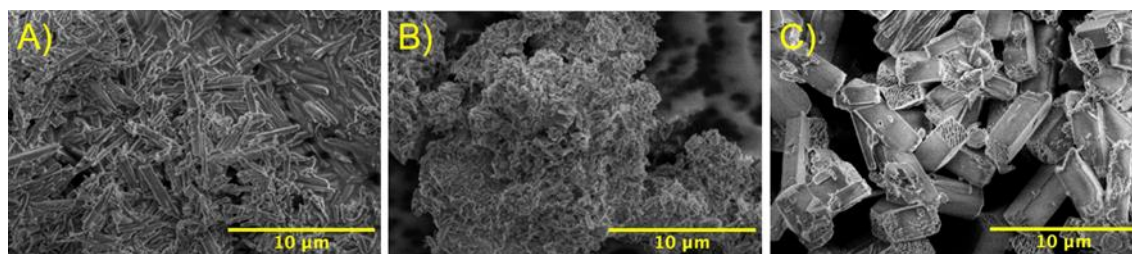


Figure 6 : SEM pictures of the different U-MOF morphologies obtained from the organic phase using DHBQ in different conditions

Moreover, regardless of the solvent used to dissolve the linker, a certain crystalline phase is always observed (Figure 7). This underlines the modularity of the material morphology compared to the experimental procedure. Thus, illustrating another advantage that this process displays for the nuclear fuel reprocessing.

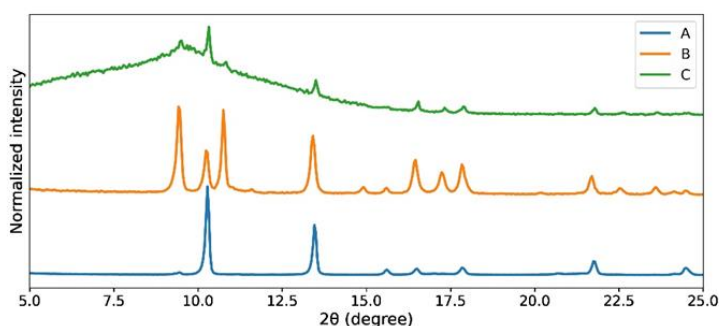


Figure 7 : X-ray diffraction patterns of U-MOF obtained from the organic phase using DHBQ in different conditions

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SEP P07 – Developing a Process to Decontaminate Effluent and Recover Uranium and Plutonium

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Nuclear research and development facilities produce effluents containing alpha radioelements, which must be eliminated before being released. Applied to Atalante effluents, a solid-phase extraction decontamination process has been developed, with the additional aim of recovering purified materials of interest (U and Pu), which can be recycled within the facility.

A first silica column impregnated with DHOA is used to quantitatively fix U and Pu, while a second silica column impregnated with TEHDGA is dedicated to the co-fixation of americium and curium. A third silica column impregnated with MDDDMBA is designed to decontaminate the plutonium into uranium from the eluate of the first DHOA column. The process recovers an alpha-decontaminated effluent, a uranium flow, a plutonium solution and an americium-curium flow. The design also takes into account the need to minimize the volume and acidity of the solution generated.

The process has been tested at an intermediate activity level (using U, Pu and Am) on a laboratory scale. Large-scale tests on genuine solutions are scheduled for 2024.

SEP P08 – Commercializing Isotope Recovery from UNF Recycling and Transmutation

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There are >90,000 tons of used nuclear fuel (UNF) in temporary storage at nuclear power plants across the United States. Every year, this number keeps rising. And despite being considered a waste, UNF represents a significant untapped opportunity to not only secure industrial radioisotope independence, but also mine for critical elements.

SHINE Technologies, LLC (SHINE) is leading a venture to address the nation's UNF disposal challenge by developing a game-changing set of interlinked technologies that reduce the environmental and economic impact of nuclear energy generation via recycling and, ultimately, transmutation of UNF. A key factor for this initiative is SHINE's focus on recovering as many value-added radioactive and stable isotopes as possible for commercial sale. The overall approach will help a) reduce the longevity, heat, and long-term radiotoxicity of high-level waste, b) improve reprocessing economics via value-added isotope extraction, and c) advance technologies to enable fusion energy generation. SHINE is leveraging design, construction, and operational experience gained from the development of first-of-its kind medical isotope (Mo-99) production facility to design an end-to-end UNF processing, recycling, and transmutation system.

SHINE is designing a comprehensive extraction facility to fractionate UNF into U, U/Pu, Np, minor actinides (MA, e.g., Am and Cm), lanthanides, and fission products (FPs). This is a critical step in the larger effort to reduce the volume of high-level waste in storage and includes tangible progress towards implementing a cost-effective transmutation system. Table 1 provides a list of the targeted isotopes and elements for separation, along with the rationale for that capture.

Table 1. Recoverable isotopes/elements of interest for the envisioned UNF recycling facility, along with their key application.

Isotope/Element	Reason for Capture
U/Pu	LWR or HALEU fuel
U	LWR fuel (after re-enrichment)
Np-237	Pu-238 production (radio-battery)
Kr-85	Industrial applications
T ₂	Fusion fuel
C-14	Agricultural/research applications
Ce	Industrial applications
Pr	Industrial applications
Nd	High Temp Superconductors
Cm-244	Radio-battery applications
Am-241	Industrial applications
Ra-226	Medical isotope production
Rh, Ru, Pd	Industrial applications
Sr-90	Radio-battery applications
Y-90	Medical isotope
Cs-137	Industrial applications
Pm-147	Radio-battery applications

The synergy between reprocessing and transmutation technologies enables a holistic solution to the used fuel disposal challenge, and the cost effectiveness of the enhanced liquid-liquid separation system and final disposal forms is key to commercialization.

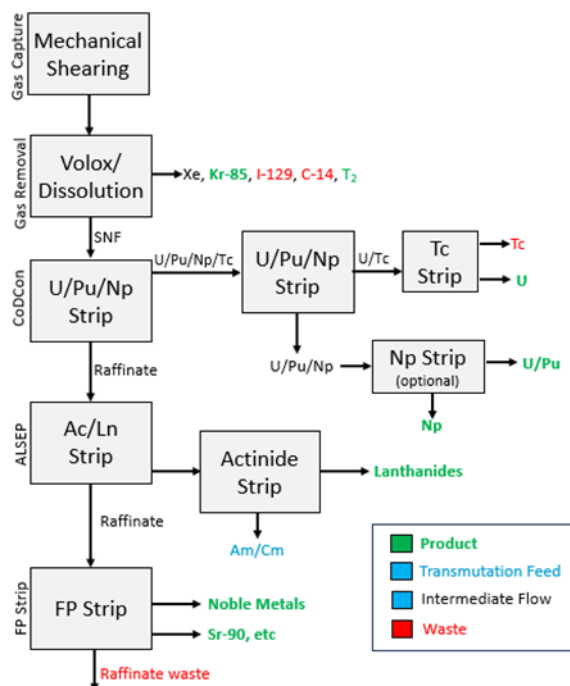


Fig. 8 High-level process flow in SHINE recycling facility

A high-level view of the envisioned separation process is provided in Fig. 1. The separation process will begin with conventional shearing of fuel rods to expose the fuel pellets. The resultant pellets and hulls will be subjected to a voloxidation process to remove volatile radionuclides from the process stream. This material will then be dissolved in nitric acid, clarified of particulate matter, and moved into a modified PUREX-type separation process to generate U+Pu and U output streams. The primary output of this step is moved to an Actinide-Lanthanide Separation (ALSEP) process to isolate the minor actinides for transmutation. Additionally, the lanthanides are segregated in this step, some of which may be value-added products. The raffinate from the ALSEP process is sent to a final fission product capture step, where valuable stable and radioactive elements are harvested. Sr-90 and the platinum group metals are of particular interest for separation due to their value. The remaining raffinate is packaged as waste, either via vitrification or cementation depending on the final waste categorization.

A key objective of SHINE's commercialization strategy is to bring UNF recycling with isotope recovery to market on an aggressive timeline. As such, a recycling process based on state-of-the-art liquid-liquid extraction (LLE) technology has been chosen as the core separation strategy. SHINE investigated alternate separation approaches and concluded that LLE is most likely to be operationally viable within five years since it: a) is demonstrated commercially and at scale, i.e. high technology readiness level; b) has robust supply chain for equipment; c) has partners from across industry and the national labs who will support this proven technology, and who have already invested time and effort in proving out; d) has sufficient support from industry stakeholders, investors and public. SHINE believes the coupling of key improvements in LLE with targeted extraction of radioisotopes and stable elements with commercial value can make this approach to UNF recycling significantly more attractive on a techno-economic basis. When ultimately coupled with a transmutation concept, the holistic recycling/transmutation concept will provide a broad spectrum of valuable isotopes and dramatically reduce waste volume that needs to be stored for geologic timeframes.

SEP P09 – Industrial Manufacturing Process of AmO₂ Powder from a Pu Solution: Separation, Conversion and Calcination

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After irradiation of the fuel, many radionuclides are found in the spent fuel that is reprocessed at the La Hague plant, throughout the activities of recycling.

The major part, composed of U and Pu, can be reused to make new fuel. Up to now, fission products and minor actinides (such as Americium) are remaining and considered as wastes either to be dissolved in glasses for long time storage [1] (both minor actinide and fission products) or burnt in future reactors [2] (only for minor actinides). Nowadays, some technological applications are under development that might require small quantities of Americium powder like neutron sources [3] or high quantities like autonomous power generators for Earth and space [4]. To explore these new technologies, Orano is developing an industrial process to obtain AmO₂ powder from aging plutonium oxide stored at La Hague. Using the solution obtained from the already existing Unit for Plutonium Redissolution at the La Hague plant, the first step of the process is the separation of the Americium from the solution. Then, this solution is converted into an oxalate precipitate, and finally calcined to form the dioxide powder.

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SEP P10 – Study of Ruthenium and Palladium Transfer Kinetics and Optimization of Waste Nuclear Fuel Separation Process

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Liquid-liquid extraction serves as a fundamental separation technique in the processing of spent nuclear fuel through the PUREX (Plutonium-Uranium Reduction Extraction) process. In this method, uranium and plutonium are separated and purified using tri-n-butyl phosphate (TBP) as an extractant, diluted in hydrogenated tetrapropylene (TPH). However, the extraction of ruthenium, although being weakly extracted by TBP, is problematic. Ruthenium contributes to beta-gamma emissions and constitutes 7 to 9% of the total mass of fission products^[1], posing a challenge in the treatment process. In addition, palladium, another fission product generated during nuclear fission, is extracted enough to disturb also the PUREX process^[2].

Monoamides have been explored as an alternative to TBP because they are incinerable, reducing the volume of secondary waste, and enable the separation of Pu(IV) from U(VI) without the need for redox reactants^[3]. The development of liquid-liquid extraction processes necessitates a deep understanding of the thermodynamic performances of the extracting system and precise kinetics data. While process schemes traditionally rely on equilibrium data, the kinetics of mass transfer are typically studied and optimized afterwards.^[4]

Our studies involving two monoamides, namely N-methyl, N-octyl ethylhexanamide (MOEHA) and di-2-ethylhexylbutyramide (DEHBA), aim at determining the mass transfer kinetics of ruthenium and palladium from nitric acid solutions. The investigation has focused on the influence of solutes and extractant concentrations, nitric acidity, and the nature of the extractant structure on the kinetics of extraction. Results have been used to understand the effect of the monoamides' structure on the extraction kinetics of ruthenium and whether chemistry or diffusion processes control the kinetics.

The determination of the global transfer constants from aqueous to organic phase of these metals with each extractant was performed using the single drop technique. Various analytical techniques, including infrared spectroscopy, Raman spectroscopy, and ICP-OES, have also been employed to assess the influence of the extractant on ruthenium speciation and the distribution coefficient ratio of ruthenium.

The outcomes of these studies will provide insights into the relationship between mass transfer kinetics, the ion/extractant system, and the molecular phenomena occurring in each phase during the transfer process, paving the way for advancements in liquid-liquid extraction processes and for the optimization of the handling of ruthenium and palladium in the fuel cycle.

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SEP P11 – The Effect of Phosphonates on Lanthanide Separation for Surface-Grafted Porous Zirconia

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Lanthanides exhibit a variety of photophysical, magnetic, and nuclear properties that offers the possibility of a wide range of applications. However, their effective utilization requires elaborate separation and preconcentration due to their presence in trace amounts in nature. Lanthanide separation is also important in terms of the nuclear cycle of 4th generation power reactors since lanthanides are often found in nuclear waste as a mixture of actinides. Successful separation of lanthanides may allow effective transmutation of certain actinides and long-lived fission products, which is considered a feasible method to reduce the volume and radiotoxicity of the waste, offering new technical options for the next nuclear power generation and the recycling of nuclear fuel. Despite these potential benefits, the separation of individual lanthanides is very challenging due to their similar physicochemical properties.

The successful application of inorganic-organic hybrid materials for the separation of f-block elements has been demonstrated, owing to their synthetically alterable morphology and coordination selectivity. This study investigated the effect of phosphonate groups on selective lanthanide sorption across a series of hybrid materials.

Hybrid materials were synthesized by attaching functional ligands with an increasing number of aminomethylenephosphonate groups (Fig.1) to a porous zirconia matrix via post-synthetic grafting. Successful surface grafting was confirmed using FTIR and ³¹P MAS-NMR spectroscopies. Additionally, deconvolution of peaks of ³¹P MAS NMR spectra confirmed the presence of “free” phosphonate groups within the attached ligands, plays a major role for the Ln sorption.

pH dependence of lanthanide uptake was studied in batch mode using a radiotracer method, with stable Lu(NO₃)₃ solution and ¹⁷⁷Lu tracer. Intra-lanthanide selectivity was assessed in both batch and column mode using MP-AES. All synthesized hybrid material clearly showed uptake of Lu³⁺ at lower pH region (about 100 μmol/g at pH 3). The material grafted with a longer ligand exhibited higher selectivity, with materials grafted with longer ligands showing enhanced selectivity (Fig. 2). For instance, the one with the longest ligand (SG85-TTHMP) demonstrated a high separation factor of 87.4±9.8 for Lu³⁺ over La³⁺. Selectivity was particularly obvious for heavier lanthanides than for middle-sized ones, which is assumed to be a result of increase of ion-dipole interaction due to lanthanide contraction, hydration coordination change, and tetrad effect (stabilization caused by configuration of 4f electron shell). Fixed-bed column experiments also showed the materials' favored uptake of Lu³⁺ over La³⁺ at pH 3. Notably, the materials exhibited promising reusability, with only partial (~30%) uptake decrease observed after five loading-eluting cycles, indicating their applicability to actual separation settings.

In conclusion, our study demonstrated that hybrid materials composed of a porous zirconia matrix and organic ligands with a greater number of phosphonate groups realized higher selectivity and stability, which provides valuable insights into the selection of organic ligands for hybrid sorbent synthesis and offer promising strategies for advancing lanthanide separation techniques.

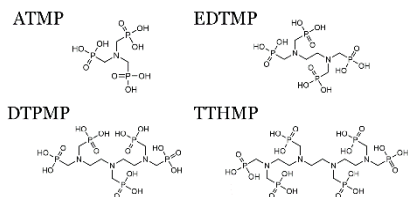


Fig. 1. Structure of functional ligands.

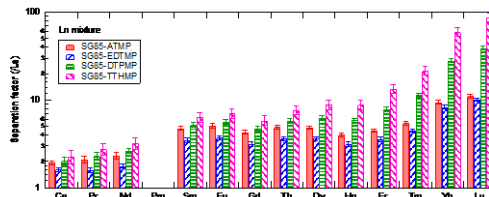


Fig. 2. Separation factors for La over other lanthanides

SEP P12 – Uranium(VI)/Plutonium(IV) Separation from Mixed Oxide Spent Nuclear Fuels Using a Single Monoamide Extractant

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In the framework of plutonium multi-recycling, a new N,N-dialkylamide extractant for mixed oxide spent nuclear fuels reprocessing is proposed instead of TBP currently used in the PUREX process. This new solvent extraction process allows extraction and purification of uranium and plutonium towards the fission products in one single cycle without redox. Indeed, after uranium and plutonium extraction from concentrated nitric acid solution, plutonium is selectively back extracted by decreasing the acidity of the aqueous phase whereas, in the PUREX process, selective plutonium back-extraction is achieved by reducing the plutonium oxidation state, using reducing agent and nitrous scavengers.

Therefore, monoamide process is easier and safer to operate because plutonium is in a stable oxidation state through all the process. This new process will be more suitable for the recovery of plutonium from spent LWR MOX and then from FR MOX fuels in which Pu/U ratio will be higher than in current fuels.

Beforehand, batch experiments were performed to study the behaviour of water, nitric acid, uranium(VI), plutonium(IV) and some fission products towards their extraction by this monoamide to determine extraction isotherms. Experimental distribution data are described with a physicochemical model which is integrated into the CEA-Orano PAREX+ code. It was used to find the correct flowsheet to obtain uranium and plutonium at very high purity and to achieve considerable recovery efficiencies.

Then, four pilot tests, using mixer-settlers, were successfully performed with this extractant.

The first test was conducted with a surrogate feed representative of MOX fuels (Pu/U=10%) in alpha-shielded line (ATALANTE facility) to confirm the uranium/plutonium partition feasibility and compare experimental data with calculated values obtained with the PAREX+ code.

Afterwards, this flowsheet was applied to the treatment of actual high activity solutions in the CBP hot cell (ATALANTE facility).

Recovery ratios (99.6%), purity rate and decontamination factors ($\sim 10^5$) were achieved in accordance with formal requirements.

These successful tests allow to pursue the development of this process and scaling up flowsheets for industrial purposes.

SEP P13 – Safety Assessment of the TEHDGA– Impregnated Silica–Based Adsorbent for Extraction Chromatography

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The management of high-level radioactive waste (HLW) generated after spent fuel reprocessing is an important issue for nuclear fuel cycle. One of the advanced technologies to reduce the volume of radioactive waste and radiotoxicity is the partitioning and transmutation (P&T) of minor actinides (MA: Am, Cm). For the wet process, the former relies on the extraction ability of an extractant; for example, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) [1]. Japan Atomic Energy Agency has developed a column separation technology, namely extraction chromatography, in which an extractant is impregnated in a silica-based support. Over the past two years, a two-step separation using the *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (TEHDGA, Fig. 1(a)) adsorbent for Ln+MA co-recovery and the *N,N,N',N',N'',N''*-hexaoctylnitritoltriacetamide (HONTA, Fig. 1(b)) adsorbent for Ln/MA separation has been evaluated for MA separation [2–3]. The safety assessment was investigated by radiolysis of gamma and He²⁺ ion beam irradiations to determine the *G*-values (*H*₂), decay constants and degradation products of these adsorbents at the irradiation doses.

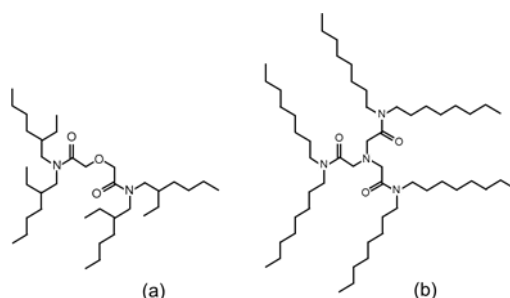


Fig. 1 Molecular structure of (a) TEHDGA and (b) HONTA

The gamma irradiation was performed at the ⁶⁰Co Irradiation Facility of the Takasaki Institute for Advanced Quantum Science, National Institutes for Quantum Science and Technology (QST). The TEHDGA adsorbents were sealed in a glass vial and irradiated at an average dose rate of 4.0 kGy/h at ambient temperature. These samples were subjected to GC analysis for the *H*₂ gas measurement. After acetone washing, the organics were subjected to LC/MS analysis for the decay constants and degradation products of the impregnated extractant.

The He²⁺ ion beam irradiation was performed at the ion injection beamline of Wakasan Energy Research Center (WERC). A portion of the adsorbents was poured in the sample holder, and the Ti film (0.03 mm) was placed to cover it. The He²⁺ ion beam accelerated to 10 MeV in the tandem accelerator was scanned through the sample holder to ensure uniform irradiation over the irradiation area. The Ti film decelerates the He²⁺ ion to 5.5 MeV, which is an emitted energy of the alpha ray of ²⁴¹Am. These samples were subjected to LC/MS analysis for degradation products of the impregnated extractant.

The results indicated that no safety equipment or treatments were required for the current MA separation process, except for the MA desorption after the pump degradation.

This work was carried out as a part of the research project "Basic Research Programs of Vitrification Technology for Waste Volume Reduction (JPJ010599)", commissioned by the Ministry of Economy, Trade and Industry (METI), in FY2019 – 2023.

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SEP P14 – Small-Angle Neutron Scattering Diffractometer SANS-J for Nuclear Separation Chemistry: Joint Collaborations between ICSM and JAEA

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In many ways, neutron scattering is a useful complement to X-ray scattering each other in the study of material structures, mainly because the neutron cross-section varies randomly among elements, whereas the X-ray atomic scattering factor increases with atomic number. The large difference in the scattering cross-section between hydrogen and deuterium in particular is crucial in the use of neutron scattering to analyze the microscopic structure of various materials, so that the difference enables us to observe only the structures formed by one specific component among scatterers composed of other multiple components. Recently, we have developed small-angle neutron scattering (SANS) diffractometer, SANS-J [1], at research reactor, JRR-3, of the Japan Atomic Energy Agency (JAEA), Tokai, Japan, and the various kinds of studies in chemical separation systems, such as biphasic solvent extraction [2], flotation process [3], and solids-liquid separation using adsorbent materials, which are well related to the nuclear process, have been conducted in the place. Here we will present our small-angle scattering diffractometer, SANS-J, which is a typical apparatus installed at the research reactor for neutron scattering, as well as some representative results obtained.

Since 2022, joint collaborations between CEA and JAEA in the field of solvent extraction, that is, "Understanding soft matter organization in solvent extraction for nuclear fuel processes", was started as a specific topic of cooperation (STC) no. 4.11, where the correspondents in JAEA and CEA are Dr. Ryuhei Motokawa and Dr. Sandrine Dourdain (Marcoule Institute in Separation Chemistry; ICSM), respectively. Based on this project, an environment has been established in which researchers (and students) affiliated with CEA (or others) can visit JAEA for neutron scattering experiments at SANS-J, JRR-3. Several research topics have been treated at SANS-J through the proposal submissions from the researchers of ICSM, and some of those studies deal with nuclear fuels such as uranium and thorium as samples. We would like to discuss the possibility of collaborative research with French institutions not limited to solvent extraction systems.

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SEP P15 – Diversification of Suppliers on Diluent (TPH) at La Hague Plant

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Fuel processing at La Hague involves uranium/plutonium separation by liquid-liquid extraction using tributylphosphate (TBP) as extractant and (TPH) hydrogenated tetrapropylene as diluent. The latter is a mixture of C10-C13 alkanes (isoparaffines). Like in other facilities, its primary function is to reduce the density and viscosity of the organic phase to improve hydraulic properties and allow phase separation. A secondary function was given to the diluent in UP2-800 and UP3 plants: the Diluent Washing function whose role is to remove by solvent extraction most of TBP dissolved and entrained in the aqueous phases downstream from contactors to limit its consequences on downstream functions. TPH is therefore essential to the operation of the process.

Historically, difficulties in diluent supplying have regularly been encountered due to production stoppages by suppliers or non-renewal of contracts. In 2019, only one supplier was qualified to supply La Hague plants with TPH. To overcome this single-provider supplier situation, a Working Group was launched this year to investigate available alternatives. The group involved researchers, engineers, and technical experts from CEA, Orano Projects and operators of the La Hague reprocessing plants.

Firstly, safety and process requirements and its criteria acceptance were established by Orano Projects engineers through a functional analysis in compliance with La Hague qualifying processes. In a second time a wide range of commercial products were listed, and five industrial scale production C10-C13 isoparaffines were selected. The next stage consisted of establishing and completing an R&D roadmap to evaluate safety and process requirements on these diluents. For this purpose, a large panel of laboratory measurements, assays and analyses was carried out mostly at CEA Marcoule and Saclay laboratories but also at Intertek Caleb Brett and La Hague laboratories. Among them, common parameters were studied and compared between the different diluents: density, viscosity, surface tension, refractive index, Br index (alkenes content), flash point, impurities contents (F, Cl, Si), distillation range using mainly international standardized methods (ISO, ASTM).

Diluents composition was thoroughly analyzed by recent techniques. The difficulty of determining the composition of these mixtures lies in the large number of components from isoparaffinic family lying in a very short distillation range. For this reason, a combination of infrared spectroscopy, ¹H and ¹³C NMR spectroscopy and multiple gas chromatography methods was used. Other important physico-chemical property linked to chemical process and safety requirements is the third phase formation domain in presence of tetravalent uranium and plutonium. These properties were finely studied at Atalante facility laboratories with a method redeveloped specifically for this project. Also, properties linked to diluent washing and settling times were measured at CEA Marcoule GI facility.

This work allowed us to qualify several industrial scale commercial solvents complying with safety and chemical process requirements previously defined and available now for using as diluents in Orano La Hague reprocessing plants. Likewise, the working methodology developed by the working group could be applied for the future in-depth qualification of new commercial diluents.

SEP P16 – Simulation of a Non-Homogeneous Precipitator in the Actinides Separation Context

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1. Introduction

Oxalic precipitation is a crucial step on the actinide 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. Continuous precipitation of actinides is conducted in a vortex reactor. The internal flow pattern produces two macro mixing zones and the concentration of the reagents strongly depends on the spatial position in the vessel.

The population balance equation (PBE) is a well-known statement used to predict crystal size distribution in precipitation processes. Nowadays many PBE numerical solution strategies are reported in the literature due to the lack of a general methodology adapted to any context.

This work focuses on the solution of the population balance equation at steady state in presence of nucleation, crystal growth and loose agglomeration, by combining hydrodynamics and crystallization principles in order to predict the characteristics of both solid and liquid phases leaving the vortex reactor.

2. Methods

The first step consisted in studying independently (i) mixing and (ii) precipitation. CFD simulations were performed at the macro scales to study the local mixing conditions and to reproduce the flow behavior. Due to a strongly anisotropic turbulence originating from the dominance of the tangential velocity, a Large Eddy Simulation (LES) approach was adopted [1]. As result, the flow is schematically represented as a combination of several interconnected well-mixed zones (Figure 1). Crystallization mechanisms were studied separately in order to determine supersaturation expressions and nucleation, growth and agglomeration kinetics.

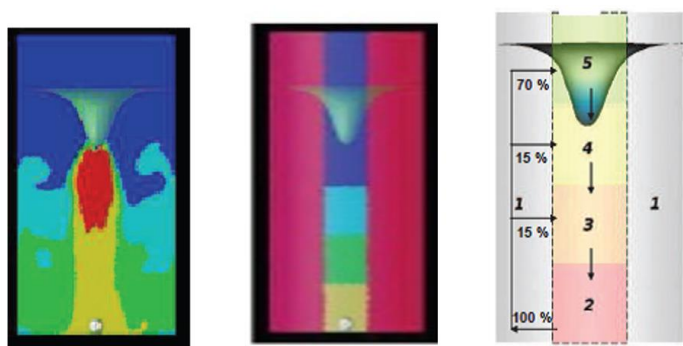


Figure 1 : Compartmental-based approach for vortex reactor simulation [5].

In a first time a tool to model the behavior of one compartment is developed: the nucleation, growth and agglomeration kinetics are included in the same model to verify their coherence. The model developed allows algorithm solution, critical variables and convergence criteria to be identified. Following this approach, the vortex reactor modelling is decomposed in three steps: (i) The simulation of a Mixed Suspension Mixed Product Removal (MSMPR) reactor, (ii) the study of the interaction between two elementary blocks (MSMPR) and (iii) the implementation and solution of the multi-compartment model.

3. Results and discussion

A numerical methodology to solve the steady state population balance including nucleation, size-independent growth and loose agglomeration is developed. It is based on a discretization method and the fixed-point algorithm coupled with convergence acceleration methods [2]. In a first time, the oxalic precipitation of neodymium and uranium in a well-mixed reactor is simulated [3]. The results demonstrated to fit the experimental measurements in a wide range of operational conditions. In addition, the crossed secant acceleration method is performant to solve the agglomeration population balance equation whether the agglomeration kernel is size dependent or not.

The same methodology is suitable to the simulation of the multi-compartmental model. Again, an accelerated fixed-point algorithm is implemented in order to solve the recycling streams. The population balance equation algorithm is integrated in the 5 compartments model describing the vortex reactor. As result, local properties of the liquid and solid phase are predicted. As an example, the local crystal size distribution is depicted in Figure 2.

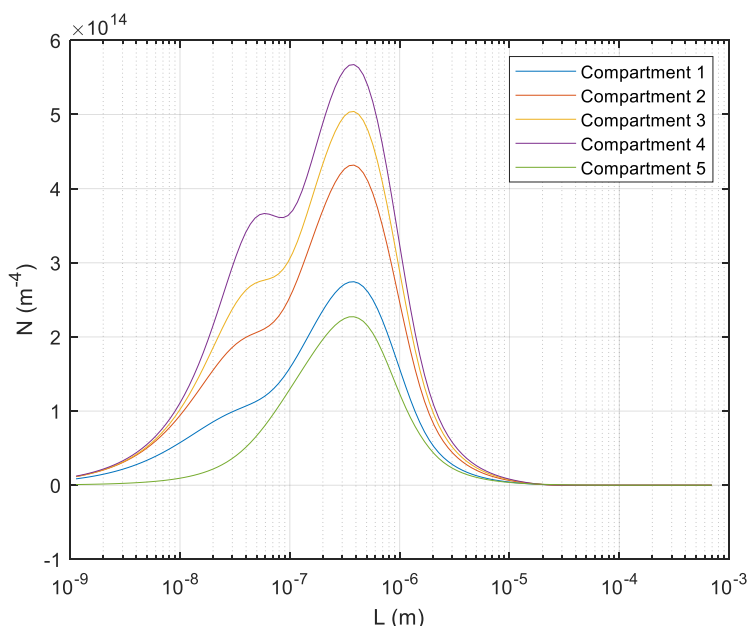


Figure 2. Crystal size distribution evolution in the vortex reactor.

The simulation of the vortex reactor is performed by the implementation of looped accelerated fixed-point algorithms. Detailed information of both, liquid and solid phase can be approached: supersaturation, concentration, crystal and monocrystals size distribution are determined in every compartment describing the flow pattern in the vortex reactor. Robustness and accuracy are ensured by modifying the operational conditions and the species to be precipitated.

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SEP P17 - Influence of TODGA Degradation Compounds in the Separation of Am/Cm in the AmSel Process.

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One of the most sustainable solutions toward the proper management of nuclear waste is through the so-called Advanced Nuclear Fuel Cycle. This method involves separating minor actinides like Neptunium (Np), Americium (Am), and Curium (Cm) from Lanthanides (Ln) and other fission products with the aim of generating new fuel or transmutation materials for advanced nuclear reactors [1]. Within the MA recovery, there has been a growing interest in selectively recovering Am alone, as creating new fuel containing Cm poses significant challenges. However, separating Am from Cm remains a considerable challenge due to their similar chemical properties. As a result, different approaches are being devised and developed such as the new AmSel (Americium Selective Extraction) [2] process, which relies on liquid-liquid extraction techniques and is intended to be used following the recovery of uranium and plutonium via the PUREX (Plutonium Uranium Reduction EXtraction) process.

The AmSel process involves a first step (co-extraction step) in which the Ln(III) and An(III) are co-extracted from the PUREX 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 water-soluble SO₃-Ph-BTBP (6,6'-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine) molecule separates Am(III) from Cm(III) and the Ln(III), thanks to the inverse selectivity of SO₃-Ph-BTBP and TODGA towards Am and Cm [2] (Figure 1). A limiting point for the development of these processes is the degradation of the previously mentioned ligands due to the harsh operation conditions (mainly the high HNO₃ concentration where nuclear fuel is dissolved and the high radioactive field). This main ligands degradation produces degradation compounds, which can lead to 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.

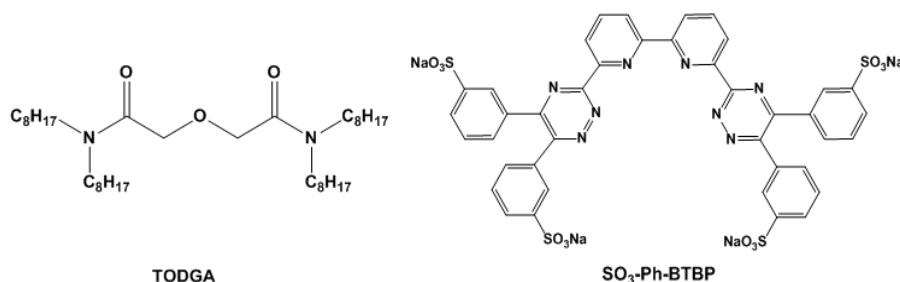


Figure 1. AmSel reference molecules.

So far, TODGA is considered one of the extractants with higher possibilities to be applied to industrial scale, since it has demonstrated most of the required needs related to extraction properties and degradation resistance for processes development. In recent years, TODGA stability has been extensively studied, as its degradation compounds (Figure 2) have been characterized [3], [4], [5], and their extraction properties have been evaluated [6]. However, their influence on the separation of Am and Cm has not been studied yet.

On the one hand, this work shows fundamental studies of the accumulation and selectivity of TODGA degradation compounds, individually and combined, for the separation of Am and Cm in the stripping step of the AmSel process. For this, the isotopes used have been ²⁴¹Am and ²⁴⁴Cm; and results are given by the distribution ratio of each isotope, obtained by gamma and alpha spectrometry.

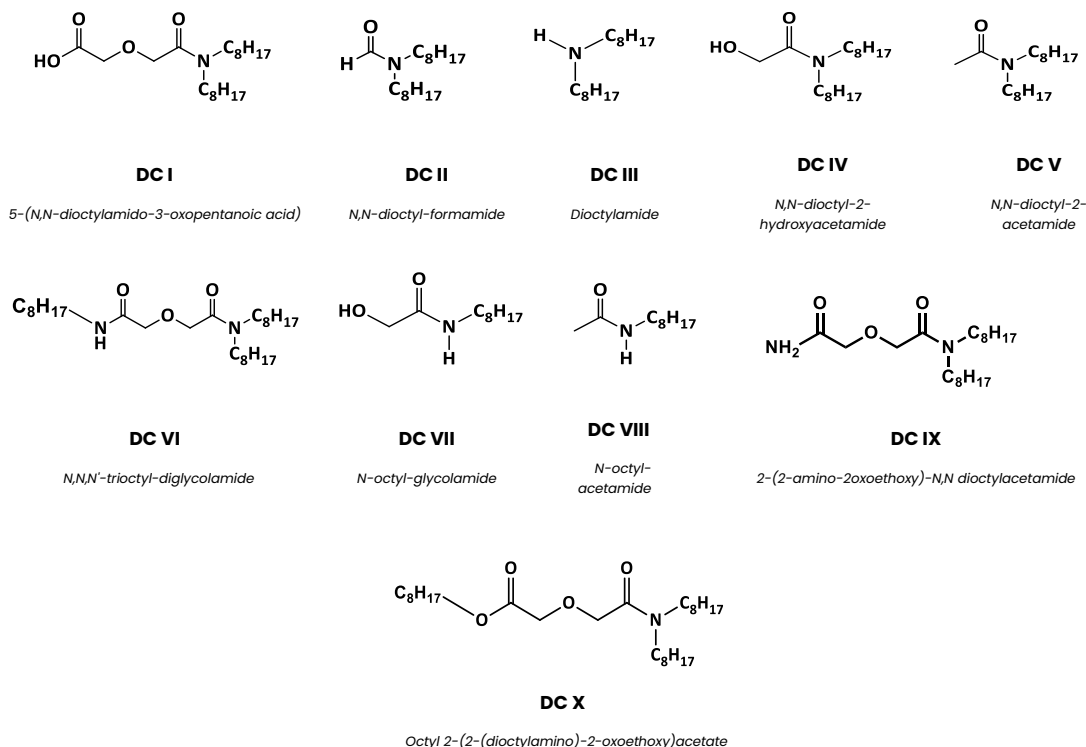


Figure 2. Structures of TODGA degradation compounds.

On the other hand, more realistic scenarios related to a real process operation were also considered, where the organic phase is stripped of metals, fed with non-irradiated TODGA (to keep the initial concentration of TODGA due to it degrades during the process, losing efficiency) and reintroduced into the process [2]. These situations involve the combined action of fresh TODGA and the different degradation compounds generated in previous cycles. In this way, the Am/Cm separation efficiency of an organic phase containing TODGA and its degradation compounds capable of extracting Cm, individually or collectively, were evaluated for the AmSel stripping step.

Results prove that the accumulation of degradation compound VI (*N,N,N'*-trioctyldiglycolamide, TrODGA), due to its structural similarity to TODGA, is the one with greatest influence on Am/Cm separation, being able to contribute positively. However, the accumulation of other main degradation compounds such as IV (*N,N*-di-octyl-2-hydroxyacetamide, DOHyA) and VII (2-hydroxy-*N*-octylacetamide) have a significantly negative impact on this separation, so their accumulation in a real process operation must be carefully controlled.

This work has been developed and funded under the framework of the European project H2020 PATRICIA (No. 945077).

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SEP P18 – Strategy and Feedback on Industrial Decontamination Using Innovative and Highly Selective Cs Sorbant Called Sorbmatech®Cs

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Removal of Cs and Sr radionuclides at the source in the nuclear industries by plug-and-play facility would benefit since operating parameters can thus be tuned for higher removal efficiency and lower secondary waste production.

Sorbmatech®Cs is Cs selective sorbant, whose production is patented by Orano and CEA, and whose efficiency is around 10⁵ mL/g regarding radioactive Cs removal. Sorbmatech®Cs is considered to perennially trap Cs, as well as some other radionuclides for storage. Inactive and active tests had been performed in laboratory scale at CEA during the whole Sorbmatech®Cs production development. The industrial demonstration is now on-going for the Cs removal of Orano industrial wastewater, using a two steps strategy to evaluate the efficiency of Sorbmatech®Cs for each kind of wastewater in order to design future industrial decontamination facility.

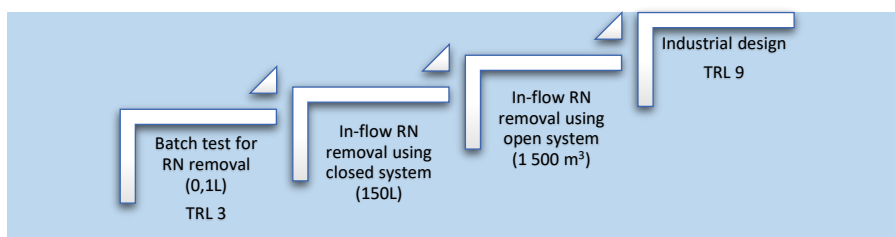
The first step called “batch test” consists in pouring small quantity of Sorbmatech®Cs into known volume of Orano wastewater then analyzing the residual Cs concentration in the liquid phase after 24 hours of contact to estimate each radionuclide distribution factor. Since Sorbmatech®Cs is Cs selective sorbant, the Cs distribution factor evaluates the interest to move forward in-flow test and is used to simulate the expected breakthrough curve of open system.

The second test consists in the decontamination of the Orano wastewater using a pilot equipped with small laboratory column filled with Sorbmatech®Cs. For this in-flow demonstration, two configurations have been tested: the first configuration is in situ decontamination of a tank (closed system), while the second configuration is a double tanks system, one tank for feeding the column and the second one for storing the decontaminated effluent (open system). Single tank is indeed recommended in case that low decontamination factor is required to downgrade wastewater into decontaminated effluent acceptable for release in the environment, while double tank configuration is recommended for high decontamination efficiency.

CEA and Orano also developed modeling of breakthrough curve to simulate this two tanks system. This model was useful to set up the open system in-flow test, especially to determine the sampling strategy as low as reasonably pertinent, while this model is expected to optimize the design of future industrial decontamination facility regarding the used sorbant volume production.

Industrial demonstration is currently on progress using legacy wastewater of the La Hague reprocessing nuclear plant which is saline solution whose total activity consists in around 95% of Cs-134 and Cs-137.

Batch test confirmed the high efficiency of Cs removal, while the single tank in-flow system estimated the long-term Cs removal efficiency of Sorbmatech®Cs in saline conditions.



SEP P19 – How the Choice of the Counter-ion/Diluent Pair Tunes the Solvent Extraction of Cesium by Calixarene-crown-ethers

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Calixarene-crown-ethers have been investigated for cesium extraction from spent fuel for several decades, among which DOC[4]C6 (dioctyl-1-oxycalixarene[4]crown-6) and MAXCalix (3,7-dimethyl-1-dioctyloxycalixarene[4]benzocrown-6) being the most studied ligands. Their main drawbacks are their low solubilities in the aliphatic diluents commonly used in the nuclear fuel cycle. Alternative diluents or mixtures with a modifier have been investigated[1], [2]. In nitrate media, for most diluents, the expected 1:1:1 ligand:metal:counter-ion stoichiometry is obtained, and the formation constant is correlated to the dielectric constant of the diluent by an affine function (Figure 9). A few diluents present hypo- (e.g. chloroform) or hyper- (e.g. ketones) nitrate stoichiometries[3]. The hyper-stoichiometry is especially interesting for a process, as it increases the difference of distribution ratios at the extraction and stripping steps, thus lowering the number of stages required. This phenomenon can be explained by either the formation of an additional species such as $\text{LCsNO}_3 \cdot \text{HNO}_3$, or the formation of aggregates.

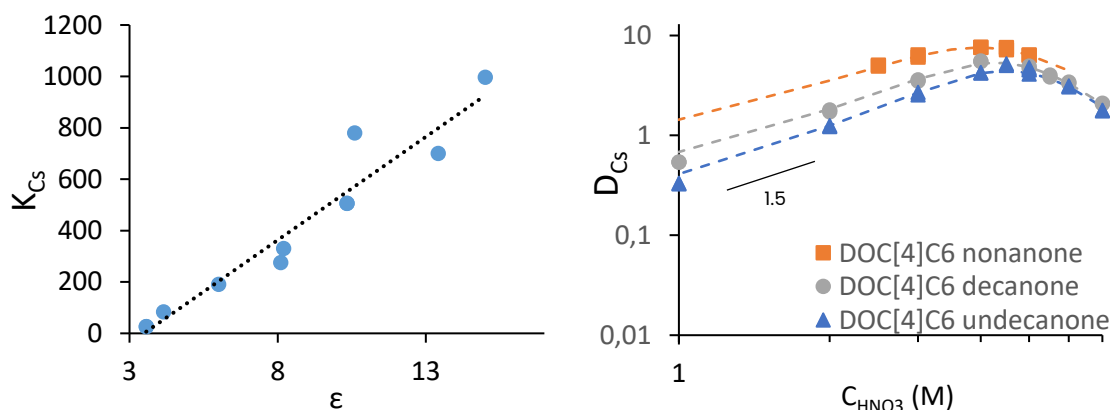


Figure 9: Fitted DOC[4]C6 formation constant versus the dielectric constant of the diluent[4] and Cs distribution ratio at 0.01 M DOC[4]C6 in alkylketones

Since the spent fuel is dissolved in nitric acid, most reported experiments used nitrates as counter-ions. However, in the case of cesium remediation from contaminated areas, such as under accidental releases (e.g. Fukushima) or leaks, other aqueous conditions have to be considered, especially chloride salts. The effect of other inorganic anions has thus been investigated for the extraction with ketone diluents. Surprisingly, a reversed extraction trend occurred with all anions except for the nitrates (Figure 10 left). A similar decreasing trend is observed for octanoic acid and chloride anion, but not for alcohol and chloride anion, for which the chloride apparent stoichiometry depends on the octanol content (Figure 10 right). However, to keep the charges balanced, each cesium cation is accompanied by a counter-ion in the organic phase. A chloride stoichiometry lower than 1 induces that either hydroxy anions, or deprotonated 1-octanol anions, replace the missing counter-ions, rather unlikely at pH 2. Considering the anomalies in both left and right of the Figure 2, the most likely hypothesis is that, at low ionic strength, an additional cesium species forms, the composition of which has been investigated by several techniques (UV-Vis, NMR, ESI-MS).

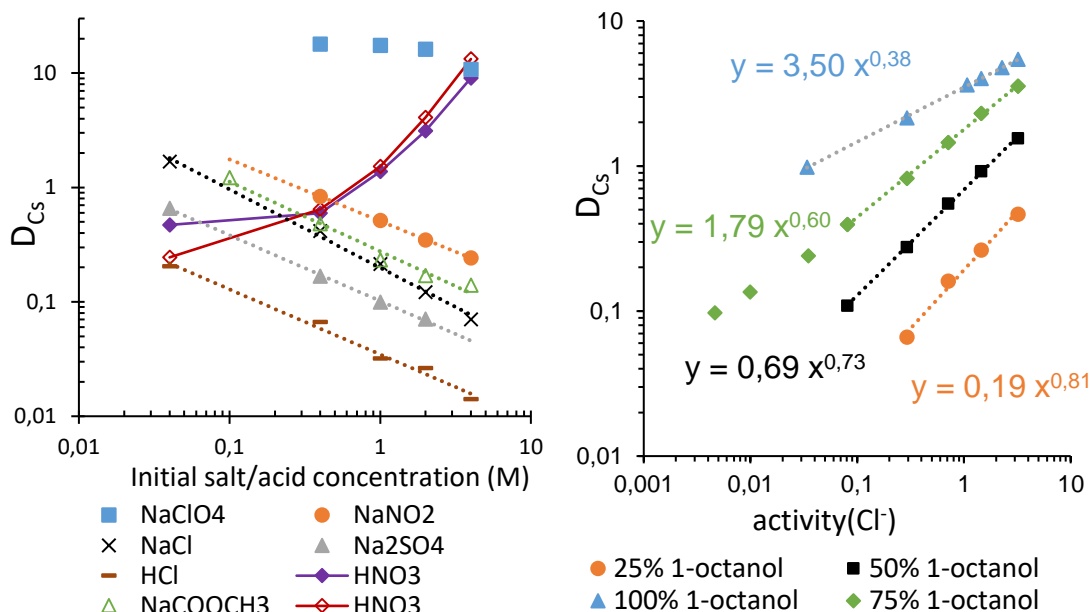


Figure 10: Left: D_{Cs} distribution ratios from different aqueous media with MAXCalix in nonanone; Right: D_{Cs} distribution ratios versus the calculated chloride activities with MAXCalix in kerosene/1-octanol mixtures

The Table 1 summarizes the apparent stoichiometries as observed from the slope analyses for several diluent/counter-ion pairs; the choice of this pair determines the overall extraction of Cs with the same extractant.

Table 1: Summary of the effect of the counter-ion/diluent pair on Cs extraction

	Nitrate	Chloride
Alcohol	1:1:1	Hypo-stoichiometry
Ketone	Hyper-stoichiometry	Reverse trend
Carboxylic Acid	1:1:1	Reverse trend

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SEP P20 – Extraction of Nitric Acid by Tripodal Amides

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Traditional solvent extraction flowsheets for recycling U and Pu from spent nuclear fuel employ tributyl phosphate in an aliphatic organic diluent. Although this approach is well-established, the products from radiolytic solvent degradation are known to decrease separation efficiency. Furthermore, solid waste is formed upon incineration of spent solvent due to the presence of phosphorus. There is therefore interest in the development of alternative extractants containing only carbon, hydrogen, oxygen, and nitrogen (CHON).^c

Tripodal amides (Figure 1) are an emerging class of CHON extractants that have been identified as promising candidates for An/Ln separation^d, in-group An separation^{ef}, and TcO_4^- extraction^g. These systems are prone to third-phase formation at high metal loadings, but this can be mitigated through modification of the ligand alkyl chain length or addition of a phase modifier (typically a long-chain aliphatic alcohol). However, the impact of these modifications on HNO_3 extraction and on the physiochemical properties of the system (e.g., interfacial tension, viscosity, and density) is not well-understood. Further fundamental studies are therefore needed to predict and understand the behavior of these systems in solvent extraction equipment.

Studies of the mechanism of HNO_3 extraction by the ligand *N,N,N',N',N'',N''*-hexaoctylnitritoltriacetamide (HONTA) will be presented. As shown in Figure 2, the distribution ratio for extraction of HNO_3 by 0.1 M HONTA in *n*-dodecane decreases with increasing HNO_3 concentration. Modelling of these data suggests the presence of $\text{HONTA} \cdot (\text{HNO}_3)$, $\text{HONTA} \cdot (\text{HNO}_3)_2$, and $\text{HONTA} \cdot (\text{HNO}_3)_3$ species under these conditions.

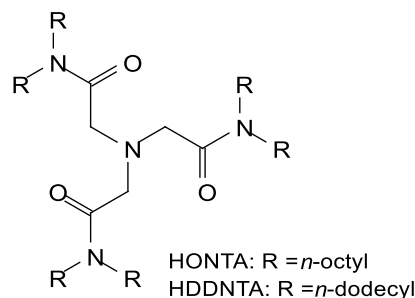


Figure 1. Structure of tripodal amide ligands HONTA and HDDNTA.

^c Nash, K. L. Twenty-First Century Approaches to Actinide Partitioning. In *Separation for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G. J.; Nash, K. L.; Clark, S. B.; Friese, J. I., Eds.; American Chemical Society: Washington D.C, 2006; pp 21–40.

^d Sasaki, Y.; Tsubata, Y.; Kitatsuji, Y.; Morita, Y. Novel Soft–Hard Donor Ligand, NTAamide, for Mutual Separation of Trivalent Actinoids and Lanthanoids. *Chem. Lett.* **2013**, 42, 91–92. DOI: 10.1246/cl.2013.91.

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^f Karak, A.; Mahanty, B.; Mohapatra, P. K.; J. M. Egberink, R.; Valsala, T. P.; Sathe, D. B.; Bhatt, R. B.; Huskens, J.; Verboom, W. Highly efficient and selective extraction of Pu(IV) using two alkyl-substituted amides of nitrilotriacetic acid from nitric acid solutions. *Sep. Purif. Technol.* **2021**, 279, 119584. DOI: 10.1016/j.seppur.2021.119584.

^g Wang, X.; Ding, S.; Wang, Z.; Song, L.; Yang, X.; Xiao, Q.; Xu, H.; Wang, J.; Shen, Z.; Wang, H. A H-Bonding and Electrostatic Interaction Combined Strategy for TcO_4^- Separation by a Nitrotriacetate-Derived Amine-Amide Extractant. *Inorg. Chem.* **2021**, 60, 10899–10908. DOI: 10.1021/acs.inorgchem.1c00111

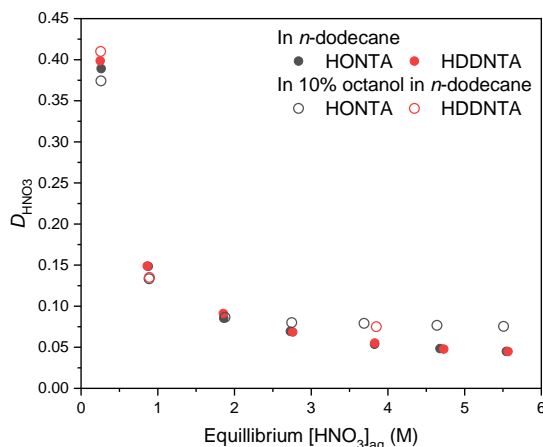


Figure 2. Distribution ratios for extraction of HNO₃ by 0.1 M tripodal amide ligand in dodecane or in 10% octanol in dodecane.

corresponds to a free energy of activation of 52.7 kJ/mol for the proton chemical exchange process. Association of HNO₃ with the carbonyl moieties is also supported by the broadening of the carbonyl band in FT-IR spectra of the post-contact organic phase.

At low HNO₃ concentrations, the addition of 10% 1-octanol as a phase modifier has very little impact on the HNO₃ distribution ratio. At higher HNO₃ concentration, the HNO₃ distribution ratio is slightly higher in the presence of 1-octanol, which can be attributed to the extraction of HNO₃ by 1-octanol.¹ Analogous experiments with *N,N,N',N',N'',N''*-hexadodecyltrinitriacetamide (HDDNTA) indicate that ligand alkyl chain length does not significantly change the mechanism of HNO₃ extraction. Likewise, the concentration of water in the post-contact organic phase is higher in the presence of 10% octanol but is similar for HONTA and HDDNTA. Comparisons of the physiochemical properties (interfacial tension, viscosity, and density) of HONTA and HDDNTA in the absence and presence of 1-octanol will also be discussed.

In conclusion, the mechanism of HNO₃ extraction by 0.1 M HONTA in *n*-dodecane has been examined. Spectroscopic studies demonstrate that HNO₃ associates with the central amine even at low acid concentration, and that HNO₃ associates with the carbonyl moieties of the ligand at higher acid concentration. HNO₃ and H₂O extraction are increased in the presence of the phase modifier 1-octanol but are not significantly impacted by changing the ligand alkyl chain length.

^h Verma, P. K.; Karak, A.; Sahu, P.; Aswal, V. K.; Mahanty, B.; Ali, S. M.; Egberink, R. J. M.; Huskens, J.; Verboom, W.; Mohapatra, P. K. Aggregation Behavior of Nitrilotriacetamide (NTAmide) Ligands in Thorium(IV) Extraction from Acidic Medium: Small-Angle Neutron Scattering, Fourier Transform Infrared, and Theoretical Studies. *Langmuir* **2022**, 38, 14745-14759. DOI: 10.1021/acs.langmuir.2c02394

ⁱ Geist, A. Extraction of Nitric Acid into Alcohol: Kerosene Mixtures. *Solv. Extr. Ion Exch.* **2010**, 28, 596-607. DOI: 10.1080/07366299.2010.499286.

SEP P21 – Synthesis of Chiral Ligands for Actinides Extraction

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Uranium extraction and spent fuel reprocessing are the subject of many researches aiming to improve and to understand the different mechanisms involved in conventional as well as in innovative processes. Whether upstream or downstream of the nuclear fuel cycle, many processes (PUREX, URPHOS, AMEX...) require a liquid-liquid extraction (LLE) stage. The LLE consists of contacting acidic leachate (resulting from the leaching of uranium ores or spent fuels) with a diluent oil (kerosene, hydrogenated tetrapropylene...) containing a lipophilic ligand. The used ligand must show high affinity and selectivity towards the targeted element in order to allow the efficient transfer of this latter in organic phase.

In a first instance, our research has focused on alternative ligands claimed as new promising candidates in two well-known processes: the *N,N*-di(2-ethylhexyl)butanamide (DEHBA) which may replace advantageously the *n*-tributylphosphate in the PUREX process¹ and the butyl-*N,N*-bis(ethylhexyl)carbamoylnonyl phosphonate (DEHCNPB) as an useful ligand for URPHOS process². It turned out that these ligands contain several asymmetric carbons and thus present several diastereoisomers. Moreover, it has been shown in the literature that the absolute configuration of the various asymmetric centers of a given chiral ligand have an impact on the silver extraction³, lanthanide extraction⁴ and plutonium extraction⁵.

Therefore, in the second part of our research, we investigated the effect of chirality on the actinides extraction. The principle of these studies was to develop an enantio/diastereoselective synthesis of a model chiral ligand and to compare the extraction properties of each diastereoisomer with those of the unresolved mixture. Our first experiments were carried out with the monoamide DEHBA and its diastereopure forms. The DEHBA bears two asymmetric carbons in β position of the amine function of both alkyl chains and presents a couple of enantiomers (*R,R*) and (*S,S*) and one diastereoisomer (*R,S*), which is an achiral mesoform. We therefore developed a synthesis leading to each optically pure molecule that was assessed in PUREX conditions in order to evaluate the distribution ratio and the selectivity of actinides extraction. We further completed our study by trying to characterize the impact of the ethyl position on alkyl chain (steric hindrance of the complexing site) on the extraction properties of the ligand. Two DEHBA regioisomers, namely the *N*-(2-ethylhexyl)-*N*-(oct-3-yl)butyramide (EHOBA) and the *N,N*-di(octan-3-yl)butyramide (DOBA) were synthesized and their LLE properties were investigated in PUREX conditions.⁶ These studies allowed us to conclude that chirality of DEHBA and the regioisomerism have an effect on the plutonium distribution ratio and on the U/Pu separation factor.

The amidophosphonate DEHCNPB includes three asymmetric carbons: two of them are in β position of amine function of both alkyl chains and the third is on the methylene bridge. For this molecule, the synthesis of optically pure isomer is a real challenge because this requires an enantioselective alkylation which has not yet been described in literature. The distribution ratio and the selectivity of these optically pure molecules will be studied in various media according to their utility in front-end (nitric media)⁷ or back-end (phosphoric media, URPHOS process) of the fuel cycle.

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SEP P22 – Partitioning of Neptunium in TBP–HNO₃ System for Optimization of the CoDCon Flowsheet

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The CoDCon process (Co-DeContamination) is a tributyl phosphate (TBP)-based process that allows for co-extraction of Pu and Np with U. However, controlling Np partitioning is difficult due to its varied chemical speciation. After dissolution of used nuclear fuel (UNF) in a strongly oxidizing environment by refluxing HNO₃, it is expected that neptunium is predominantly present as Np(V) and Np(VI). Np(IV) may also be present due to disproportionation of Np(V) if the solution is in storage for an extended period. Because Np(IV) and Np(VI) are extracted by TBP, while Np(V) remains in the aqueous phase, Np oxidation state control is vital for partitioning of Np to a single outlet stream.

The goal of this work is to find favorable conditions for full extraction of Np by TBP while minimizing the addition of reagent salts. Oxidation of Np(V) to Np(VI) is promoted by a high HNO₃ concentration and is autocatalyzed by the presence of low concentrations of HNO₂ and radicals like •OH, •NO₂ that form due to radiolysis of nitric acid and water. In this work, we utilize Argonne's 3-MeV Van de Graaff generator (VDG) which can deliver beta and gamma dose rates that can exceed those produced by actual UNF assemblies. Thus, VDG irradiations provide redox conditions that approach those expected during UNF processing. Irradiation of nitric acid solutions at a variety of concentrations is used to find optimal conditions for oxidation of Np(V) to Np(VI) during solvent extraction.

Using a single-stage annular centrifugal contactor, Np-bearing irradiated nitric acid solutions are contacted with TBP dissolved in dodecane to measure the partitioning of Np into the organic phase under various nitric acid concentrations and radiation doses. Argonne's additively manufactured centrifugal contactors are used to simulate the continuous processing conditions of a solvent extraction process. To keep the volume of solution required for testing low, 1.25-cm rotor diameter contactors are used. Changes in the concentrations of Np in the aqueous phase are monitored using online UV-Vis-NIR spectroscopy. The key absorbance features are Np(IV) at 650–900 nm, Np(V) at 980 nm and Np(VI) at 1223 nm. The real-time concentration of HNO₂ is monitored using UV-Vis in the 350–400 nm region. The sensitive redox chemistry of Np(V) in a continuous two-phase system, where Np(IV) and Np(VI) are continually removed from aqueous phase by their extraction into TBP, should lead to a more realistic approximation of the processing conditions present in a reprocessing plant.

Data from single-stage contactor testing will enable optimization of the CoDCon flowsheet by using the new experimental data to develop more accurate redox chemistry simulations with the AMUSE code (Argonne Modeling for Universal Solvent Extraction). AMUSE calculates the steady-state composition of the organic and aqueous phase in each stage for a user-specified process flowsheet. The product compositions generated by AMUSE provides the information required to identify the conditions necessary to achieve >99% recovery yield of Np. Experimental results that demonstrate the effect of the concentration of HNO₃ and NO₂ in the aqueous feed on the extraction of Np into TBP for a single-stage centrifugal contactor will be reported.

SEP P23 – New Synthetic Pathway towards the Hydrophilic 2,9-Bis-Triazolyl-1,10-Phenanthroline Ligand for Selective Americium Stripping

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In 2017, a clear step forward was provided towards proper management of spent nuclear fuel (SNF). The first CHON compliant hydrophilic 1,10-phenanthroline derived ligand (BTrzPhen-diol **1**) for the selective separation of Am(III) was then reported by Edwards et al.¹ This ligand is a promising alternative for the non-CHON compliant SO₃-Ph-BTBP/BTPhen **2** ligands which have been studied extensively in Americium Selective Extraction (AmSel) processes. The AmSel process consists of two steps in which Am(III), Cm(III) and the lanthanides are co-extracted from an aqueous HNO₃ solution with a non-selective ligand like TODGA **3** in a first step, followed by the selective stripping of Am(III) by a hydrophilic ligand. When Am(III) was stripped with BTrzPhen-diol (0.01M) from a TODGA (0.2M) containing loaded organic phase a separation factor for Am(III)/Eu(III) of 47 was obtained at an HNO₃ concentration of 0.33M. Additionally, a Am(III)/Cm(III) separation factor of 2.5 was obtained which is similar to SO₃-BTBP and SO₃-BTPhen.² BTrzPhen-diol was synthesized by the well-known copper(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC). Two novel 2,9-bis-triazolyl-1,10-phenanthroline derivatives (DS-BTrzPhen and DAA-BTrzPhen) were recently published by Wan et al. 2023, and were also synthesized *via* this method.³ For this reaction, the addition of the rather expensive TBTA complexing agent is necessary to prevent copper from binding with the phenanthroline ligand. Moreover, column chromatography is needed to purify all the intermediate compounds of BTrzPhen-diol, making this strategy unsuitable when scaling up to industrial processes.

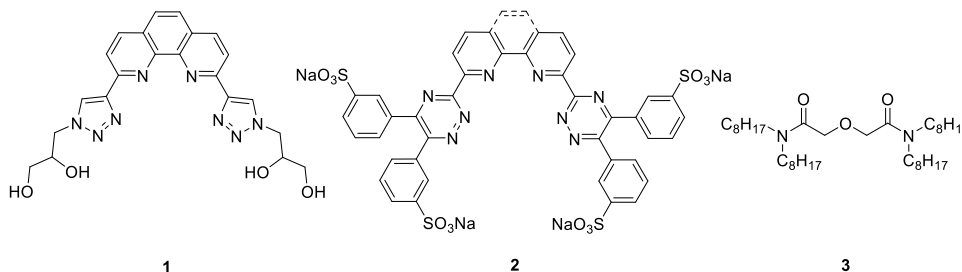


Figure 11: Molecular structures of BTrzPhen-diol **1**, SO₃-Ph-BTBP/BTPhen **2** and TODGA **3**.

In this work, an alternative synthetic route towards BTrzPhen-diol was developed. This synthetic pathway is reproducible, scalable (gram scale), and provides higher yields which are significant improvements. Additionally, more extensive extraction/stripping studies were performed with the combination of TODGA and BTrzPhen-diol. This included a study of the kinetics, the influence of the HNO₃ and ligand concentration on the distribution ratios of Am(III), Cm(III) and Eu(III) and the influence on the co-stripping of yttrium and the lanthanides (La, Ce, Pr, Nd, Sm, Gd, Dy and Yb) together with Am(III) and Cm(III).

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SEP P24 – Shaping of Hybrid Materials and Modeling of the Column Process for the Selective Extraction of Uranium from High Sulphate Concentration Solutions

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The extraction of uranium from complex media with high sulfate concentrations resulting from mining leaching requires the development of efficient and competitive materials for industrial-scale column processing. The CEA is developing the formulation of this type of material on a laboratory scale. The physico-chemical nature of these materials is now well characterized and the latest results highlight families with interesting properties, both in terms of uranium capacity and selectivity with respect to impurities (e.g. Fe(II/III), Mo(VI)). The next step is to establish and optimize the column process for Uranium extraction. This will be achieved with extraction and re-extraction studies in fixed-bed process conditions, coupled with equilibrium and continuous process modeling (**Erreur ! Source du renvoi introuvable.**).

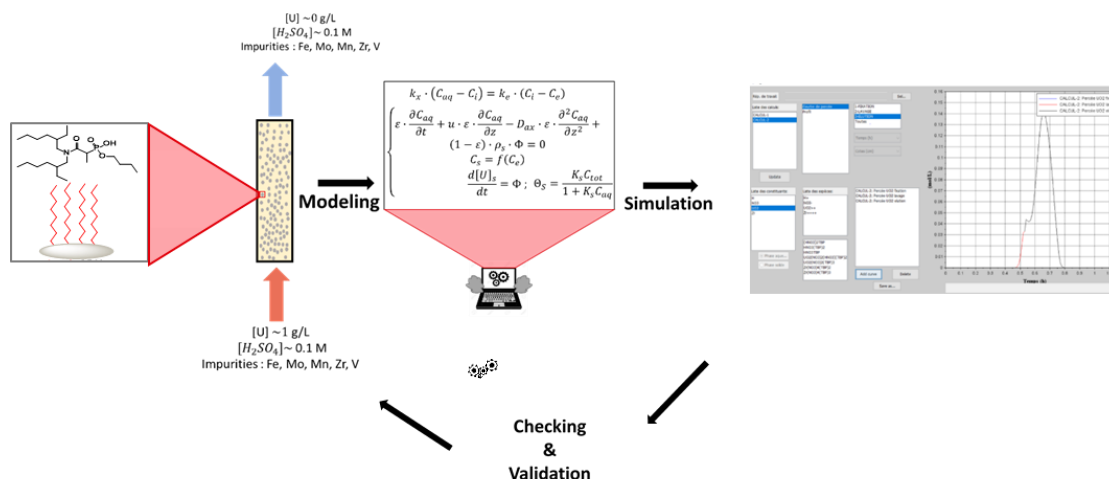


Figure 1. Model-building process

The objective of this work is to shape multi-scale functionalized materials, to characterize these hybrid materials and to evaluate their extracting properties in "batch" then in continuous process, first on simulated juices then on real solutions. The data collected as well as the input parameters (concentrations, temperatures, and flow rates in the column...) will help to model the dynamic behavior of these materials (modeling of thermodynamic, kinetic and hydrodynamic parameters during extraction and elution). This modeling will both guide the shaping studies and allow the acquisition of data for the dimensioning studies, with a future use in mining site as perspective.

SEP P25 – Differences in Extraction Mechanisms between Fluorous and Organic Extraction Systems: Structuring Extractants at the Interface and in the Bulk Extracting Phase

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The extraction of Zr(IV) as a major fission product from aqueous HNO₃ solutions have been investigated extensively because the presence of Zr in the tri-*n*-butyl phosphate (TBP)-based PUREX process for reprocessing spent nuclear fuel is problematic.^[1] We have recently shown that a Zr-loaded organic phase from liquid-liquid extraction with TBP shows hierarchical aggregation behaviors of Zr(NO₃)₄(TBP)₂ coordination complexes, which self-assemble into primary clusters that coalesce further to form superclusters. This supercluster formation portends the formation of the third phase and interfacial cruds.^[2] In this study, we develop a fluoroalkylated phosphate, tris(4,4,5,5,6,6,7,7,7-nonafluoroheptyl) phosphate (TFP), for Zr(IV) extraction to increase the extractability and prevent third-phase formation. Fluorous solvents have excellent chemical properties and immiscibility with both water and organic solutions.^[3] Considering these properties, the hierarchical aggregating behaviors of Zr(IV) and the highly hydrophobic fluorous extractant should be different from that of Zr(IV) with TBP, and this may reduce the formation of a third phase and interfacial crud. We investigated the extraction performance and mechanism of TFP extraction of Zr(IV) from HNO₃ solutions into perfluorohexane and compared them with the conventional organic extraction system using tri-*n*-alkyl phosphate (TAP) in *n*-hexane.

The extraction experiments were carried out by the batch method. The fluorous and organic phases were 0.05 M TFP in perfluorohexane and 0.50 M TAP in *n*-hexane, respectively. The aqueous phase was prepared by mixing the 1.12 M Zr(IV) stock solution and the 15.6 M HNO₃ solution to obtain the 0.01 M Zr(IV) and the 0.1–15 M HNO₃ solutions. Equal volumes of both phases were mixed at 25°C and 1800 rpm. After phase separation, the Zr(IV), HNO₃, and H₂O concentrations were measured by inductively coupled plasma mass spectrometer, ion chromatography, and Karl-Fischer titration, respectively. The distribution ratio of Zr(IV) was calculated by the mass balance. In addition, ³¹P nuclear magnetic resonance, small-angle neutron scattering, and neutron reflectometry were used to observe the bulk and interface structure of the extracting phases after Zr(IV) extraction. Despite TFP concentration being one-tenth of that of TAP, the 0.05 M TFP had a much higher Zr(IV) extraction performance. Moreover, no third phase formed, even as the concentration of TFP was increased. To verify the reason for the superior Zr(IV) extraction performance of TFP, the compositions of each phase before and after water, HNO₃, and Zr(IV) extraction were determined using both TFP and TAP. The concentrations of water and HNO₃ molecules in the fluorous phase lowered during Zr(IV) extraction, indicating that, unlike with TAP, water and HNO₃ molecules do not preferentially interact with TFP. In this work, a new fluorous phosphate extractant, TFP, was synthesized and its extraction performance for Zr(IV) from HNO₃ aqueous solution was evaluated. The Zr(IV) extraction strength of TFP in the perfluorohexane was much higher than that of TAP in *n*-hexane. We believe that the superior performance of TFP in perfluorohexane makes it suitable as an alternative extractant to TAP in the Zr(IV) extraction system and to other conventional organic extraction systems.

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SEP P26 – Removal of Plutonium and Americium from Nitrate Solution by Precipitation

G. VERWAERDE, S. FAURE

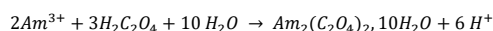
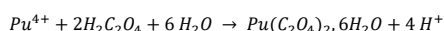
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Oxalate precipitation is a well-known method to recover plutonium from acid media as its product, plutonium oxalate, can be converted into plutonium dioxide by calcination.

This method is used at the end of the PUREX process to convert plutonium nitrate into plutonium oxalate. In this process, large volume of concentrated plutonium solutions are treated with excellent efficiency, since Pu oxalate has a low solubility for a large domain of nitric acid concentration.

In the frame of a facility decommissioning preparation program, CEA/Valduc has to treat an aged plutonium nitrate solution where plutonium is associated with americium. Concomitant Pu and Am oxalate precipitation has been assessed as process opportunity for this project.

Literature¹ shows the possibility to form Am(III) oxalate for a more restricted domain of nitric acid concentration than for Pu(IV). The global reactions of precipitation are:



In the present study, laboratory scale investigations were carried out for the simultaneous removal of Pu and Am from nitric acid solutions. The purpose of these experiments was to find a domain where Pu(IV) and Am(III) oxalate can be both precipitated.

The results show a good precipitation yield for both americium (80%) and plutonium (98%) when the nitric acid concentration is low (1,5M). However, the residual activity in the oxalate effluent remains too high to be discarded to the active effluent treatment workshop without additional treatment.

¹ G.A Burney and J.A. Porter, Solubilities of Pu(III), Am(III) and Cm(III) oxalates, Savannah River Laboratory, E. I. du Pont de Nemours and Co. Aiken, South Carolina 29801.

SEP P27 – Monitoring Plutonium Concentration in Process Solutions through UV-Vis Spectrophotometry and Multivariate Analysis

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Reliable analyte quantifications are necessary for process control applications such as nuclear fuel recycling. Standard determination of plutonium concentration in nitric acid solutions, performed through UV-Vis spectrophotometry, requires chemical preparation such as complete oxidation to Pu(VI), reduction to Pu(III) or pH control before analysis, as the UV-Vis spectral response of Pu(IV) not only depends on Pu concentration but also on HNO₃ concentration and the presence of interfering species.

In order to limit chemical preparation, contaminated waste and operators' exposure, chemometrics provides a statistical approach to overcome the complexity of this whole system through multivariate analysis. This study applies a partial least square regression (PLS) model on various calibration sets including either lab-produced solutions of set [Pu] and [HNO₃] concentrations, process solutions or both, to get the best prediction on a validation set composed of a large range of process solutions. Model parameters are adapted in order to decrease errors and get the best fit between offline measurements and model predictions.

The results show that the PLS model can get a reliable estimation of plutonium concentrations at the different process checkpoints, and identify outliers, provided that the solutions used to build the model are representative of process solutions in terms of [Pu], [HNO₃] and fluoride concentrations. It confirms the potential of UV-Vis spectrophotometry coupled to multivariate analysis to be implemented for on-line measurements.

ACTINIDE MATERIALS AND NUCLEAR FUELS

MAT P01 – Preparation of Mixed Actinide Oxides by Colloidal Sol-Gel Route

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The MOX nuclear fuel used in nuclear reactors is traditionally prepared by powder metallurgy. To improve the distribution homogeneity of actinides in the MOX and avoid the hot spots coming from local accumulation of fissile elements, new synthesis methods are studying. Recently, Lu and al have used sol-gel colloidal route to prepare stable sols of nanometric thorium colloids by a control of the pH and the use of a complexing agent. These two key parameters allow the limitation of the hydrolysis and condensation reactions of the polynuclear actinide species $An_x(OH)_n^{(2x-n)+}$ and thus, a control of the size of the particles, as well as their interaction, whether attractive or repulsive [1]. After a freeze-drying process and a thermal treatment, the accessible macroporous-microporous ThO_2 powder obtained was easily impregnated by a simulating minor actinide solution and thermally treated to prepare a mixed actinide oxide.[1].

In this work, we extended the method used by Lu and co-workers to others lanthanides and actinides (M): Ce(III) and U(VI). For this, the sols were prepared dissolving salt of thorium, cerium or uranium nitrates in solution of amino-caproic acid (ACA) used as the complexing agent. The pH was then adjusted using a solution of NH_4OH at a pH range from 3 to 6. The stable sols were then freeze dried to concentrate and assemble the colloids and the paste thermally treated to obtain actinide oxide powders. The sols and the final materials were characterized by Small Angle X-ray Scattering (SAXS), scanning and high-resolution electron microscopies (SEM and HRTEM). The results highlight that the sol stability and the final material morphology depend on the element M, the ratio M/ACA and the pH. First, for Th, simulations of SAXS data shows that two types of particles in thorium sols. When $Th/ACA \leq 0.5$, the particle consists in thorium hexamer cored surrounded by an ACA shell. When $Th/ACA > 0.5$, the particles are core-shell nanoparticles having a ThO_2 core and a shell of ACA. Finally, when $pH = 6$ and $Th/ACA = 2$, sol is not stable and a precipitate is formed. With Ce, whatever the Ce/ACA ratio and for $3 \leq pH \leq 5$, the sols obtained are stable and present the same 15% of polynuclear Ce species having a nanometric size. For $pH=6$, a mixture of Ce polynuclear species and nanoparticles having size around 10 nm were observed. Similar polynuclear species having nanometric size were obtained with U but only at pH 3. For higher pH, an uranium phase precipitates.

After freeze-drying and a thermal treatment, macro and microporous powders were obtained and consist in loose packings of ThO_2 , CeO_2 and UO_2 nanoparticles with an ordered distribution of interparticular porosity and in some cases a fraction of nanometric crystallites. Specific surface area and pore volume were determined by SAXS analysis. Finally, the powders obtained were impregnated with a simulating minor actinide solution of $HfCl_4$ and thermally treated to prepare mixed oxides. The SEM-EDX analyses highlight a high homogeneities of the element distributions at a microscopic scale

This methods is of interest could therefore contribute to research into the transmutation of minor actinides and the synthesis of mixed actinide fuels.

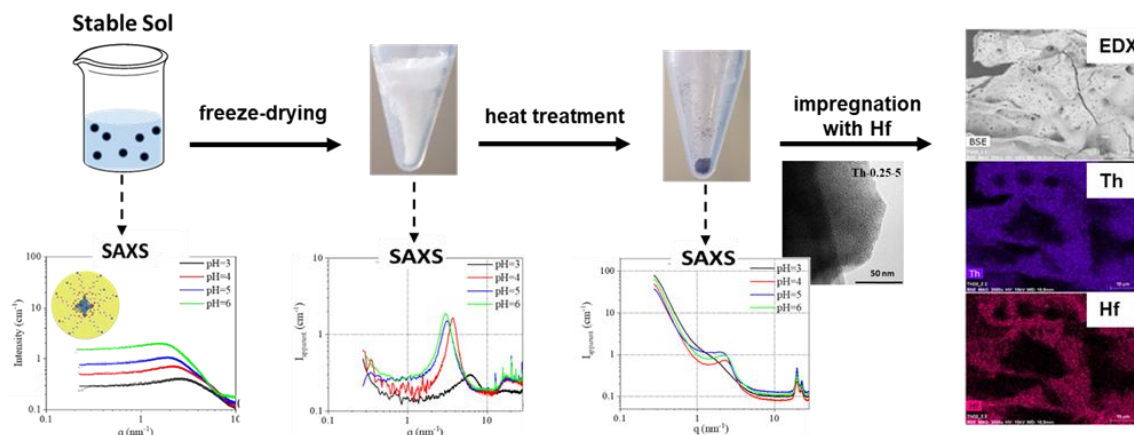


Figure 1: Description of the mixed oxide powder $\text{ThO}_2/\text{HfO}_2$ preparation from the sol to the final material with SAXS figures, HRTEM image of the ThO_2 powder before impregnation, and the Energy dispersive X-ray (EDX) cartographies of Th and Hf of the final material.[3]

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MAT P02 – Exploring Predictive Laws for the Flowability of Powder Mixtures: the Case of UO₂ Powder

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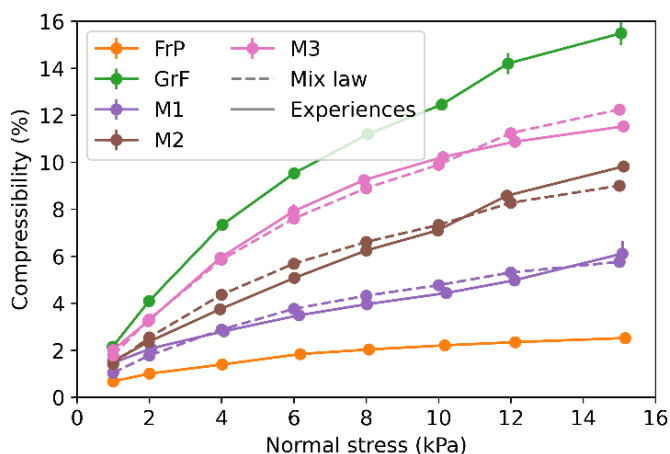
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Dynamic behaviour of granular media is of crucial importance for many industrial processes. Better understanding of the powder rheology allows better control of the final properties of the manufactured product such as tablets or pellets and avoids specific problems occurring during powder conveying such as segregation or clogging of pipes and silos. In the nuclear field, powder flowability issues can lead to increased radiation exposure for workers who unclog pipes. Thus, in the context of nuclear fuel pellets fabrication, we explore flowability of mixtures of uranium oxides powders.

In this work, model powders were first developed to provide particles with "simplified" characteristics compared to conventional UO₂ powders. To do so, model UO₂ powders are prepared by two different granulation process, involving pressing and sieving, in order to obtain samples with different agglomerate shape, size distribution and strength. After determining particle physical characteristics of each powder, the flowability of these samples is studied by several indicators measured with a powder rheometer and other rheology characterization technics (repose angle, compressibility etc...). The flow properties measured on these powders are analyzed in relation to the physical characteristics of the particles.

In a second step, binary mixtures were prepared using a cohesive model powder and a free flowing model powder. The flowability data was interpreted along three different axes: results analysis considering simple mixing laws, the use of correlation matrices to process data statistically, the use of models based on inter-particle forces and a multi-component population-dependent granular. Thus, it appears that mixing laws can be effectively deduced to predict certain flow properties from individual powders properties. Moreover, the results obtained using correlation matrices appear promising: they highlight the existence of some trends for certain properties as a function of particle characteristics. Finally, it has been demonstrated that the flowability index of UO₂ powders follows a power law in function of Bond number, as inactive powder mentioned in the literature.



Compressibility of UO₂ powder mixtures

MAT P03 – Application of Thermal Analysis for Future Advanced Fuel Cycles and Waste Management

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The Laboratory of Materials Research (LBM) at the National Center for Nuclear Research conducts scientific, testing, and diagnostic work on advanced construction and functional materials used in nuclear reactors. The LBM includes the Thermal Research Laboratory, equipped with modern devices for comprehensive thermal analysis. In the course of researching materials potentially used in high-temperature gas-cooled reactors (HTGR), investigations are conducted, including the measurement of the coefficient of thermal expansion (CTE), shrinkage, anisotropic behavior for various types of materials (e.g., ceramics, glass, metals, composites, polymers, etc.) at temperatures up to 1600°C in air or in a protective gas atmosphere. Measurements also cover changes in mass, temperature stability, oxidation/reduction reactions, analysis of the composition of evolved gases, phase transition temperatures, oxidation reactions, and specific heat in the temperature range of RT-1600°C in a protective gas atmosphere and up to 1250°C in a steam atmosphere. Moreover, the laboratory's equipment allows for the determination of diffusion and thermal conductivity, including volumetric materials in the range from 0.01 to 1000 mm²/s with an accuracy of up to 3% over the entire temperature range from RT to 1250°C. This is achieved using a xenon lamp with a wavelength of 150-2000 nm in a controlled gas atmosphere. Furthermore, the determination of diffusion and thermal conductivity is possible for layers with thicknesses of (i) metallic 0.1-20 µm, (ii) ceramic 0.3-5 µm, (iii) insulating materials from 30 nm to 2 µm.

The authors would like to highlighting the potential applications of the mentioned thermal analysis research for the broad theme of safeguards and analytical methods developments for actinide materials and fuel fabrication methods.

In this study, materials-substrates of ceramic matrices obtained by two different techniques were compiled and compared. The first technique was the "wet route" synthesis using the Complex Sol-Gel Process (CSGP), and the second was the "dry route" based on a mechanical alloying process in a planetary ball mill under the argon atmosphere. Both techniques were applied to synthesize stabilized zirconia with neodymium and/or cerium oxide with a content of 10 mol% as surrogates of potential Minor Actinides. The spark plasma sintering (SPS) technique was applied to consolidate the prepared powder mixtures.

Subsequently, material microstructure, phase composition, and properties were assessed using thermal analysis (TG-DSC, dilatometry, laser flash method), as well as ICP-MS&LIBS, Raman spectroscopy, SEM observation, XRD phase analysis, Vickers hardness, and surface Nanoindentation testing. The presented results enable significant in-depth characterization of this material and an assessment of the impact of the selected method of powder preparation and additives on the properties of the sintered material. Such a comparison is also important in the context of obtaining other advanced materials used in nuclear reactors.

Acknowledgement

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MAT P04 – Preparation of (U,Pu)O₂ Mixed Oxides By Hydroxide Route

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In France, nuclear fuel recycling is currently based on the recycling of plutonium from spent fuel. The plutonium retrieved is then used to produce Mixed Oxide fuels (U,Pu)O₂ (MOx) by co-grinding the PuO₂ obtained by oxalic route with UO₂ through the MIMAS (Micronized MASTER blend) process[1]. Such MOx fuel is used in PWR. In the framework of new generation of Fast Neutron Reactor (FNR), several alternative MOx fuel synthesis processes are under investigation. Among them, the hydroxide route [2] constitutes a promising option. This synthesis route is based on the quantitative precipitation on An(III)/An(IV) compounds by ammonia in specific chemical conditions, leading to production of highly reactive powders with homogeneous cationic distribution on the nanometric scale. With this new wet process, the problem of powder dissemination encountered during MIMAS process can be overcome and, consequently, the number of stages during manufacturing can be reduced. This method also allows the preparation of very representative homogeneous model compounds doped with fission products, which are very useful for the understanding of spent fuel behavior [3–7].

However, this method was never applied to (U,Pu)O₂ synthesis yet. The transposition of this method to the real uranium-plutonium system raise questions on the experimental methodology used, the physico-chemical characteristics of the powders produced, and their influence on the shaping and sintering stages. These issues have prompted a multidisciplinary R&D approach to explore the potential of this innovation for MOx fuel fabrication. In this context, the aim of this work was firstly to study the influence of various synthesis parameters (reactant concentrations, redox, addition rate, drying temperature, calcination temperature...), in order to optimize the reference hydroxide precipitation synthesis route. Therefore, a multi-parametric study was performed, coupled with crossed characterization techniques (SEM, XRD, TGA, UV-vis, IR and Raman spectroscopies, microprobe analyses, BET, dilatometry, XAS).

The aim of this poster will be to present the results obtained by this approach on the optimal parameters for (U,Pu)O₂ synthesis by hydroxide pathway.

Keywords : Fuel, MOx, hydroxide precipitation, synthesis parameters

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MAT P05 – Wet Chemistry Route to Prepare a Panel of Irradiated MOx Fuel Model Compounds

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Irradiated fuel can be an interesting source of platinum group metals (PGMs, ruthenium, rhodium and palladium) that are all considered as critical metals¹. These metals are created by nuclear fission of ²³⁵U, ²³⁹Pu and ²⁴¹Pu in the light water reactors (LWRs) and are associated in white phases, also called ϵ particles². According to the IRSN (Institut de Radioprotection et de Sûreté Nucléaire)³, approximately 8400 tons of UO₂ and 120 tons of MOx are produced each year in France. The amount of ϵ phases within the irradiated fuel is approximately 1 wt. %, it can increase up to 1,97 wt. % in MOx from P. Dehaut⁴. They are composed of: ruthenium (30 wt. %), rhodium (5 wt. %), palladium (20 wt. %), technetium (10 wt. %), molybdenum (35 wt. %)⁵. That produces between 42 and 85 tons of PGM that can be valued each year in France. The PREPAC project (Procédé de REcupération des Platinoïdes en Aval du Cycle) proposed by the CEA & CNRS consortium, aims to study various processes to recover PGMs from nuclear fuels. In this context, the use of less radioactive and more easily handled simulants of irradiated nuclear fuel is necessary for the development of new recovery methods. On the other hand, irradiated MOx prepared by powder metallurgy (*i.e.* MIMAS process³) is an extremely heterogeneous material in terms of its chemical composition and microstructure. Fresh MIMAS MOx fuel is mainly composed of three phases that exhibit different Pu content⁴: Pu rich agglomerates containing 20 wt. % of Pu, UO₂ matrix incorporating 3 wt. % of Pu and coating phase incorporating 7,5 wt. % of Pu. The use of model compounds is thus also required to gain into our understanding of the behaviour of the fission products (FPs) within these different phases.

This work describes a way to prepare a panel of model compounds for irradiated MOx, called "SIMMOx". Plutonium was replaced by thorium in the SIMMOx. The use of Th as Pu analog⁶ is justified by the similarity of their ionic radius⁷ and oxidation state⁸ in the MOx and the high chemical durability of PuO₂ and ThO₂⁹. First, homogeneous SIMMOx pellets were synthesized containing 3, 7.5 and 20 wt.% of Th. Then, different families of FPs were incorporated in the SIMMOx separately, then simultaneously to increase progressively the complexity of the model materials. Ru, Rh, Pd, Mo and Re were added to simulate the fission products forming metallic precipitates in irradiated fuels¹. La, Ce, Nd, Pr, Sr were chosen to represent FPs dissolved in the matrix. Fission gas, volatile FPs and FPs forming separated oxide phases were not considered at this stage.

The SIMMOx pellets were synthesized following the hydroxide route¹⁰. The cations (our case U(IV), Th(IV)) from tetrachloride solutions were mixed with ammonia solution (NH₃.H₂O, 4M, in excess of 400%) to obtain hydroxide precursors. Ammonia solution was put in the stirring solution of cations (introduced in the appropriate proportions) controlling the dripping. The precipitate obtained was then washed with ammonia solution (0,25 M), water and ethanol, and dried in an oven at 90°C. It was then calcined at 800°C during 8 hours to obtain oxide powder that was pelletizing and sintered at 1600°C during 4 hours in order to obtain densities in the range of irradiated MOx fuel. In a second time, the same experiment is done adding the fission products in the cations solution in the target proportions^{4,5}.

In order to identify the nature of the phases formed and the spatial distribution of the FPs, SIMMOx were characterized using SEM, EDX and XRD. The density of the pellets obtained after sintering was determined using geometrical measurements and He pycnometry. Only the group of FPs dissolved in the matrix was put in the first batch. XRD analysis were important in order to verify their influence on the crystallographic structure on the matrix. In the second batch, only FPs forming metallic precipitates have been incorporated. Their sizes and their spatial distribution in the pellets (observed by SEM) have been compared with real spent fuel. Then, the two families of FP were put together in the synthesis in order to get closer to a real system.

The goal of all the synthesis is to perform a multiparametric study of their dissolution in a nitric acid solution (4M). The influences of the FPs on the elemental releases and on the preferential zones of dissolution will be studied. A special attention will be given to the dissolution residues in order to find the optimal conditions to recover the elements of interest. This study will be a preliminary step of a process of recovering PGMs from the spent nuclear fuel.

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MAT P06 – Adaptation of MOX MIMAS Process to the Isotopic Evolution of Plutonium – Research of Alternative Lubricant and Poreformer

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The evolution of the MOX product is associated with the degradation of the isotopic composition of plutonium, with an increase in the ^{238}Pu content (for instance linked to the increase in the burn-up rate of UOx fuels [1]) and the ^{241}Am content (linked to the storage of PuO_2 powder between its treatment and its introduction into the MOX manufacturing process). This leads to an increase in temperature and radiolytic activity within the powder blends [2].

Preliminary experiments have been carried out using PuO_2 powders with a degraded isotopic composition. It showed that increasing temperature damages the lubricating properties of zinc stearate, while increasing radiolytic activity reinforces the radiolysis phenomenon of azodicarboxamide (ADCA). In the long term, the loss of additives properties could finally hinder the pelletizing process.

For these reasons, Melox is engaged in the selection of alternative compounds to zinc stearate and ADCA. The work presented will focus on the development of MOX pellets with calcium stearate and oxamide under degraded isotopic conditions. It will highlight the quality of the products obtained and the performance gains compared to historical additives.

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MAT P07 – Evaluation of Dissolution Behavior of Unirradiated Fugen MOX Pellets

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Advanced Thermal Reactor "Fugen", which locate in Tsuruga, Japan, operated from 1978 to 2003 and has proceeded to decommission by Japan Atomic Energy Agency (JAEA). Spent fuels of Fugen, which are stored in the domestic facilities, are planned to be transported to France for reprocessing by Orano based on Inter Governmental Agreement.

For the reprocessing of Fugen fuel, it is necessary to consider the dissolution process, because MOX pellets are expected to be difficult to dissolve in comparison to UOX pellets. However, experimental data on dissolvability of "Fugen" MOX pellets are limited. Therefore, in this study, dissolution of unirradiated Fugen MOX pellets was performed to evaluate dissolution behavior as a preliminary test before reprocessing actual irradiated fuel.

The dissolution experiments were conducted using unirradiated Type-B Fugen MOX pellets, which Pu content is about 1.7 %, at the Chemical Processing Facility (CPF). After the dissolution under the condition of Table 1, dissolution solution and undissolved particles were separated by filtration using 0.45 μm pore size filter in Run1. In Run2, it was filtered twice, the first is 10 μm pore size, and the second is 0.45 μm pore size for evaluating the size of the undissolved particles. Undissolved particles were completely dissolved by nitric acid solution with small amount of hydrofluoric acid around 373 K for 30 hours. The concentrations of U, Pu, and ^{241}Am in undissolved particles dissolution solution were analyzed by ICP-AES and radioactivity analysis, and calculated dissolution yields by compering to the amount in undissolved particles and in loading of them.

Appearance of the dissolution solution and the undissolved particles are shown in Fig2. The reaction was finished in sight after 4hours of heating. The results are shown in Table 2. The dissolution yields of Pu, U and ^{241}Am were 99.9 %, which reproduced the result in the case of over 373 K⁽³⁾. Pu / (Pu + U) values of the undissolved particles were 23% (Run1) and 44% (Run2), They are more than 10 times higher than that of Fugen MOX pellets before the dissolution. From this result, the cause for generating undissolved particles is considered that locally high concentrations of Pu in the matrix remained undissolved. The ratio of Pu and U in the undissolved particles was more than 90% for both runs, and it was confirmed that almost all of the residues were 10 μm or larger.

In addition, applicability of the fragmentation model⁽⁴⁾⁽⁵⁾ was evaluated using obtained Fugen MOX dissolution data. This model needs to set a parameter "f", which is the ease of penetration and diffusion of nitric acid into the fuel matrix, and when it is 7×10^{-3} , It is found to be in good agreement between experimental curve and calculated curve on Pu dissolution. Thus, the fragmentation model adapting for fast reactor fuel is prospected to adapt for low Pu content fuel.

Dissolution behavior obtained in this study will be contributed to the reprocessing of Fugen spent fuel at Orano.

Table 1 Dissolution experiments condition

Item	Run1	Run2
Nitric acid initial concentration	7.7 M	
Nitric acid initial volume	260 mL	
Dissolution temperature	365 K	
Target of heavy metal concentration	200 g/L	
Dissolution hours	4 hours	5 hours
Pore size of filter	0.45 μm	10 μm and 0.45 μm

Table 2 The result of dissolution test

Items		Run1	Run2(sum)	Run2(10 μm)	Run2(0.45 μm)
Input amount (g)	Total amount	60.439	60.474		
Undissolved particles (g)	Total amount	9.9×10^{-3}	7.6×10^{-3}	5.9×10^{-3}	1.7×10^{-3}
	Pu	6.7×10^{-4}	3.9×10^{-4}	3.7×10^{-4}	1.5×10^{-5}
	U	2.3×10^{-3}	5.0×10^{-4}	5.0×10^{-4}	$< 5.0 \times 10^{-4}$
	^{241}Am	4.7×10^{-5}	2.8×10^{-5}	2.6×10^{-5}	1.6×10^{-6}
Dissolution yields (%)	Total amount	99.9	99.9		
	Pu	99.9	99.9		
	U	99.9	99.9		
	^{241}Am	99.9	99.9		

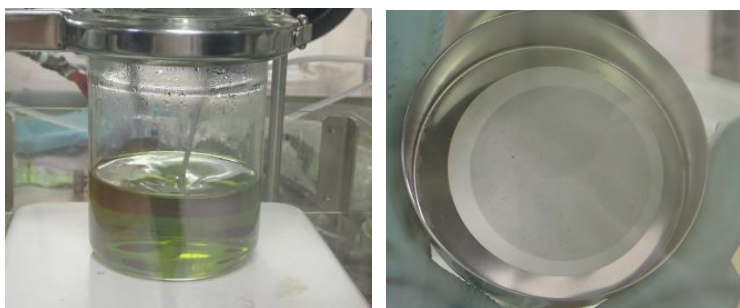


Fig1. (left) Appearance of the dissolver solution after heating for 4 hours. (right) Appearance of the undissolved particles.

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MAT P08 – Comparison of the Dissolution Kinetics and Mechanisms of UO_2 and U_3O_8 in Nitric Acid

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The widespread use of Mixed Oxide (MOx) fuel in Pressurized Water Reactor associated with a plutonium multi-recycling is an option currently studied in France. Such strategy has gained increasing attention as a way to stabilize the plutonium inventory. The dissolution of spent fuel in nitric acid is one of the main step of the nuclear fuel recycling. However, a decrease in $(\text{U,Pu})\text{O}_2$ dissolution kinetics with the increase in Pu content is observed [1-2].

An innovative process is currently studied to enhance MOx reprocessing at industrial rates. This process consists of extracting the fuel from its cladding upstream the dissolution, in order to increase the fuel surface area in contact with concentrated nitric acid and thus facilitate its dissolution. Currently, the most promising solution involves high temperature oxidation of the MOx spent fuel, which induces phase transformations leading to the collapse of the ceramic into a more reactive powder.

However, the MOx fuel presents multiphase structure that includes different agglomerates with various uranium and plutonium concentrations (**Figure 1**): one with high uranium concentration (blue), one with high plutonium concentration (red) and agglomerates stack where the plutonium concentration is similar to the fuel average one (green). Therefore, the over-oxidation of a MOx pellet will lead to the formation of different phases depending on plutonium content: U_3O_8 , $(\text{U,Pu})_3\text{O}_8$, $(\text{U,Pu})_4\text{O}_8$, $(\text{U,Pu})\text{O}_{2+x}$. It is therefore necessary to ensure that these phases are highly soluble in nitric acid. To this date, there is no (case of Pu-containing phases) or little (case of U_3O_8) data available in the literature on the behavior of these hyperstoichiometric phases during dissolution, making it difficult to optimize the reprocessing of over-oxidized irradiated MOx fuels.

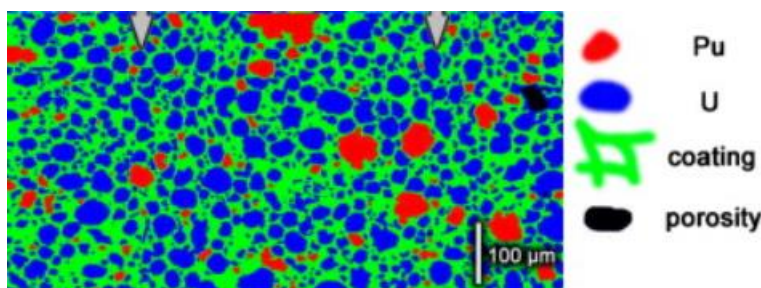


Figure 12. Electron probe micro analysis (EPMA) mapping obtained on an irradiated MIMAS MOX pellet with a $\text{Pu}/(\text{U}+\text{Pu})$ ratio of 4.62 wt.% [3].

The aim of this PhD project is to fill this gap by investigating the kinetics and mechanisms governing the dissolution of each phase resulting of the over-oxidation of $(\text{U,Pu})\text{O}_2$. During this conference, we will compare the dissolution of (i) a single phase UO_2 representative of the U-rich phase in the MOx, and (ii) its resulting over-oxidized phase, U_3O_8 . A homemade experimental set-up (**Figure 2**) was developed for this purpose, which allows us to carry out dissolution experiments in controlled conditions while continuously monitoring the release of U cations *via in situ* UV-Vis spectrometry analysis.

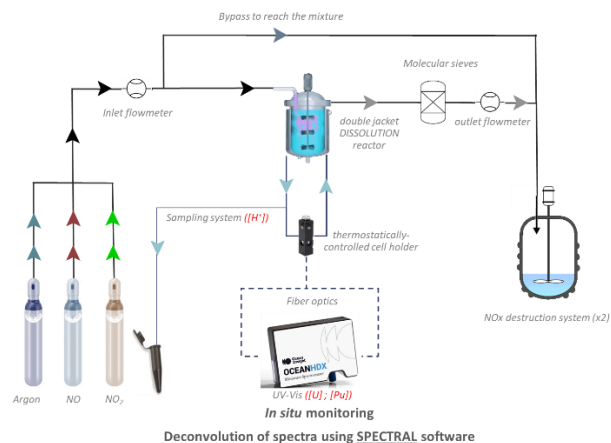


Figure 13. Experimental dissolution set-up.

Interrupted dissolution tests will also be carried out to study the evolution of the powder by characterizing it upstream, downstream and during the experiments. The *ex situ* solid-state characterizations will be based on BET, XRD, SEM, Raman spectroscopy, etc. All the experimental data will be used to compare the reaction mechanisms involved during the dissolution of UO_2 and U_3O_8 , and to highlight the impact of the over-oxidation on the dissolution behavior of uranium oxides.

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MAT P09 – Impact of AMSEL Ligands (Ph-SO₃-BTBP) on the Conversion Strategy to Obtain the Final Zirconia-Based Matrix

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The feasibility of preparing Zr oxide-supported CERCER targets (for AmO₂) has been developed by an advanced thermal denitration route. Experiments on Nd, as Am surrogate, have been carried out to study the impact of AMSEL ligands (Ph-SO₃-BTBP^k) on the conversion strategy to obtain the final oxide. Two routes, dry and wet, have been studied and compared by direct co-precipitation and internal gelification, respectively. In this preliminary study, we have focused on a simplified system, such as ZrO₂ as an inert matrix. In our case, the co-precipitated solid was aged, washed, filtered, dried, and finally calcined but not sintered; therefore, the addition of trivalent elements as Sc³⁺, Y³⁺ or rare-earths, necessary for the ZrO₂ solid phase stabilization,^l has not been employed. Another important parameter to take into account is the nominal content of trivalent doping cations, in this case, Nd. In the literature, very different Minor Actinides (MA) levels can be found depending on their future use as a fuel. This fraction drops to 2.5%-10%^m for large and medium-sized sodium-cooled fast reactors, and in contrast, accelerator-driven systems could allow for MA fractions up to almost 50%.ⁿ Thus, a wide range of Nd concentrations has been used, from 0 to 50 wt%, to expand its applicability. However, it is well known that the more MA added, the greater the amount of Ph-SO₃-BTBP and its fragments from the stripping solution.

First of all, we tried a direct co-precipitation of Zr and Nd, both from nitrate aqueous solutions by indirect ammonia addition (by urea/HMTA degradation), which is a carbon free-oxide powder after conversion of the starting precursors.^o A similar procedure was previously developed at CIEMAT for ammonium diuranate (ADU) precipitation where we recover and purify uranium from samples of different origins, and precipitate it for new fuel fabrication^p. As one of the main objectives is to carry out the fabrication by wet route (avoiding the manipulation of powder with a high content of MA) we also applied a sol-gel technique based on the formation of microspheres by internal gelation from the same type of solutions previously described, dropped into a column filled with hot silicon oil (90-100°C), which acts as a heat carrier. These solid samples with varied Zr and Nd proportions (0, 3, 5, 10, 30 and 50 wt% of Nd) were analyzed by the different techniques available at CIEMAT (TGA/DSC, ICP-MS, SEM-EDX, Raman spectroscopy and XRD).

^k Geist, A., *et al.* Selective aqueous complexation of actinides with hydrophilic BTP and BTBP: Towards improved i-SANEX processes. In 11th Information Exchange Meeting Actinide and Fission Product P&T (2010) 1-9. OECD-NEA. San Francisco, USA.

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^p Milena, A. *et al.* Thermal air oxidation of UO₂: Joint effect of precursor's nature and particle size distribution. Progress in Nuclear Energy 159 (2023) 104629. <https://doi.org/10.1016/j.pnucene.2023.104629>

Once the methods for the co-precipitation and internal gelation were ready, the effect of the presence of degraded Ph-SO₃-BTBP samples on the conversion methodology was also studied along the process.

The research leading to these results has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945077, and the Spanish Project IONMAT, which is an interdisciplinary and multidisciplinary consortium funded by the State Plan for Scientific and Technical Research and Innovation (PEICTI) 2021-2023.

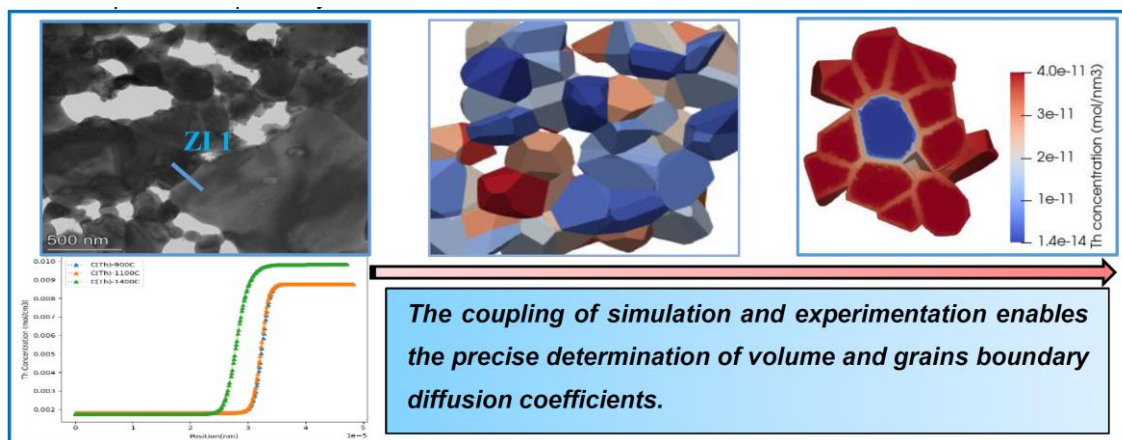
MAT P10 – A Novel Approach to Studying Thorium Diffusion in UO_{2+x} Single Crystals

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Sintering is a crucial step in the manufacturing process of MOX fuel. During this process, uranium dioxide and plutonium dioxide pellets are exposed to controlled atmosphere and temperatures. Under these conditions, only the high-temperature diffusion of uranium and plutonium cations allows for homogenization at the crystalline lattice. The distribution of plutonium in uranium obtained during this process is an important characteristic of MOX fuel, with implications for chemical reprocessing and power distribution during irradiation. As the sintering process takes place, the microstructure of the pellets evolves from particles in contact to a 95% dense compact. The mechanisms that cause mass transport in response to the driving force [1] include volume diffusion (VD), surface diffusion (SD), and grain boundary diffusion (GBD). Determining the diffusion coefficients of uranium and plutonium species is crucial for understanding and controlling the transport phenomena. An original study methodology has been developed and tested on a surrogate material, namely $(\text{U}_{0.75}\text{Th}_{0.25})\text{O}_2 / \text{UO}_{2+x}$, due to the challenges in handling plutonium oxide. This approach enhances the understanding of the inter-diffusion of uranium and thorium-uranium metallic species in the 25% thorium mixed oxide $\text{U}_{0.75}\text{Th}_{0.25}\text{O}_2$. In this study, the volume diffusion of Th cations in UO_2 was investigated using a composite material with micrometer-sized grains of $(\text{U}_{0.75}\text{Th}_{0.25})\text{O}_2$ and submicrometer-sized grains of UO_{2+x} . This composite is elaborated to ensure that the grains are adjoined while limiting the diffusion of thorium. Thin films were extracted by the Focused Ion Beam technique (FIB) at the intergranular zone and then tungsten-welded onto a heating support. Nanoscale tracking up to 1100°C was performed using transmission electron microscopy (TEM), acquiring concentration profiles at different times along a line crossing two grains of different initial compositions. This allowed, for the first time, the determination of volume diffusion coefficients in single crystals of these materials (Figure below). 3D finite element simulations were conducted in order to adjust volume diffusion coefficients and grain boundary diffusion coefficients, using Fick's laws for multicomponent systems. These simulations successfully reproduced the experimental profiles acquired by TEM.



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MAT P11 – Surface Decontamination Techniques for HALEU Metal Ingots

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Recovery of uranium metal has been a feature of the electrometallurgical treatment of irradiated Experimental Breeder Reactor – II fuel at Idaho National Laboratory since deployment of the technology in the late 1990's. This treatment technique was selected by the U. S. Department of Energy as a means of conditioning the sodium bonded used fuel for geologic disposal. With the recent application of High Assay Low Enriched Uranium in many fuel designs for advanced reactor concepts, interest in using the HALEU recovered from EBR-II fuel has gained significant attention. In response to this interest, the EBR-II treatment program has deployed uranium metal casting techniques that produce reduced radiological content material intended to facilitate its use as feedstock in advanced reactor applications. Casting of the HALEU metal occurs within an inert atmosphere hot cell in close proximity to where highly irradiated used fuel is handled resulting in general hot cell contamination becoming adhered to the surface of the metal ingots. The presence of this surface contamination creates radiological exposure challenges in removing the HALEU metal from the hot cell and preparing for reuse as fuel fabrication feedstock. In response to these challenges, the INL is investigating deployment of techniques that can reduce surface contaminants and as result reduce the radiological exposure associated with handling the recovered uranium metal. Sonication has emerged as a leading candidate for near term deployment based on results from initial research trials. The research to be presented will provide an overview of the additional techniques considered, the advantages associated with the sonication approach and the results of the trials conducted thus far.

MAT P12 – In-Depth Analysis of Volatile Fission Products in High Burnup SFR Fuel Using a (U,Pu)O₂ SIMMOx Approach

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In the context of Generation IV Sodium-cooled Fast Reactor (SFR), the U_{1-y}Pu_yO_{2-x} Mixed Oxides (MOx) containing 20 % to 30 % Pu/(U+Pu) have been identified as the best candidate for fuels [1]. Under nominal operation conditions, at the level of the maximum neutron flux plane, the temperature at the core of the pellet can reach up to ~2473 K and up to ~873 K at the periphery. These values significantly exceed those observed for PWR fuels. Moreover, the physico-chemical and microstructural properties of the fuel are significantly affected by the continuous generation of Fission Products (FPs) within (U,Pu)O₂ matrix [2]. Such a high thermal gradient leads to fuel restructuring during irradiation and migration of volatile FPs such as iodine and cesium to the colder fuel regions. At high burnup, this phenomenon leads to the development of a layer enriched with volatile FPs, commonly referred to as “Joint Oxyde-Gaine” (JOG) [3]. Consequently, for the successful development of such reactors, it is mandatory from a nuclear safety perspective to understand the effect of irradiation on the fuel, particularly focusing on the effect of FPs and the JOG formation.

Due to its very high radiotoxicity, the characterization of irradiated fuel presents inherent challenges [4]. Isolating and studying distinct parameters such as porosity, FPs, JOG, oxygen-to-metal ratio (O/M), among others, remains challenging. Furthermore, these materials have complex compositional dynamics that change continuously throughout their lifecycle. To overcome these challenges, a “separate effect” approach using innovative materials referred to as “SIMFuel” [4,5] or “SIMMOx” [6,7], is required. These materials consists of fresh fuel doped with stable isotopes of FPs, thereby limiting the radiological risk associated with experimentation. Furthermore, both FPs number and content in these materials can be tailored to investigate the effects of selected FPs. As illustrated by the recent examination of SIMMOx, information has been collected about the speciation of FPs and the interaction between FPs and (U,Pu)O₂ matrix with a Nd local enrichment with higher Pu content [6,7]. Moreover, there is currently no research addressing the influence of volatile FPs, responsible of JOG formation, on a MOx including all other FPs.

In our work, we are developing a new approach to incorporate volatile FPs into SIMMOx and study the JOG formation. This process starts with a diffusion couple between volatile FPs compounds and SIMMOx, in order to incorporate iodine and cesium in material, using temperature activation. Preliminary tests on UO₂ matrix have demonstrated the successful incorporation of iodine and cesium into the material thanks to different migration/transfer mechanisms induced by the temperature gradient. Additionally, the microstructure (porosity and defects) would be representative of the spent nuclear fuel.

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MAT P13 – Thermodynamic and Kinetic Effects of Impurities in Uranium Alloys.

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Metallic uranium alloyed to stabilize the body centered cubic structure (γ -U) are superior nuclear fuels because of their inherent machinability, thermal conductivity, uranium atom density and dimensional stability during irradiation inside the reactor. However, the thermodynamic and kinetic effects of impurities severely impact the physical properties and accelerate the degradation of metallic uranium by formation of deleterious precipitate phases especially within the U-Ti-Nb-C-X system. A comprehensive understanding of the driving forces for carbide formation, distribution, and migration is lacking but necessary to better tailor processing pathways and manufacturing of metallic uranium. This work presents an integrated framework that provides insight into predicting the impurity and alloying effects in uranium alloys using a tailored experimental and multiscale CALPHAD-based modeling approach. Predictive models that go beyond equilibrium thermodynamics are used to explore the complex interrelationship between thermodynamics and kinetic driving forces responsible for impurity formation.

Keywords: kinetics, actinides, diffusion, impurities

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WASTE CONDITIONING AND GEOLOGICAL REPOSITORY

WAS P01 – Radionuclide Complexation with TBP and DBP: Thermodynamic Data Generation for the ThermoChimie Database

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Tri-n-butyl phosphate (TBP) is the most used extractant and is widely used to recover uranium and plutonium from spent nuclear fuel in the Plutonium Uranium Refining Extraction (PUREX) process (Schulz et al., 1990). TBP is decomposed by radiological and chemical reactions and changed into the acid phosphates such as di-n-butyl phosphates (HDBP), mono-n-butyl phosphate (H₂MBP) and phosphoric acid (H₃PO₄). To date, minimal attention has been directed towards understanding the behaviors of TBP and DBP under conditions relevant for radioactive waste disposal, specifically in the presence of hyperalkaline media resulting from the cementitious environment. Hence, this study investigates the degradation kinetics of TBP and DBP and their complexation with several radionuclides (Eu(III), Th(IV), Pu(IV), Np(V)). The research focus on the degradation products and complexation mechanisms in order to elucidate the influence of cationic species on the interactions between phosphates and radionuclides. The ternary complexation of TBP and DBP with cationic species (Ca, Mg and Fe) will also be the objective of this work. The formation of such species has been found to be relevant for other organic ligands in similar conditions as the ones studied in this work (DiBlasi et al., 2022). Additionally, the study will assess the impact of environmental factors, including pH and oxic/anoxic conditions, on degradation kinetic and complexation efficiency. Understanding these variables is crucial for adapting complexation strategies to diverse environmental conditions, ensuring the applicability and effectiveness of the basic knowledge (i.e. datasets) derived in this work.

The findings of this research will contribute to the development of new thermodynamic data for species missing from current thermodynamic databases (i.e. ThermoChimie) used for geochemical calculations in the context of radioactive waste disposal.

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WAS P02 – Modelling the Gas Generation of Actinide Bearing Materials in Storage Containers

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Actinides reprocessing generates by-products with low contents of radioactive elements. These products are placed in dedicated packaging arrangements involving several containers for medium to long-term storage. However, during storage, the products evolve by generating gases because of chemical and radiochemical reactions. Indeed, molecules of the plastic elements of the packaging (containers, plastic bags), adsorbed water and matrix material of the product (salts) can be decomposed under ionizing radiation. Radiolysis generates primary radicals that can react with each other or with surrounding materials by homogeneous reactions to form stable gases (H_2 , HCl , CO_2) [1-5]. These phenomena may cause safety issue in storage vaults.

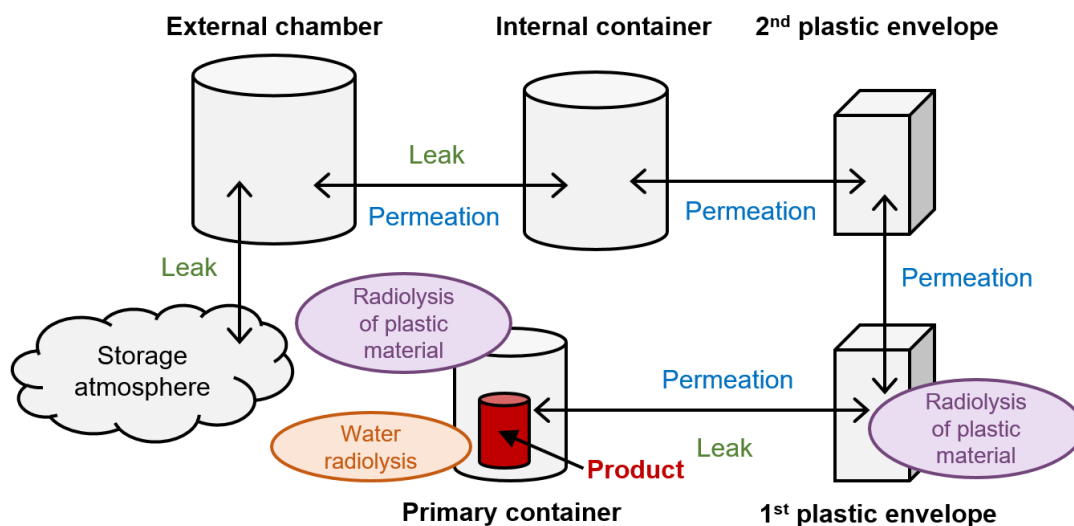


Figure 1: Scheme of each phenomenon taken into account in the model

To improve our knowledge of the evolution of these alpha emitters containing products, a model was developed using a macroscopic approach. This phenomenological model can be divided in two parts. First, plastic and water radiolysis models were implemented to evaluate gas generation closed to the nuclear materials. Secondly, the transportation of gases between the different containers were evaluated. The model takes into account two transfer phenomena: leakage as a result of a total pressure difference between two compartments and permeation as a result of a partial pressure gradient from each side of a plastic wall. The model was computed in Matlab using ODE solvers and was confronted to experimental measurements. Chosen key parameters were adjusted to fit the experimental data. The model allows us to highlight the key parameters influencing the gas generation.

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WAS P03 – Continuous Radioactive Organic Liquid Waste Treatment Technology Using an Emulsion Flow Apparatus

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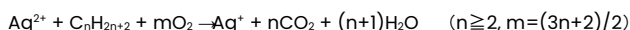
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Radioactive liquid wastes are generated through various experiments and/or analyses in nuclear facilities. These liquid wastes containing both radioactive elements and chemical reagents have been stored in nuclear facilities due to a lack of efficient treatment procedures. To give appropriate treatment procedures for the stored radioactive liquid wastes, the STRAD (Systematic Treatment of RAdioactive liquid waste for Decommissioning) project is conducted by the Japan Atomic Energy Agency (JAEA) with several collaborators.

Aqueous and organic solutions containing various chemical materials are this project's targets, and radioactivity removal technologies from them have been developed. Treatment of organic compounds is one of the most difficult challenges of this project. Basic studies for applying solidification treatments such as geopolymer to the organic liquid are still ongoing. However, solid wastes remain after those treatments. To reduce the amount of waste as much as possible, complete mineralization of organic compounds is required. Oxidative decomposition is a promising procedure for mineralization, and currently, we are conducting fundamental studies for the decomposition of organic compounds. One of the decomposition methods is a combination of oxidation by metal ions and an emulsion formation technology. Ag²⁺ has strong oxidation power and can be applied to the decomposition of organic compounds. The decomposition reaction of hydrocarbon compounds by the Ag²⁺ oxidation is written as follows;



Since the Ag²⁺ oxidation reaction proceeds at the boundary of the aqueous phase containing Ag²⁺ and the organic phase, efficient mixing of the two phases is necessary for effective decomposition. In this study, we investigated the applicability of an emulsion flow technology that has been developed for efficient solvent extraction by mixing and separating an organic solvent and an aqueous solution continuously. The emulsion flow apparatus consists of a column in which an emulsion state is generated and pumps for supplying organic and aqueous solutions. The two phases are supplied into the column from opposite ends, and the counter-current forms an emulsion state inside the column. The supplied liquids go out from the column from different ends. A part of the organic compounds supplied into the column are decomposed inside the column, and residual organic compounds are discharged from the column. Thus, circulating an organic liquid and an aqueous solution containing Ag²⁺ is expected to achieve continuous treatment.

In this study, to confirm the decomposition performance inside the emulsion flow apparatus, decomposition tests of the PUREX solvent (30% TBP in dodecane) were carried out, where Ag²⁺ ions were generated by electrolysis of Ag⁺ ions in AgNO₃ solution. Efficient mixing of two phases was successfully done in the column, and the decomposition of organic liquid was progressed in the emulsion flow device system. Carbon dioxide (CO₂) was generated as a decomposition product of organic substances. The total organic carbon (TOC) analysis on the aqueous phase after the tests detected water-soluble decomposition products. Based on these results, the emulsion flow technology was shown to be applicable to the treatment of organic liquid waste. To identify the degradation products of the organic compounds and the decomposition mechanisms, LC-MS analysis on the aqueous phase will be carried out.

In the future, an engineering-scale apparatus with durability against radiations and chemicals will be developed, and genuine liquid wastes accumulating in laboratories will be treated.

WAS P04 – The Effect of pH and Radiation Damage on Diffusion, Dissolution and Precipitation during Glass Corrosion.

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In addition to pH and temperature, glass corrosion is also affected by radiation damage. There are essentially three components, diffusion, dissolution, and precipitation, in glass corrosion and there is evidence that the rate and onset of all three of them is affected by radiation damage. By combining, high-temperature high-speed AFM, high-energy ToF-ERDA, white light interferometry and electron microscopy, we have measured from a few minutes to a few hours all the three components as a function of pH (from 1.7 to 12) and radiation damage in dilute conditions (stage-I) on ISG2 glass. This has also allowed us to measure the diffusion coefficients of B (and its isotopes), Na and H/H₂O at different pH's as a function of radiation damage. We will discuss the use of these techniques, their potential in unraveling the different components of glass corrosion and how they are affected by radiation damage.

WAS P05 – Uranium Hexafluoride Reduction Chemistry in Ionic Liquid Medium

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The enrichment of uranium for nuclear fuel results in the waste product depleted uranium hexafluoride (UF_6), a remarkably corrosive material with a high vapor pressure. Due to the extreme hazards of this material, both transport and storage become extremely problematic.^{1,2,3} Thus, the conversion of UF_6 to a more chemically stable form of uranium is necessary. Conversion has dual benefits, as it leads to safer storage and transportation conditions while providing worthwhile resources. This study explores efficient pathways for the reduction of UF_6 , with a focus on the recovery of uranium tetrafluoride (UF_4) which has crucial applications. UF_4 holds promise as a nuclear fuel in advanced nuclear reactors, as well as serving as a precursor to uranium metal.⁴ Recent advancements in the use of room temperature ionic liquid (IL) offer new possibilities for UF_6 stabilization and uranium recovery.

The reduction of UF_6 to UF_6^- has been demonstrated by dissolution into IL, which donates an electron from the IL anionic species, bis(trifluoromethanesulfonyl)imide, rendering the nuclear material chemically inert.⁵ Over long periods of time, a second electron donation will take place from the IL, causing a precipitation of the reduced uranium coordinated with the IL cation, $[UF_6][1\text{-methyl-1-propylpiperidinium}]_2$. However, a more rapid recovery of uranium from IL was achieved through the addition of aqueous and nonaqueous extraction agents. Vigorous mixing of the uranium/IL solution and extraction agent induced a competing reaction in the solution, in which the uranium was recovered in a mixed valency state. A portion of uranium was reduced to solid UF_4 , while the other portion was oxidized to a uranyl (UO_2^{2+}) species and remains in the phase of the extraction agent. Removal of the agitation step following addition of extraction agent increased the product yield of UF_4 and revealed that the precipitation of the solid UF_4 occurred at the IL/extraction agent interface. The uranium concentrations were analyzed via inductively coupled plasma atomic emission spectroscopy (ICP-AES). The solid, UF_4 , was analyzed using powder x-ray diffraction (pXRD) and thermal gravimetric analysis (TGA). Reaction kinetics were also investigated by monitoring the production of UF_4 using UV-visible spectroscopy. Additionally, the experiment was repeated at various temperatures to calculate the reaction's activation energy.

Although the nuclear fuel enrichment process gives rise to nuclear waste, that waste may be converted and reused in various ways, providing an important uranium supply. This research aims to examine the recovery pathways of UF_6 using IL to provide safe working conditions. Conversion of UF_6 to chemically stable compounds will reduce the risk involved with storage and transportation while also contributing valuable uranium resources.

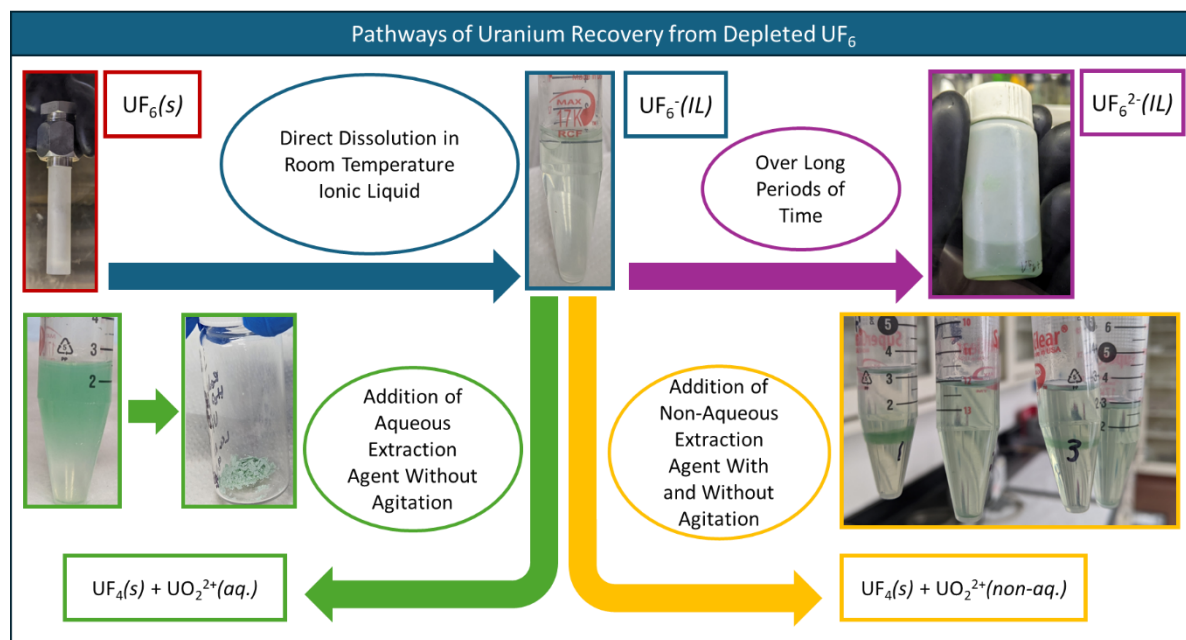


Figure 1: Flow chart of recovery pathways for uranium hexafluoride using room temperature ionic liquid medium.

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WAS P06 – Long-Term Storage and Aging of PuO₂ Powder up to 50 Years Old

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The UK has accumulated a large inventory of separated plutonium from spent fuel reprocessing operations that is largely stored as plutonium dioxide (PuO₂). The PuO₂ has been in storage for up to 50 years already and continued storage will be required until a process for re-use or disposal is implemented. Consequently, some materials may require storage for over 100 years.

During storage, the PuO₂ powder and the storage containers are subject to conditions of elevated temperature and intense radiation. To understand the effects of long-term storage, Sellafield Ltd undertakes a package surveillance programme that, in addition to inspections within the storage facilities, includes a programme of destructive examination of PuO₂ packages. Characterisation is performed in the High Alpha Inventory Laboratories within the UK National Nuclear Laboratory's Central Laboratory.

In the UK, PuO₂ powder was mainly produced by either the reprocessing of Magnox metallic fuel in the Magnox reprocessing plant or from reprocessing oxide fuel in the THORP reprocessing plant. Magnox PuO₂ is packaged in a screw-top aluminium inner can that holds the PuO₂, a layer of polythene that is used to contain the inner can when it is removed from the glovebox and a welded stainless-steel outer can. The THORP package is an all-stainless-steel package design with a screw-top stainless-steel inner can, a breathable intermediate stainless steel can fitted with a sintered metal filter and a welded stainless steel outer can. Both package types can be opened for destructive examination.

Packages are punctured, opened (Figure 1) and sampled before conditioning PuO₂ by heating in a furnace and repacking it for continued storage. Characterisation of the PuO₂ includes Specific Surface Area (SSA) analysis, ThermoGravimetric Analysis (TGA), pore-size analysis, powder X-ray Diffraction (XRD), water adsorption, chemical and isotopic analysis. In addition, the gas composition within each package is determined, the polythene is examined and metallographic examination of the cans is performed.



Figure 1: Opening a Magnox package

The UK population of PuO₂ powders provides a unique opportunity to study the effects of aging of many decades because there are PuO₂ powders with a range of initial physical properties that were characterised at the time of production. The evolution of the gas composition in storage packages and changes in the physical properties of PuO₂ occur over several years and decades. These changes may influence future reuse in MOX fuel production or disposal as well as behaviour during continued long-term storage. The results of these studies will be summarised and the implications discussed.

WAS P07 – Underwater Weathering of UO_x/MO_x Fuels

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In France, the single recycling of irradiated fuel leads to the medium-term storage of irradiated Mimas[®] MO_x (Mixed Oxide) fuel assemblies in pools, with a view to recycling or final disposal. In this context of underwater storage, it is important to consider an incidental scenario involving a defect in the cladding. Given that the pool water is oxidizing due to the presence of radiolytic products such as H₂O₂ and OH[•], leaching by this water promotes the dissolution of uranium from the fuel through an oxidative dissolution mechanism, followed by its reprecipitation as studtite [(UO₂)(O₂)(H₂O)₂].2(H₂O). It is therefore important to study these degradation mechanisms, with the aim of recovering the rods after several years and decades of storage, and limit contamination of the pool water by the release of radionuclides into the water.

To this end, a three-step scientific approach has been implemented. First, we studied the dynamic leaching of model materials (U, Th)O₂ using a multiparametric approach, aimed at establishing a set of kinetic laws that can be extrapolated to real fuel, in order to feed chemistry-transport models. In parallel, studies on the static leaching of MIMAS MO_x fuel under gamma radiolysis were conducted. These studies, which coupled Raman spectroscopy and image analysis, allowed us to propose a precipitation process for studtite on the surface of Mimas[®] MO_x fuel.

Finally, an original experimental methodology involving the use of ¹⁸O isotopes and Raman spectroscopy has been developed. These studies were conducted to enhance our understanding of the mechanisms of studtite precipitation on the fuel surface. The results obtained are consistent with each other and have allowed us to propose a mechanism for the formation of studtite, which is presented in **Figure 14**. The link between the formation of uranyl-peroxide bonds in the solid phase and the nature of the oxidizing species produced by water radiolysis has been elucidated.

It appears that there is a direct chemical relationship between the peroxo ligands within studtite and the peroxide entities of the H₂O₂ molecule in the solution. Under alpha radiolysis, the formation of H₂O₂ results from the primary radiolytic yield during the heterogeneous chemistry step involving the recombination of OH[•] + OH[•]. In the meantime, under gamma radiolysis, the formation of H₂O₂ results from a reaction mechanism involving dissolved oxygen in the solution. Regarding the uranyl bond, the characterization of its isotopy has allowed us to specify the oxidation mechanism occurring at the UO₂/water interface. It appears that under gamma radiolysis, the primary oxidation mechanism of UO₂ involves the incorporation of oxygen atoms from OH[•] radicals. In contrast, under alpha radiolysis, there is a significant contribution from H₂O₂, whose oxidation mechanism occurs in two steps. The first step involves a simple electron transfer between UO₂ and H₂O₂, followed by a second step where an oxygen atom is incorporated via OH[•] radicals produced as a reaction product from the first step.

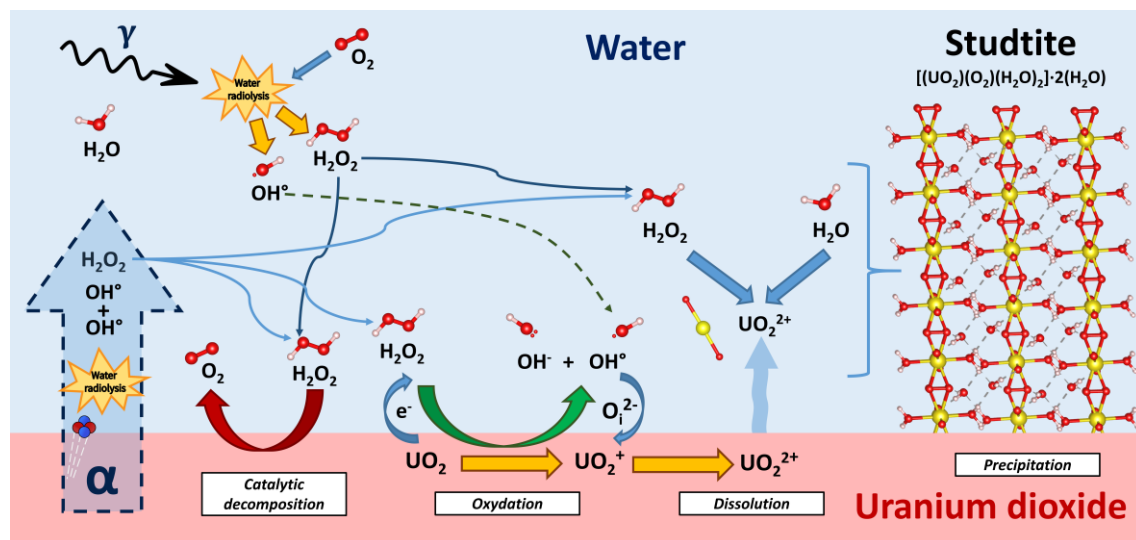


Figure 14. Reaction diagram for studtite formation on the fuel surface

WAS P08 – Irradiation Effects on the Leaching of Nuclear Waste Glasses: Understanding and Modeling of Leaching Mechanisms

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In France, borosilicate glass, known as R7T7, is used to contain high-level, long-lived nuclear waste from spent fuel reprocessing [1]. The glass canisters containing these wastes are destined to be stored in deep geological repository. After several hundred years, groundwater is expected to come in contact with the glass, which will have been self-irradiated by the radioactive elements it contains. Alteration of the glass by water, whose structure and properties will have been modified by the effects of its self-irradiation [2], represents the most important source of radionuclide dispersion in the environment.

Insofar as the alteration phenomenon takes place on a time scale that is inaccessible, modeling enables to simulate the very long-term glass behavior. In this case, the GRAAL 2 model [3], which will be used during this Ph.D. study, allows the prediction of the glass constituent elements releases in solution. Nevertheless, GRAAL 2 does not allow the distinction between the alteration of a pristine glass and a radioactive glass yet.

In order to better understand the alteration mechanisms of nuclear glasses and to adapt the GRAAL 2 parameters to radioactive glasses, this work focuses on the study of the alteration mechanisms of a simplified borosilicate glass, called ISG (International Simple Glass). Its simple chemical composition (SiO_2 , B_2O_3 , Na_2O , Al_2O_3 , CaO , ZrO_2) exacerbates some phenomena, such as leaching and irradiation-induced structural modifications, and makes characterization and modeling easier [4]. In order to simulate the various irradiation sources of a radioactive glass, we will study two types of samples in parallel:

- Radioactive curium-doped ISG glass, which has accumulated electronic and nuclear doses for several years;
- Non-radioactive ISG glasses, which will be irradiated using external beams under different scenarios (electrons, He, Au, Xe, Si, Ne...) to simulate the effect of self-irradiation.

The methodology chosen to study the effects of irradiation on the structure and properties of the two types of glasses as well as their behavior under alteration by water will be presented and supplemented by the first results obtained. The stored energy of each sample depending on the irradiation scenario will be quantified using calorimetric studies carried out by DSC (Differential Scanning Calorimetry) [5], and different leaching protocols will be used to favor some alteration mechanisms over the others and thus independently measure the impact of irradiation on each of them.

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WAS P09– Redox Reactivity of Selenium(VI) in the Presence of Fe(II) and S(–II) Bearing Mineral Phases Under the Conditions of Callovo–Oxfordian Pore Water

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Due to its long half-life of 3.27×10^5 a [1] and high activity, ⁷⁹Se is an important radionuclide to monitor for a correct assessment of the safety of nuclear waste repositories. Selenium is present in five oxidation states in nature ranging from –II, –I, 0, +IV, and +VI. Selenium solubility is controlled by its oxidation state, hence depends on the redox conditions present in soils, sediments, rocks, and aquifers. The –II, –I and 0 oxidation states are commonly predominant in reducing anoxic environments, while the +IV and +VI states predominate in oxidizing environments [2]. Selenate [Se(VI)], the most oxidized form of Se, is an anion with high mobility in the pore waters of the Callovo–Oxfordian (COx) clayey formations that could potentially host the French repository for high-activity and long-life nuclear wastes (HLW). It is therefore important to evaluate the possible redox reactions that could lead to a decrease of its mobility, with a change in its oxidation state, in the environmental conditions of the repository.

It is known that magnetite, a Fe(II)–containing solid phase resulting from the corrosion of the steel canisters and present in natural COx clayrock, can reduce selenate to elemental Se, a non-mobile solid species [3,4]. Selenate is an oxyanion that is typically adsorbed via the formation of outer-sphere complexes, and for which kinetic barriers for electron transfer could be high. The interactions with Fe(II) and S(–II)–bearing redox active solids– mediate the oxido-reduction kinetics of selenium oxyanions, playing an important role in the control of Se speciation [5]. Regarding Se(VI), it has been found to be metastable (far from thermodynamic equilibrium) and to co-exist in different oxidation states in the COx pore waters. The reduction of Se(VI) by magnetite, much slower than for Se(IV), has been described to include different steps: adsorption, reduction to Se(IV), and further reduction to less soluble Se phases, each of them imposing a kinetic barrier for the whole reduction process [3]. At present it is not clear whether the Se(VI) initial adsorption or its reduction to Se(IV) are concomitant or not [4], and extra work needs to be done in this direction to establish the reduction pathway.

Though it has been shown that Se(VI) can be reduced by Fe(II)–bearing solids [3,4] such as magnetite or pyrite, little is known about the potential competition with ubiquitous ions present in the COx porewater such as carbonate or sulfate. These ions have been shown to adsorb forming both outer and inner-sphere complexes, therefore potentially limiting the contact of Se(VI) molecules with the Fe(II)–bearing solids, and therefore potentially inhibiting the electron transfer necessary for Se(VI) reduction.

The aim of this work is to study the redox reactions of Se(VI) with magnetite and pyrite under neutral pH conditions at both macroscopic and molecular levels by combining batch sorption studies and advanced spectroscopic techniques. In addition, the influence of sulfate and carbonate ions will be investigated.

A series of batch experiments were performed at pH 7 under anoxic conditions by pre-equilibrating (14 days) the magnetite suspension with sulfate and then introducing selenate. Another series was performed by simultaneous addition of sulfate and selenate. In both cases, a reduced uptake of selenate with increasing sulfate concentrations was noticed at the macroscopic level. As shown from XANES measurements (Figure 1), the competing effect of sulfate slows down the electron transfer from the magnetite to the aqueous selenate. Indeed, a higher degree of reduction of the selenate to elemental Se is observed in the absence of sulfate. This result points to a limited electron transfer under sulfate-rich conditions, probably due to specific interactions of the magnetite surface with the sulfate ions.

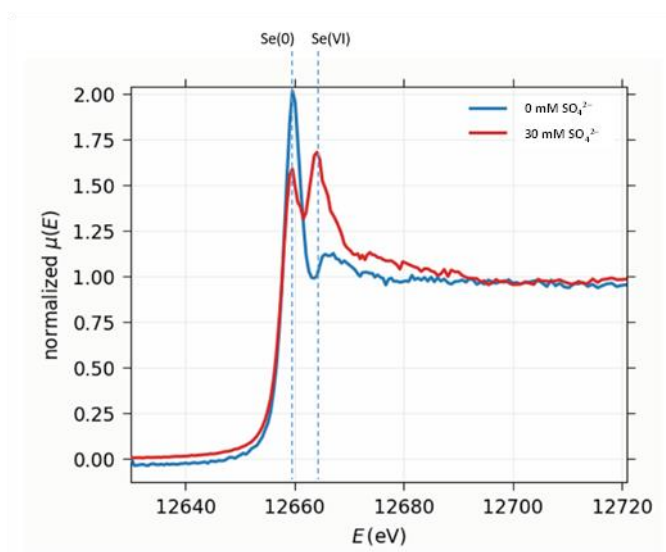


Figure 1. Se K-edge XANES spectra of two samples of magnetite reacted in the presence and absence of sulfate at pH 7 and equilibration time of 3h (sequential addition).

These results will be complemented by IR and XPS experiments. The impact of carbonate ions will also be investigated. Further experiments will be conducted with synthetic COx porewater in the pH range 7-9. The same approach will also be applied with pyrite, an ubiquitous mineral present in COx clayrock.

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WAS P10 – Radionuclide Leaching Model for Spent BWR Tie Plate in Geological Disposal: Factors Affecting ^{14}C Leaching and Post-Closure Safety Assessment

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Introduction

Carbon 14 (^{14}C) is a key radionuclide in activated metal waste management due to its large inventory, long half-life (5730 years), rapid release rate, and mobility. In the Japanese preliminary safety case [1,2], the leaching of radionuclides from the metal matrix is regarded as the corrosion-related congruent release, where some conservative parameters such as a rapid corrosion rate were assumed. This study aimed to redesign the leaching model for a fuel component (BWR lower tie plate) based on a realistic approach, including the new research findings and the novel techniques [3-5], in order to ensure the safety and to mitigate radiological impact on the post-closure assessment.

Leaching models and post-closure safety assessment

The leaching model and parameters for the lower tie plate were improved in the following order:

- Model-1: conventional model applied to the current safety case [1,2]. The waste form (i.e., tie plate) was assumed to be a thin flat plate with a 0.34 mm thickness that corrodes at a rate of 0.02 $\mu\text{m}/\text{y}$. The content of activation products was obtained by a simple activation calculation (e.g., ORIGEN-2).
- Model-2: modeling the three-dimensional shape of the tie plate [3] to be applied time-varying practical surface area.
- Model-3: the content of activation products was obtained by the detailed activation calculation using the Monte Carlo burnup calculation system (MCNP-BURN2 [5]).
- Model-4: in addition to the above, the realistic corrosion rate obtained from the long-term experiment [4] was applied.

A post-closure safety assessment of radionuclide migration in a groundwater scenario [1] was performed using Monte Carlo simulation software GoldSim [6]. The models and migration parameters for the engineered and geological barrier systems were based on the reference safety case [1].

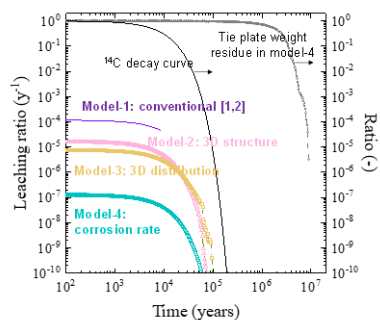


Fig. 1. Leaching ratio of ^{14}C from BWR tie plate for different leaching models together with ratios of the tie plate weight

Results and discussion

Fig. 1 shows the ^{14}C leaching ratio (i.e., leached ^{14}C /initial ^{14}C /year) for each model along with the residual tie plate weight (Model-4) and the ^{14}C decay curve (half-life; 5730 years). Compared to the leaching ratio for Model-1 ($1/8500 \text{ y}^{-1}$), the initial leaching ratios for Model-2, -3, and -4 were reduced to be approximately $1/14$, $1/30$, and $1/1200$, respectively. As shown by contour in Fig. 2, representing the evolution of ^{14}C activity in the tie plate, the original shape was kept for 10,000 years and ^{14}C decays in the metal matrix without leaching. Finally, Fig. 3 shows the dose by ^{14}C in the post-closure safety assessment for the four models (relative value to the peak dose in Model-1). The improved leaching models contribute to dose reduction. In particular, the realistic shape (Model-2) and corrosion rate (Model-4) are found to be the key factors for the safe disposal of activated metal wastes.

residue and ^{14}C decay.

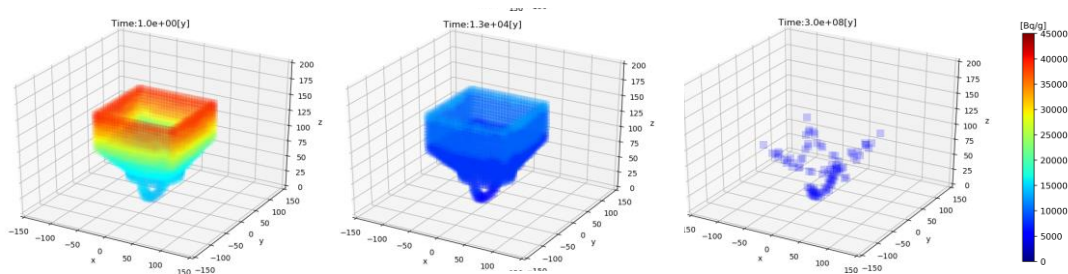


Fig. 2. Simulation of the corrosion-related leaching model showing the varying ^{14}C activity in the BWR tie plate owing to ^{14}C decay (half-life; 5730 years) and corrosion thinning.

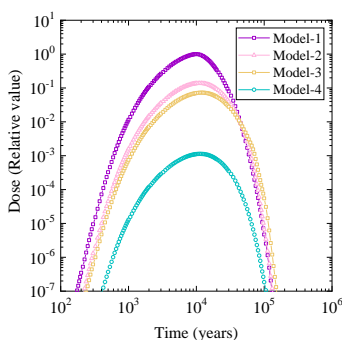


Fig. 3. Results of radiological dose by ^{14}C for different leaching models in the post-closure safety assessment.

Acknowledgement

This study was conducted as a part of R&D supporting program titled “Advanced technology development for geological disposal of TRU waste (2022 FY)” under a contract with the Ministry of Economy, Trade and Industry (METI) (Grant Number: JPY007597).

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WAS P11 – Co-Precipitation of Uranium (IV) and Cerium (III)

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Spent nuclear fuel is mainly $\text{UO}_2(\text{s})$ and thus very insoluble in deep groundwaters which are anoxic and reducing. Dissolution of spent nuclear fuel in a future deep repository is a very complex process and is caused mainly by the radioactivity of the fuel itself. Ionizing radiations cause ionisation or bond breaking of water molecules (radiolysis), producing both oxidants and reductants in similar amounts. For kinetic reasons, molecular oxidants will predominantly react with the fuel causing its oxidative dissolution. It is well known that dissolved molecular hydrogen, which is usually inert under repository temperatures, contributes in consuming part of the oxidants in solution through its reaction with the OH^\cdot -radical:



Recent studies have shown that the effects noticed in tests of spent fuel leaching under hydrogen are much stronger and mainly due processes occurring at the fuel surface (Cui et al. 2008).

Despite the multiple observations of the effect of hydrogen in the oxidative dissolution of the spent fuel and alpha doped UO_2 , the only explanation offered presently is based on the effect of the metallic ϵ -particles present in spent fuel. The effect of these particles has been already thoroughly investigated (Broczkowski et al. 2005, Trummer et al. 2009) and their interaction with dissolved H_2 has been used in models which predict the absence of oxidative dissolution for fuel older than 100 years in presence of only 0.1 bar H_2 (Jonsson et al. 2007).

In most of the spent fuel leaching tests carried out in the presence of hydrogen, a decrease in the concentrations of uranium and other actinides such as Np and Pu is observed in the first days to weeks of the test and afterwards, they remain very low and constant during several months to years. This has led most of the authors to conclude these actinide elements, originating from a pre-oxidized fuel layer are reduced and precipitate as the corresponding reduced amorphous oxides. Their constant concentrations during months or years afterwards were interpreted as due to equilibrium with the corresponding reduced state amorphous oxides, i.e. $\text{UO}_2(\text{am})$, $\text{NpO}_2(\text{am})$ and $\text{PuO}_2(\text{am})$ or $\text{Pu}(\text{OH})_3(\text{am})$. In some of these publications (Cui 2008, Fors 2009, Ekeroth 2020, Puranen 2020) it has been observed that the measured concentrations of Np and Pu in solution are much lower than what is predicted from thermodynamic equilibrium data (Guillamont et al. 2005, Grenthe et al. 2020). $\text{NpO}_2(\text{am})$ and $\text{UO}_2(\text{am})$ have very similar solubilities, about $3 \cdot 10^{-9}$ M, thus similar concentrations of Np and U would be expected if they are at equilibrium with the corresponding amorphous oxides. This is not the case in fuel leaching tests under hydrogen: Np is about three orders of magnitude lower than U. Further, the concentrations of Np and Pu in solution are lower than the concentration in equilibrium with the corresponding reduced oxide by the same factor as their concentration is lower than that of uranium in spent nuclear fuel. In spent fuel there is usually ~95% U, ~0.9 % Pu and < 0.1 % Np and the observed Pu and Np concentrations are ~100 respectively 1000 times lower than $\sim 10^{-9}$ M, which is the measured concentration of uranium. The possibility that these actinide ions co-precipitate with each other is high, given the similarity of their ionic radii with eight coordination 0.96 Å (Pu (IV)), 0.98 Å (Np (IV)), 1.00 Å (U(IV)), 1.0 Å (Pu (III) six coordination) (Shanon 1976) and of the fluorite type structures of their tetravalent oxides.

It is therefore important to investigate if a solid solution of these actinide oxides can be formed during spent fuel leaching and to determine if the solid solution formed is regular and homogenous. A study of the co-precipitation of U and other actinides in waters which simulate repository conditions was undertaken in this work. In this study, the coprecipitation of U(IV) and Ce (III) was carried out where Ce was used as a surrogate for Pu. The composition of U and Pu in the spent fuel was used to simulate the possibility of their co-precipitation formation under reducing conditions.

WAS P12 – Study of Ca-Actinyl(VI)-CO₃ Complexes Using CE-ICP-MS with Polyetheretherketone Capillaries

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Ca-Actinyl(VI)-CO₃ complexes have attracted extensive attention since Ca-U(VI)-CO₃ was identified in seepage waters of a German uranium mine in the 1990s.^[1] Ca-Pu(VI)-CO₃ was identified recently.^[2] Considering the abundance of carbonate and calcium in natural waters, it is necessary to study the thermodynamic properties of these complexes for the understanding and modelling of actinide migration in the geosphere and biosphere. Adsorption studies have suggested the presence of Ca²⁺ could influence the adsorption of U(VI) on minerals and enhance its mobility in aqueous environment.^[3, 4]

Fused silica capillary is predominately used as capillary material in capillary electrophoresis (CE) for its high durability, low thermal expansion and UV-transparency. Nevertheless, depending on the chemical system studied, undesirable band broadening and peak distortion can occur due to the high surface reactivity of fused silica. A great deal of effort has been done to minimize the interaction between the capillary and analytes including surface modification and additives.^[5, 6] Dynamic modification could be convenient but also easily removed by rinsing thus requiring occasional regeneration between each experiment, while permanent modification usually needs time-consuming coating processes. Organic polymer capillaries could be an attractive alternative as they are more inert than fused silica. However, few studies have been conducted with these materials yet.^[7, 8]

In this work polyetheretherketone capillary (PEEK) was chosen to investigate the behavior of Ca-U(VI)-CO₃ complexes. Experiments were performed with a CE coupled to inductively coupled plasma mass spectrometry (ICP-MS), in 0.1 M NaCl at 25°C. U(VI) concentration was fixed at 5×10⁻⁶ M, carbonate concentration was controlled by atmospheric CO₂ and the samples were prepared by varying both pH and total Ca concentration to avoid precipitation of calcite and schoepite.^[9] Evaluation of Joule effect was conducted to limit thermal interference and the voltage was set to ± 4 kV, positive and negative voltage were both applied to further verify and improve the accuracy. Tris buffer (25 mM) was used to stabilize the pH during electrophoresis. Since PEEK capillaries are not transparent to UV, a highly stable neutral complex Ga-NOTA (1,4,7-triazacyclonane-N,N',N''-triacetic acid) was selected as the electroosmotic flow (EOF) marker^[10]. Cs was added as a reference to monitor the electrophoretic runs.

In Figure 1 the graph on the left shows the effect of complexation on electrophoretic mobility of U(VI). The two peaks in the middle were the reference without any voltage; when -5 kV of voltage was applied, the U(VI) peak with the presence of Ca showed lower mobility than the peak without Ca, which suggested a decrease of charge caused by complexation. The figure on the right illustrates the relation between the observed mobility of Ca-U(VI)-CO₃ complexes and calculated total charge from the speciation of these complexes.^[9] It could be observed that when pH decreases with the increase of total Ca concentration, UO₂(CO₃)₃⁴⁻ was gradually complexed by Ca²⁺. This was leading to the formation of Ca_nUO₂(CO₃)₃⁽⁴⁻²ⁿ⁾⁻, the decrease of total charge and correspondently the decrease of electrophoretic mobility. Experimental data were in accordance with the calculations, validating the performance of PEEK for capillary electrophoresis and suggested a promising strategy for further application in this field to other actinyl(VI).

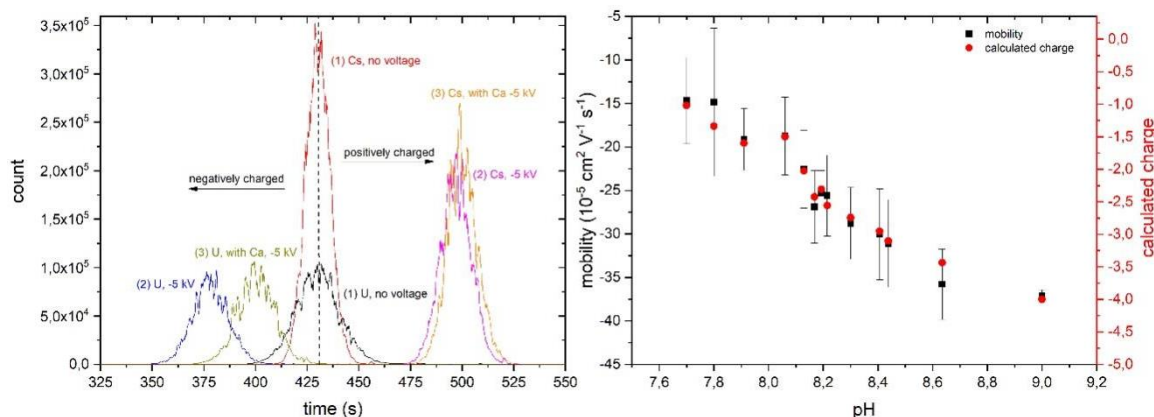


Figure 15 left: Comparison of three U(VI) samples with Cs reference at pH 9

(1) no Ca no voltage ; (2) no Ca -5 kV ; (3) 5×10^{-3} M Ca -5 kV

0.1 M NaCl, 25°C, $c(U) = 5 \times 10^{-6}$ M, 100 mbar, in equilibrium with atmospheric CO₂

right: Comparison of observed mobility and calculated charge of the complexes

0.1 M NaCl, 25°C, ± 4 kV, $c(U) = 5 \times 10^{-6}$ M, 100 mbar, in equilibrium with atmospheric CO₂

Acknowledgement This work is financed by ONDRAF-NIRAS.

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WAS P13 – Determination of Cl-36 Distribution in Spent BWR Tie Plate Using Accelerator Mass Spectrometry

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Introduction

Cl-36 is one of the important radionuclides for safety assessment of the deep geological disposal because it has a long half-life (301,000 years) [1] and migrates in groundwater as anion. When Cl-36 concentration is determined by β -ray measurement, overestimation due to the influence of interfering radionuclides and deterioration of detection limits due to background radioactivity have been issues. In this study, accelerator mass spectrometry (AMS) was applied to accurately quantify Cl-36 concentrations in spent boiling water reactor (BWR) tie plate (stainless steel). Activation calculations of Cl-36 were also conducted to discuss the conservatism of the Cl-36 inventory in a safety assessment.

Materials and Methods

Three test specimens (Fig. 1) were collected from different positions of the lower tie plate of a BWR spent fuel assembly[2][3] (9×9A-type fuel, average burnup 35 GWd/tHM). After adding Cl carrier to the specimens, these specimens were dissolved with concentrated sulfuric acid in a distillation vessel, and the temperature was increased to 350°C to distill chlorine. In the distillation process, C-14 associated with Cl-36 was removed by sodium carbonate, and γ -ray emitting nuclides (Co-60 etc.) were removed by iron hydroxide coprecipitation and cobalt sulfide coprecipitation. To remove S-36, which causes isobaric interference in AMS, cobalt nitrate and ammonia were added until cobalt hydroxide was formed, and the precipitates were filtered. The procedure was repeated until cobalt hydroxide was formed. The supernatant was reacted with silver nitrate to form AgCl, and Cl-36 concentrations were determined by AMS at Micro Analysis Laboratory, Tandem accelerator (MALT) in the University of Tokyo. The activation calculation was also performed by ORIGEN2.2-UPJ[4] according to the burnup history.

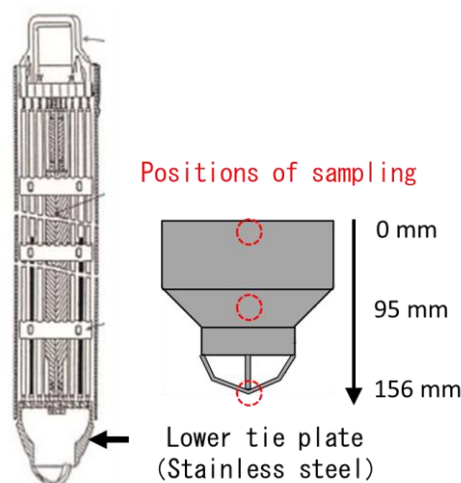


Fig. 1 BWR fuel assembly, lower tie plate,

Results and discussion

Cl-36 concentrations determined by AMS were more than one order of magnitude lower than the detection limit of the β -ray measurement (plastic scintillator), and Cl-36 concentrations decreased with increasing distance from the fuel zone (Fig. 2). This indicates that Cl-36 is produced by irradiation. In the presentation, Cl-36 concentrations determined using AMS are compared with those obtained from activation calculations, and the conservatism of the safety assessment will be discussed.

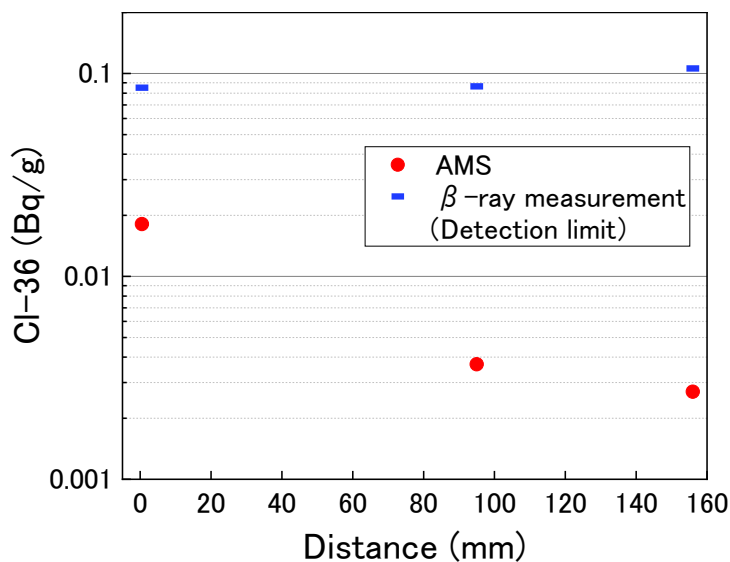


Fig. 2 Cl-36 concentrations determined using AMS

Acknowledgement

This study was conducted as a part of a R&D supporting program titled "Advanced technology development for geological disposal of TRU waste (2022 FY)" under a contract with the Ministry of Economy, Trade and Industry (METI) (Grant Number: JPJ007597).

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Fig. 2 Cl-36 concentrations determined using AMS

WAS P14 – Radionuclide Complexation with Phthalate: Thermodynamic Data Generation for the ThermoChimie Database

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Long-lived, intermediate-level and high-level radioactive waste produced by nuclear power generation and related industries is planned to be put into underground repositories for long-term disposal. One of the design criteria for these repositories is to delay the release of radionuclides into the environment from radioactive waste degradation for thousands to tens of thousands of years. Mitigation of the movement of radionuclides outside of the disposal system (repository plus host rock) involves studying the solution chemistry (i.e. solubility, speciation, sorption, etc.) of these radionuclides and compiling that data into geochemical databases, like ThermoChimie (www.thermochimie-tdb.com).^{1,2} In doing so, geochemical models of the repositories can be created and used to assess the transport of contaminants (radionuclides, chemotoxic elements, etc.) in the environment.

A gap in the thermochemical data has been identified for radionuclide complexation with phthalate, an organic molecule whose derivatives are added to plastics and cement. Adam et al., 2021, focused on a larger number of organic molecules and their interactions with Nd(III), Th(IV), and U(VI) at pH 9 and 13,³ showed that phthalate had little effect on the solubility of the three radionuclides studied at $[L] \leq 2 \cdot 10^{-3}$ M. Reiller et al., 2017 also focused on a wider range of organic ligands, but with Eu(III), in an alkaline solution and demonstrated similar results.⁴ So, the overall goal of this work is to evaluate the effect of phthalate on the solubility of several actinides (Cm(III), Pu(IV/V), Np(IV/V), Th(IV) and U(VI)) and lanthanides (Nd(III) and Eu(III)) between pH 9-13. To that end, the solution chemistry of phthalate will be studied using solubility experiments, analyzed with UV-Vis spectroscopy and TOC analysis, and potentiometric titrations for complexation with Ca and Mg. The data obtained will then be used to plan future radionuclide experiments, in accordance with the stated goal.

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WAS P15 – Insight into the Transport Behaviors and Interface Mechanisms of Actinide Colloids

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The occurrence forms and migration behaviors of actinide in the environment are crucial for nuclear environmental safety assessment. Based on the geochemical process of actinide in the environment, radionuclide migration models are constructed to describe and predict nuclide migration behaviors and laws. However, the migration distance of on-site monitoring is often greater than the predicted migration results, and a large number of studies have found that colloids play an important role in radionuclide migration. The actinide elements are prone to form intrinsic colloids under groundwater environment conditions, and also easily associate with the widely existed environmental colloids to form pseudo colloids. The existence of colloidal phase will significantly affect the occurrence mode and migration law of actinide. In this work, aiming at the migration behavior and interface mechanism of typical actinide colloids, the column experiment method was used to reveal the transport law of actinide colloids, the colloidal interface reaction process and microscopic mechanism were clarified with the aid of advanced spectroscopic technologies, and the migration law of actinide colloids under different environmental conditions was revealed, and a radionuclide migration model considering colloidal phase was constructed. The retention, distribution, migration, and fate of key actinide colloids in different types of environmental media were elucidated. Relevant achievements provide theoretical basis and technical support for the migration mechanism of actinide in geological media and the remediation of contaminated soil, and provide important reference for nuclear environmental safety assessment.

WAS P16– Dissolution Rates of Cerium and Zirconium Dioxide Nanoparticles in Nuclear Fuel Debris Retrieval in Batch and Continuous Systems

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Nanoparticles of various types and sizes are generated during the mechanical and laser cutting of fuel debris retrieval following the Fukushima-Daiichi nuclear power plant accident. Understanding the distribution of metal mass and its impact on the denaturation of fuel debris is critical. Certain metal species have adverse effects on the dissolution of (U, Zr)O₂, leading to disruptions in the retrieval process. To ensure the safety of retrieval and storage management, we selected cerium oxide nanoparticles as surrogates for plutonium oxide. We aim to evaluate variations in its dissolution and denaturation behaviour in a simulated chemical environment in the presence of zirconium oxide, taking into account nano-size effects. In this study, we focus on how H₂O₂ affects the dissolution of nanoparticles. H₂O₂ is the main oxidant radiolytically formed inside reactors and may induce the degradation of nanoparticles. To investigate this, we prepared acidic solvents with different H₂O₂ concentrations as the reaction solvent and conducted experiments by mixing CeO₂ and (Ce, Zr)O₂ nanoparticles with the reaction solvent in both batch and continuous systems. To gain a fundamental understanding of the thermodynamic behaviour and mechanisms of nanoparticle denaturation and to analyse their effects on the nuclear fuel debris retrieval, we characterized the structural variations of nanoparticles after mixing and quantitatively evaluated the dissolved metals.

Experiments were conducted in two parts. In batch experiments, CeO₂ and (Ce, Zr)O₂ suspensions were prepared and mixed with a reaction solvent in a stirred reactor under a specific agitation velocity. The H₂O₂ concentration corresponds to the ionizing irradiated aerated water present in the plant. Supernatant was collected at specified intervals using a syringe with a 0.2 µm filter. The concentration of dissolved metals was measured using microwave plasma atomic emission spectrometry, while morphological variations of the particles during the reactions were explored using dynamic light scattering and transmission electron microscopy. The experiments during flow were conducted in microchannels using two syringe pumps, containing the reaction solvent and the nanoparticle suspensions, respectively, as figure 1 shows. This setup allowed for precise control of flow rates. Reactions were induced when the two solutions collided in the microchannel T-junction outlet. Samples were collected at the channel end while the physicochemical analysis followed the same approach as in the batch-scale experiments.

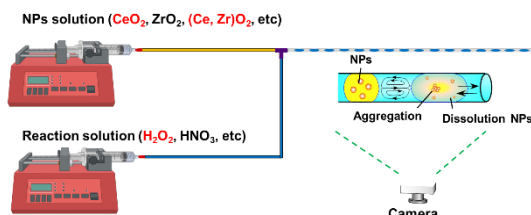


Figure 1 Schematics of continuous systems

Our experiments revealed that H₂O₂ can induce interesting phenomena in the redox dissolution reactions of cerium oxide nanoparticles. Morphological results indicated different aggregation and dissolution behaviour of needle shaped CeO₂ nanoparticles in the batch and the continuous experiments, possibly attributed to the distinctive prooxidant activities of CeO₂ nanoparticles. Furthermore, the results from the flow experiments showed different dissolution rates of (Ce, Zr)O₂ nanoparticles in the reaction solvent compared with CeO₂ nanoparticles, attributed to the high Zr-doping. These results suggested that specific interfacial reactions between generated alpha particles and irradiated water occur during mechanical and laser cutting in nuclear plants, contributing to complex chemical environments in solutions. Furthermore, co-existing particles showed effects on the denaturation process. Our findings provide valuable insights into nano-scale interfaces and will facilitate the study of their interactions.

SAFEGUARDS AND ANALYTICAL CHEMISTRY

ANA P01 – New Insights for the Use of Ultra-Low $^{236}\text{U}/^{238}\text{U}$ Isotope Ratio by ICP-MS/MS for Environmental Analysis

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Uranium isotopes measurement is of increasing interest for environmental sciences, nuclear safeguards, and nuclear forensics. Recently, several studies focused on the minor isotopes of uranium in the environment. In fact, minor isotope as ^{236}U is of prime interest for the determination of uranium sources investigation due to the variation of its isotope ratio (i.e., $^{236}\text{U}/^{238}\text{U}$) regarding their origin. The isotopic variations of the $^{236}\text{U}/^{238}\text{U}$ isotope ratio between the geochemical background ($10^{-14} - 10^{-12}$), the uranium ore ($10^{-12} - 10^{-10}$) and the global fallout ($10^{-9} - 10^{-7}$), make this ratio a relevant fingerprint of uranium sources in the environment.

However, detection of ^{236}U in environmental samples is quite challenging due to its extremely low abundance and for this reason specific instrumentation disposing high sensitivity and high-resolution capabilities is required. The analytical science community has been working for several years to reduce the detection limit of the $^{236}\text{U}/^{238}\text{U}$ isotopic ratio using mass spectrometry (in particular AMS), and recently by using the inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). Recent works focused on the determination of very low isotope ratios by improving the hydride formation, the peak tailing, etc. [1], [2], [3]. In a previous work, the lowest isotope ratios measured using the ICP-MS/MS technology in UO^+ mode was about 1×10^{-10} [4].

The latest generation of ICP-MS/MS, recently commercialized, has improved performance, including better ion transmissions and an extended dynamic range of mass detection. This allows the measurement of isotopes up to mass to charge ratio of 280. This is a great improvement as uranium ions could now be measured as UO^{2+} rather than UO^+ which shows important advantages in terms of sensitivity and hydride formation. In this work we explored the capabilities of the new model of ICP-MS/MS, Agilent 8900, in terms of hydride formation rate and the lowest achievable $^{236}\text{U}/^{238}\text{U}$ isotope ratio in UO^{2+} mode. To this end, measurements of certified reference materials and environmental samples were performed.

These improvements as well as the coupling with an efficient desolvating module (APEX Ω) and the addition of oxygen in the collision/reaction cell allowed an important sensitivity increase and an effective decrease of the interferences on $^{236}\text{U}^+$ ion measurements: the sensitivity increased to 4.3×10^6 cps/ppb while reducing the main interference with an hydride formation rate of 7.2×10^{-10} . These values are one order of magnitude better than previous published values and allow ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios measurement.

For the first time a precise determination of the $^{236}\text{U}/^{238}\text{U}$ isotopic ratio up to 10^{-11} was demonstrated by ICP-MS/MS [5], validated by the analysis of certified reference materials and environmental samples previously measured by AMS. This new limit is a new milestone in the determination of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios and open the way to various geochemical applications.

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ANA P02 – Enabling Fuel Cycle Safeguards through a Solvent Extraction Digital Twin coupled to Real-Time Online Monitoring

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The recycling of spent nuclear fuel is necessary to maximize the extractable energy and minimize waste associated with the nuclear fuel cycle. Solvent extraction methods such as the PUREX process are currently the principal methods for recycling nuclear fuels. Even minor modifications to the extraction conditions such as organic-to-aqueous (O/A), liquid flow rates, acid pH, etc. could affect the direction of streams of nuclear material and thus ensuring that these processes are operating optimally is of utmost importance. To this end, we present the development of a novel solvent extraction digital twin which combines online spectroscopic process monitoring with multi-stage solvent extraction modeling and machine learning anomaly detection to feed a real-time digital twin that can be utilized for nuclear fuel recycling monitoring. The feed concentrations of extractable and non-extractable actinide surrogates are monitored and ingested into an INL developed data warehouse, from which other digital adaptors can operate on the data providing real-time predictions of actinide species concentrations in the loaded organic and raffinate streams, correlations of the expected and measured concentrations at each location, and anomaly detection if expected and measured concentrations diverge. In this work, we discuss the characterization of this solvent extraction digital twin under normal operating conditions, and under various abnormal operating conditions that could result unwanted diversion of actinide material. The ability to monitor the solvent extraction process in real-time could enable the rapid identification and mitigation of these process upsets and potential proliferation events.

ANA P03 – Quantification of Lanthanides from Three Optical Spectroscopic Techniques across Three Pathlengths on a Microfluidic Device

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Microfluidic devices (MFDs) provide numerous benefits including low fabrication costs,¹ rapid sampling of small volumes^{2,3} and the ability to perform small volume reactions.⁴ Within the nuclear field, MFDs offer a platform on which to characterize processes from fundamental chemistry of actinides to actinide-bearing processes, while providing reduced radiation exposure, minimized waste costs,⁵ and small-footprint analyses.

Optical spectroscopy provides a means of on-line analysis on MFDs. Optical spectroscopy has been successfully deployed on MFDs for the detection and quantification of liquid phase analytes,^{3,6} including lanthanide⁵ and actinide⁷ cations as well as some fission products in dissolved spent nuclear fuel.

Here, samples are measured in a polymethylmethacrylate (PMMA) microfluidic system utilizing three optical spectroscopies. The PMMA MFD is utilized for its optical transparency and for the ability to fabricate complex channel, lens, and mirror geometries.¹ Fiber optics mounted within the PMMA chip allow for ultraviolet (UV)-visible and near infrared (NIR) excitation light to be directed along three portions of a flow channel within the chip. The channel lengths measure 1.0, 2.5, and 10 mm.

Transmitted light is collected and processed using two custom fiber optic spectroscopic UV-visible and NIR instruments⁸ from Spectra Solutions Inc. Discrete fibers and regions of the detection array in the spectroscopic instruments process the light from each of the three channels on the MFD. An external Raman microprobe is utilized, being set perpendicular to the MFD. The 70 μm focal width of the probe is focused within the outlet channel, capturing signal from solutions exiting the MFD.

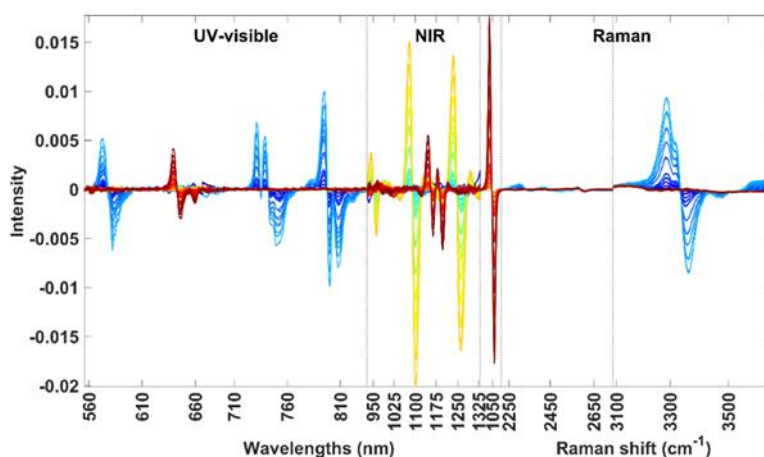


Figure 16. Multiblock processed spectra combining ultraviolet (UV)-visible and near infrared (NIR) absorbances of aqueous neodymium, holmium, and samarium nitrates in microfluidic channels measuring 1.0, 2.5, and 10 mm, and Raman signal. Dashed vertical lines indicate breaks in the x-axis.

Absorbance spectroscopies are utilized to quantify neodymium, holmium and samarium cations in aqueous solutions along all channel lengths. From Raman spectra, neodymium and nitrate are quantified. By utilizing multiple spectroscopic techniques, signal overlap, low analyte signal, or background signal in one type of spectra can be compensated for by the inclusion of another type of spectra.^{7,8}

After signal processing, chemometric models are created to quantify neodymium, holmium, samarium, and nitrate concentrations in sample solutions containing up to three lanthanide nitrates in solution. The preprocessed spectra are shown in Figure 1.

Chemometric models are constructed from several arrays of spectra and compared. The simplest models incorporate spectra collected using one spectroscopic technique at one channel length. Through normalization and wavelength correction, the absorbance spectra collected across the three channel lengths are made comparable, and lanthanide concentrations are quantified using a linear principal component regression (PCR) model for each of the spectroscopy methods. Additionally, multiblock modeling is conducted, in which simultaneously collected UV-visible, NIR, and Raman spectra are concatenated to create hybrid-technique spectra for each channel length. This allows for measurement of all lanthanides and nitrate from a single linear PCR model for each channel length. Finally, quantification is conducted by combining UV-visible, NIR, and Raman spectra at all channel lengths, providing the greatest range of quantitation for all four analytes from a single model at all channel lengths.

Root mean square errors for models encompassing spectra from multiple pathlengths remain comparable to models incorporating spectra from a single pathlength. The multi-channel length models allow for quantification in a greater range of analyte concentrations than is possible in a single channel length. The multiblock models provide reduced errors for neodymium and holmium, which produce signal in two of the three spectroscopic techniques utilized herein.

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ANA P04 – Understanding the Acidification Mechanisms of Alkaline Ru Solutions, for a Robust ICP-OES/MS Analysis

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Ruthenium has a complex chemistry, with ten stable oxidation states and multiple species. As it is a fission product (FP) of uranium and plutonium, its consideration in nuclear fuel reprocessing studies is of a great interest. Ruthenium proportion in FP increases with combustion rate or plutonium presence in the initial fuel^[1]. As France aims to increase fuel multi-recycling, an increase in ruthenium waste quantity is expected. A good understanding of its chemistry in nuclear process is then essential for nuclear fuel reprocessing.

Atalante facility is dedicated to research on the back end of the fuel cycle. The Atalante analytical laboratory provides an analytical support to research laboratories on their respective topics. Considering this context, some laboratories need ruthenium quantification initially in an alkaline environment. Usually, the analytical techniques used for this purpose (mostly ICP-OES or ICP-MS) are less suitable for analysis in an alkaline environment and require an acidification of the matrix. During this step, sample integrity is not guaranteed and the ruthenium concentration is affected of an unknown uncertainty. Indeed, a variable quantity of ruthenium precipitate or evaporate, leading to a false concentration value.

Erreur ! Source du renvoi introuvable. summarises this issue. Furthermore, there is no certified ruthenium solution in a alkaline medium so the measurement bias cannot be known. Finally, Ru can be quantified in alkaline medium with a UV-Visible spectrometer. However, this method suffers from poor reliability, especially at low concentrations. In addition, other species can easily interfere the measurement by absorbing at the measurement wavelength.

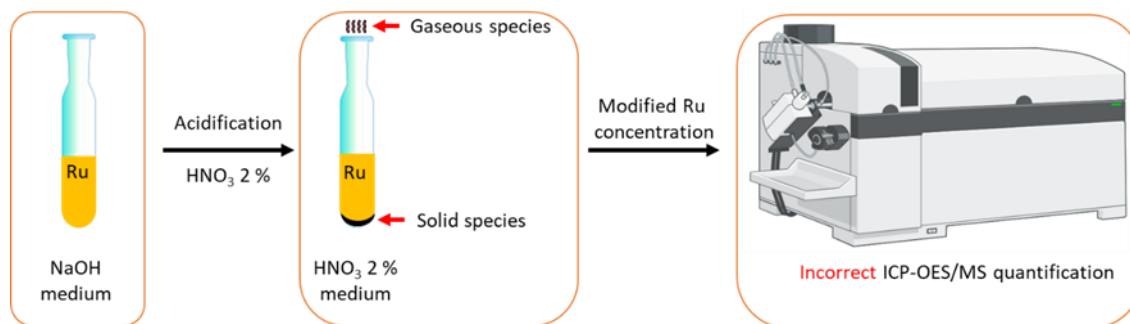


Figure 17: Scheme of acidification process of ruthenium basic solution prior an ICP-OES/MS determination

A previous study of the acidic and alkaline medium speciation was performed, followed by a study of the precipitation and volatilization product of the acidification. Two leads are followed to investigate the ruthenium integrity issue. The first one is to maintain a high potential in solution to prevent precipitation, the second one is a prior conversion in stable chlorinated species before acidification.

Before testing them, confirmation of their viability is done by studying the acidification byproducts. X-Ray diffraction analysis, thermogravimetric analysis, and other analytical techniques are used to characterise solid species while gas collector and UV-Vis measurement are going to be used for gaseous ones. An *In-situ* UV-Vis probe will also be used, coupled to a fast detector to better identify intermediate species and understand their formations mechanisms.

Then, to keep Ru from changing state, a high potential solution is maintained, with a strong oxidant such as potassium persulfate. In this case, the presence of lower oxidation degree solid species, such as ruthenium dioxide (RuO_2) can be minimized and even totally prevented in few weeks, depending on Ru and acid concentration^[2,3]. With a strong oxidant, Ru is kept in the soluble +VIII species: H_2RuO_5 and HRuO_5^- . **Erreur ! Source du renvoi introuvable.** shows a basic solution of r

uthenium with **Erreur ! Source du renvoi introuvable.**a a black deposit and **Erreur ! Source du renvoi introuvable.**b the vanishing of this deposit after adding potassium persulfate.

The viability of this solution needs to be studied in an analytical way, to determine whether ruthenium is kept in solution. The main drawback of this method is the plausible evaporation of a part of the ruthenium in the RuO_4 form. This study will verify if the volatilization phenomenon is enhanced by the presence of a strong oxidizer and thus, if it is at a constant or variable rate. The impact on the uncertainty also needs to be estimated. The concentration of an alkaline ruthenium solution will be certified by others methods, such as the catalytic kinetic method with UV-Visible spectroscopy^[4,5].

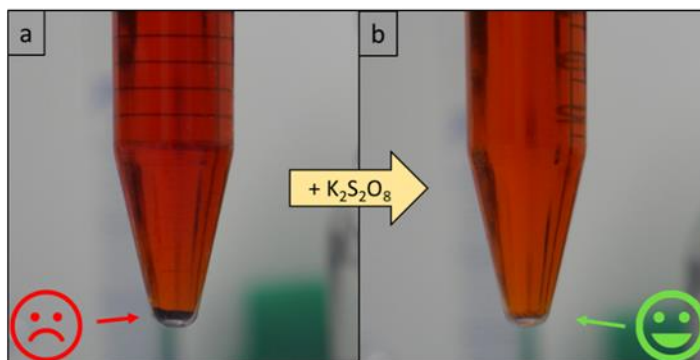


Figure 18: Ru in a NaOH solution before (a) and after (b) adding potassium persulfate

The second method to prevent ruthenium losses is a prior conversion in stable chlorinated species, especially in RuCl_6^{3-} , RuCl_n^{3-} and binuclear complexes depending on the Cl^- concentration. The favored way to do this is to add concentrated hydrochloric acid to the alkaline solution. Ruthenium volatilization is more difficult in HCl than in HNO_3 , and also stable in much more longer time scale^[6]. A certified alkaline solution of Ru can also be useful for this lead. It will estimate uncertainty and optimize the protocol to have the better quantification limits.

The final step is to study the quantification of ruthenium from alkaline medium and acidification with real solutions and simulated interfering elements. The goal will be to identify whether interferers enhanced or catalyze the formation of binuclear ruthenium complexes, potentially leading to variable uncertainty.

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ANA P05 – Acoustic Measurements of Solvent Extraction Processes in Support of Safeguards

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The proposed poster focuses on using acoustic monitoring to advance detection techniques for reprocessing equipment in support of nuclear safeguards. The usage of free air acoustic monitoring has been previously demonstrated at Idaho National Laboratory (INL) at facilities such as the Advanced Test Reactor and the National Security Test Range. However, this work focuses on a deployment environment dedicated to monitoring separation processes, using solvent extraction equipment such as centrifugal contactors. This environment offers an opportunity for signal discovery and in characterizing acoustic signatures of the equipment in operation. This data can support the development of safeguards by design and security by design measures for aqueous reprocessing facilities. Furthermore, this type of monitoring can aid in early detection and identification of removed materials indicating diversion, which is essential for initiating material recovery and actor identification. The results of this work include data from nine low-frequency acoustic sensors used to investigate potential acoustic characteristics of centrifugal contactors used in multi-stage processes. The results also discuss the correlation between the signatures and the operation of the contactor banks.

ANA P06 – Advancing Analytical Chemical Processing to Support Molten Salt Reactor Fuel Performance Analyses and Safeguards

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Advanced molten salt reactors (MSRs) have been proposed for providing long-term, carbon-free energy. Despite their promise, however, the liquid nature of MSR cores poses unique challenges to both optimizing the reactor's operational efficiency as well providing materials accountability and safeguards during their operation.

Actinide and fission product isotopic analyses are key to supporting both these objectives. However, new approaches to performing these analyses are currently needed. For example, while traditional solid fueled reactor analyses are performed months to years after fuel extraction from the reactor core, the liquid nature of MSR cores necessitates temporal analysis as close to near real-time as possible.

Current state-of-the-art approaches for actinide and fission product analyses included both radiometric (i.e., gamma spectrometry, alpha spectrometry, etc.) and mass spectrometric techniques. Direct application of these techniques to near-real time analysis of irradiated molten salts, however, is complicated by several factors including: 1) high sample radioactive doses, and 2) analytical complexity of fresh nuclear fuel samples (e.g., isobaric and gamma spectrometric interferences, combined with challenging fission product decay schemes). To overcome these analytical challenges, new chemical processing approaches for rapid dissolution and chemical separation of irradiated molten salts are needed.

We report initial research into developing a near-real time analytical chemical dissolution and separation system for high-activity, freshly irradiated molten salt samples. This approach implements both 1) novel analytical chemical systems engineering to enable sample dissolution and rapid chromatographic chemical separation, and 2) innovations in fundamental chromatographic separations approaches. To enable the success of this approach, a series of fundamental studies advancing chemical separation distribution data surrounding new extraction chromatographic resins is also reported. The results from this research have diverse applications ranging from improving analytical chemical separations of the actinides, fission products, and stable elements, to improving the efficiency, decreasing the costs, and improving the safety associated with analytical nuclear fuel samples analyses (both molten salt and traditional solid fueled samples).

ANA P07 – Achievement of Electrochemical Analyses on Stainless Steels in a Hostile Nuclear Environment

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KEYWORDS: Electrochemical cell, remote manipulator, fission products, boiling nitric acid

Introduction

As most industries, the nuclear industry and particularly the fuel reprocessing plants face with many issues about corrosion. The study and understanding of these corrosion phenomena are essential for Orano at La Hague plants (France) in the objective of sustaining the highest production rates at the best achievable nuclear and work safety standards.

Applied electrochemistry and electrochemical analytical methods enable to study the various interdependencies between metals corrosion and solutions chemistries. However, this field of science is not the same in common chemistry laboratories and at the vicinity of highly radioactive substances. Thus, an electro-chemical cell was designed to be operated in hostile environments and to study materials corrosion for example in actinides fission products in boiling nitric acid solutions.

Electrochemical techniques

The cell development was undertaken in the frame of a project for which it was required to perform several electrochemical measurements.

Open Circuit Voltage (OCV) is a very common experimental technique which requires a set of only two electrodes and a voltmeter (no current). The method provides useful information concerning the passivation state of a metal or indications on the rate of the cathodic reaction at the electrode.

Cyclic Voltammetry (CV) and potentiodynamic step polarization at quasi-steady state are two other very simple and common electrochemical techniques. However, these methods require to use a potentiostat and a generator and is thus a bit more complex to set up. CV and polarization are used to acquire information about electrochemical reactions occurring at the electrode interface.

The cell design takes into account these requirements. The cell also enables to perform Electrochemical Impedance Spectroscopy or galvanic current measurement by Zero Resistance Amperometry.

Cell description

The electrochemical cell is a three-electrode cell: the working electrode (WE) being the material studied, a counter electrode (CE) being platinum in our case and the reference electrode (Ref.) with a fixed potential. This cell is connected to a potentiostat to record the different electrical signals.

The cell is made to operate in a solution of boiling nitric acid with fission products coming from the reprocessing of spent nuclear fuel with the Purex process. A particular effort has been made in the design of a reference electrode system with a low impedance and a good temperature stability with a resistance to the pollution by the studied solution. A small vapor cooling system is associated to the cell, avoiding concentration of the boiling solutions during electrochemical measurements (total reflux con-denser).

The approach followed was to choose a chemically-resistant, electrically insulating material and adapt it to be handled by a remote manipulator inside a shielded enclosure. The material has therefore to be shock proof. Then, electrical connectors were adapted to be handled by a remote manipulator and connected to the potentiostat which is located outside of the shielded enclosure (Figure 1).



Figure 1 : Shielded enclosure with a remote manipulator

During the preliminary inactive commissioning/qualification, the electrochemical cell was submitted to some improvements. For example, a miniaturization of the cell was performed to enable the heating of the solution by a graphite heating block. The material of the cell lid was changed (Figure 2) for mechanical and machineability reasons.



Figure 2 : Figure 2 shows from left to right, the evolution of the cell

The qualification of the cell was a three-stage process including:

- an initial qualification in an inactive chemistry laboratory,
- an inactive remote operation qualification,
- an active qualification with dummy fission products solutions then with real active fission products solutions.

The initial qualification took place at HRB (Hall de Recherche de Beaumont). Ability to reach boiling solutions, efficiency in cooling vapours, impact of the length of electrochemical cables and repeatability of the electrochemical signal in several solutions have been checked.

The qualification of the remote manipulation of the cell in an inactive testing environment took place at HEF (Hall d'Essais et de Formation) in Orano- La Hague fuel reprocessing plant. At this stage the cell safety and surety have been approved.

This cell was then approved during a test campaign in 2020 in the fuel reprocessing plant. An austenitic stainless steel was studied in a fission products boiling solution.

Several electrochemical measurement campaigns have been carried out on site since.

Conclusion

This study and the cell qualification enabled Orano to perform complex remote electrochemical measurements in highly radioactive and chemically aggressive environment. Currently the cell is maintained in a radiation shielded enclosure at Orano La Hague nuclear fuel reprocessing plant to be used on demand in the frame of R&D tests. The tests performed concern either metals (constitutive of process equipment) or solutions properties (by changing the working electrode).

PYROCHEMISTRY AND CHEMISTRY FOR MOLTEN SALTS

PYR P01 – A Novel Glove-box Scale Testbed for Fundamental Pyroprocessing Research and Development

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Pyroprocessing is an ideal approach for reprocessing metallic nuclear fuels from fast breeder reactors. INL has engaged in pyroprocessing research since the 1980's as a potential method to prepare legacy spent fuel for long term geological storage. Despite decades of research and operations in several pilot scale pyroprocessing facilities around the world, including the Fuel Cycle Facility (FCF) at Idaho National Laboratory, numerous scientific questions remain regarding the fundamental mechanisms of actinide and fission product dissolution, diffusion, electrodeposition, and chemical speciation. In order to continue to push the frontiers of pyroprocessing science, the authors have established a LiCl-KCl eutectic molten salt electrolytic test-bed for confirming the fundamental scientific characteristics associated with the partitioning of actinides and fission products in real-time during pyroprocessing operations.

The project consists of two phases; first, a cold-surrogate study aimed towards validating system design and establishing operating constraints for various fission product and actinide elements which do not lend themselves to radiometric analysis at the proposed scale. And second, evaluation of radiological fuel simulants incorporating uranium and a suite of fission products.

The small scale electrolyzer, and associated instrumentation, provide the capability to spatially resolve the electrodeposition of fuel surrogates in real time through pinhole gamma spectroscopic imaging. This should help inform chemical mechanisms of 1) initial fuel dissolution, 2) actinide and fission product diffusion, 3) uranium and/or impurity electrodeposition at the cathode, and 4) gaseous fission product production and evolution. In order to enable imaging, simulant studies employing gamma emitting radiotracers such as uranium-237 and neptunium-239 are employed, along with short-lived fission products. Results from initial studies using this novel glovebox-scale test bed will be presented at this conference.

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PYR P02 – Chemical Behavior of Fission Products in NaOH-KOH Molten Salts

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The decommissioning of the first-generation of nuclear reactors, corresponding mainly to the uranium naturel graphite gas (UNGG) reactors in France, has generated a large volume of radioactive metallic wastes, which have to be managed. The fuel for these reactors was composed of an uranium metal rod with two Mg-Zr alloy tails, surrounded by a magnesium sheath, the whole being introduced into a graphite jacket. The waste generated was stored in silos at ORANO (La Hague) and at CEA (Marcoule) after mechanically removing the uranium rod. This waste mainly contains graphite and magnesium, but also small quantities of uranium and fission products.

These metallic wastes are considered as intermediate level waste and their main way of management is their encapsulation in a cementitious matrix. However, magnesium is a reactive metal that can be oxidized inside the matrix, with production of hydrogen gas and corrosion products. The corrosion of the metallic wastes has to be limited as much as possible to ensure the confinement of the radioactivity. While the massive waste can be directly immobilized in a specific conditioning matrix, the fine particles of waste present at the bottom of the silos, which are too reactive due to their high specific surface, cannot be managed in the same way. Currently, it was proposed an innovative process to manage the powdery metal waste by integrating a dissolution step of the metal before the preparation of the cementitious matrix. The metal being oxidized during the dissolution, it is no more reactive with water during the conditioning. By this process, hydrogen gas is produced under well-controlled conditions during the dissolution reaction.

Studies have then been developed on the dissolution of reactive metal, especially magnesium, in hydroxide molten salts, NaOH-KOH (51.5-48.5 mol%) containing water, at 225°C. The results have shown the high efficiency of this process to inert the Mg wastes before conditioning. However, because the wastes contain other elements, such as some fission products, it is important to study their reactivity in such medium. Thus, our goal was to determine the speciation of the main fission products contained in the silos: strontium, cesium and iodine. A double approach has been applied for this study:

- Thermodynamic calculations to define the stability domains of the elements in the molten hydroxide salt as a function of the potential and the water contain,
- Experimental studies, mainly by electrochemistry, to define the chemical and electrochemical behavior of these elements.

The results obtained by thermodynamic calculations and electrochemistry are in good agreement: the stable species of Sr, Cs and I in NaOH-KOH are $\text{Sr}(\text{OH})_2$, $\text{Cs}(\text{OH})$ and NaI . Moreover, the electrochemical study on iodine showed that the O_2^- species is more stable than the O_2^{2-} species in this hydroxide molten salt.

PYR P03 – Chemical Durability of Ceramic Materials in Molten Salts: Application to Nuclear Materials Pyroprocessing

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Ceramic crucibles are widely used in pyrochemical processing; it offers good chemical and thermal resistance under severe conditions. However, chlorine salts can corrode ceramic materials, leading to brittleness or impregnation of the crucible by the salt. When pyroprocessing nuclear materials, the latter can result as contamination of the crucible.

A study was carried out to understand the phenomenon of ceramics impregnation by molten salts. Ceramic samples were placed in contact with salts and the surface state of the samples was characterized afterwards.

Ceramics such as Y_2O_3 -doped MgO , Al_2O_3 and Y_2O_3 -stabilized ZrO_2 (YSZ) were studied whereas the salts are pure $CaCl_2$ and $NaCl-KCl_{(eut.)}$. Oxide ions concentration was controlled by CaO addition.

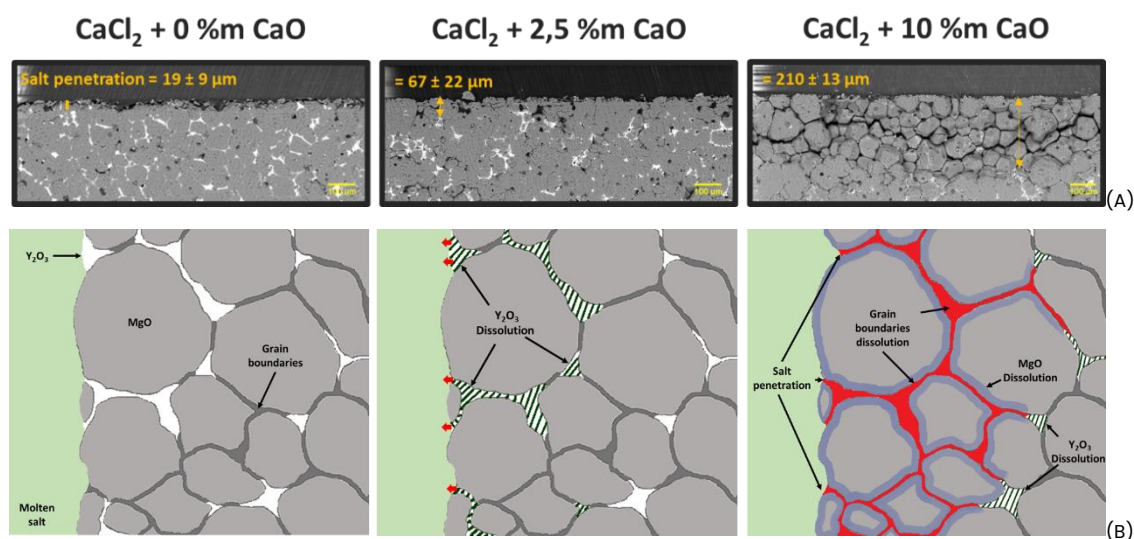


Figure 1. (A) SEM images highlighting salt penetration through grain boundaries dissolution of Y_2O_3 -doped MgO in calcium chloride molten salt with various content of O^{2-} ions and (B) the proposed mechanism to describe the dissolution of Y_2O_3 -doped MgO ceramic in molten salts.

Concerning MgO , Y_2O_3 is mostly located at grain boundaries to limit open porosity and this phase can exhibit a lower chemical durability in molten salts. It showed a preferential dissolution route through grain boundaries, and thus the formation of a pathway for the salt to penetrate. Chemical analysis performed on the salt revealed the presence of elements composing the ceramic. The results finally showed a very strong impact of oxide ions concentration (pO^{2-}) on the dissolution of Y_2O_3 . Similar results were obtained with Al_2O_3 samples, as a quantitative dissolution was observed. YSZ offers a more challenging behavior as Y and Zr form a unique phase. Lower dissolution of Y could be expected but its dissolution led to a destabilization of ZrO_2 with a structural phase transformation from tetragonal ZrO_2 to the more reactive monoclinic ZrO_2 , creating cracks and secondary phases such as $CaZrO_3$.

In a parallel step, an innovative route to prepare ceramic materials is studied, involving 3D printing. It allows the manufacturing of ceramic pieces with complex geometry, which are difficult to produce with conventional methods. We investigated two printing processes, the fused deposition modeling (FDM) and laser stereolithography (SLA). Both techniques led to high-density ceramics with an equivalent chemical durability than the conventional ones.

PYR P04 – Chemical Behavior of Uranium in Chloride Molten Salts

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The molten salt reactor is one concept selected by the Generation IV forum in 2001. This concept, based on the use of a liquid fuel, consists of salts mixture melted at high temperature. The first concepts were based on the U/Th fuel cycle. Recently, researches have been carried out in order to adapt this concept to the U/Pu fuel cycle which is the French reference cycle. Neutronic studies evidenced the requirement to replace the fluoride salt with a chloride salt because the fluorides thermalize the neutron spectrum.

Fluoride salts were the subject of studies for many years. The use of chloride salts necessitates academic research in chemistry field, some issues being the evolution of the salt composition during reactor operation and its influence on the molten salt chemistry, the state of the fission products when they are produced in the salt, the way to extract them from the salt during the reprocessing step and the control of the fuel redox potential in order to mitigate the corrosion.

Thermodynamic calculations and electrochemical measurements are used to determine fundamental parameters of elements in molten salts, such as redox potentials, diffusion coefficients and activity coefficients to deduce the solvation Gibbs energy.

Based on thermodynamic calculations, it was shown that the presence of uranium chloride in the fuel salt is able to stabilize the redox potential of the salt and to limit the corrosion of structural materials. Experimental determinations are required to compare the thermodynamic data and experimental measurements, to study the stability of uranium chloride in the salt with time and to measure the redox potential of the salt with and without uranium chloride.

This talk presents a preliminary study on the chemical and electrochemical behavior of uranium in a chloride molten salt and the influence of chloro-acidity on its behavior. The chloro-acidity is defined by the amount of free chloride ions in the salt which influences the solvation of the solutes. Two different chloride molten salts in term of chloro-acidity (NaCl-CaCl₂ (salt A) and LiCl-KCl (salt B) at 550°C) were chosen in order to compare their solvation properties with respect to uranium chloride.

The electrochemical systems UCl₃/U and UCl₄/UCl₃ are clearly observed by electrochemistry and the salt redox potential measured on a tungsten electrode is ranging between these two systems. It was shown that the potential measured is closed to the theoretical one calculated from the thermodynamic data of pure compounds and is linked to the nature of the molten salt through the free chloride amount in the salt.

PYR P05 – NaCl- UCl_3 Synthesis Routes for Molten Salts Fast Reactors

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Ensuring clean and affordable energy is key to achieving all 17 sustainable development goals set by the United Nations at COP21. That's why the energy of the future needs to be secure, equitable, carbon-free and decentralized.

Nuclear power is seeing renewed interest as a potential energy source due to society's commitment to low-carbon sources to deal with climate change. Molten salts fast reactors are considered a promising technology in this context, thanks to their greater efficiency in generating electricity and/or heat, in addition to offering advantages in terms of radioactive waste management.

NAAREA's XAMR* (eXtrasmall Advanced Modular Reactor) concept uses long-lived nuclear waste in the form of a ternary NaCl-PuCl₃-UCl₃ salt as fuel to produce safe, abundant and dispatchable energy that can be deployed as close as possible to industrial consumers around the world. To produce the fuel, the binaries NaCl-UCl₃ and NaCl-PuCl₃ salts need to be separately prepared. Although the use of NaCl-UCl₃ in molten salts reactors has been discussed for decades, scarce information is available on the most effective synthesis routes for producing it on a large scale.

Different synthesis routes are possible to produce NaCl-UCl₃. The choice of one in particular will depend on several criteria, such as the conversion yield of the reaction, the availability of raw materials, the chemical hazards of the reagents/by-products and the equipment needed to meet the required reaction conditions. The synthesis routes consist of obtaining the NaCl-UCl₃ salt directly, without additional steps, or obtaining UCl₃ or UCl₄, where additional steps are required.

Pyrochemical methods allow the binary salt to be obtained in a one-step process by reacting the U metal in NaCl medium with chlorinating agents such as NH₄Cl, FeCl₂, ZnCl₂ and CdCl₂. U metal powder is required in the reaction with NH₄Cl, which increases the complexity of the process in terms of safety because of its pyrophoric behavior [1]. When considering FeCl₂, ZnCl₂ or CdCl₂ as a chlorinating agent, one of the challenges is the separation of the metal chloride reactant or associated metal reaction product [2], [3], [4]. Therefore, it is necessary to investigate alternatives to guarantee the purity of the binary salt in large-scale production.

Gaseous chlorinating agents can be used to synthesize high purity products. The contact of U metal with Cl₂ or HCl gases favors, however, forms of uranium chloride other than UCl₃. On the other hand, UCl₃ can be produced through the thermal decomposition of NH₄Cl into HCl [5]. Particular attention needs to be given to the fact that the reactants need to be charged in an airtight reactor to obtain UCl₃ as the main product. Since UCl₃ is the main product of the reaction, an additional step is required to obtain NaCl-UCl₃.

Other synthesis routes available consist of obtaining UCl₄ by chlorinating UO₂ or U₃O₈ with CCl₄ and by chlorinating UO₂(NO₃)₂ with hexachloropropene. Both methods have the advantage of avoiding the pyrophoric risks involved with U metal but require the additional steps of reduction of UCl₄ to UCl₃ and the preparation of the binary salt. When using CCl₄ as the chlorinating agent, due to the toxicity of the reagents and by-products released, a study of gas management is required [6]. When using hexachloropropene, the management of purification steps and reaction exothermicity should be investigated for large-scale production [7].

For ATALANTE 2024, NAAREA will present its advances in NaCl-UCl₃ synthesis routes with the aim of enabling large-scale production.

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PYR P06 – Study of the Behavior and Precipitation of Lanthanides in Molten Chloride.

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The spent salts produced during plutonium recycling must be treated to separate nuclear materials from salt matrix. The salts consist of eutectics mixtures NaCl-KCl, NaCl-CaCl₂ and pure CaCl₂, containing several actinides species with oxidation degree varying from 0 to IV (metal, chlorides, oxychlorides and oxides). The strategy is to separate actinides from their chloride matrix by a 3 steps process shown in Fig.1. To achieve this goal, the conversion of the actinide species into oxide form is realized by oxidizing species addition in molten salt. This step has to be investigated to know the key parameters of successful conversion.

In this study, lanthanide chlorides (CeCl₃ or PrCl₃) have been used as plutonium chloride surrogate, and two reactants (Na₂CO₃, CaO) were compared to perform lanthanide precipitation. The effect of carbonate cation, temperature and carbonate dissociation has been studied. Indeed, carbonate can either decompose and donate oxide ions or be stabilized and adopt an oxidizing behavior.

First, this work presents the electrochemical study of Ln(III) on the working electrode (Mo and W). The electrochemical methods were used to investigate reduction of Ln(III). This made it possible to quantify the amount of cerium in the salt during reactant additions and to study precipitation mechanisms.

In the second stage, two reagents were used to precipitate lanthanides into insoluble species such as LnO₂, Ln₂O₃. The study focuses on quantifying the different species formed and on conversion yields. The results show that NaCl-KCl oxidized spent salt reaches a high decontamination factor, and that CaCl₂ have a different behavior.

Electrochemical studies enable in-situ visualization of metal behavior in salt baths. This will enable the study of precipitation mechanisms via metered additions. Results obtained depend on the process conditions : this highlight the need for in-depth study of the influence and nature of the atmosphere.

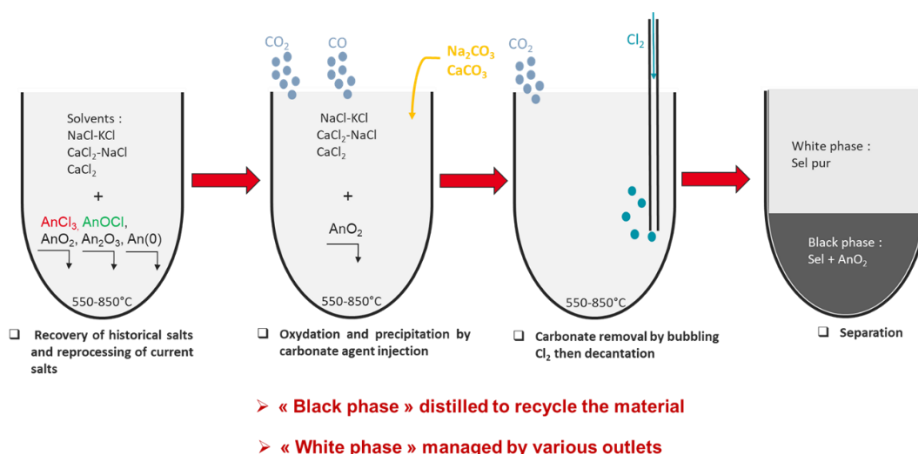


Figure 19 : Simplified diagram of the process

PYR P07 – Precipitation Phenomena of Actinide and Lanthanide in a NaCl–CaCl₂ and NaCl–MgCl₂

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This work is part of the French program on the development of a molten salt reactor (MSR) dedicated to transuranic elements (Am, Pu) transmutation in a molten chloride fuel salt. This reactor uses a liquid fuel NaCl–MgCl₂–PuCl₃–AmCl₃ (500°C–650°C). In the molten salt media, the presence of oxygen and/or humidity can lead to formation of poorly soluble or insoluble species such as actinide oxides AnO₂, An₂O₃ or oxychlorides AnOCl. These insoluble species can have a negative impact on the homogeneity of the liquid fuel in the reactor, leading potentially to safety issues.

In this work, the stability of plutonium and lanthanides was studied (CeCl₃ and NdCl₃ as PuCl₃ simulant or as fission products present in the salt). A number of lanthanide precipitation tests in NaCl–CaCl₂ have been carried out by adding oxide ions or air as precipitating agents. The results of DRX and ICP–AES analyses show the formation of insoluble oxides when air is added and oxychlorides when oxides are added, which is coherent with already published data. The precipitation slope of CeCl₃ with oxide ions is close to unity in coherence with the formation of CeOCl. When MgCl₂ is added to NaCl–CaCl₂, CeCl₃ precipitation slope is smaller (close to 0,3) without observing Mg²⁺ precipitation as MgO as mentioned in the bibliography. Lanthanide and actinide oxychloride solubility in MgCl₂ based salt, discussed in the literature, could explain the observed phenomena. In order to better understand the role of MgCl₂, solubilization tests of lanthanide oxides and oxychlorides (LnO₂, Ln₂O₃ and LnOCl) at various MgCl₂/Ln ratios were carried out, showing the positive role of MgCl₂ as a retardant of precipitation as well as oxide's solubilization agent. Plutonium precipitation/solubilization experiments were also tested, and their results are almost identical. Even if the mechanism of precipitation/solubilization is not clearly understood, the study tends to show that the presence of MgCl₂ in a MSR chloride fuel salt should have a favorable effect regarding precipitation phenomena.

PYR P08 – Chlorine Isotopes Separation for Fast-Spectrum Molten Salt Reactors

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Nuclear power is seeing renewed interest as a potential energy source due to society's commitment to low-carbon sources to deal with climate change. Molten salts fast neutron reactors are considered a promising technology in this context, due to their greater efficiency in generating electricity and/or heat, in addition to offering advantages in terms of safety and radioactive waste management.

NAAREA's XAMR® (eXtrasmall Advanced Modular Reactor) concept uses long-lived nuclear waste in the form of a ternary NaCl-PuCl₃-UCl₃ salt as fuel to produce safe, abundant, dispatchable, carbon-free and decentralized energy that can be deployed as close as possible to industrial consumers around the world.

Natural chlorine contains two stable isotopes: 75% of ³⁵Cl and 25% of ³⁷Cl. During irradiation, ³⁶Cl is mainly produced from ³⁵Cl by neutron capture, but also to a minority from ³⁷Cl. Since ³⁶Cl has a half-life of 301,000 years and is highly mobile in the biosphere, its production during irradiation must be limited. Calculations show that a ³⁷Cl enrichment of 100% in the initial molten salt reduces the amount of ³⁶Cl produced after irradiation by a factor 400. In addition, ³⁷Cl has a lower capture cross section than ³⁵Cl, which improves the performance of the chlorine fuel salt in the reactor. Thus, chlorine isotope separation is highly considered to produce chlorine enriched with ³⁷Cl (> 99%).

For that purpose, several isotopes separation techniques such as ultracentrifugation, gas diffusion, thermal diffusion and distillation are considered.

Chlorine isotopes separation by ultracentrifugation was demonstrated by Beams and al. [1] in the 1930s, years before uranium isotopes separation using this technique. In this case, the gas molecule containing the heavy isotope is projected to the periphery, while the gas molecule containing the light isotope migrates to the middle of the centrifuge. For uranium enrichment, the lower part of the centrifuge can also be heated, which creates a convection motion in which to the top of the column central part is enriched in ²³⁵U, while the ²³⁸U migrates downwards. This technique is used, for example, in the Georges Besse II plant (Tricastin) for uranium enrichment.

By thermal diffusion, a proof of concept was made by Kranz and al. [2] decades ago for chlorine isotopes separation. In this case, the gas molecule containing the light isotope diffuses to the hot wall of an inner column and then to the upper part by thermal convection, while the gas molecule containing the heavy isotope diffuses to the cold wall and an outer column and then to the lower part by thermal convection. Thus, this technique is very efficient to recover enriched ³⁷Cl using several columns in a serial/cascade process.

Other well-known techniques developed for gas separation are considered, such as gaseous diffusion and distillation. The phase distribution of chlorine isotopes at the liquid/vapor equilibrium is investigated to design a distillation columns process for ³⁷Cl enrichment at industrial scale. The gaseous diffusion is based on the small mass difference between two isotopes molecules, a separation can then take place by filtering a mixture of both isotopes through suitable membranes. This process was used in the Eurodif plant for uranium enrichment until 2012. In the case of chlorine isotopes separation using hydrogen chloride (HCl), several challenges such as corrosion or decomposition are identified. However, no proof of concept was made for chlorine isotopes enrichment using distillation and gaseous diffusion.

Considering some of these techniques, a progress of report chlorine isotopes separation will be made with the aim of producing a large quantity of enriched ³⁷Cl for molten salts reactors fuel and coolant.

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ACTINIDE AND FISSION PRODUCTS CHEMISTRY

ACT 01 – X-Ray Analyses on Radioactive Matter at the Mars Beamline of Synchrotron Soleil

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The MARS (Multi-Analyses on Radioactive Samples) beamline at the SOLEIL synchrotron (Saint-Aubin, France) has been operating in collaboration with an international community to probe radioactive samples since 2010 [1-3] and has been built thanks to a close partnership with the CEA. The radioprotection specifications of the beamline satisfy the French ASN (Autorité de Sureté Nucléaire) regulations, opening the door to allowing a diverse variety of radioactive samples to be analysed. The maximum total equivalent activity present at a given time, including the storage on the beamline, is 185 GBq with a maximum of 18.5 GBq (0.5 Ci) per sample.

The MARS beamline is fully devoted to advanced structural and chemical characterizations of radioactive matter (solid or liquid) using tender to hard X-rays, 3.5 to 35 keV energy range. With multiple end-stations available, the beamline can perform several techniques: Standard X-ray absorption spectroscopy including XANES and EXAFS, while high-resolution X-ray spectroscopy is well established too [4,5]. Transmission X-ray diffraction (TXRD), high-resolution X-ray diffraction (HR-XRD) [6], and associated X-ray microbeam techniques (μ XRF/ μ XRD/ μ XAS). Small-angle and wide-angle X-ray scattering (SAXS/WAXS) are also available [7].

The status of the beamline with particular emphasis on the foreseen upgrades of the high-resolution spectrometer will be discussed in addition to some recent achievements on a selection of disciplines.

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ACT 02 – Structural and Microstructural Heterogeneities: Which Impact on Dissolution Kinetics?

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During irradiation in the reactor, MOX (Mixed Oxide) fuels that are composed of uranium and plutonium oxides undergo strong elemental and microstructural changes. Irradiated fuels exhibit cationic heterogeneity, with the presence of plutonium-enriched zones that are resistant to dissolution above a precise content, namely $x \approx 0.35$ in $U_{1-x}Pu_xO_2$ compounds [1]. Irradiation also leads to the formation of fission products (FP), present in the gaseous form, as metallic precipitates and oxides, as well as those included in the matrix [2]. The presence of these heterogeneities and FP could modify the dissolution kinetics of the fuel during reprocessing, and lead to the formation of insoluble residues. The existing literature offers scarce insights into the dissolution of irradiated heterogeneous fuels. Nevertheless, a very recent study [3] focused specifically on the dissolution of heterogeneous model compounds $(U,Th)O_2$ with different heterogeneity contents using thorium as a plutonium surrogate (Figure 20). Therefore, the preparation, then dissolution of such heterogeneous model compounds $(U,Th)O_2$ incorporating metallic (Ru, Rh, Pd, Mo, Re) and lanthanide (La, Ce, Pr, Nd) elements is of strong interest. It would underline the impact of FP on the dissolution kinetics. In this study, thorium and rhenium have been considered as surrogates of plutonium and technetium, respectively and free from FP elements [4,5].

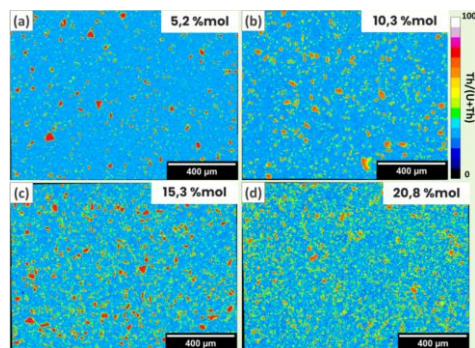


Figure 20 : X-EDS micrographs of heterogeneous model compounds $(U,Th)O_2$ at different heterogeneity contents [3]

In a first stage, precursors were synthesized by the wet chemistry route, namely hydroxide precipitation [6]. The advantage of this method of synthesis lies in the ability of the elements to co-precipitate, resulting in a homogeneous powder with a high reactive surface suitable for sintering. Cationic heterogeneities within the pellets were introduced by mixing homogeneous powders with different thorium contents. Then, the doping elements (metal and lanthanide) simulating FP were introduced directly into the solution containing uranium and thorium to promote their co-precipitation. A forthcoming additional experiment will be also dedicated to the simultaneous incorporation of all the studied FP (Figure 21).

Dissolution experiments will be then carried out in concentrated nitric media, demonstrating the influence of cationic heterogeneities and the presence of metallic and lanthanide elements on the dissolution kinetics for such heterogeneous model compounds. A multiparametric study will be also carried out through a dual approach to obtain simultaneous macro- and microscopic description of the dissolution. The macroscopic scale will provide information on the elemental release inventories in the solution, while the microscopic scale will enable the microstructure of the pellet to be analyzed by ESEM and the zones that dissolve preferentially to be evidenced during the dissolution process.

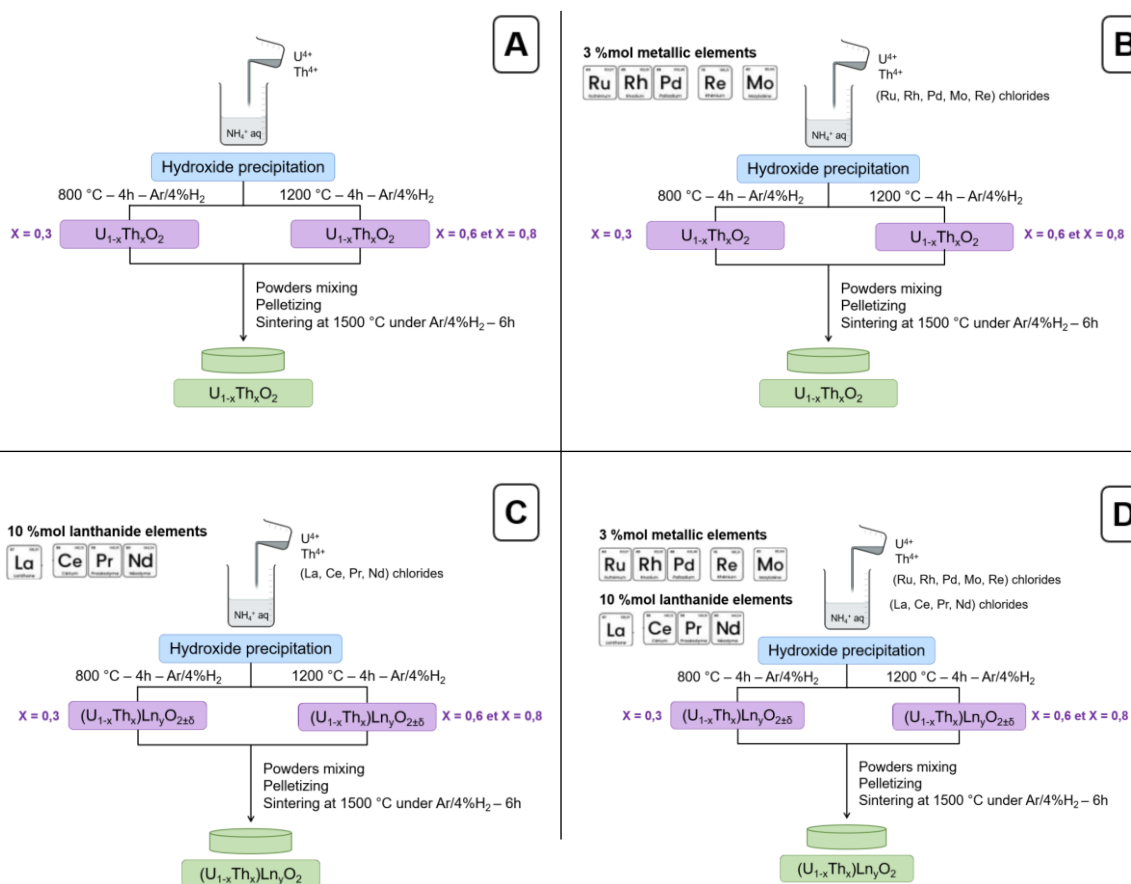


Figure 21 : Schematic representation of hydroxide synthesis used to prepare heterogeneous mixed oxides without doping FP elements (A), by adding metallic FP (B), by adding lanthanide elements (C) and by adding all the studied FP (D)

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ACT 03 – PuO₂ from Calcination of a Pu(IV) Peroxo Complex: Preliminary Results

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In France, the fuel used in the current nuclear reactors consists of uranium oxide (UOx) or mixed uranium and plutonium oxide (MOx). The plutonium is obtained by reprocessing UOx spent fuel, during which Pu is separated and purified from U and the fission products using the PUREX process. It is then industrially converted from Pu(IV) in nitric acid media into plutonium oxide, PuO₂, by precipitation of a Pu(IV) di-oxalate complex and its calcination. Although this process is well mastered, several research avenues are currently being explored to improve or to substitute it. One of the explored pathways involves the calcination of a Pu(IV) peroxo complex [1, 2, 3]

The goal of this study is to conduct a comparative analysis of the morphological characteristics of PuO₂ materials derived from various precursor materials, with a specific focus on elucidating differences between peroxide and oxalate Pu(IV) complexes.

The initial results presented in this study focus on the characteristics of the PuO₂ powders, such as the variation of its specific surface area with calcination temperature, studied by BET. X-ray diffraction analysis is used to follow both the evolution of the crystallite size and their structure. Information about the molecular structure, including chemical bonds and functional groups, as well as the presence of adsorbed species, is examined using Raman spectroscopy. The evolution of morphology from peroxide to oxide is studied using scanning electron microscopy (SEM). Additionally, the temperatures at which species are eliminated are investigated through thermogravimetric analysis (TGA).

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ACT 04 – Complexation of Curium(III) and Europium(III) with Aqueous Phosphates: a Combined Experimental, Thermodynamic, and *ab initio* Study

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The environmental fate of radionuclides (RN), such as actinides and fission products, disposed of in underground nuclear waste repositories is a major concern. Long-term safety assessments of these disposal sites depend on the ability of geochemical models and thermodynamic databases (TDBs) to predict the mobility of RNs over very long time scales. One example where TDBs still have large data gaps is related to the complexation of trivalent actinides and lanthanides with aqueous phosphates. Indeed, solid phosphate monazites are one of the candidate phases for the immobilization of specific high-level waste streams for future safe storage in deep underground disposal facilities, therefore potentially and locally increasing the presence of phosphate at the final disposal site.

Recent work [1-3] obtained reliable complexation constants at 25 °C and at elevated temperatures and thus, partially closed some knowledge gaps. Laser-induced luminescence spectroscopy was used to study the complexation of Cm(III) and Eu(III) as a function of total phosphate concentration in the temperature regime 25-90 °C, using NaClO₄ as a background electrolyte (I = 0.5 to 3.0 M). These studies have been conducted in the acidic pH-range (-log₁₀ [H⁺] = 1.00, 2.52, 3.44, and 3.65) to avoid precipitation of solid Cm and Eu rhabdophane. For the first time, in addition to the presence of the 1:1 CmH₂PO₄²⁺/EuH₂PO₄²⁺ species [1-3], the formation of Cm(H₂PO₄)₂⁺ [2] and Eu(H₂PO₄)₂⁺ [3] was unambiguously established from the collected luminescence spectroscopic data. The conditional complexation constants of all aqueous complexes were found to increase with increasing ionic strength and temperature [1-3]. Extrapolation of the obtained conditional complexation constants to infinite dilution at 25 °C and elevated temperature was performed by applying the Specific Ion Interaction Theory (SIT). Using the integrated van't Hoff equation, both the molar enthalpy of reaction ΔH_m^o and entropy of reaction ΔS_m^o values were derived.

During complexation, depending on the concentration of phosphate, monodentate or bidentate Cm(III)/Eu(III)-phosphate complexes can form with different overall coordination numbers (8,9). Obtaining additional information about the complex structures from spectroscopic data only is often challenging, especially at the low metal-ion concentrations used in the experiments.

Thus, relativistic quantum chemical (QC) methods can be considered as an additional tool to complement experimental observations. In this study, the structural properties, electronic structures, and thermodynamics of the 1:1 and 1:2 Cm(III) and Eu(III) phosphate complexes were solved using state-of-the-art QC calculations. In particular, the QC methods allowed i) to investigate the complexation strength of Cm(III) and Eu(III) with aqueous phosphate, ii) to understand the possible change of the coordination number with increasing temperature and iii) to investigate the nature (ionic/covalent) of the Cm/Eu bonds with water and phosphate.

Combining the information obtained from quantum chemical calculations with the observed spectral changes facilitates the decisive determination of the structures of the formed phosphate complexes and their overall coordination [2,3].

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ACT 05 – Ultrasound-Assisted Conversion of UO_2 into U(VI) Peroxides in Aqueous Solution Saturated with Ar/O_2

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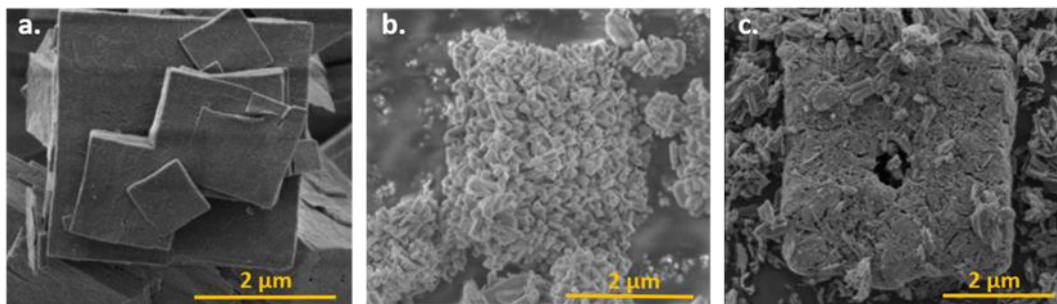
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In the French nuclear industry, uranium is used as nuclear fuel in the oxide form $\text{U(IV)}\text{O}_2$. After being used in the reactor, spent nuclear fuel is very damaging for organisms and must be safely contained for thousands of years. During storage, the potential intrusion of groundwaters through containment failures could result in the production of radiolytic species such as H_2O_2 that can contribute in the corrosion of UO_2 -based matrices and promote the dissolution and release of radionuclides into the surroundings. Sonochemistry provides an original route to slowly accumulate H_2O_2 in solution through the acoustic cavitation phenomenon. [1-3]

This work focuses on the sonolysis of uranium dioxide in pure water and slightly acidic media under oxygenated atmosphere. After the preparation of well-characterized uranium dioxide platelets using the oxalic route, their complete conversion into (meta-)studite $[(\text{UO}_2(\text{O}_2)(\text{H}_2\text{O})_2) \cdot x\text{H}_2\text{O}]$ is observed under ultrasound. Detailed investigations on the remaining solutions (UV-Visible absorption spectroscopy and ICP-OES) and solid residues (SEM, XRD, and FTIR techniques) allowed us to attribute this behavior to the sonochemical generation of hydrogen peroxide and physical effect from acoustic cavitation phenomenon.

The formation of crystalline studite structures was observed on the surface of uranium dioxide platelets with a preservation of the morphology suggesting a complex formation mechanism other than classical dissolution/reprecipitation. Interestingly, under specific sonochemical conditions, center-holed platelets are observed. A mechanism based on a sonocapillary effect providing the circulation of the reactants within the oxide was proposed leading to a publication and will be discussed during the conference. [5].

Figure 1: a) SEM image of UO_2 platelets synthesized from the oxalate route b) and c) SEM image of the uranyl peroxide observed after sonication of UO_2 in H_2SO_4 5.10^{-4} M at 346 kHz (20 W.mL^{-1} , 20°C , Ar/O_2 , and 6h)



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ACT 06 – Machine Learning Methods for Fission Gas and Defect Diffusivity Modeling in Advanced Oxide Fuels

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Fission gas production and diffusion is one of the primary factors limiting nuclear fuel performance and achievable discharge burn-up. As gases like xenon and krypton are produced through fission events, their diffusion through the fuel lattice, segregation at grain boundaries, and formation of bubbles leads to significant fuel swelling. The eventual release of such gases from the fuel matrix and into the fuel-cladding gap generates increased pressure on the cladding and decreases thermal conductivity across the gap. These phenomena significantly impact fuel performance as a function of burn-up. Therefore, with longer burnup-times becoming increasingly advantageous for advanced reactor designs, it is desirable to develop a more complete kinetic and thermodynamic understanding of fission gas diffusion in nuclear fuel matrices. There is particular interest in elucidating these processes in doped uranium dioxides, advanced fuel forms which incorporate dopants like chromium, aluminum, titanium, and manganese into the UO_2 lattice to improve fuel performance. Molecular and cluster dynamics simulations provide valuable insights into such diffusion processes, including both fission gas and defect diffusivity. The accuracy of these simulations, though, depends on the quality of a potential energy surface describing the forces acting on all atoms in the fuel lattice. While these potential energy surfaces are typically computed using density functional theory (DFT), strong f -electron correlations in actinide-based materials lead to significant increases in computational cost and complexity. Computational expense also limits the system size that can feasibly be modeled using DFT. This system size limitation is especially detrimental for modeling doped oxide fuels, whose microstructure can only be captured using larger unit cells. Machine learning methods present an alternative to these expensive and size-constrained DFT calculations, achieving DFT-quality calculation accuracy at a fraction of the computational cost. We report the use of higher-order equivariant message passing to fit machine learning interatomic potentials for uranium dioxide fuels. Irradiation effects are also considered by using training data reflective of defect evolution within the crystal lattice as a function of burnup. Following validation, we use our model to calculate a number of thermodynamic and kinetic parameters for molecular and cluster dynamics calculations modeling fission gas diffusion processes. Furthermore, we highlight the utility of using machine learning methods to overcome difficulties in accurately capturing the microstructure of doped uranium oxides. This paves the way for computational models to corroborate findings that the altered fuel chemistries and characteristically-enlarged grain sizes of doped fuel forms improve retention of gaseous fission products.

ACT 07 – Synthesis and Characterization of Polynuclear Actinide(IV) Species

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The actinide chemistry is largely influenced by the formation of polynuclear species that have attracted valuable interest over the last decades. These species have been proven to play a potential role in the management of waste, fuel reprocessing and even in biological media. The polynuclear species of tetravalent actinides (i.e., actinides clusters) discussed here materialize as molecules containing multiple metal centers connected by oxo and/or hydroxo groups. This forms the core of the cluster, often described by its nuclearity, N , which represent the number of actinides in it. These entities are formed through condensation reactions (referred to as ololation and oxolation reactions) in the presence of water and are surface-stabilized by organic or inorganic ligands.^[1]

In the solid state, various polynuclear species of actinides(IV) have been identified from XRD crystal structures, with various nuclearities ranging from 2 to 38. However, the hexamer consisting of 6 plutonium atoms (Pu_6) is frequently observed.^[1] This nuclearity has been studied and stabilized several times in the form of the $[\text{Pu}_6\text{O}_4(\text{OH})_4]^{12+}$ core. Takao *et al.* investigated the formation of hexanuclear clusters of neptunium, uranium, and thorium in solution, in the presence of carboxylate ligands.^[2] Our group have also studied the formation of plutonium hexameric clusters under various conditions. The results revealed similarities in UV-Vis spectra associated with this nuclearity.^[1] However, studies in aqueous solutions are still inadequate, and it remains difficult to identify these polynuclear species in solution.

Additionally, recent studies suggest that these species could play a role in the formation mechanism of PuO_2 colloidal nanoparticles.^[6] Indeed, some hexanuclear Pu(IV) clusters have been identified as reactive intermediates in this process. Colloid formation is an irreversible process that may pose challenges in the context of used nuclear fuel reprocessing. Understanding the formation of polynuclear actinide species is thus crucial for comprehending and mastering the formation of colloids in solution.

The first objective of this study is to develop reliable spectroscopic databases, in order to help the identification of polynuclear species in solution. This work begins with the synthesis of plutonium(IV) single crystals characterized by X-ray diffraction (SCXRD), which specific spectra are collected with UV-visible and vibrational spectroscopies (IR and Raman). This approach will simplify the identification of these species in solution, enhance the understanding of the mechanisms involved in the formation of polynuclear species, as well as their evolution towards the formation of colloids. Preliminary results will be presented in the poster.

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ACT 08 – Exploration of Predominant Factors of U(VI) Precipitation Formation in the Advanced Reprocessing Technology using Diamide Ligands.

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Various amide ligands are frequently employed in advanced reprocessing technologies to separate nuclear fuel materials such as U, Pu, and Th from the spent fuels [1]. The amide ligands usually exhibit strong affinity with UO_2^{2+} and M^{4+} ($\text{M} = \text{Pu}, \text{Th}$), and well meet requirements from the “CHON” principle and radiation resistivity. There are two main principles of such advanced spent fuel reprocessing, *i.e.*, solvent extraction and precipitation. In the former method, *N,N*-dialkylated monoamides [1] prefer to form stable complexes with UO_2^{2+} and M^{4+} to be recycled. As a result, these metal ions significantly tend to be extracted from $\text{HNO}_3(\text{aq})$ to an organic phase. For the process feasibility, precipitation of any materials must be prohibited. In contrast, well-designed amide ligands such as 2-pyrrolidone or γ -lactam derivatives such as **L1** in Fig. 1 may afford sparingly soluble crystalline nitorato complexes of UO_2^{2+} and M^{4+} in $\text{HNO}_3(\text{aq})$ [2]. In this principle, crystallization with amide ligands must be enhanced for efficient recovery of the nuclear fuel materials. Hence, knowing what determines occurrence of precipitation is the most important to design and optimize molecular structures of amide ligands to be employed in these advanced reprocessing principles having the conflicting requirements mentioned above. While steric effects of different ligand structures have been proposed to explain $\text{UO}_2^{2+}/\text{Pu}^{4+}$ selectivity found in the solvent extraction [3], no details have been well discussed yet how to control precipitation through the spent fuel reprocessing. In this study, we investigated how the precipitation behavior of UO_2^{2+} is decided by the molecular structures of the amide ligands. For this purpose, we rather focused on the precipitation here, because the single crystal X-ray diffraction (SCXRD) provides detailed molecular and crystal structures with precise atomic coordinates of the formed complexes.

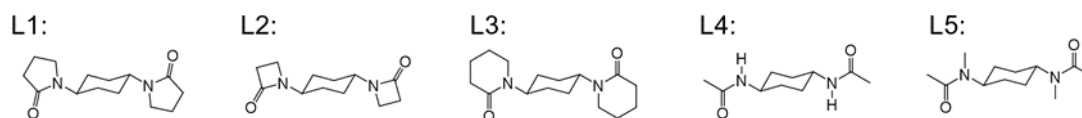


Fig. 1 Schematic structures of diamide ligands (**Lx**) studied here.

Figure 1 shows diamide ligands studied in this work. **L2–L5** are derived from **L1**, which has already been demonstrated as an excellent precipitant for UO_2^{2+} [4] and M^{4+} [5,6]. Stock solutions of UO_2^{2+} in 3 M $\text{HNO}_3(\text{aq})$, 3 M $\text{HNO}_3(\text{aq})$, and a selected ligand (**Lx**, $x = 1-5$) were layered from bottom to top of the $\phi 5$ mm glass tube, where total concentrations of UO_2^{2+} , **Lx**, and HNO_3 after equilibration were 70 mM, 77 mM, and 3.0 M, respectively. The crystalline deposits obtained were structurally characterized by SCXRD as well as IR and elemental analysis. When no precipitation occurred in the aqueous system, methanol or ethanol was used as an alternative solvent instead. The U concentrations in the solution phases were measured by ICP-AES to evaluate the precipitation ratio (ppt%) as follows,

$$\text{ppt}\% = \frac{[\text{U}]_{\text{init}} - [\text{U}]_{\text{sup}}}{[\text{U}]_{\text{init}}} \times 100$$

where $[\text{U}]_{\text{init}}$ and $[\text{U}]_{\text{sup}}$ are the U concentrations at the initial state and that in the supernatant, respectively.

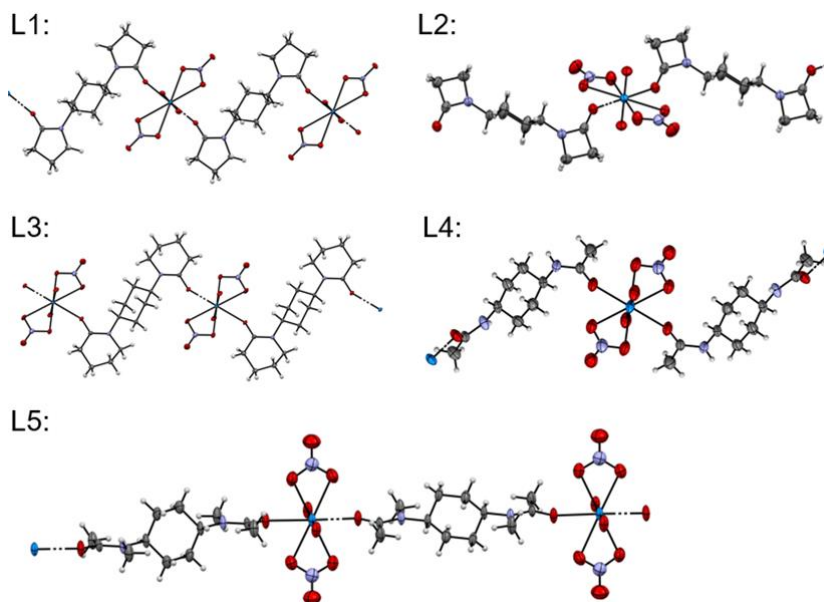


Fig. 2 ORTEP views of $[UO_2(NO_3)_2(Lx)]_n$ at the 50% probability level ($x = 1-5$). Blue: U; red: O; purple: N; grey: C; white: H.

As shown in Fig. 2, all diamide ligands (**Lx**) resulted in one-dimensional coordination polymers with stoichiometry of $[UO_2(NO_3)_2(Lx)]_n$. These results are the same in principle with that of **L1** we reported previously [5]. Two NO_3^- are coordinated to U in the bidentate manner, and located at the *trans*-positions in the equatorial plane of UO_2^{2+} . In-between them, the O atoms of the amide ligands are present to form a typical hexagonal bipyramidal coordination of this class of UO_2^{2+} complexes. There were no significant differences in structural parameters. On the other hand, ppt% were significantly dependent on difference in **Lx** as summarized in Table 1. Since packing efficiency in a crystal structure may affect solubility of a molecule of interest [7], we examined relationship between ppt% and packing efficiency (ξ) defined by ZV_m / V_{cell} , where Z , V_m , and V_{cell} are the number of molecules in a crystal lattice, molecular volume, and cell volume, respectively [8]. As shown in Table 1, the order of ppt% basically follows that of ξ . That is, **L1** showing the highest ξ has the highest ppt%. In contrast, **L2** and **L4** having lower ξ resulted in no precipitation from 3 M $HNO_3(aq)$. These results suggest that ξ of the crystalline $[UO_2(NO_3)_2(Lx)]_n$ remarkably affects ppt% of UO_2^{2+} . More details about dependency of ppt% on the ligand structures are also being investigated.

Table 1. Relationship between Precipitation Ratio (ppt%) and Packing Efficiency (ξ) of $[UO_2(NO_3)_2(Lx)]_n$

Lx =	L2	L4	L3	L5	L1
ppt% [%]	0	0	81	83	90
ξ [%]	64.90	65.46	65.28	65.82	68.19

*This work was supported by JSPS KAKENHI (No. JP20KK0119).

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ACT 09 – Exploring the Formation Mechanism of PuO₂ Colloidal Nanoparticles

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Enhancing the comprehension of the structural and physicochemical characteristics of colloidal plutonium oxide (PuO₂) nanoparticles holds significance not only in understanding their environmental dispersion behavior but also for a potential advancement in nuclear fuel technologies.[1] The colloidal suspensions resulting from the hydrolysis of Pu(IV) are described as crystalline PuO₂ nanoparticles with an average diameter of approximately 2 nm, and exhibiting structural irregularities attributed to a surface effect.[2,3] By using a H₂O/D₂O isotopic effect occurring during hydrolysis, recent investigations identified a Pu(IV) hexameric oxo-hydroxo cluster as an intermediate in the nanoparticle formation process.[4] This work questioned the contribution of smaller and bigger entities in the formation mechanism. In this context, the combination of small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS, encompassing XANES/EXAFS) available at the synchrotron SOLEIL/MARS beamline emerges as particularly relevant techniques for elucidating both the morphological characteristics and atomic environment evolution during the nucleation and growth phases of PuO₂ colloidal nanoparticles.

To facilitate the monitoring of Pu hydrolysis within the facility, a specific heating module has been developed, while matching to the safety standards for the manipulation of radioactive samples. The module will enable the kinetic evaluation of Pu(IV) hydrolysis through the thermal degradation of a complexing agent stabilizing Pu(IV). Preliminary assessments have demonstrated the viability of this chemical approach, wherein the decomposition of a Pu(IV) peroxide complex at approximately 80°C yielded Pu(IV) colloids which accumulation was followed through UV-Vis absorption spectroscopy. Using this approach, the in-situ formation kinetics will be followed using both SAXS and XAS techniques in order to propose a valuable mechanism for the formation of the PuO₂ nanoparticles in aqueous solution. The heating module has been previously tested on an analogous system in which zirconium was used as a substitute for Pu. The initial results confirmed that zirconium can be protected from hydrolysis by complexing with H₂O₂, and that heating this chemical system triggers the formation of Zr colloids. This presentation will showcase the progress of this project by discussing the steps required for the development of the heating module, as well as the preliminary results obtained with Pu and Zr.

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ACT 10 – Comparing Transmutation Fuel Irradiation between a Fast Neutron Spectrum and a Cd-filtered Thermal Spectrum

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The FUTURIX-FTA experiment is an international collaboration between the Department of Energy (DOE) in the United States and the Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA) in France. FUTURIX-FTA irradiations were conducted for the DOE Advanced Fuels Campaign (AFC), which is part of Nuclear Technology Research and Development (NTRD) program. FUTURIX-FTA irradiations in the Phénix reactor sought to investigate fuel compositions that could transmute long-lived transuranic actinide isotopes of Pu, Am and Np contained in spent nuclear fuel via fast reactor technology.

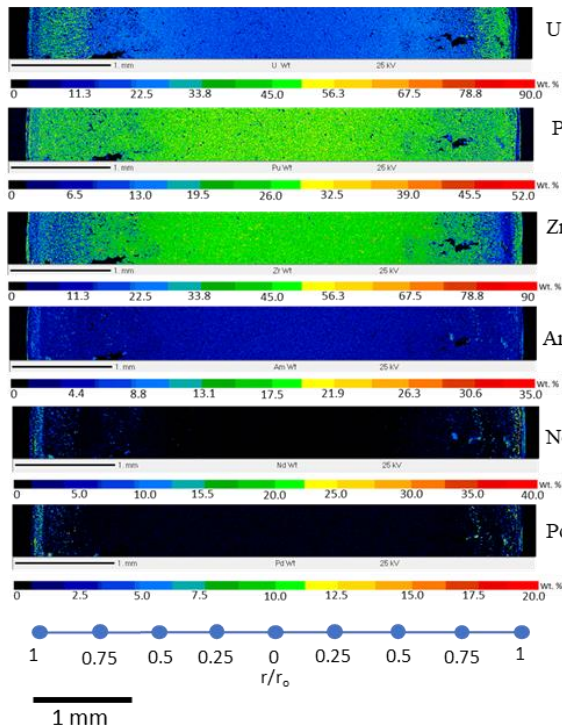
Concomitant with the Phénix reactor transmutation fuel irradiation campaign, the US DOE elected to test duplicate fuel specimens in the US-based Advanced Test Reactor (ATR) using a Cd-filtered thermal neutron spectrum to mimic the prototypic fast neutron spectrum produced by the Phénix reactor. When considering fuel performance, the pin irradiated under a true fast neutron spectrum will produce a uniform power distribution because the mean free path of neutrons exceeds the pin's diameter. In contrast, irradiation under a thermal spectrum tends to produce an uneven power distribution due to self-shielding of the fuel center. Use of Cd shrouds to filter the thermal neutron spectrum allows most of the thermal energy neutrons to be filtered out of the neutron spectrum experienced by the fuel pin. This work focuses on electron probe microanalysis (EPMA) of two rods with the composition of 34.1U-28.3Pu-3.8Am-2.1Np-31.7Zr (where the values are in weight %)—one of which was irradiated in the fast spectrum Phenix reactor to a burnup of 9.5% fissions per initial metal atom (FIMA) and the other was irradiated in the a Cd-filtered AGR reactor thermal neutron spectrum to a burnup of 20.5 % FIMA.

Figure 1 shows that the phenomenon known as constituent redistribution, wherein the elemental fuel components become heterogeneously distributed following irradiation, has occurred in both fuel pins. U has moved away from the fuel center toward the cladding while Zr has moved toward the fuel center. Am tends to co-occur with lanthanide (Ln) elements, while there is also formation in both fuels of Ln-Pd phases. However, the details of the constituent redistribution and the specific phases that form suggest that the temperature gradient along the pins' radius differed from one another.

The U and Zr radial chemical profiles in the thermal spectrum irradiated pin appear to be relatively flat for most of the pin radius, and do not appear to change composition until $r/r_0 = 0.8$. In contrast, the radial chemical profiles of U and Zr in the fast spectrum irradiated pin appear more variable, with both increases and decreases in elemental concentration between the center and the cladding. Ln, Am, and Ln-Pd phases appear to be much larger in size and more abundant in the pin irradiated under the fast neutron spectrum, than are apparent in the thermal spectrum-irradiated pin.

This presentation will compare secondary phase compositions and constituent redistribution between the two pins to elucidate performance differences that might result from Cd-filtered thermal irradiation compared to those that result from a true fast spectrum.

Cd-filtered Thermal Spectrum Neutron Irradiation



True Fast Spectrum Neutron Irradiation

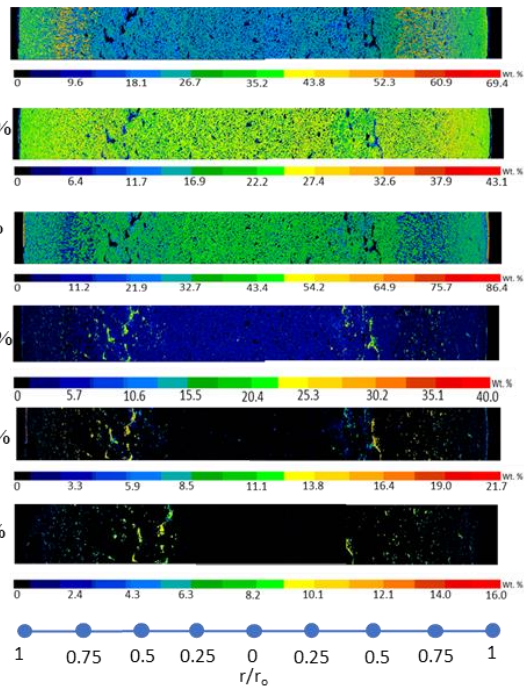


Figure 1. Shows radial X-ray maps of U, Pu, Zr, Am, Nd, Pd for the pin irradiated in the ATR (left column) and the Phénix reactor (right column).

ACT II – Thermodynamics of Ln(III)–EDTA Systems in Highly Alkaline Solutions.

Marcin Ziobro, Rafał Janicki

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According to the global trends nuclear energy consumption will grow to the 6% or 10% level in 2040 and 8% or 13% level in 2060 in comparison to the 5% level in 2015 [1]. Nuclear energy sources have numerous advantages in comparison to coal or oil, however, they are not free from environmental impact. The most difficult problem generated by nuclear power plants is waste management. According to the IAEA calculations, 1150 tons of spent fuel are generated each year only in France [2].

Besides citrates, succinates and oxalates, EDTA is one of the main organic ligands, which is present in liquid radioactive waste due to its use in the separation process and decontamination operations in the nuclear industry [3]. For instance, the Hanford mixed waste alone contains about 240 tons of radioactive waste containing the EDTA ligand, with initial concentrations of 0.1 M EDTA [3,4]. This waste has unique characteristics of being extremely heterogeneous and highly basic and having high ionic strength [3,5]. Knowledge about complexation equilibria between actinides and lanthanides with polycarboxylic acids is required to understand the migration of nuclides into the soil. Moreover characterization of lanthanide compounds with EDTA and other organic acids may develop a new approach for Ln/An separation as lanthanides cause neutron poisoning preventing the transmutation of the radioactive actinides.

The main aim of the study was to obtain thermodynamic parameters of erbium(III) complexes with EDTA in highly alkaline solutions. The comparative analysis of the high resolution UV–vis–NIR absorption spectroscopy results of crystals and solutions led to the identification of the $[\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})_{n-1}]^{2-}$ aqueous species. Equilibrium constants of the reaction $[\text{Er}(\text{EDTA})(\text{H}_2\text{O})_n]^- + \text{OH}^- \rightarrow [\text{Er}(\text{EDTA})(\text{OH})(\text{H}_2\text{O})_{n-1}]^{2-} + \text{H}_2\text{O}$ in various ionic media (NaCl, KCl, $[\text{C}(\text{NH}_2)_3]\text{Cl}$) were determined and extrapolated to the zero ionic strength using the Specific Ion Interaction Theory (SIT) formula.

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ACT 12 – Study of the Interaction between Actinides and Peptide Ligands

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Actinides are radioactive metals of high importance in civil and military nuclear activities. Trace amounts of these elements may be found in the environment due to historical nuclear tests and accidental releases. Most actinides being alpha emitters, it is essential to investigate their behavior within the human body. While the targeted organs are well-known, the transport mechanism and molecular interactions remain unidentified. Proteins have been identified as actinide targets in the event of human contamination. Although the literature on the interactions between actinides and proteins is scarce, metalloproteomic studies have shown that several calcium-binding proteins have a strong affinity for actinides¹. As a model for all calcium-binding protein, the **calcium-modulated protein** (calmodulin) was chosen for its EF-hand motif site, which is widely present in calcium-binding proteins, and its high importance in cellular regulatory function. L. Daronnat investigated the interaction of plutonium (IV) with several variants of the calmodulin and observed various behaviors of the plutonium depending on the variant of calmodulin used²: the formation of a Pu(IV)-calmodulin complex, the formation of a Pu(III)-calmodulin complex and the formation of hexanuclear clusters of plutonium. CaME (Engineered Calmodulin) is a variant of calmodulin developed especially to bind plutonium(IV). This variant has an extra carboxylate ligand in its complexation loop (shown in figure 1), increasing its affinity for actinides IV.

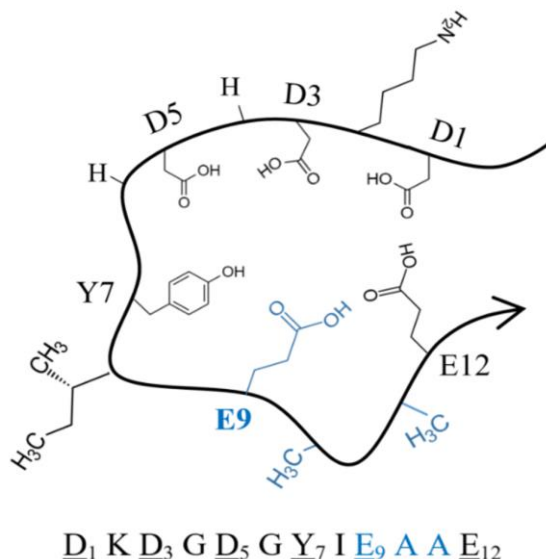


Figure 22 – Structure and sequence of the coordination site of CaME

This particular variant was the only which did not promote the formation of plutonium clusters. Instead, it only generated 1:1 complexes. Additionally, an unexpected change of the oxidation state of plutonium (from IV to III) was noticed in presence of CaME.³ To get a better understanding of this behavior, a deepened characterization of the species formed between CaME and actinides have been undertaken.

This work aims to characterize the complexes formed between CaME and actinides (Th, U, Np, Pu), using different experimental techniques. Electrospray Ionization Mass Spectrometry was used to determine the stoichiometry of the

complexes and UV-Vis-NIR Spectroscopy was used to characterize the environment of the actinide. Structural data were obtained through two or three-dimensional NMR spectroscopy. For that, an extra batch of CaME was synthesized and enriched with ^{13}C and ^{15}N , allowing for ^1H - ^{13}C - ^{15}N NMR analysis. The paramagnetic properties of the plutonium are used to identify the amino acid involved in the coordination sphere of the metallic ions.

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ACT 13 – Interaction of Plutonium (IV) With Proteins: Focusing on the Impact of Amino Acids on the Plutonium Speciation

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Plutonium, a prominent actinide, draws significant attention due to its high chemo- and radio-toxicities, historical dispersion from nuclear tests and the potential for pollution or contamination through accidental releases. If released into nature, the actinide mobility depends on biogeochemical compounds and can access the population. Despite identifying target organs in humans, understanding the transport and accumulation mechanisms of plutonium in the body remains limited. This research aims to investigate the interaction mechanisms between plutonium and specific target proteins through a molecular approach.

Recent publications showed that proteins could play an important role in actinide mobility in the environment, like the natural protein Lanmodulin which exhibits strong affinity and selectivity for actinides against lanthanides.¹ In the human body, recent studies have reevaluated Pu interaction with transferrin,² an iron carrier in the blood, suggesting the involvement of the transferrin Pu/Fe complex in cellular internalization.³ Additionally, investigations into plutonium's interactions with the iron-storage protein ferritin⁴ and the liver-derived plasma protein fetuin have revealed intriguing insights.⁵ Other calcium-binding proteins were also identified as possible Pu targets.⁶ Pu⁴⁺, UO₂²⁺ and Fe³⁺ share some characteristics with Ca²⁺ like hard cation – strong Lewis acid behaviors. Calcium forms electrostatic interactions with 7 to 8 oxygen atoms (Figure 1).

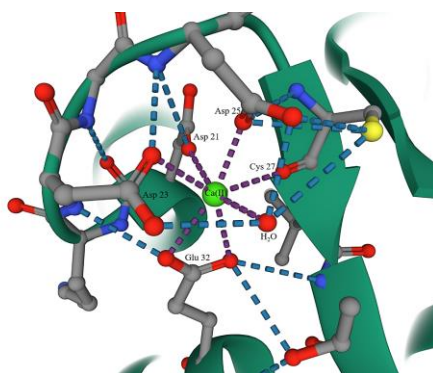


Figure 23 : Calcium binding site EF-1 of the *Arabidopsis thaliana* (PDB 5a2h). Oxygen atoms are represented in red, carbon atoms in grey, nitrogen atoms in blue, and sulfur atoms in yellow. The purple dashed lines represent the interactions between the complexation loop and calcium, while the blue dashed lines represent hydrogen bonds.

This work focuses on investigating the interaction of plutonium with the calcium-binding EF-hand motifs of calmodulin, a protein expressed in all eukaryotic cells involved in numerous signal transduction pathways. Previously, it has been demonstrated the possibility of increasing the affinity of the metal binding loop for uranyl by engineering the protein and replacing amino acids in the coordination loop.^{7,8} This new study considers the impact of Pu speciation and pH levels on protein-Pu interactions. It involved optimizing experimental conditions to observe these interactions at physiological pH.⁹

Several variants of the EF-hand motif with different amino acid sequences were produced, and their behavior in the presence of plutonium (III) and (IV) were studied using a multi-technique approach: UV-visible spectrophotometry, XANES and EXAFS, electrospray ionization mass spectrometry, capillary electrophoresis coupled with inductive plasma mass spectrometry.

At micromolar concentrations of plutonium and proteins, 1 : 1 Pu : Calmodulin complexes were observed, demonstrating a robust affinity for plutonium (IV), with stability constants ranging from $\log(K) \approx 23.2$ to 24.5 (or dissociation constants (K_d) on the order of $K_d \approx 10^{-24}$ to 10^{-25} mol.L⁻¹). The stability constant of these complexes exhibited a linear variation with the charge of the complexing loop. At higher plutonium concentrations ($> 100 \mu\text{mol.L}^{-1}$), diverse behaviors were observed, including the formation of 1 : 1 Pu(IV) : CaM complexes, 1 : 1 Pu(III) : CaM complexes, and the formation of hexanuclear clusters of Pu(IV). These three species are interconnected through chemical equilibria (Figure 2) depending on the plutonium concentration and the nature of the amino acids in the complexation loop.

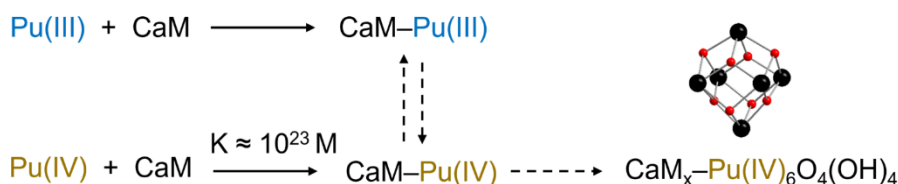


Figure 24 : Proposed reaction scheme in accordance with the experimental observations.
Dotted arrows represent the reactions that depend on concentration and amino acid sequence in the coordination loop.

A higher number of carboxylic acid functions could be responsible for the reduction of Pu(IV) to Pu(III), and the hydrophobicity of some amino acids, by limiting water molecule access to plutonium, could reduce the formation of hexanuclear clusters of Pu(IV). With the high potential to modulate amino acids in the coordination loop and the development of a robust methodology, the next step involves the development of an engineered coordination loop with a high affinity and selectivity for actinide and lanthanide separation.

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