



**Nuclear Fuel Cycle: a Chemistry Conference
May 4-5th, 2021.**

Book of Abstracts

Supported by the **H2020 GENIORS** program, the **NFC3** conference is organized jointly by the French Alternative Energies and Atomic Energy Commission (CEA), the University of Montpellier (UM) and the French National Centre for Scientific Research (CNRS). The conference intends to provide a unique platform dedicated to discussions on the latest chemistry research progress and breakthroughs within the nuclear fuel cycle community. The 2021 edition includes Keynote lectures and contributed talks. Oral presentations cover the following topics dedicated to the nuclear fuel cycles:

- Actinide and fission product chemistry
- Actinides separation
- Actinide materials: nuclear fuels and radwaste matrices
- Waste conditioning and Geological repository



Nuclear Fuel Cycle: a Chemistry Conference (NFC3) – 2021

May 4

10:00	<i>introduction</i>		
	ACT K1	K. TAKAO	
	<i>10 min questions</i>		
10:55	ACT O1	G. CHUPIN	
	ACT O2	E. MONTOYA	
	ACT O3	R. ONO	
	ACT O4	B. PERRIN	
11:55	<i>20 min questions</i>		
12:15	END OF SESSION		
	<i>lunch time</i>		
13:30	SEP K1	E. MOSSINI	
	<i>10 min questions</i>		
14:10	SEP O1	P. WEßLING	
	SEP O2	G. COLOMBO DUGONI	
	SEP O3	D. MORENO MARTINEZ	
	SEP O4	I. SÁNCHEZ GARCÍA	
15:10	<i>20 min questions</i>		
15:30	<i>15 min break</i>		
15:45	SEP K2	J. SHAFER	
	<i>Questions 10 min</i>		
16:25	SEP O5	D. MAERTENS	
	SEP O6	M. EDDY	
	SEP O7	A. DRESSLER	
	SEP O8	E. MAKOMBE	
17:25	<i>20 min questions</i>		
17:45	END OF SESSION		

May 5

10:00	<i>introduction</i>		
	MAT K1	C. SCHREINEMACHERS	
	<i>10 min questions</i>		
10:55	MAT O1	P. FOUQUET-MÉTIVIER	
	MAT O2	L. GONZALES	
	MAT O3	M. MASSONET	
	MAT O4	K. KOTTRUP	
	MAT O5	J. SIMEON	
12:10	<i>20 min questions</i>		
12:30	END OF SESSION		
	<i>Lunch time</i>		
14:00	W&G K1	G. THOROGOOD	
	<i>10 min questions</i>		
14:40	W&G O1	D. COMANDELLA	
	W&G O2	M. COT-AURIOL	
	W&G O3	A. MATVEENKO	
	W&G O4	C. GILLET	
15:40	<i>20 min questions</i>		
16:00	<i>15 min break</i>		
16:15	W&G O5	E. PERRY	
	W&G O6	R. PÉNÉLOPE	
	W&G O7	A. RODIONOVA	
	W&G O8	S. A. KULIKOVA	
17:15	<i>20 min questions</i>		
17:35	END OF SESSION		

ACTINIDE AND FISSION PRODUCT CHEMISTRY

ACT K1	<i>Coordination Chemistry of Actinide(VI, IV) Nitrates for Development of Nuclear Fuel Materials Selective Precipitation (NUMAP) Reprocessing</i>	Koichiro TAKAO Tokyo Institute of Technology
ACT O1	<i>Synthesis and Characterization of a hexanuclear plutonium(IV) in acetate solution from EXAFS and DFT</i>	Geoffroy CHUPIN CEA
ACT O2	<i>DFT Study on the Chemical Behavior of High Yielding Fission Products (Cs-137, I-129) in a UO₂ Framework</i>	Eduardo MONTOYA University of Nevada, Las Vegas
ACT O3	<i>Crystal Structures of Tetravalent f-Block Metals with Bis(2-pyrrolidone) Linker Molecules at Different HNO₃ Concentration</i>	Ryoma ONO Tokyo institute of technology
ACT O4	<i>Plutonium alpha radiolysis of nitric acid solutions</i>	Brandon PERRIN CEA

ACTINIDES SEPARATION

SEP K1	<i>PyTri-Diol behavior at conditions relevant for i-SANEX and EURO-GANEX processes</i>	Eros MOSSINI Politecnico di Milano
SEP O1	<i>Activating the Aromatic Core of the Water-soluble Complexing Agent PTD</i>	Patrik WEBLING Heidelberg University
SEP O2	<i>Deep Eutectic Solvents: promising co-solvents for Spent Nuclear Fuel reprocessing</i>	Greta COLOMBO DUGONI Politecnico di Milano
SEP O3	<i>Speciation in solvent extraction organic phases studied by molecular dynamics simulations: bifunctional amidophosphonic acid extractants</i>	Diego MORENO MARTINEZ CEA
SEP O4	<i>Development of a gamma irradiation loop and the evaluation of the EURO-GANEX process resistance</i>	Iván SÁNCHEZ GARCÍA CIEMAT
SEP K2	<i>Technical Opportunities for Decreasing Cost and Proliferation Hazard Associated with Reprocessing Technologies</i>	Jenifer SHAFER ARPA-E
SEP O5	<i>Use of TBP and N,N-dialkylamides for uranium extraction with 25 mm annular centrifugal contactors: effect of residence time on extraction performance</i>	Dominic MAERTENS SCK CEN / KU Leuven
SEP O6	<i>How Aqueous Complexes Shape ALSEP Kinetics</i>	Madeleine EDDY Colorado School of Mines
SEP O7	<i>The effect of immobilization mode of amidophosphonate ligands onto silica surfaces on the uranium extraction efficiency</i>	Aline DRESSLER CEA
SEP O8	<i>Malonamides for the multi-recycling of nuclear spent fuel.</i>	Elizabeth MAKOMBE CEA/ICSM

ACTINIDE MATERIALS: NUCLEAR FUELS AND RADWASTE MATRICES

MAT K1	Structural changes of Nd- and Ce-doped ammonium diuranate during the conversion to $U_{1-y}Ln_yO_{2\pm x}$	Christian SCHREINEMACHERS Forschungszentrum Jülich GmbH
MAT O1	Study of melting temperatures of (U,Pu)O ₂ SFRs fuels: influence of Pu and Am contents and oxygen stoichiometry	Pauline FOUQUET-MÉTIVIER CEA
MAT O2	Chromium doped Uranium Nitride as an advanced technology fuel	Luis GONZALEZ Chalmers University of Technology
MAT O3	Impact of the method of preparation and sintering conditions on the dissolution of (U,Ce)O _{2±δ}	Malvina MASSONNET ICSM/CEA
MAT O4	Molten salt irradiation and waste management	Konstantin KOTTRUP NRG
MAT O5	Sintering map approach on MOX SFR nuclear fuels with various plutonium contents	Julie SIMEON CEA

WASTE MANAGEMENT & GEOLOGICAL REPOSITORY

WG K1	Pb₂Tc₂O_{6.86}, a Stable Valence V Technetium Oxide?	Gordon THOROGOOD ANSTO
WG O1	Electrospun microporous membranes loaded with cerium oxide nanoparticles for the decontamination of nuclear wastewaters	Daniele COMANDELLA European Commission - JRC
WG O2	Sonochemical conversion of UO ₃ into U(VI) intrinsic colloids in near-neutral conditions	Manon COT-AURIOL CEA/ICSM
WG O3	Matrices for the immobilization of waste from pyrochemical processing of spent nuclear fuel	Anna MATVEENKO Lomonosov Moscow State University
WG O4	Effects of complex irradiation scenarios on ISG nuclear glass structure, properties and leaching behaviour	Célia GILLET CEA/ICSM
WG O5	The Fabrication and Oxidative Dissolution of Mixed Oxide Fuels under the Reducing Conditions of a Geological Disposal Facility	Emma PERRY University Of Cambridge
WG O6	Development of iodine filters directly convertible into conditioning matrices	Raphaël PÉNÉLOPE CEA
WG O7	Sorption and spatial distribution of radionuclides onto fractured rocks of the exocontact zone of the Nizhnekansky granitoid massif	Anastasiia RODIONOVA GEOKHI RAS
WG O8	Immobilization of metal chlorides in magnesium potassium phosphate compound	Svetlana A. KULIKOVA Vernadsky Institute, Russian Academy of Sciences

ACTINIDE AND FISSION PRODUCT CHEMISTRY

Coordination Chemistry of Actinide(VI, IV) Nitrates for Development of Nuclear Fuel Materials Selective Precipitation (NUMAP) Reprocessing^[1]

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Nuclear fuel recycling is a promising option to overcome the increasing energy demands in the current and future societies. Spent fuel reprocessing aims recovery of recyclable nuclear fuel materials from spent fuels and reduction of the radioactive waste volume. Solvent extraction is extensively employed as a useful and well-experienced method for reprocessing, while there would be still some space to explore the diversity of reprocessing methodology. During these two decades, we have extensively dedicated our effort to investigate crystallization of hexavalent and tetravalent actinides from HNO₃ aqueous systems to develop a simple and versatile reprocessing principle based on selective precipitation of the nuclear fuel materials. Herein, I intend to introduce an outline of our development of NUclear fuel MAterials selective Precipitation (NUMAP) method.^[1]

Uranium usually stays at +6, and forms a dioxo molecular cation, uranyl ion ([O≡U≡O]²⁺, UO₂²⁺). The positive charge of UO₂²⁺ is compensated by coordination of 2 NO₃⁻ to form a D_{2h}-symmetric UO₂(NO₃)₂(L)₂ (Fig. 1a), where 2 additional monodentate ligands (L) are also involved to fulfill the remaining coordination sites. If the molecular structure of L is appropriately designed, high symmetry and enough hydrophobicity will be provided to allow crystallization of a sparingly soluble UO₂(NO₃)₂(L)₂ from a HNO₃ solution dissolving the spent nuclear fuels. For this purpose, we employed *N*-alkylated 2-pyrrolidone (NRP, Fig. 1b), and recently shifted to more sophisticated molecular design of double-headed NRP (DHNRP) which allows to connect the [UO₂(NO₃)₂] monomeric units to afford an infinite 1-dimensional coordination polymer of [UO₂(NO₃)₂(DHNRP)]_n (Fig. 1c). Especially in the latter concept, the solubility of UO₂²⁺ in 3 M HNO₃(aq) decreases down to 10⁻³-10⁻⁴ M after addition of DHNRP appropriately selected, corresponding to > 99% recovery of U from the feed solution. Furthermore, we have also found that some of DHNRPs efficiently precipitates An⁴⁺ (An = Th, U, Np) to form less-soluble crystalline phases of (HDHNRP)₂[An(NO₃)₆]. Interestingly, there are no direct chemical bonds between An⁴⁺ and DHNRP. Instead, H⁺ is trapped between neighboring DHNRP molecules with hydrogen bonding for charge compensation of [An(NO₃)₆]¹²⁻. The solubility of (HDHNRP)₂[An(NO₃)₆] is 10⁻³ M, allowing to expect efficient recovery of nuclear fuel materials in tetravalence such as Pu⁴⁺ and Th⁴⁺.

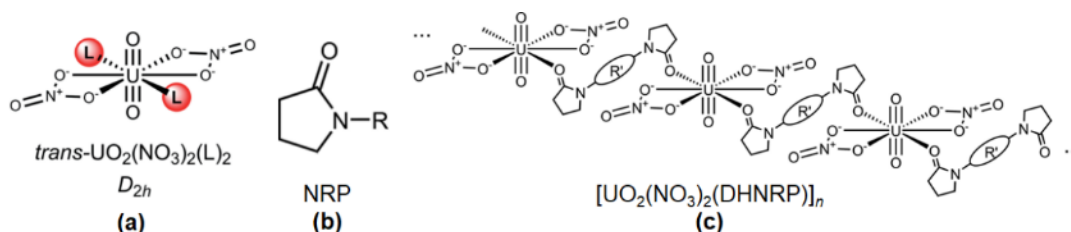


Figure 1: Schematic structures of UO₂(NO₃)₂(L)₂ (a), NRP (b), and [UO₂(NO₃)₂(DHNRP)]_n (c).

[1] K. Takao, Y. Ikeda, *Eur. J. Inorg. Chem.* **2020**, 3443-3459.

Synthesis and Characterization of a hexanuclear plutonium(IV) in acetate solution from EXAFS and DFT

G.Chupin [1], D. Guillaumont [1], C. Tamain [1], T. Dumas [1], P-L. Solari[2] and P. Moisy [1]

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Polynuclear actinide complexes (or clusters) are molecular entities composed of several metallic centers. Beyond the different types of clusters, we are interested in molecules in which actinide atoms are connected through aquo, hydroxo or oxo ligands. Those structures require further complexation by organic or inorganic ligands (Cl^- , SO_4^{2-} , NO_3^- or RCOO^-) to be stabilized [1]. This project focuses on tetravalent actinide, especially Pu(IV) in acetate solutions. In order to obtain plutonium cluster, pH and ligand concentration was set to allow both condensation and complexation. First, the Vis-NIR absorption spectroscopy at $[\text{AcOH}] = 1\text{M}$ and $\text{pH} = 4.5$ suggested the Pu(IV) complexation with acetate, without colloid formation. Secondly, the EXAFS spectrum evidence the formation of a polynuclear plutonium cluster in solution. In order to confirm this observation, the *ab initio* EXAFS spectrum of the expected $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ complex were calculated using DFT method. The k^3 -weighted simulated signal was compared to the experimental one and confirmed its synthesis in solution (figure 1). Finally, in order to observe if this signal was specific to hexanuclear system, plutonium clusters EXAFS spectra from dimer to hexamer were simulated by DFT. The cluster geometry and nuclearity have an impact on the EXAFS simulated signal and confirmed the indisputable $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ stoichiometry. This result highlights the importance of polynuclear species for plutonium speciation in hydrolytic conditions and the necessity to study them to revise speciation diagram.

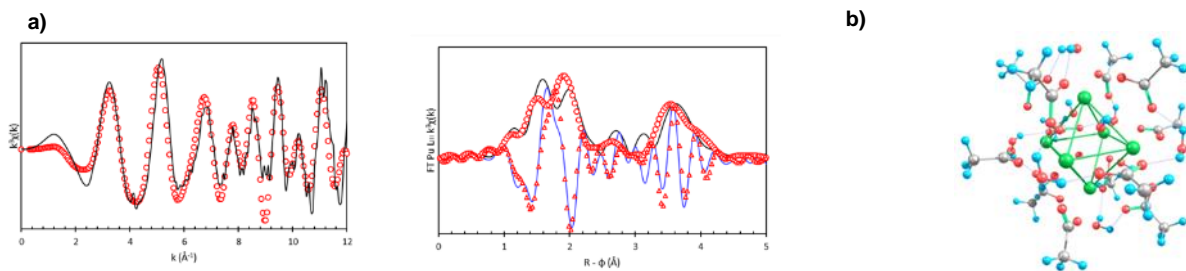


Figure 1. a) Experimental $k^3\chi(k)$ signal, corresponding FT (solid black line) and imaginary part (solid blue line) and *ab initio* EXAFS spectra simulation of $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ (red open circle) and its imaginary part (red open triangle). b) Corresponding $\text{Pu}_6\text{O}_4(\text{OH})_4(\text{AcO})_{12}(\text{H}_2\text{O})_6$ DFT optimized structure (B3LYP/6-31G(d,p)/ECP82/solvent)

[1] Knope, K. E. et al., Chem. Rev. 113, 944 (2013).

DFT Study on the Chemical Behavior of High Yielding Fission Products (Cs-137, I-129) in a UO₂ Framework

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The lack of confidence in the safety and performance of current long-term storage solutions for spent nuclear fuel (SNF) is a major concern for both the scientific community and the general populace. This innate fear on the potential impact of leaked SNF on the environment stems from a cultural understanding that nuclear science is both dangerous and malicious towards environmental and public health. Advances in computational sciences have granted researchers the opportunity to dive headfirst into predicting the arrangement of elements using probability statistics and quantum theory as tools that safely and conveniently improve upon our knowledge on atomic behaviour. By using already established work in thermodynamics and formation kinetics, a density functional theory (DFT) study can be conducted to simulate the potential chemical behaviour that SNF may exhibit under certain conditions in both natural and synthetic settings. This research simulates bulk spent oxide fuel (UO₂) as it reacts with high yielding fission products (FP), including Cs-137 and I-129. Results from the DFT study are then recreated under laboratory conditions to improve on both methods, especially in accuracy and efficiency in data collection. Validity of both theory and experimental results are confirmed using characterization methods such as x-ray diffraction (XRD) and scanning electron microscopy (SEM). Using an *ab initio* program such as VASP, we can solve for the Schrödinger equation to find stability in a [UO₂] cell matrix where the FP [Cs, I₂, and CsI] are included in the matrix as a defect. Various combinations of the defects are explored, including different molar concentrations and arrangements with neighbouring atoms. Multiple established theoretical conditions are tested due to the unique electronic behaviour uranium exhibits as a mott-insulator. A generalized gradient approximation (GGA) accurately predicts the crystallographic behaviour of uranium, while GGA+U (where U is the addition of a Hubbard term) is most beneficial in predicting the magnetic behaviour of the same system.

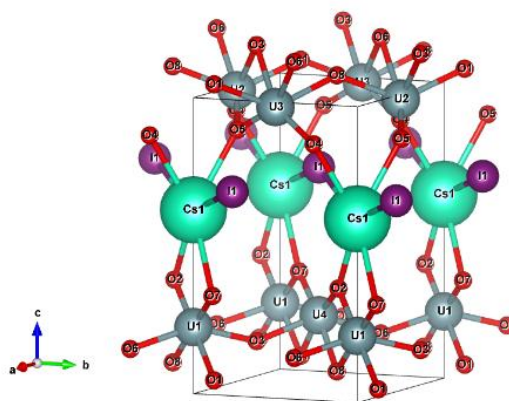


Figure 1: Optimized UO₂ geometry where CsI is interstitially added to the cell

Crystal Structures of Tetravalent f-Block Metals with Bis(2-pyrrolidone) Linker Molecules at Different HNO₃ Concentration

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Recovery of tetravalent actinides (An(IV)) is the most essential in reprocessing processes for U/Pu and Th/U nuclear fuel cycles. In our recent development of a precipitation-based simple and versatile reprocessing method, we have found that *N,N'*-*trans*-cyclohexane-1,4-diylbis(pyrrolidin-2-one) (Figure 1a, **L**) crystallizes with An(IV) (An = U, Np) in 3 M HNO₃(aq) to form sparingly soluble (HL)₂[An(NO₃)₆] [1, 2]. This would be also the case for Th(IV) and Pu(IV) because of chemical similarities of them through the actinide series. Ce(IV) is another tetravalent f-block metal ion compatible with aqueous systems. Therefore, the structural chemistry of Ce(IV) nitrate complexes with **L** will provide a good contrast between lanthanides and actinides, and therefore is of great interest to promote understanding of the f-block chemistry relevant to nuclear fuel cycles. Herein, we aim to compare the structure of compounds between An(IV) (An=Th, U) nitrate complexes and **L** with that of Ce(IV), in HNO₃ aq with various concentrations.

Figure 1b shows a molecular structure of [Ce₂O(NO₃)₆L₂]_n deposited from 3 M HNO₃(aq). In this Ce(IV) compound, [Ce(NO₃)₃]⁺ units are connected by μ-O²⁻ (O(1)) and crosslinking **L** to form a three-dimensional metal organic framework. The number of coordinated NO₃⁻ is smaller than that in [Ce(NO₃)₆]²⁻ commonly available. The remaining positive charge on [Ce(NO₃)₃]⁺ is compensated by μ-O²⁻ (O(1)) shared between 2 Ce⁴⁺ centers. The μ-O²⁻ occurring in this structure is most probably generated by oxolation of Ce(IV). This was unexpected, because its mother liquor (3 M HNO₃) was still strongly acidic. All above results imply that coordination chemistry of Ce(IV) in HNO₃(aq) is strongly dependent on [HNO₃]. Indeed, (HL)₂[Ce(NO₃)₆] (Figure 1c) deposited from 9 M HNO₃(aq), where [Ce(NO₃)₆]²⁻ and H⁺-involved hydrogen-bonded polymer of [H⁺...L]_n are present. This structure is also common to (HL)₂[An(NO₃)₆] [1, 2]. We have found that there is a boundary between [Ce₂O(NO₃)₆L₂]_n and (HL)₂[Ce(NO₃)₆] at [HNO₃] = 4.3 M. On the other hand, Th(IV) at [HNO₃] = 2-9 M does not show any oxolation to give μ-O²⁻ like Figure 1b of Ce(IV), but always forms (HL)₂[Th(NO₃)₆]. This contrast is a critical difference between lanthanides and actinides in the coordination chemistry of f-block metals.

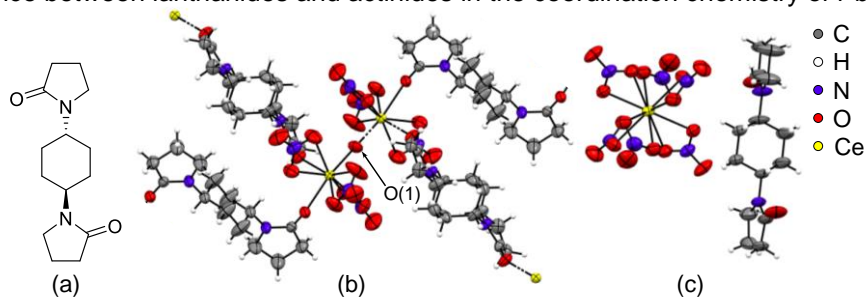


Figure 1. Schematic structure of **L** (a), and molecular structure of [Ce₂(μ-O)(NO₃)₆L₂]_n from 3 M HNO₃ aq (b), and (HL)₂[Ce(NO₃)₆]_n from 9 M HNO₃ aq (c).

[1] K. Takao *et al*, *RSC Adv.*, **10** 6082-6087 (2020).

[2] K. Takao *et al*, *Angew. Chem. Int. Ed.*, **58** 240-243 (2019).

Plutonium alpha radiolysis of nitric acid solutions

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Nitric acid is widely used in the nuclear industry. During the reprocessing of spent nuclear fuel, nitric acid is subject to an intense radiation field leading to the degradation of the aqueous phase and the formation of numerous radiolytic products. Some of these radiolytic products (mainly H_2O_2 and HNO_2) have redox behaviour that can be detrimental to the reprocessing process [1],[2]. Moreover, the formation of gaseous radiolytic products (H_2 , NO_x , ...) can raise safety concerns [3].

The radiolytic yields of some species have been investigated as a function of HNO_3 concentration from the α -radiolysis of solutions containing plutonium at different initial oxidation state, with or without sulfamic acid (Fig. 1) and the redox behaviour of plutonium have also been monitored (Fig. 2).

The results have shown that the radiolytic yields of H_2 , N_2O and HNO_2 depend on the HNO_3 concentrations as well as the initial oxidation state of plutonium. The dependence on the initial oxidation state decreases with increasing HNO_3 concentration.

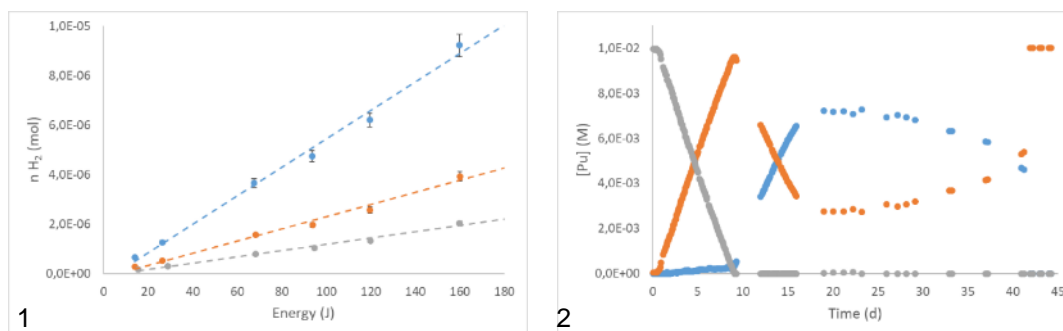


Figure 1: Formation of H_2 from nitric acid solutions containing plutonium. $[\text{Pu(IV)}] = 0.01\text{M}$, $\bullet [\text{HNO}_3] = 1\text{M}$, $\circ [\text{HNO}_3] = 3\text{M}$, $\square [\text{HNO}_3] = 6\text{M}$.

Figure 2: Evolution of the oxidation state of plutonium under α -radiolysis of a nitric acid solution containing plutonium with sulfamic acid. $[\text{HNO}_3] = 1\text{M}$, $[\text{H}_2\text{NSO}_3\text{H}] = 0.1\text{M}$, $[\text{Pu}] = 0.01\text{M}$, $\square \text{Pu(VI)}$, $\circ \text{Pu(IV)}$, $\bullet \text{Pu(III)}$.

[1] G Garaix et al., *Rad. Phys. Chem.* **2015**, 106, 394–403

[2] G P Horne et al., *J. Phys. Chem. B* **2017**, 121, 4, 883–889

[3] C R Gregson et al., *J. Phys. Chem. B* **2018**, 122, 9, 2627–2634

ACTINIDES SEPARATION

PyTri-Diol behavior at conditions relevant for *i*-SANEX and EURO GANEX processes

Eros Mossini[1]*, Annalisa Ossola[1], Elena Macerata[1], Nathalie Boubals[2], Mario Mariani[1]

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The Partitioning and Transmutation of long-term radiotoxic TRAnsUranium elements (TRU) is a valid approach for minimizing the high-level waste and optimizing both natural resources exploitation and final repository environmental footprint. Among several processes developed so far, the *i*-SANEX (innovative-Selective ActiNide EXtraction) and EURO-GANEX (EUROpean-Grouped ActiNide EXtraction) concepts target the selective separation of Minor Actinides (MA: Am and Cm) or, more ambitiously, of all TRU from lanthanides (Ln) and fission products. The well-established TetraOctyl-DiGlycolAmide (TODGA) ligand is typically employed to co-extract Ln and MA from the aqueous feed, in association with DiMethyl-DiOctylHexylEthoxyMalonAmide (DMDOHEMA) if all TRU need to be extracted. Afterwards, a hydrophilic complexing agent is required to achieve the selective actinide separation. To this aim, among several molecules proposed so far, the CHON PyTri-Diol ligand exhibited promising TRU extraction selectivity and efficiency, and unprecedented radiolytic and hydrolytic stability [1][2].

In view of possible future industrial implementation, PyTri-Diol behavior has been studied in conditions closer to the process ones. The effect of temperature on PyTri-Diol extraction capability has been investigated by means of solvent extraction experiments in the temperature range of interest, namely between 10 and 50°C. Even if the MA/Eu separation factor decreases at increasing temperature, the system remains sufficiently selective for MA. Furthermore, the effects of Am and Pu loading on PyTri-Diol performances have been studied. In order to demonstrate the applicability to *i*-SANEX and EURO-GANEX processes respectively, solvent extraction experiments were performed with synthetic aqueous feeds containing real-waste concentration of ²⁴¹Am(III) and ²³⁹Pu(IV). The tests were performed with fresh, aged (1 month) and irradiated (up to 200 kGy with 2.5 kGy/h ⁶⁰Co source) PyTri-Diol solutions, in some cases containing AcetoHydroxamic Acid (AHA) to enhance Pu(IV) back-extraction. Remarkably, whether fresh, aged or irradiated, PyTri-Diol alone efficiently and selectively recovers Am(III) and, synergistically with AHA, Pu(IV) present in macro-concentrations.

These results are very encouraging and furtherly support the implementation of *i*-SANEX and EURO-GANEX processes based on PyTri-Diol system.

Financial support for this research was provided by the European Commission (GENIORS project, H2020-Euratom Grant agreement ID: 755171).

[1] Macerata E., et al. (2016) Hydrophilic Clicked 2,6-Bis-Triazolyl-pyridines Endowed with High Actinide Selectivity and Radiochemical Stability: Toward a Closed Nuclear Fuel Cycle. *Journal of the American Chemical Society* **138**: 7232-7235

[2] Mossini E., et al. (2019) Radiolytic degradation of hydrophilic PyTri ligands for minor actinide recycling. *Journal of Radioanalytical and Nuclear Chemistry* **322**: 1663-1673

Technical Opportunities for Decreasing Cost and Proliferation Hazard Associated with Reprocessing Technologies

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There has been a recent, significant investment in advanced reactor technologies in the U.S, with some technologies slated to be operational before the end of the decade. Concomitant with the development of these technologies, is the need to develop an appropriate fuel source. While high-assay low enriched uranium (HALEU) has broadly been considered the fuel of choice for such technologies, a mixed actinide fuel containing uranium, plutonium, neptunium and americium may have certain benefits. The material could be derived from used commercial nuclear fuel available in the U.S. and would provide a pathway for transmutation of long-lived actinide isotopes to much shorter-lived fission products. However, such an approach is not without technical challenges. Current reprocessing technology is probably too expensive to encourage significant interest from commercial entities and safeguarding a facility with sufficient precision to foster wide acceptance of the technology has not been demonstrated. This presentation will consider potential opportunities to address these technical challenges while seeking broader feedback from the expert community about the viability and impact of such approaches.

Activating the Aromatic Core of the Water-soluble Complexing Agent PTD

P. Weßling [1,2], M. Trumm [1], E. Macerata [3], A. Ossola [3], E. Mossini [3], M.C. Gullo [4], A. Arduini [4], A. Casnati [4], M. Mariani [3], C. Adam [1], A. Geist [1], P.J. Panak [1,2]

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Several solvent extraction processes for separating actinides from irradiated nuclear fuel developed in European research programs make use of 3,3',3'',3'''-(pyridine-2,6-diylbis(1,2,4-triazine-3,5,6-triyl))tetrabenzenesulfonate (SO₃-Ph-BTP) to selectively strip actinides from organic phases loaded with actinides and lanthanides. [1] As a "CHON" compliant alternative to SO₃-Ph-BTP, 3,3'-(pyridine-2,6-diylbis(1H-1,2,3-triazole-4,1-diyl))bis-(propan-1-ol) (PTD) was developed. Although performing satisfactorily for selectively stripping actinides, the stability constant of the [Cm(PTD)₃]³⁺ complex is lower by more than one order of magnitude compared to the [Cm(SO₃-Ph-BTP)₃]³⁺ complex, demonstrating its weaker complexation strength. [2]

Consequently, PTD-OMe was synthesized, bearing a methoxy group on the central pyridine ring to increase its basicity and hence complexation strength. Time-resolved laser fluorescence spectroscopy (TRLFS) confirms the ligand's improved complexation properties ($\log \beta_3(\text{PTD-OMe}) = 10.8 \pm 0.4$ vs. $\log \beta_3(\text{PTD}) = 9.9 \pm 0.5$). However, PTD-OMe proves to be less efficient than PTD in solvent extraction experiments. This is explained by the increased basicity of the ligand ($\text{p}K_a(\text{PTD-OMe}) = 2.54 \pm 0.08$ vs. $\text{p}K_a(\text{PTD}) = 2.1$). This increased basicity leads to a reduced free ligand concentration under solvent extraction conditions (0.44 mol/L HNO₃), explaining the inferior performance compared to PTD.

Both DFT calculations and NMR measurements confirm that protonation occurs at the pyridine nitrogen atom. The lower selectivity of PTD-OMe compared to PTD is explained by the unfavourable changes in polarizabilities of the nitrogen atoms.

This work comprehensively demonstrates how activating the aromatic core of a ligand benefits its complexation properties. However, solvent extraction performance is compromised due to more pronounced ligand protonation if the pH of the system is smaller than the $\text{p}K_a$ value of the ligand.

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Deep Eutectic Solvents: promising media for Spent Nuclear Fuel reprocessing

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In this communication, we report on the use of Deep Eutectic Solvents (DES) for processing nuclear waste, and in particular in Selective ActiNide EXtraction (SANEX) process, allowing to selectively recover Actinides from spent nuclear fuel solutions.

DES are an interesting new class of solvents.[1] They are eutectic mixtures of hydrogen bond acceptor (HBA) and donor (HBD), generally liquid at room temperature. The large variety of combinations of the components allows to modulate the solvent properties.[2,3]

Herein, a novel family of choline acetate-based DES is proposed. Some representative DES of this family were tested as co-solvent for actinides/lanthanides partitioning based on liquid-liquid extraction within the frame of the hydrometallurgical reprocessing of spent nuclear fuel. The DES here described were designed in accordance with the CHON rule to avoid secondary waste production at the end of life.

As a first step, we obtained information regarding the DES containing solvents radiochemical stability. The pure DES and the 3 M HNO₃ solutions containing DES (5-50% in wt.) were irradiated up to 100 kGy by a Co-60 source and then analyzed by electrospray ionization mass spectrometry (ESI-MS). The analyses confirmed the excellent radiochemical stability of the systems.

Preliminary extraction experiments were performed at controlled temperature (25°C) by exploring i) a library of DES, ii) different DES concentrations in the aqueous phase, and iii) different mixing time. ²⁴¹Am(III) and ¹⁵²Eu(III) were used as representatives of minor actinide and lanthanide families present in the aqueous feed to be decontaminated. The aqueous phase consists of 3M HNO₃ and DES as co-solvent in different concentrations. The organic phase is the lipophilic ligand CyMe₄-BTBP. The DES performance was checked with respect to CyMe₄-BTBP dissolved in 1-octanol (0.015M)[4]. CyMe₄-BTBP has been chosen since it is the reference ligand for selective extraction of Am(III). Kinetic studies underline a catalytic effect of DES leading to enhanced CyMe₄-BTBP extraction and selectivity.

Results, advantages and drawbacks of the use of DESs in advanced partitioning processes are summarized in the present communication. The promising results obtained justify further investigations on these co-solvents to understand the rationale of their action as well as to improve the Actinides selectivity.

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Speciation In Solvent Extraction Organic Phases Studied By Molecular Dynamics Simulations: Bifunctional Amidophosphonic Acid Extractants

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DEHCNPB (Butyl-N,N-di(2-ethylhexyl)carbamoyl-nonylphosphonate) is an amido-phosphonic acid developed for the separation of uranium from wet phosphoric acid. The bifunctional molecular structure of DEHCNPB was developed assembling the organic functions of HDEHP and TOPO, two molecules used as synergistic mixture for this separation [1]. Although previous studies have been done [2], a detailed characterization of the DEHCNPB organic solutions at the supramolecular and molecular scales is missing. In the present work, we use classical Molecular Dynamics (MD) coupled to experimental data, in order to describe the aggregation for the bifunctional extractant DEHCNPB as well as the speciation of uranium (VI) in such organic solutions. We provide a fine description of the population of species in the organic solution, as well as the interactions within aggregates themselves and with the extracted water. In addition, we shed light on the extraction mechanism. Two to three extractant molecules are found to coordinate uranyl by their phosphonate groups. Uranyl is not fully dehydrated in the organic solution. The amide groups are found to form H-bonds with the remaining water molecules bound to uranyl. These H-bond networks around the metallic cation stabilize the complexes and facilitate the extraction. These results underline the importance of considering weak interaction in the understanding of extraction processes and show also how coupling molecular modelling with experiments leads to a fine exploration of the molecular interactions and supramolecular organization of such systems.

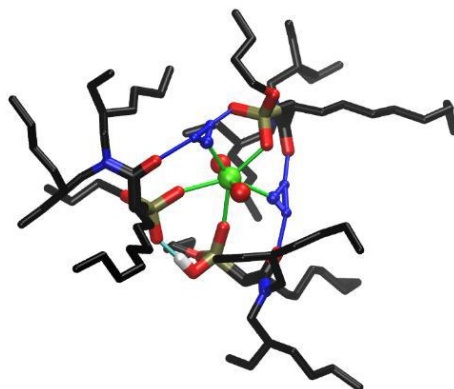


Figure 1. Snapshot of a typical uranyl complex formed during the simulation. The phosphonate-phosphonate interactions are represented in cyan, the water interactions in blue, and the uranium coordination bonds in green.

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Development of a gamma irradiation loop and the evaluation of the EURO-GANEX process resistance

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One of the current R&D trends for the development of advanced nuclear fuel cycle is the Partitioning and Transmutation (P&T) strategy. It consists of recovering not only the U and Pu from the spent nuclear fuel (SNF), as in the PUREX process, but also the minor actinides (MAs: mainly Np, Am, and Cm), for the subsequent conversion into short-lived nuclides by transmutation process. MAs have a special attention because together with Pu, they are the main responsible of the long-term radiotoxicity of the SNF [1].

From the point of view of security, the resistance to the existing highly radioactive field and the high acid concentration where fuel is dissolved is a constraining factor for the development of extraction processes. Ligands used for selective extraction tend to suffer hydrolytic and radiolytic degradations that can lead to changes in the composition of the extraction system, reducing their concentration, producing degradation compounds and modifying the initial physicochemical and chemical properties. All these effects result in less efficiency, an increase of secondary wastes and possible mal-operation situations. In that sense, resistance studies of extraction systems are very useful to know and predict the long-term behaviour during a normal or mal-operation in a future reprocessing plant, which is one of the priorities within the European framework [2].

In order to simulate real reprocessing conditions of a process as much as possible, a new irradiation loop design for resistance studies of extraction systems has been developed at CIEMAT. This system has a really low volume requirement and its step by step configuration permits an easy modification of settings, adjusting experiments depending on the study interest. This irradiation loop has been initially set up to test the main EURO-GANEX process steps: the lanthanides (Ln) and actinides (An) co-extraction follows-up the stripping of the transuranic elements (TRU) [3]. During the process, behaviour of An and Ln, presence of stainless steel corrosion products, effects of acidity, solvent degradation as well as new possible degradation compounds have been explored.

The performance and changes in the composition have been analysed along the irradiation experiment by different techniques: gamma spectrometry and ICP-MS to know the extraction and corrosion behaviour of the full system, and HPLC-MS and Raman spectroscopy to determine the degradation of the organic and aqueous solvents, respectively. The results obtained evidence the importance of developing realistic irradiation experiments where different factors affecting the performance can be easily studied and isolated.

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Use of TBP and N,N-dialkylamides for uranium extraction with 25 mm annular centrifugal contactors: effect of residence time on extraction performance

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Tri-*n*-butyl phosphate (TBP) is used as solvating extractant in the PUREX process, but *N,N*-dialkylamides can also extractant uranium from HNO₃ and have the particular advantage that they comprise only the elements carbon, hydrogen, oxygen and nitrogen (CHON).

Annular centrifugal contactors (ACCs) have interesting characteristics and advantages in continuous solvent extraction processes compared to e.g. mixer-settlers. Besides their small footprint, very short contact times in the annular mixing zone can be achieved, limiting solvent degradation. An experimental setup consisting of 16 stages of 25 mm \varnothing ACCs made from 316 L stainless steel was used for SX R&D at SCK CEN (Mol, Belgium). The housing in which the rotor is spinning, is made from acrylic glass, which allows direct visual observation of the annular mixing zones. The R&D setup can be easily converted from an extraction-scrubbing process to a back-extraction configuration. It was investigated how the efficiency of solvent extraction processes can be optimized by changing the contact time in the centrifugal contactor.

The SX Process software package was used to create a model for U extraction by 1.1 M TBP as a function of the HNO₃ and free TBP concentrations [1]. Distribution isotherms were constructed from available literature data and data fitting was performed in MATLAB. Flow sheets with high saturation of the organic phase were modelled to maximize decontamination of fission products. Several experiments were performed to assess the TBP benchmark system. Ru and Zr decontaminations were less efficient than predicted by the model, in agreement with literature reports [2]. Increasing the residence time in the mixing zone by increasing the mixer volume improved the efficiency of the scrubbing process, indicating that a kinetic effect is responsible.

Batch extraction experiments were performed to determine distribution isotherms of 1.1 M D2EHBA and 1.1 M D2EHiBA for U and HNO₃ at different HNO₃ concentrations. The multi-stage extraction experiments with D2EHiBA confirmed a better performance of Ru and Zr decontamination compared to TBP. Where it was found that for the TBP process, only 4 extraction stages are required to achieve a decontamination factor of $>10^5$ for U, for D2EHiBA 8 stages are required, while comparable throughput was obtained.

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How Aqueous Complexes Shape ALSEP Kinetics

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The Actinide Lanthanide SEParation (ALSEP) process is a modern approach to the separating minor actinides from lanthanide fission products, which is an essential step in closing of the nuclear fuel cycle. ALSEP achieves this separation by incorporating aqueous polyaminocarboxylate ligands, aided by carboxylate buffers, to selectively complex the minor actinides, leaving the lanthanides behind in the organic phase. This actinide stripping step experiences relatively slow kinetics, making the overall process difficult to use at the industrial scale. This kinetic barrier is not unique to ALSEP, with other TALSPEAK-like processes experiencing the same slow rates of metal transfer. The root cause of this slow kinetics has been minimally studied throughout the years, with no research reported on the kinetic mechanism of the ALSEP stripping step.

This presentation will highlight current efforts to understand the kinetic limitations of the ALSEP process through systematic study of each component in the system. Microfluidic techniques using Nd and Am, coupled with unique biphasic UV-vis spectroscopy of Nd, were used to measure the effects of component concentration on the solvent extraction kinetics of the phase transfer reaction. Of particular interest is the effects of aqueous ligand and buffer pairs – as the identity of these species will impact both kinetics and aqueous equilibrium species stoichiometry. The two ligand/buffer pairs of particular interest to this study are N-(2-hydroxyethyl)-ethylenediaminetriacetic acid with citric acid and diethylenetriaminepentaacetic acid with malonate – both choices stemming from the original ALSEP design. These pairs exhibit vastly different equilibrium behaviours, with HEDTA/citrate forming a 1:1:1 ternary metal complex and DTPA/citrate forming only a 1:1 binary DTPA metal complex. This difference in aqueous complex identity allows the citrate and malonate buffers to take on fundamentally different roles in the metal transfer process. Understanding this relationship between complexation and kinetics on the aqueous side of the ALSEP stripping step is an essential part of the process to modify and design the next generation of solvent extraction separations more effectively.

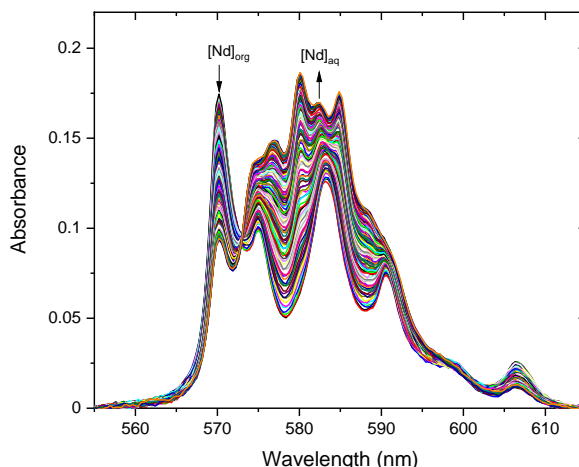


Figure 1: Real-time biphasic UV-Vis spectra for the ALSEP strip using an HEDTA/Citrate system.

The effect of immobilization mode of amidophosphonate ligands onto silica surfaces on the uranium extraction efficiency

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Various functionalized silica materials were investigated as uranium solid-phase extractants from different sulfuric acid solutions. Silica supports were functionalized with amidophosphonate moieties either grafted by peptide coupling (*Grafted@D60*) or by non-covalent impregnation (*AdsC8@D60* and *AdsMiMBr@D60*). Prior to impregnation, the surface of the supports were modified either by alkyl chains or by ionic liquid chains. The impact of the functionalization pathways towards uranium extraction was evaluated in two sulfuric medias: the first is a low sulfate solution ($[\text{SO}_4]^{2-}/[\text{U}] = 50$, $\text{pH} = 2$) and the second is a high sulfate solution ($[\text{SO}_4]^{2-}/[\text{U}] = 900$, $\text{pH} = 1$). These media represent, respectively, the composition of typical effluent solutions from uranium mining plants and uranium mining leaching solutions. Two sorts of extraction experiments were conducted: sorption isotherms in the absence of competitive ions to determine the maximum uranium extraction capacity of the materials and selectivity experiments to evaluate the impact of the competitive cations such as Fe and Mo. The sorption isotherms show that all materials shown good results in terms of extraction efficiency in both media (Fig. 1).

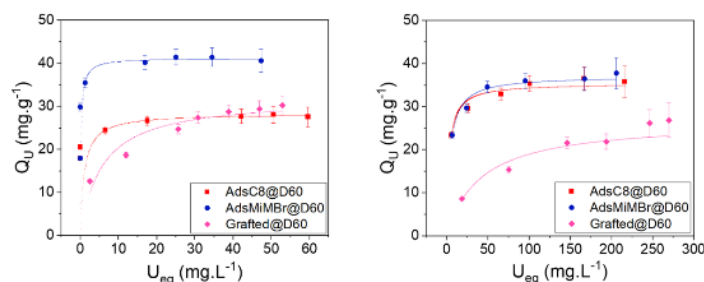


Figure 1: Uranium extraction isotherms measured for the three studied materials in "effluent" (left) and "mining" (right) isotherm conditions and the corresponding fits to a Langmuir model.

In effluent conditions, *AdsMiMBr@D60* require around 2.0 amidophosphonates ligands per uranium, while *AdsC8@D60* and *Grafted@D60* reveals 2.7 and 2.4 ligands per uranium, respectively. This suggests that the ionic liquid moieties either ease the uranyl group migration in the organic layer and/or help the amidophosphonate moieties to organize itself and then complex uranium. In addition, the Langmuir modelling confirms that this material shows the higher affinity to uranium. In mining conditions the grafted material needs 2.6 ligands to extract a uranyl ion, while both adsorbed materials only needs on average 2.1 ligands to complex uranium, whose superior uranium affinity has also been confirmed by higher Langmuir constants. Considering the extraction tests performed in the presence of Fe and Mo, both impregnated materials shown higher selectivity towards uranium than the grafted one in both media, mainly in mining conditions. Indeed, the non-covalent impregnation of the ligands probably increase their mobility and allows an easier coordination around uranium. EXAFS studies and/or modelling could validate this hypothesis.

Malonamides for the multi-recycling of nuclear spent fuel

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Nuclear energy is the principal source of electricity in France; the actual nuclear fuel consists of either uranium oxide or a mixture of uranium and plutonium oxide. After its use in the nuclear reactor, spent nuclear fuel still contains a significant amount of uranium and plutonium, which can be recovered and reused as nuclear fuel. The actual recycling process PUREX (Plutonium Uranium Refining by Extraction) involves a liquid-liquid extraction process using TriButylPhosphate (TBP) as extracting molecule. Although this solvent has been used for decades, it presents some limitations such as its non-incinerable nature, the formation of troublesome degradation products moreover; the uranium/plutonium separation is performed by using a reducing agent. As an alternative, malonamides molecules can be used to extract uranium (VI) and plutonium (IV) from spent nuclear fuel [1]

Malonamides show to be good extractants of uranium (VI) and plutonium (IV). These molecules are only composed of C, H, O and N atoms hence they are entirely incinerable solvents, and their degradation products are less disturbing to the recycling process.[1] However, malonamides also co-extract minor actinides and Lanthanides.[2] This work aims to study the possibility of adapting malonamides family to extract selectively U (VI) and Pu (IV), without extracting minor actinides and lanthanides also develop a simple formulation that separates uranium (VI) and plutonium (IV) without modifying their oxidation state. Deep characterization using spectroscopy techniques (IR, NMR ...), SAXS, ESI-MS and ICP-MS will then performed to understand extraction and selectivity properties establish the speciation, have a description of the cation's coordination sphere and solution organization

Thus, several malonamides systems (Ligands/diluents) have been investigated on U (VI) and Th (IV). The effects of structural modifications on extraction performances and separation possibility have been evaluated. Third phase formation (splitting of the organic phase into two different phases) and aggregation influence on extraction process has conjointly been taken into account.

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**ACTINIDE MATERIALS: NUCLEAR FUELS AND
RADWASTE MATRICES**

Structural changes of Nd- and Ce-doped ammonium diuranate during the conversion to $U_{1-y}Ln_yO_{2\pm x}$

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In an advanced nuclear fuel cycle, partitioning and transmutation (P&T) is a key strategy to reduce spent nuclear fuel's radiotoxicity and heat generation. Long-lived minor actinides (MA) are partitioned from spent nuclear fuel and subsequently converted into fuel or targets materials for use in fast reactor systems, where the actinides are fissioned to short-lived radionuclides. The sol-gel route via internal gelation is a process that is currently explored for the production of such MA containing transmutation fuel, by converting an actinide-containing solution into a homogeneous precipitate with spherical geometry. Those precursors are thermally treated and can be used as particle fuel or compressed into fuel pellets. The advantages of the process are to avoid handling of fine powder and to facilitate automation for the production of nuclear fuel precursors.

Within this study, the structural changes in Nd- and Ce- doped ammonium diuranate (ADU) gels, prepared by internal gelation during the conversion to $U_{1-y}Ln_yO_{2\pm x}$ were investigated. Nd and Ce molar metal fractions up to 30 mol% were introduced, acting as surrogates for the actinides Am and Pu. Nd was used in its trivalent oxidation state, while both trivalent and tetravalent cerium were tested. The dried Ln-doped ADU gels were characterised by optical microscopy and X-ray powder diffraction (XRD). Those precursors were thermally treated in two individual steps: (1) calcination under oxidising conditions at a maximum temperature of 900 °C, followed by (2) sintering in reducing atmosphere at a maximum temperature of 1600 °C (10 h). The behaviour of the dried gels during both thermal treatment steps was studied *in-situ* by high temperature scanning electron microscopy (HT-SEM) and thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC) and evolved gas analysis mass spectrometry (EGA-MS).

The material prepared with the trivalent dopant precursors behaved significantly different during the decomposition in air compared to mixtures prepared with Ce(IV), which indicates different crystallinities and/or initial compositions. The calcined products were identified as (Ln-doped) α - U_3O_8 for dopant contents up to 10 mol%. For higher Ln contents, a more complex mixed-phase behaviour was found. The introduction of a reducing atmosphere led to a sudden mass loss. Particle shrinkage occurred significantly later, pointing out that the shrinkage observed within the sintering is controlled by a general densification of the material and insignificantly by the volume change due to the transition of the orthorhombic (Ln-doped) α - U_3O_8 phase to the cubic (Ln-doped) $UO_{2\pm x}$ phase. The sintered products were identified as single phase solid solutions according to the formula $U_{1-y}Ln_yO_{2\pm x}$ for Nd contents up to 30 mol% and Ce contents up to 20 mol%. In this contribution we will report and discuss the experimental results.

Study of melting temperatures of (U,Pu)O₂ SFRs fuels: influence of Pu and Am contents and oxygen stoichiometry

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Innovative mixed oxide (MOX) (U,Pu)O_{2±x} fuels for sodium fast neutron reactor (SFRs) systems are currently studied within the framework of the development of advanced nuclear reactors (GEN-IV). With a plutonium content ranging between 20 and 40 mol.%, the fuel will contain few mol.% of ²⁴¹Am, daughter element generated by ²⁴¹Pu decay. Furthermore, the oxygen stoichiometry (Oxygen/Metal ratio) of the SFRs fuels needs to meet precise specifications (i.e. to be between 1.95 and 1.99) to minimize cladding corrosion and avoid fuel melting. Thus, in order to foresee the fuel behaviour during irradiation, an accurate knowledge of its thermodynamic and structural properties, especially at high temperature, is mandatory. Moreover, several parameters can affect these properties such as the plutonium content, the americium content and/or the oxygen stoichiometry. The prediction of the formed phases in the fuel and their compositions under specific temperature and oxygen potential conditions is then crucial for safety perspectives. However, the determination of these data as a function of the plutonium content and the O/M ratio still represents an experimental challenge, despite its improvement over the last decades [1,2].

To this aim, the melting temperature of five various U_{1-y-z}Pu_yAm_zO_{2±x} nuclear fuels is currently measured at the JRC-Karlsruhe hot lab facility (0.005 < z < 0.03 and 0.235 < y < 0.44) by a laser heating technique [3]. The latter has proven to be suitable to investigate high temperature properties thanks to its rapidity (<1 second) and its self-crucible setup, which limit the chemical interaction between the sample and the surroundings. Thanks to the recent addition of oxygen gauges to the setup monitoring the atmosphere inside the chamber, the variation of the oxygen partial pressure will be assessed during the experiments.

The corresponding solidus/liquidus temperatures will be presented and the influence of the Pu and Am contents will be discussed. For the first time, the variation of the oxygen stoichiometry of the sample during the shots will be estimated, based on the oxygen gauges measurements. Thermodynamic calculations using the CALPHAD method will also be compared to the experimental results. With the help of other analyses performed at CEA Marcoule (XRD, Raman Spectroscopy, Electron Microscopy...), new input data for the TAF-ID, thus for the modelling of the U-Pu-Am-O system, will be selected.

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Chromium doped Uranium Nitride as an advanced technology fuel.

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Uranium nitride has been proposed as an advanced technology fuel (ATF) due to its enhanced thermal properties compared to the standard UO_2 . However, due to its low oxidation resistance, its implementation in water cooled reactors has been denied. A method to improve the corrosion resistance is by doping this ceramic material with oxide scale forming elements such as aluminium or chromium. In this work the effect of chromium on the oxidation resistance of uranium nitride was investigated. Chromium doped uranium nitride microspheres were produced by an internal gelation method followed by carbothermic reduction and nitridation.

Chromium precipitations were observed on the surface of the microspheres produced, indicating low solubility of Cr in the UN matrix. Chromium volatilization was also observed during the heating treatment, as up to 80% of Cr content was lost during this process. During the oxygen exposure experiments, the doped spheres with chromium increased the maximal reaction rate temperatures to values between 330 and 367 °C from 307 °C in the undoped microspheres.

These microspheres were also pressed and sintered into pellets using SPS to reduce the sintering time and avoid further chromium losses due to volatilization. High density pellets (>95%) were manufactured with this method. Although the heating and cooling process is extremely fast in SPS, chromium precipitations were still observed, however, in this case the chromium was observed in the pores of the pellets.

Oxidation resistance under an oxygen atmosphere was observed to improve for pellets with high density when they were doped with low amounts of chromium. The maximal reaction rate temperatures were increased from 580 °C to 665 °C when the final Cr content was below 1%.

Impact of the method of preparation and sintering conditions on the dissolution of (U,Ce)O_{2±δ}

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In the current context of nuclear fuel reprocessing and further MOX fuel fabrication, it is important to master the synthesis and sintering of (U,Pu)O_{2±δ}. As spent MOX fuel has very complex structure and microstructure and due to the strong constraints linked to the handling of plutonium, simple model oxides must be prepared to understand the behavior of MOX during reprocessing. In this frame, cerium is often used as a surrogate, based on similar size and chemical properties [1]. This work was then focused on the sintering of (U,Ce)O_{2±δ} mixed oxides, addressing more specifically the impact of various factors (chemical composition, sintering atmosphere and temperature...) on the pellets densification and microstructure.

With this aim, analysis were performed on highly homogeneous U_{1-y}Ce_yO_{2±δ} oxides (0.1 ≤ y ≤ 0.5) prepared by hydroxide precipitation [2] heated at high temperature. Powders characterization revealed the formation of single-phase solid solutions (XRD) with nano-size particles (SEM) and homogeneous cationic distribution (EDS). A dilatometric study then evidenced the very high sintering capability of the powders, with densification temperatures lowered by 100 to 200°C compared to those used for MOX fuel elaboration. Moreover, it allowed us to master the microstructure of the samples with high relative densities (typically above 95%TD) and grains sizes ranging from few hundreds of nanometers to several tens of micrometers depending on the conditions used (temperature, atmosphere). This study showed that the sintering atmosphere had a big impact on the sintering process, with higher grain size when working under Ar atmosphere compared to reducing conditions. In order to understand such behaviour, the speciation of both uranium and cerium in the materials was followed by XANES measurements. It revealed that nearly stoichiometric samples were obtained in reducing atmosphere whereas inert atmosphere led to oxidized compounds. Some sintered pellets were submitted to first dissolution tests in 2M HNO₃ at 25°C. They underlined two different behaviours as a function of the initial sintering atmosphere. With nearly stoichiometric compounds, the typical behaviour of UO₂ dissolution [3] is recovered, but with oxidized compounds, it seems to have different step during dissolution with first a fast dissolution followed by a level. Moreover, operando dissolution tests were performed to follow the evolution of solid/liquid interface. This analysis revealed preferential dissolution of grains boundaries for the samples prepared in reducing atmosphere and of particular crystal orientation [4] for those sintered in inert atmosphere.

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Molten salt irradiation and waste management

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Due to the growing concerns about the impact of climate change, there is renewed interest in nuclear energy as a reliable source of electricity with low carbon emission.[1] In this context, molten salt reactors (MSRs) have the potential to offer a safer and more efficient alternative to existing nuclear reactor designs.[2] As a result the research interest into MSR related technologies has surged in recent years. At NRG we are conducting a molten salt research program, together with international collaborators, as part of our broader R&D efforts in the field of nuclear technologies. In this program we have several research projects dedicated to different aspects of the molten salt reactor and the corresponding fuel cycle.

The SALIENT (**SALt Irradiation Experiment**) experiment series focusses mainly on the interaction between molten salt and various materials such as graphite or metallic alloys which are relevant in an MSR context. In addition, we also study the generation and distribution of fission products in the fuel salt during burn-up. The first iteration of SALIENT is dedicated to the interaction between the salt and graphite. After 2 years of irradiation, post-irradiation examination for SALIENT-01 was started in 2020 and is currently ongoing.[3] The irradiation rig for a subsequent experiment (SALIENT-03) is currently being built in which we plan to investigate the interaction of molten fuel salt with metal alloys under irradiation conditions, specifically with respect to monitoring and mitigation of corrosion processes.

In the SAGA (**SALt GAMMA irradiation**) experiment, fluoride-based fuel salt is subjected to γ -irradiation to gather data on fluorine gas production via radiolysis.

In this contribution we discuss the design of the irradiation facilities and the (preliminary) results of the above-mentioned projects as well as the progress of our ongoing efforts towards the development of a process for the conversion of spent fluoride fuel salt to a stable waste form that is suitable for nuclear waste storage.

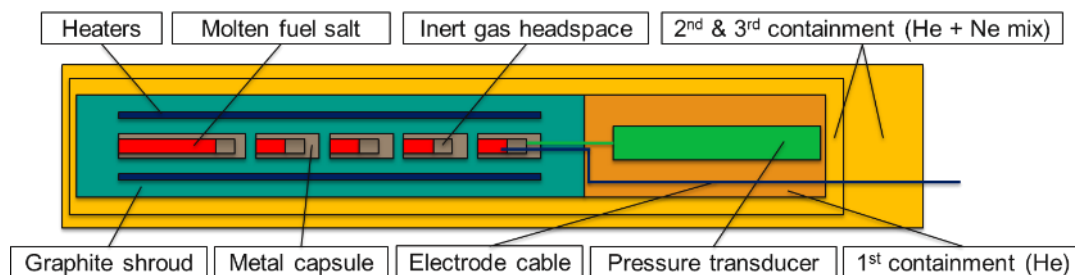


Figure 1: Schematic representation of the SALIENT-03 irradiation setup

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[2] E. Merle-Lucotte et al., *European Nuclear Conference (ENC 2007)*, **Sep 2007**, 48-53

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Sintering map approach on MOX SFR nuclear fuels with various plutonium contents

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In order to close its nuclear fuel cycle, France search new ways of plutonium reprocessing from spent nuclear fuel for the manufacture of new (U,Pu)O₂ fuels for current PWR (pressurized water reactor) or future SFR (sodium-cooled fast reactor). The present work focuses on investigating the mechanisms governing densification and microstructural evolution of the (U,Pu)O₂ fuel during sintering under a reducing controlled atmosphere (i.e. giving an oxygen-to-metal ratio between 2.00 and 1.94).

The powders investigated were prepared by freeze granulation, yielding smooth and spherical granules with great flowability and a good pelletizing behaviour. Several Pu/(U+Pu) ratios were studied in the range considered for SFR fuels, i.e. between 15 and 33 mol%. The sintering behaviour was investigated through the “sintering map” approach, by constructing the “grain size versus relative density” trajectory (example in Figure 1). High temperature dilatometer tests under a controlled oxygen potential were thus combined with microstructural characterizations (density, grain size, porosity distribution...) by optical microscopy, SEM, EPMA and XRD. Data collected were interpreted to identify the involved diffusion mechanisms controlling densification (plutonium diffusion through the grain boundaries and grain growth by the grain boundaries for the 15 mol% pellets) and to calculate activation energies (found around 525 ± 50 kJ/mol for the 15 mol% pellets) and to calculate activation energies (found around 525 ± 50 kJ/mol for the 15 mol% pellets). Diffusion coefficients were also calculated and compared to those from the literature. Predictive sintering models were finally built up to optimize the sintering cycle, i.e., to reduce of the maximum temperature and duration, while ensuring a high density (>95%).

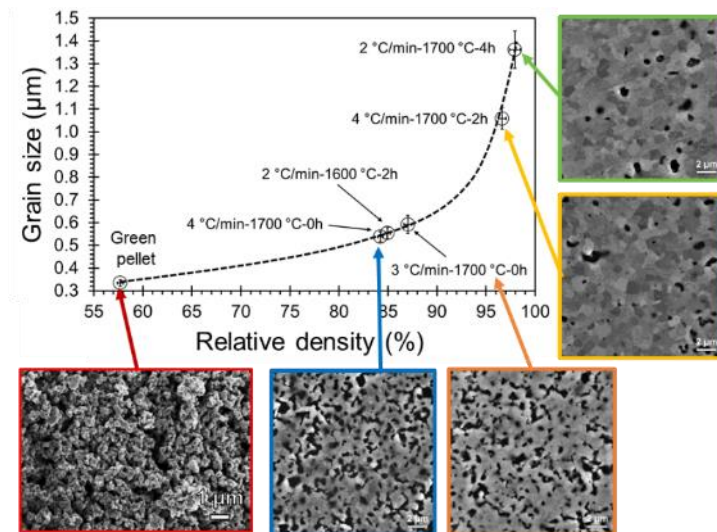


Figure 1: Sintering map of (U,Pu)O₂ with 15 mol% Pu/(U+Pu) exhibiting grain size and relative density evolutions during sintering.

**WASTE MANAGEMENT & GEOLOGICAL
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Pb₂Tc₂O_{6.86}, a Stable Valence V Technetium Oxide?

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Despite the fact that Technetium V oxides are possible there are very few reports of their existence. Most recently Lawler et.al. ¹ have reported the structure of Tc₂O₅ “tech red” and have noted that it is indeed volatile. It is apparent from this study that there is no stable form and they draw parallels with a well-studied analogue of Tc₂O₅, Re₂O₅ that disproportionates into Re(4+) and Re(7+) species. Given these parallels we investigated PbTcO₃ as reported by Muller et.al ² to be a pyrochlore in an attempt to determine if there were parallels with Pb₂Re₂O_{7-d}. The structure of lead-technetium pyrochlore has been refined in space group *Fd3m* with *a* = 10.36584(2) Å using a combination of synchrotron X-ray and neutron powder diffraction data and confirmed via Electron Diffraction. The oxide is found to be oxygen deficient with a stoichiometry of Pb₂Tc₂O_{6.86}. The displacive disorder of the Pb cations is evident from the refinements as has been observed in Bi₂Tc₂O_{7-d}. X-ray absorption measurements at the Tc K-edge demonstrate the valence of the Tc is greater than 4.0 as anticipated from the refined oxygen stoichiometry. Raman spectroscopy confirms the local coordination of the Technetium leading us to conclude that this pyrochlore is the first example of a stable valence V Technetium oxide.

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Electrospun microporous membranes loaded with cerium oxide nanoparticles for the decontamination of nuclear wastewaters

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Removal of radioactive actinides from nuclear wastewaters is a resource-intensive activity, which is routinely carried out by numerous nuclear decommissioning sites around the world. Water-suspended cerium oxide nanoparticles (CNP) recently showed a great potential in the water-phase removal of uranium via adsorption [1]. However, the successful use of CNP suspensions is hindered by their tendency to agglomerate, by complex recovery procedures and by potential loss of adsorbent material during adsorption/desorption cycles. Here, ultra-small ceria nanoparticles (CNP, < 3 nm) produced via a precipitation-hydrothermal approach [2] were incorporated into polymeric membranes made of poly(vinyl)alcohol (CNP-PVA) or cellulose acetate (CNP-CA) electrospun nanofibers (d ≈ 250 nm). The incorporation of CNP into nanofibers minimizes sorbent loss during repeated adsorption cycles (2% CNP mass loss after ten cycles). The adsorptive materials were characterised and tested in the adsorption of uranyl and europium (as non-radioactive americium homologous) ions from model water solutions. The maximum adsorption capacities, as determined by fitting with the Langmuir model, were found to be equal to about 40 mg_U/g_{CNP} and 20 mg_{Eu}/g_{CNP}, respectively. Moreover, the microporous membranes could be used as filtering unit in the continuous removal of uranyl ions from model solutions: for example, 5 mg of CNP-PVA could remove 55% of U 5 mg/L in a 30-min run at 0.2 mL/min. The membranes are currently under testing at the nuclear site of European Commission - Joint Research Centre in Ispra (Italy) for the decommissioning of real-world radioactive wastewaters.

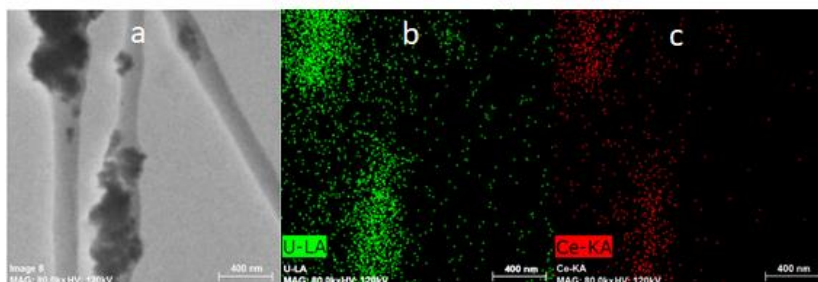


Figure 1: (a) STEM of cellulose acetate nanofibers with incorporated cerium oxide nanoparticles used to adsorb UO_2^{2+} . EDX detection (b,c) shows that U (green) is found predominantly on cerium oxide (red).

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[2] D. Prieur, W. Bonani, K. Popa, O. Walter, K. W. Kriegsman, M. H. Engelhard, X. Guo, R. Eloirdi, T. Gouder, A. Beck, T. Vitova, A.C. Scheinost, K. Kvashnina & P. Martin, *Inorganic Chemistry*, 2020, **59**, 5760-5767.

Sonochemical conversion of UO_3 into U(VI) intrinsic colloids in near-neutral conditions

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Under oxidizing conditions, the corrosion of the spent nuclear fuel may result in the leaching of water soluble uranyl(VI)-based species.[1-3] The speciation of the generated forms is complex and the potential formation of intrinsic colloids from U(VI) hydroxo complexes appears particularly poorly reported in literature. Such a phenomenon could however significantly contribute in the migration of radionuclides in the environment.[4-6] Therefore, a better knowledge in the speciation and reactivity of these species seems particularly relevant. This presentation describes the characterization of uranium(VI) intrinsic colloids obtained by sonolysis of amorphous and crystalline UO_3 in near-neutral conditions. Using carbon monoxide to inhibit the formation of hydrogen peroxide, the application of ultrasound results in the complete conversion of UO_3 powder into (meta-)schoepite precipitates and the observation of very stable uranium(VI) nanoparticles in the liquid phase. A thorough investigation of these colloids with HR-TEM, SAXS and XAS techniques confirmed the formation of quasi-spherical nanoparticles measuring ca. 3.8 ± 0.3 nm in diameter and exhibiting a schoepite-like crystalline structure (Figure 1). The possible formation of environmentally relevant U(VI) colloidal suspensions using sonochemistry appears significantly interesting for the preparation of reference systems without added ions and capping agents.

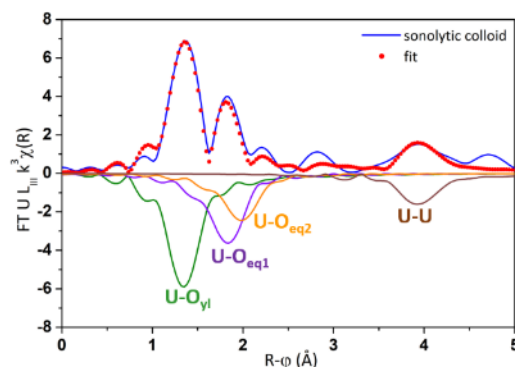


Figure 1: Fourier transforms of the k^3 -weighted range spectra of U(VI) colloids and corresponding fit. The four main wave components of the fit are plotted with negative amplitude.

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- [3] N. Priyadarshini *et al.*, *Journal of Radioanalytical and Nuclear Chemistry* **298**, 1923-1931 (2013)
- [4] P.A. Finn *et al.*, *Radiochimica Acta* **66**, 189-195 (1994).
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- [6] P. Bots *et al.*, *Langmuir* **30**, 14396-14405 (2014).

Matrices for the immobilization of waste from pyrochemical processing of spent nuclear fuel

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Nowadays countries operating nuclear power plants have an ambitious goal – closing the nuclear fuel cycle. One of the major tasks is the management of spent nuclear fuel (SNF). Processing of mixed nitride uranium-plutonium SNF suggests the use of LiCl-KCl electrolyte in the pyrochemical or combined technology. However, the industrial application of pyrochemical processing cannot be implemented until methods for the immobilization of the resulting radioactive waste (RW) are developed.

Studies with glass composite materials show that for reliable fixation of a significant amount of alkali chlorides they must be preliminary converted into the form of phosphates or oxides, i.e. conventional technological operation forms. Ceramic or glass-ceramic matrices are more reliable alternatives to vitrified matrices [1,2]. To reduce the release of radionuclides from the matrix into the biosphere, the matrix material should be as close as possible to the surrounding host rocks in its chemical and phase composition. Therefore, in this work we propose to use the bentonite clays as a possible material for matrices for a specific radioactive waste arose from pyrochemical processing of SNF. These finely dispersed materials, consisting of more than 70% of the layered mineral montmorillonite have a large specific surface, become very durable after annealing like all clays and are able to retain alkali metal ions due to their layered structure.

Specific compositions and temperature-time regimes were chosen empirically for immobilization of the spent LiCl-KCl electrolyte with addition of fission products. As a result, strong ceramic samples with an electrolyte content of up to 30 mass. % were synthesized. The addition of silicon-containing compounds to the matrix base material were investigated to increase mechanical strength characteristics and to reduce the temperature and an overall cost of the technology. The formation of new mineral phases during annealing was revealed, and the absence of the effect of radiation exposure up to 100 MGy on the resulted matrix was observed. The studied characteristics included mechanical strength, frost resistance and water resistance, phase composition, morphological structure, and hydrolytic stability [3,4]. A set of modern analytical and physicochemical methods were used to support the results: X-ray diffraction with in-situ heating in situ, ICP-AES and ICP-MS, mercury porosimetry, X-ray fluorescence analysis, etc. Thus, the fundamental possibility of using bentonite clays as a material for immobilizing the spent chloride electrolyte from pyro-processing of SNF has been demonstrated.

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Effects of complex irradiation scenarios on ISG nuclear glass structure, properties and leaching behavior

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In the context of deep geological disposal of nuclear wastes, borosilicate nuclear glasses are used to confine the radionuclides in order to control and limit their impact on the environment. The main challenge is therefore to predict their long-term behavior to ensure the safety of the disposal solution. For this, two main factors must be considered: the complex self-irradiation of the glass resulting from the radionuclides contained in the vitreous matrix and the interaction of the glass with the groundwater. This work focuses on a simplified glass (in terms of chemical composition), chosen by the international community, called ISG: International Simple Glass [1]. Pristine glass coupons are subjected to several irradiations scenarios (electrons, Au ions, electrons followed by Au ions) to simulate as accurately as possible the different sources of irradiation of a real radioactive glass. For electron irradiation, an irradiated dose of 3.25 GGy was chosen, in agreement with the dose values for which structural and properties evolutions are observed in nuclear glasses [2]. For Au ions, a nuclear dose of 40 MGy was chosen that corresponds to the value from which the structure and macroscopic properties of the glass do not evolve anymore [3]. Moreover, these dose levels also correspond to the ones expected when the glass will be in contact with water, i.e. after several hundred to thousands years of disposal.

Radiation effects on the glass structure and properties are studied by respectively Raman and NMR spectroscopies, X-ray reflectivity, density, hardness and contact angle measurements.

Pristine and irradiated glass coupons are also leached for several months in pure water, at 90 °C and at a high surface-area-to-volume ratio ($SA/V = 200 \text{ cm}^{-1}$), in order to reach quickly the residual alteration rate regime. The alteration layer is characterized by ToF-SIMS and by cryo-TEM to determine its thickness and to study its porosity.

The results showed that the electron irradiation induces very small changes of both the structure and properties of the glass, and its alteration behavior. However, the irradiation involving Au ions causes notable modifications of ISG glass structure and properties, together with an increase of the glass alteration rate. The results obtained for the sequentially (electrons followed by Au ions) irradiated glass are close to those obtained for the glass irradiated with Au ions only. It suggests that the nuclear damage induces the major modifications of the glass structure, macroscopic properties and therefore leaching behavior in the residual rate regime.

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The Fabrication and Oxidative Dissolution of Mixed Oxide Fuels under the Reducing Conditions of a Geological Disposal Facility.

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When disposing of spent nuclear fuel in a geological disposal facility, a primary pathway for radioactive release is dissolution of the fuel matrix by ground water. These ground waters contain a number of dissolved minerals, dependent on the host rock, that diminish the oxidising potential of the water and make it reducing. When alpha radiation from unirradiated or spent nuclear fuel interacts with water, radiolytic oxidants are produced. By oxidising U(IV) to U(VI) these radiolytic oxidants could increase the dissolution rate of the fuel matrix. Hydrogen peroxide is considered the dominant oxidant to simulate radiolytic effects because it is the most long lived. Hydrogen peroxide is produced close to the surface of the fuel, but it is also consumed in the dissolution of the actinide and by autocatalytic decomposition on the surface of actinide oxides to varying degrees [1,2].

Further complexity is introduced to the system by the addition of a second actinide. Mixed oxide fuels containing uranium and plutonium are used in 10 % of nuclear reactors worldwide. It was expected that mixed oxide fuels would produce more radiolytic oxidants due to an increased radioactivity and therefore have a faster dissolution rate. In actual fact, mixed uranium plutonium oxide containing up to 30 % plutonium has been observed to release uranium more slowly than unirradiated uranium oxide^[3]. This could be due to a number of factors including an increased autocatalytic decomposition effect of the mixed oxide surface or the formation of a passivating secondary phase. Studying the dissolution of a lower activity sample of mixed uranium thorium dioxide will allow the separation of competing factors and underpin the dissolution mechanisms of mixed oxides.

This poster presents preliminary results from a series of dissolution experiments with mixed uranium thorium oxide in simplified Callovo-Oxfordian ground waters under an argon atmosphere. $U_{0.75}Th_{0.25}O_2$ has been produced using an oxalic co-precipitation and a thermal decomposition. The powders were pressed into 5mm diameter pellets and sintered at 1600 degrees to 94% theoretical density with their surface areas determined by 3D SEM. The contribution of an additional actinide to the passivation of the surface is being studied by XRD, EDS and NMR by comparison with pure UO_2 and ThO_2 pellets. Hydrogen peroxide concentrations throughout the studies are monitored by indirect spectrophotometry. A peristaltic pump will be used to deliver hydrogen peroxide at equivalent rates to its production by plutonium mixed oxide fuels to create a more realistic long-term assessment of the effect of α -radiolysis than previous batch delivery methods.

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Development of iodine filters directly convertible into conditioning matrices

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The reprocessing of spent nuclear fuel generates waste of which a small part is managed as an atmospheric or marine release. As such, we find gaseous iodine 129, a long-lived intermediate-level radionuclide. Its safe management through a deep geological repository is here considered. To reach this goal, it is necessary to fix gaseous iodine on porous filters that could be directly converted into a homogenous conditioning matrix with high chemical durability under repository conditions. Within this framework, we showed the potential of a silver phosphate-based macroporous filter. This filter can be obtained by a two-step synthesis allowing in-situ functionalization by metallic silver. A high iodine capture rate of 480 mg.g^{-1} was obtained under static conditions at $110 \text{ }^\circ\text{C}$ for 16 h. After iodine capture, the filter can be transformed into an iodine-bearing phosphate glass. A heat treatment at $650 \text{ }^\circ\text{C}$ confirmed the formation of a conditioning matrix made of glass [1] and has to be optimized. A longer heat treatment at a lower temperature could reduce volatilization and improve filters transformation.

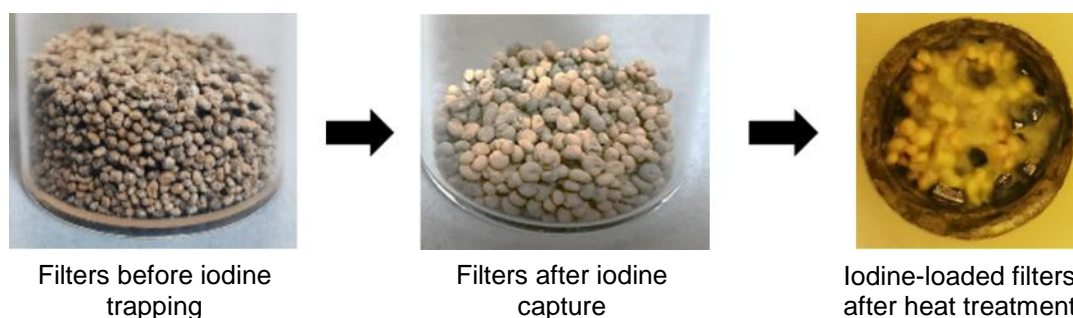


Figure 1: Photographs of the developed filters at different steps of the process

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Sorption and spatial distribution of radionuclides onto fractured rocks of the exocontact zone of the Nizhnekansky granitoid massif

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The further development of nuclear power is impossible without solving the problems associated with the accumulation of a significant amount of radioactive waste. High-level radioactive waste (HLW) containing long-lived radionuclides pose a special ecological hazard. The safest and most appropriate method for dealing with HLW is disposal of conditioned HLW in deep geological repositories.

The project on a final repository for HLW in the exocontact zone of the Nizhnekansky granitoid massif at the Eniseysky site (Krasnoyarsk region) is currently developing in Russia. To prevent radionuclides release into the environment, the concept of multi-barrier protection system was accepted, which includes both engineered and natural barriers. The last barrier preventing radionuclides release into the environment is the host rocks. Therefore, the main purpose of this work is to study the sorption and distribution of various radionuclides on natural minerals in the exocontact zone of the Nizhnekansky granitoid massif, which is characterized by a very complex heterogeneous mineral composition, the presence of various inclusions and fractured zones. Modeling of radionuclides' behavior under these conditions requires understanding that radionuclides will migrate mainly through the fractured zones.

We studied sorption of ^{137}Cs , $^{90}\text{Sr}/^{90}\text{Y}$ and ^{241}Am on scarns (high-temperature metasomatic rocks of the contact zone) from borehole R-11 from a depth of 249 m. The rock samples were represented by three polished discs, whose mineral composition and fracture distribution were characterized. According to the data obtained by scanning electron microscopy and micro-X-ray fluorescence analysis, the sample composition included various silicates (quartz, feldspars, chlorite, zeolite) as well as carbonates (calcite).

For the quantitative assessment of the sorption efficiency of individual mineral phases towards certain radionuclide, we developed a technique to determine the parameter of relative sorption efficiency (RSE), which characterizes the contribution of each mineral phase of a heterogeneous system to the overall sorbed fraction of radionuclides. The methodology for determining the RSE parameter was based on a comparative analysis of the radiogram obtained by digital autoradiography along with the SEM-image, in which the mineral phases were specified. The developed technique allowed us to estimate the contribution of mineral phases of fracture zones to retention of Cs, Sr/Y, Am. It was established that predominant mineral phase for Cs, Sr/Y retention onto the sample surface is chlorite with RSE values 2 and 1.8 respectively. In case of Am its uniform distribution onto mineral phases with close RSE values (0.97-1) was established.

The distribution coefficients of radionuclides calculated for contacting surfaces (K_a) were also obtained as a result of the study. K_a values for Cs, Sr, Am were 6.6, 0.9 and 26.1 ml/cm², respectively.

Immobilization of metal chlorides in magnesium potassium phosphate compound

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Nowadays, the Russian nuclear industry is focused on closing of the nuclear fuel cycle. As a part of the "Proryv" project, a combined pyrochemical and hydrometallurgical technology ("PH-process") was proposed for the reprocessing of mixed nitride uranium-plutonium spent nuclear fuel (MNUP SNF) of lead-cooled BREST-OD-300 reactor. Pyrochemical reprocessing of MNUP SNF involves its anodic dissolution in molten alkali metal chlorides and cathodic deposition of fissile materials using a liquid cadmium cathode. As a result, the new types of radioactive waste (RW) are generated, primarily spent electrolyte – mixture of K and Li chlorides and fission products (Cs, Sr, rare earth elements), so the conversion of RW into stable forms is required. Earlier in [1-3] promise of magnesium potassium phosphate (MPP) compound was shown to solve the tasks of problematic RW management. Therefore, the aim of our research was to approve MPP compound for solidification of spent electrolyte surrogate. The samples of MPP compound containing up to 15 wt% $\text{Li}_{0.57}\text{K}_{0.41}\text{Cs}_{0.02}\text{Cl}$ [4] and up to 12 wt% $\text{Li}_{0.40}\text{K}_{0.28}\text{La}_{0.08}\text{Cs}_{0.016}\text{Sr}_{0.016}\text{Ba}_{0.016}\text{Cl}$ [5] were synthesized. The samples of MPP compound containing about 28 wt% zeolite (Sokyrnytsya deposit, Transcarpathian region) for the Cs binding were also obtained. The phase composition, compressive strength, thermal and hydrolytic stability of MPP compound were studied.

It was found that MPP compound of the target composition $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ is the main crystalline phase of all synthesized samples, and there are also MgO and chloride phases in the compound. It was shown that increasing salt content in MPP compound leads to increasing its compressive strength and reaches 20-30 MPa, and incorporation of zeolite into the compound leads to increasing the strength to 40-60 MPa. It was shown that heat treatment of MPP compound up to 450 °C results in decreasing its compressive strength, however, the strength of heat-treated compound samples with fillers is about 10-20 MPa, which satisfies the regulatory requirements for solidified RW. It was shown that heat treatment of the obtained compound samples does not lead to a decrease in its hydrolytic stability: the leaching rate of Cs from samples at 21 days of samples contact with water is $(3-7) \cdot 10^{-4} \text{ g}/(\text{cm}^2 \cdot \text{day})$. It was shown that the quality indicators of the MPP compound meet the current requirements for solidified RW in Russia.

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