Abstract booklet 53rd Journées des Actinides

April 15th–18th, 2024

centralelille

Université de Lille

cnrs

Edited on April 20, 2024

53rd Journées des Actinides

The UCCS (Unité de Catalyse et Chimie du Solide, UMR 8181) and the PhLAM (Physique Lasers Atomes et Molécules, UMR 8523) institutes are pleased to host the 53rd Journées des Actinides international conference from April 15th to April 18th on the Lille campus.

This event series offers an informal and interdisciplinary forum for the discussion of current advances on the physical and chemical properties of lanthanide- and actinide-based molecules, compounds and alloys. The conference has a broad scope, spanning topics from fundamental to applied research:

- Inorganic and organometallic chemistry
- Strongly correlated systems, superconductivity, quantum criticality
- Materials and nanomaterials
- Theory and band structure
- Actinide production and handling
- Safety of the nuclear fuel cycle
- Nuclear safeguards and security
- Radiation protection
- Environment contamination, remediation, and decommissioning

The JDA scientific committee will offer 4 awards:

1. Life-time achievement
2. Early-career achievement
3. Best oral presentation
4. Best poster presentation

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Hello Lille

Framatome

Conference information

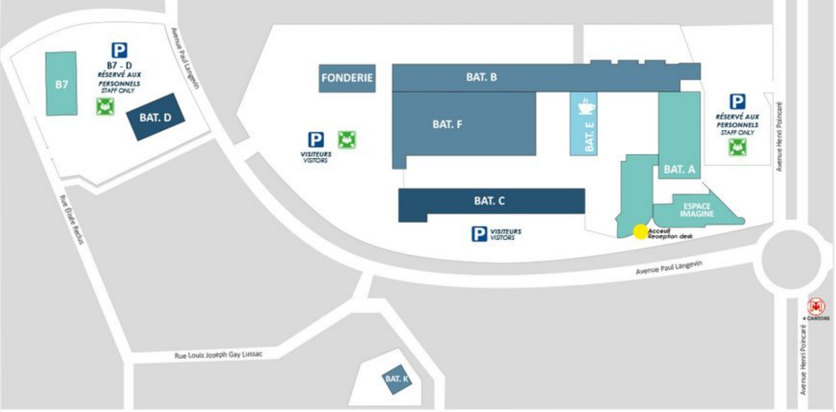
WIFI connection at Ecole Centrale Lille

- **EDUROAM** network: use your academic credentials
- **WIFI network**: password TBA

Conference location

The conference takes place at the Ecole Centrale Lille (Link to Google Maps), Amphi Cuccaroni and Espace Imagine next to the reception desk.

Map of Lille Campus



Map of Centrale Lille

Subway access

From Lille Flandres railway station

- Take subway line 1 toward “4 Cantons-Stade Pierre Mauroy”
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- Exit the subway station to the left and walk 3 minutes to the Centrale Lille main building

Getting to Lille

All travel details to access Lille city are available on the JDA 2024 website.

Conference Schedule

Start	End	MONDAY 15	TUESDAY 16	WEDNESDAY 17	THURSDAY 18
			Session 3 **Chair: V. Vallet**	**Session 7** **Chair: A. Pereira Gonçalves**	**Session 9** **Chair: F. Réal**
8:45	9:05		🟦 J. Lin	🟩 S. Harris	🟧 E. Colineau
9:05	9:25		🟩 B. Vasseur	🟧 A. Shick	🟦 R. Maurice
9:25	9:45		🟧 I. Halevy	🟦 L. Braga Ferreira dos Santos	🟩 R. Kennedy
9:45	10:05		🟦 A. Parimi	🟩 E. Clarke	🟧 W. Thomas
10:05	10:25		🟩 M. Gascoin	🟧 M. C. Notarangelo	🟦 T. Shaaban
10:25	10:55		**Coffee break**	**Coffee break**	**Coffee break**
			Session 4 **Chair: M. Virot**	**Session 8** **Chair: M. Rivenet**	**Session 10** **Chair: K. Kvashnina**
10:55	11:15		🟩 A. Pereira Gonçalves	🟦 M. Maloubier	🟧 E. Svanidze
11:15	11:35		🟧 K. Gofryk	🟧 K. Kvashnina	🟦 C. Tamain
11:35	11:55		🟦 A. van Hattem	🟦 M. Virot	🟧 E. Lawrence Bright
11:55	12:15	**Welcome Lunch**	🟩 A. Zanini	🟧 D. Legut	🟦 M. Pasturel
12:15	12:35		🟧 K. Sergii	🟦 F. Legg	🟧 C. Silva
12:35	14:00		**Lunch**	**Lunch**	**Lunch** **Meeting of scientific committee**
		Session 1 **Chair: L. Havela**	**Session 5** **Chair: I. Halevy**	**Lille guided tour**	**Sessions 11-12** **Chair: E. Colineau**
13:50	14:00	**Opening words**			
14:00	14:20	🟦 K. Lv	🟦 Q. Hervy		🟦 W. Maschio
14:20	14:40	🟧 D. Shirokiy	🟩 B. Labonne		🟩 L. Harding
14:40	15:00	🟩 H. Lu	🟧 L. Havela		🟧 M. Osipenko
15:00	15:20	🟦 N. Jordan	🟦 H. Oher		🟦 S. Bayle
15:20	15:40	🟧 A. Holdsworth	🟩 E. Dubois		🟩 R. Springell
15:40	16:10	**Coffee break**	**Coffee break**		🟦 T. Stephant
		Session 2 **Chair: E. Svanidze**	**Session 6** **Chair: M. Pasturel**		**Coffee break**
16:10	16:30	🟧 F. Bottin	🟧 J. Kolorenc		**Selection of awardee**
16:30	16:50	🟩 E. Brando	🟦 H. Cuvilliers		
16:50	17:10	🟧 E. Tereshina-Chitrova	🟩 Y. Wang		
17:10	17:30	🟦 N. Cheng	🟦 L. Huang		
17:30	19:00	**Welcome Cocktail**	**Poster Session with cocktail**		
19:30	23:00				**Conference Dinner**

🟦 **Chemistry**
🟧 **Physics**
🟩 **Materials**

Program edited on 2023/04/15

This book contains all abstracts accepted as of March 1$^{\text{st}}$, 2023. The contributions are identified by

- CT for Contributed Talk
- P for posters
- In the conference program, the **number** to the left is an hyperlink to abstract

Posters should be mounted upon arrival on Monday and will remain on display until Thursday afternoon.

CONFERENCE PROGRAM

Monday, April 15th

12:00–13:45: Welcome lunch

13:50–14:00: Opening words

14:00–15:40: Session 1
Chair: L. Havela

9 **14:00** CT-1
Kai Lv (Institute of Nuclear Physics and Chemistry, @CN)
Selective crystallization of actinide metal-organic frameworks: An evolving strategy for actinide separation

10 **14:20** CT-2
Daniil Shirokiy (Forschungszentrum Jülich (FZJ - Research Centre Juelich) @DE)
Insights into the Structural and Redox Chemistry of Cr-doped $(\mathrm{Ln,U})\mathrm{O}_2$ Materials

11 **14:40** CT-3
Haiyan Lu (Institute of Materials, China Academy of Engineering Physics @CN)
Correlated 5f electronic states in ASn_3 (A=U, Np, Pu) intermetallics

12 **15:00** CT-4
Norbert Jordan (Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology @DE)
Complexation of Cm(III) and Eu(III) with phosphates: an experimental and theoretical study

13 **15:20** CT-5
Alistair F. Holdsworth (University of Manchester @UK)
The Effects of Irradiation on the Structure and Leaching of Pure and Doped Thin-Film Ceria SIMFUEL Models

15:40 - 16:10: Coffee break

16:10–17:30: Session 2
Chair: E. Svanidze

14 **16:10** CT-6
Bottin, François (CEA @FR)
Huge anharmonic effects in delta plutonium

15 **16:30** CT-7
Edoardo Brando (CEA @FR)
Thermodynamical properties of $\mathrm{U}_3\mathrm{Si}_2$

16 **16:50** CT-8
Evgenia Tereshina-Chitrova (Institute of Physics of the Czech Academy of Sciences @CZ)
Uranium Thin Films and Multilayers: Magneto-Structural Correlations and Functionalities

17 **17:10** CT-9
Ning Chen (Soochow University @CN)
Actinide endohedral fullerenes: novel actinide bonding behaviors inside fullerene cages

17:30–19:00: Welcome cocktail

Tuesday, April 16th

08:45–10:25: Session 3
Chair: V. Vallet

18 **08:45** CT-10
Jian Lin (Xi'an Jiaotong University @CN)
Radiation Detection Based on Radiochromic and Fluorochromic Thorium-Organic Complexes

19 **09:05** CT-11
Bastien Vasseur (UCCS - Univ. Lille @FR)
Heat storage potential of the UO_3-H_2O system: study of water sorption and aging

20 **09:25** CT-12
Itzhak Halevy (Ben Gurion Uni. @IL)
Advancing Nuclear Safeguards: Automated Fission Track Analysis via Synthetic Model Generation and Image Analysis Tools

21 **09:45** CT-13
Ashutosh Parimi (University of Manitoba @CN)
Interactions Between Metals and Eudistomins of Ascidian Origin: A Computational Study

22 **10:05** CT-14
Mathieu Gascoin (CEA Cadarache @FR)
Atomistic modelling of fission products trapping and mobility properties in actinide oxides

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10:25 - 10:55: Coffee break

10:55–12:35: Session 4
Chair: M. Virot

23 **10:55** CT-15
António Pereira Gonçalves (C2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa @PT)
Laser flash melting of $(UC)_1{-}x(MC)x$ ($M = Ta, Nb, Hf$; $x = 0.05, 0.15$) solid solutions

24 **11:15** CT-16
Krzysztof Gofryk (Idaho National Laboratory @US)
Strong electronic correlations and topology in transuranic-based systems: the case of $NpTe_2$

25 **11:35** CT-17
Andries van Hattem (TU Delft @NL)
Experiments in and thermodynamic modelling of the $Bi-U-O$ system

26 **11:55** CT-18
Alice Zanini (Università degli Studi di Padova @IT)
Additive manufacturing of nanostructured uranium dicarbide/carbon nanocomposites via sol-gel technique

27 **12:15** CT-19
Sergii Khmelevskyi (Vienna Scientific Cluster Researach Center, TU Vienna @AT)
Orbital spin-singlet state in heavy fermion U-based superconductors

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12:35–14:00: Lunch break

14:00–15:40: Session 5
Chair: I. Halevy

28 **14:00** CT-20
Quentin Hervy (CEA @FR)
Plutonium speciation in presence of boric acid - A spectroscopic and electrochemical characterization

29 **14:20** CT-21
Baptiste Labonne (CEA @FR)
Atomic scale modelling results on the structural and thermal properties of stoichiometric and hypostoichiometric Am-bearing oxides

30 **14:40** CT-22
Ladislav Havela (Charles University, Faculty of Mathematics and Physics @CZ)
Tuning the band gap in f-metal Zintl phases by pressure

31 **15:00** CT-23
Hanna Oher (Univ Paris-Saclay, IJCLab/IN2P3 @FR)
Chemistry and speciation of protactinium +IV – a theoretical study

32 **15:20** CT-24
Eliott Dubois (CEA @FR)
Machine Learning Interatomic Potentials for Atomistic Simulations of Nuclear Fuel

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15:40 - 16:10: Coffee break

16:10–17:30: Session 6
Chair: M. Pasturel

33 **16:10** CT-25
Jindrich Kolorenc (Institute of Physics, Czech Academy of Sciences, Prague @CZ)
Theory of Valence-to-Core RIXS Measured at the Uranium M_5 edge: UO_2 and UF_4 Compared

34 **16:30** CT-26
Hugo Cuvilliers (UCCS – Centrale Lille @FR)
Parametric study of uranyl speciation and stability in peroxocarbonate media

35 **16:50** CT-27
Yaxing Wang (Soochow University @CN)
Ultrafiltration separation of Am(VI)-polyoxometalate from lanthanides

36 **17:10** CT-28
Li Huang (Science and Technology on Surface Physics and Chemistry Laboratory @CN)
APAWlib: New fully-relativistic projector augmented wave datasets for actinides

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17:30–19:00: Poster session & cocktail

37 P-1
Rami Babayew (NRCN @IL)
Analyzing the two-dimensional (2D) micrographs as three-dimensional (3D) representation of a Lexan fission trucks in the field of nuclear forensics

38 P-2
Luiza Braga Ferreira dos Santos (Helmholtz-Zentrum Dresden-Rossendorf @DE)
Fundamental investigations of actinide immobilization by incorporation into solid phases relevant for final disposal

39 P-3
Liwei Cheng (Soochow University @CN)
Uranium-organic hybrid materials for direct X-ray detection

40 P-4
Eric Colineau (European Commission @EU)
The Actinide User Laboratory in Karlsruhe

Wednesday, April 17th

08:45–10:25: Session 7
Chair: A. Pereira Gonçalves

55 **08:45** CT-29
Sharee Harris (Lawrence Livermore National Laboratory @US)
Hydride-Dehydride process and spheroidization: an alternative route to produce spherical metallic U-6 wt.% Nb powders

56 **09:05** CT-30
Alexander Shick (Institute of Physics, Czech Academy of Sciences @CZ)
Spin and Orbital Magnetic Moments of UTe_2 induced by the external magnetic field

57 **09:25** CT-31
Luiza Braga Ferreira dos Santos (Helmholtz-Zentrum Dresden-Rossendorf @DE)
Scaling up: syntheses and ceramic production of doped zirconia for irradiation experiments and grazing incidence analysis

58 **09:45** CT-32
Evan Clarke (Lawrence Livermore National Laboratory @US)
Two Methods for Passivating Plasma-Spheroidized Uranium Alloy Powders to Prevent Spontaneous Combustion in Air

59 **10:05** CT-33
Maria Chiara Notarangelo (CEA Cadarache @FR)
Atomic scale calculation of thermophysical properties of molten salt reactor fuel via DFT and PIM MD simulations: inclusion of Americium

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10:25 - 10:55: Coffee break

10:55–12:35: Session 8
Chair: M. Rivenet

60 **10:55** CT-34
Melody Maloubier (CNRS/IJCLab @FR)
The chemistry of protactinium solutions: the road to resilience

61 **11:15** CT-35
Kristina Kvashnina (Helmhotlz-Zentrum Dresden-Rossendorf @DE)
Electronic Structure of Actinide Oxide Nanoparticles

62 **11:35** CT-26
Matthieu Virot (CEA Marcoule ICSM @FR)
Preparation and Structural Characterization of an Original Peroxide Complex of Pu(IV)

63 **11:55** CT-37
Dominik Legut (VSB - Technical University of Ostrava @CZ)
Curie temperature in uranium hydrides

64 **12:15** CT-38
Florence Legg (University of Bristol @UK)
Investigating the oxidation of epitaxial $(UxTh_{1-x})O_2$ thin films

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12:35–14:00: Lunch break

14:00–17:00: Lille City tour

Thursday, April 18th

08:45–10:25: Session 9
Chair: F. Réal

65 **08:45** CT-39
Eric Colineau (European Commission @EU)
"Superconductivity and quantum criticality in actinide-iridium systems

66 **09:05** CT-40
Rémi Maurice (CNRS @FR)
Partial views on chemical bonding: Application to actinide molecular and solid-state systems

67 **09:25** CT-41
J Rory Kennedy (Idaho National Laboratory @US)
Nuclear Fuel and Pu Redox Studies from The Glenn T. Seaborg Institute at Idaho National Laboratory (U.S.A.)

68 **09:45** CT-42
William Thomas (University Of Bristol @UK)
Absence of induced ferromagnetism in epitaxial uranium dioxide thin films

69 **11:35** CT-43
Tamara Shaaban (PhLAM – University of Lille – CNRS @FR)
Effect of ligands on Pa^{5+} and ${PaO_3}^{+}$ relative stabilities: A computational study

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10:25–10:55: Coffee break

10:55–12:35: Session 10
Chair: K. Kvashnina

70 **10:55** CT-44
Eteri Svanidze (MPI CPfS @DE)
Searching for new arsenides

71 **11:15** CT-45
Tamain, Christelle (CEA @FR)
Coordination chemistry of Neptunium(V) and/or (VI) in organic phase in liquid-liquid extraction processes

72 **11:35** CT-46
Eleanor Lawrence Bright (The Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility, Grenoble, France, and Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden @DE)
Anisotropic Resonant Scattering at the uranium M_4 edge: Insights into U_2N_3

73 **11:55** CT-47
Mathieu Pasturel (Institut des Sciences Chimiques de Rennes @FR)
Complex magnetic behaviours in $U_6TE_4Al_{43}$ (TE = V, Nb, Ta, Cr, Mo, W) with isolated U-dumbells

74 **12:15** CT-48
Clara Silva (ESRF / HZDR) @FR, DE)
Investigation of HERFD-XANES sensitivity at the U L_3-edge to extract uranyl bond lengths

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12:35–14:00: Lunch break

14:00–15:40: Session 11
Chair: E. Colineau

Selective crystallization of actinide metal-organic frameworks: An evolving strategy for actinide separation

Kai Lv,[1] **Songzhu Qi**[2]

[1] *Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics (CAEP),*
621900 Mianyang, China e-mail: lvkai@caep.cn

[2] *National Synchrotron Radiation Laboratory, University of Science and Technology of China,*
230026 Hefei, China

The selective crystallizations of a variety of compounds covering metal borate,[1] metal complexes,[2] supramolecular assembly,[3] metal-organic frameworks[4] have recently been exploited for the challenging intragroup and congener metal separation. Our group proposed selective crystallization of actinide metal-organic frameworks (An-MOFs) for the separation of macro-amount actinides in the presence of representative ions for products in spent nuclear fuels. The resulting An-MOFs can be directly used as primary actinide waste form,[5] versatile adsorbents for radioactive species and toxic gases due to their structural integrity and reactivity.

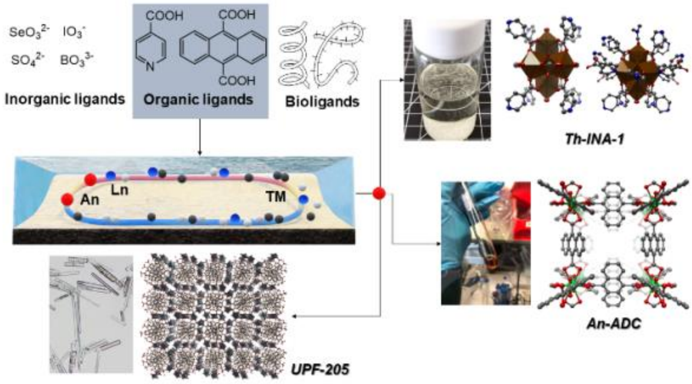

Fig.1. Selective crystallization of three types of An-MOFs for actinide separation

References

[1]Xuemiao Yin et al., Nature Communication, **14438**, 8 (2017).

[2] Alexander B. Weberg et al., Chemical Science, **6796-6805**, 13 (2022).

[3] Joseph G.O'Connell-Danes et al., Nature Communication, **4497**, 13 (2022).

[4] Huajun Yang et al., Angew Chem Int Ed, **11148-11152**, 60 (2021).

[5] Kai Lv et al., ACS Materials Lett, **536-542**, 5 (2023).

Insights into the Structural and Redox Chemistry of *Cr-doped* (Ln,U)O₂ Materials

Daniil Shirokiy,[1*] Maximilian Henkes,[1] Andrey Bukaemskiy,[1] Kristina O. Kvashnina,[2] Martina Klinkenberg,[1] Philip Kegler,[1] Dirk Bosbach,[1] and Gabriel L. Murphy[1]

[1] Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany, e-mail: d.sirochii@fz-juelich.de
[2] The Rossendorf Beamline at ESRF, The European Synchrotron, CS40220, 38043, Grenoble, Cedex 9, France

Cr-doped UO_2 nuclear fuels have endured sustained interest from industry and researchers due to the superior in-reactor performance they possess over traditional non-doped variants (UO_2). The ubiquitous generation of spent nuclear fuel (SNF) is a challenge that impacts many nations, regardless of fuel type. Direct disposal of SNF into deep geological repositories is the preferred method for nations including German and Finland among many others but requires long-term understanding of the SNF stability that is often ensured for 1 000 000 years according to StandAG §1. Consequently, researching the structural and chemical stability of SNF is crucial aspect of nuclear waste management. Despite high, increased in-reactor performance and reduced in bulk waste generation of Cr-doped UO_2 fuels, their chemistry and structural properties within SNF are still poorly studied. Specifically potential interaction of Cr with trivalent cations of lanthanides (Ln) and minor actinides (MA) (e.g., Nd^{3+}, Gd^{3+}, Am^{3+}, Cm^{3+}) and Pu^{+3} may lead to the formation of alteration phases such as perovskite (($Ln^{3+}/MA^{3+})Cr^{3+}O_3$) which may impact stability both in-reactor and as SNF. Accordingly, we have been exploring the formation of such phases via the preparation of model system materials, under conditions that are relevant to Cr-doped UO_2. This involves the systematic synthesis of Cr-doped (($U_{1-x}Ln_x)O_2$) for Ln = La, Ce, Pr, Gd, Ho, Lu. These materials have been subject to high resolution structural and redox analysis using synchrotron X-ray powder diffraction (S-PXRD) and high-energy resolution fluorescence diffraction-X-ray absorption near-edge structure spectroscopy measurements (HERFD-XANES) performed at BM20 beamline of the European Synchrotron Radiation Facility (ESRF). These measurements, supported by Raman spectroscopy mapping and scanning electron microscopy, allow the occurrence of specific alteration phases to be observed in Cr-doped UO_2 when encountering lanthanides. These results will be discussed in detail with respect to the current knowledge of Cr-doped UO_2 and classical UO_2 chemistry in the context of nuclear waste management. In summary the findings might potentially have important implications for the long-term performance of nuclear waste repositories and the design of new materials for nuclear applications.

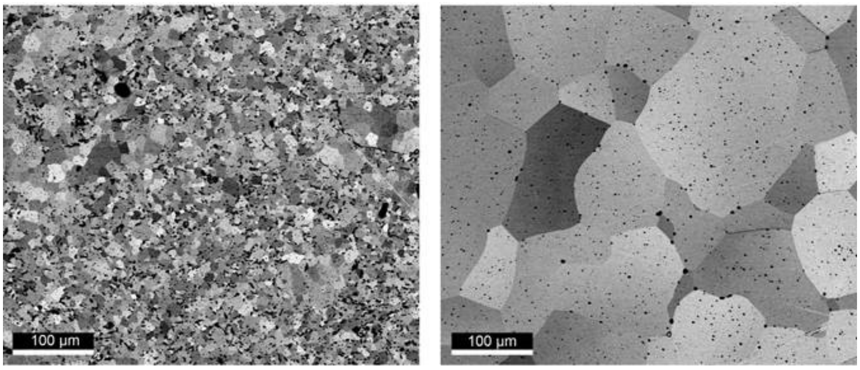

Fig. 1. SEM showing grain size difference of pure UO_2 (left) and Cr-doped UO_2 (right)

Correlated 5*f* electronic states in *A*Sn_3 (*A*=U, Np, Pu) intermetallics

Haiyan Lu,[1] Li Huang[1]

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The 5*f* series dependence of itinerant-localized 5*f* states and strongly correlated electronic states has been systematically investigated in archetypical cubic compounds *A*Sn_3 (*A*=U, Np, Pu) by using a combination of the density functional theory and the embedded dynamical mean-field approach[1-4]. The reproducibility of theoretical band structure and x-ray photoemission spectrum for USn_3 not only guarantees the reliability of calculation, but also supports the hypothesis of enhanced localization of 5*f* states with increasing atomic series from uranium to plutonium. The suppression of valence state fluctuations, which is characterized by the strength of valence state fluctuations $V(USn_3) > V(NpSn_3) > V(PuSn_3)$, is quantitatively described. The study reveals that these fluctuations are closely related to the itinerant nature of 5*f* states, as evidenced by significant hybridization between 5*f* states and conduction bands, as well as pronounced spectral weight around the Fermi level. Particularly, the emergence of prominent quasiparticle multiplets in $PuSn_3$, distinct from USn_3 and $NpSn_3$, is attributed to the interplay between competing atomic eigenstates of 5*f* electrons and 5*f* valence state fluctuations. It is proposed that a detailed understanding of the electronic structure dependence on the actinide series in *A*Sn_3 (*A*=U, Np, Pu) intermetallics compounds can provide valuable insights and promote further experimental research in this field.

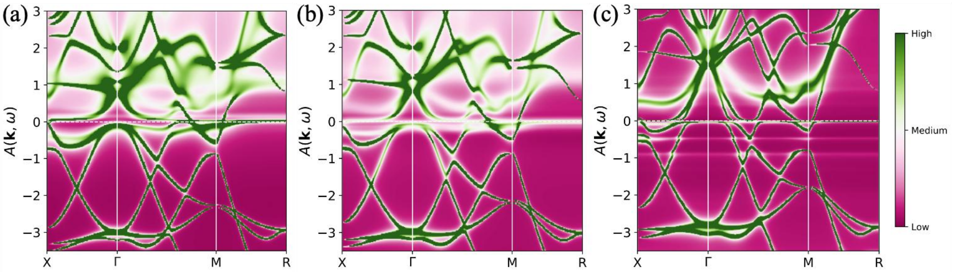

Fig. 1. Momentum-resolved spectral functions of USn_3 (a), $NpSn_3$ (b) and $PuSn_3$ (c) at 116 K calculated by the DFT+DMFT method. The horizontal lines denote the Fermi level

References

[1] Haiyan Lu* and Li Huang, *Phys. Rev. B* **108**, 165109 (2023).
[2] Haiyan Lu* and Li Huang, *Phys. Rev. B* **103**, 205134 (2021).
[3] Haiyan Lu* and Li Huang, *J. Phys.: Condens. Matter* **34**, 215601 (2022).
[4] Haiyan Lu* and Li Huang, *J. Phys.: Condens. Matter* **33**, 435603 (2021).

Complexation of Cm(III) and Eu(III) with phosphates: an experimental and theoretical study

<u>Norbert Jordan,</u>[1] Isabelle Jessat[1], Nina Huittinen[1], Florent Réal[2], Valérie Vallet[2]

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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, 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 $NaClO_4$ as a background electrolyte. These studies have been conducted in the acidic pH-range to avoid precipitation of solid Cm and Eu rhabdophane. In addition to the presence of the $CmH_2PO_4^{2+}$/$EuH_2PO_4^{2+}$ species [1-3], the formation of $Cm(H_2PO_4)_2^+$ [2] and $Eu(H_2PO_4)_2^+$ [3] was unambiguously established from the collected luminescence spectroscopic data. The conditional complexation constants of all aqueous complexes were extrapolated to infinite dilution by applying the Specific ion Interaction Theory. Using the integrated van´t Hoff equation, both the molar enthalpy of reaction $\Delta_rH_m°$ and entropy of reaction $\Delta_rS_m°$ values were derived.

Depending on the concentration of phosphate, monodentate or bidentate Cm(III)/Eu(III)-phosphate complexes form with different overall coordination numbers (8,9), but obtaining such information from spectroscopic data only is often challenging. Thus, 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 relativistic quantum chemical (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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The Effects of Irradiation on the Structure and Leaching of Pure and Doped Thin-Film Ceria SIMFUEL Models

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When studying hazardous materials such as highly radioactive spent nuclear fuel (SNF), the minimisation of sample volumes is essential [1], for example, the bulk behaviour of urania (UO_2) can be mimicked by appropriately-engineered thin films of sufficient thickness [2]. Alternatively, chemically-similar but inactive surrogates [1], such as ceria (CeO_2) can be used [3] to study effects within the normally radioactive systems used to fuel nuclear fission in most commercial power reactors. However, thin film properties are sensitive to the preparative method, many of which require costly and highly toxic precursors and specialised apparatus e.g. chemical or physical vapour deposition [4]. To address this, we present the development of a flexible, tunable, scalable method for the preparation of thin-film CeO_2 SIMFUEL models with a thickness of ≈ 5 μm [5]. These films were prepared on silica substrates using a polymer-templated deposition drop-casting approach with low-toxicity aqueous precursors and low-temperature (≤ 200 ºC) calcination [5,6], representing a new preparative route to materials. The effects of γ irradiation (up to 100 kGy) and dopants including trivalent lanthanides (Ln^{3+}, Ln = Nd, Eu, as surrogates for fission products and/or the trivalent minor actinides Am and Cm) and simulant ε-particles (Pd nanoparticles) on the structure (as determined by XRD, SEM, and solid-state Eu fluorimetry) and long-term leaching of these systems under SNF storage conditions [5,7] are explored. It was found that the sensitivity of CeO_2 films to reduction upon irradiation, particularly in the presence of simulant ε-particles results in increased leaching of Ce (as Ce^{III}, formed via reduction from Ce^{IV}) [8], while trivalent lanthanides (Nd^{3+} and Eu^{3+}) had minimal effect on Ce leaching and may even stabilise the structure of the material [9]. The relatively low crystallinity of the samples studied here means that this approach may be useful in modeling higher levels of damage at lower dose rates than is observed with more crystalline bulk ceramics. The context of these results within further work is also discussed.

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Huge anharmonic effects in delta plutonium

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Several long-debated dynamical and elastic unusual properties of δ-Pu [1,2] are captured within an unprecedented unified theoretical framework. This outcome is achieved thanks to machine learning accelerated *ab initio* simulations [3,4] enabling a fine description of strong electronic correlations [5] and explicit temperature effects [6,7,8]. First, the experimental negative thermal expansion and equilibrium volume of pure δ-Pu are correctly depicted. Secondly, the extreme softening of the phonon spectrum, related to huge anharmonic effects, is demonstrated to be responsible for the anomalous decrease of the bulk modulus with temperature, as measured experimentally (see Fig. 1). Lastly, our model successfully reproduces experimental elastic properties of alloyed δ-Pu between T = 100 K and 800 K.

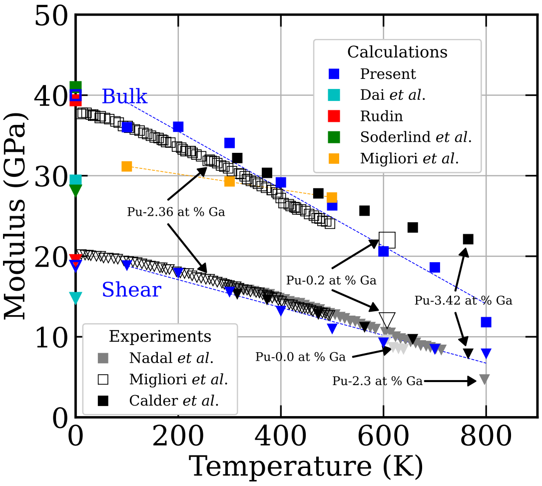

Fig. 1. Bulk and shear modulus of δ-Pu between T = 100 K and 800 K.

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Thermodynamical properties of U_3Si_2

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Exploration of uranium silicide compounds, particularly U_3Si_2, has been undertaken as a viable alternative to uranium dioxide fuel, in particular concerning material testing reactors. These compounds exhibit advantageous characteristics such as increased thermal conductivity and higher uranium density. Thermodynamic parameters, including specific heat, thermal expansion, and conductivity, play a pivotal role in fuel design. These quantities are directly connected to atomic vibrations, and their extraction involves analyzing phonon spectra and crystal structure.

In this study, we present our efforts in optimizing the calculation setup within ABINIT to obtain ab initio results closely mirroring experimental outcomes for both volume and crystal structure. Through this refined setup, we conducted phonon spectra calculations using MLACS, comparing our findings with prior computations. Employing the obtained phonon spectra, we proceeded to compute thermodynamic properties and compared them with earlier results. Our analysis highlights the distinctive characteristics of the crystallographic structure of this compound, emphasizing its pronounced impact on temperature-dependent behavior. Notably, even slight variations in volume exert a considerable influence on the phonon spectra, thereby affecting thermodynamic properties.

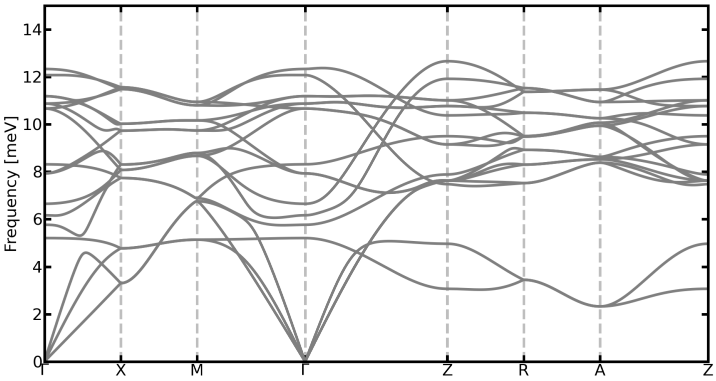

Fig. 1. Phonon spectra of U_3Si_2. The lines represent the ABINIT calculation, whilst the dots are experimental results.

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Uranium Thin Films and Multilayers: Magneto-Structural Correlations and Functionalities

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Uranium plays a crucial role as the fundamental component in the majority of nuclear fuels. Its compounds exhibit a diverse range of unique physical, chemical, and magnetic properties due to the intricate nature of its 5f electrons. Despite the systematic study of bulk properties of actinide metals, alloys, and compounds since the Manhattan Project, the exploration of thin film actinides remains relatively limited. The slow progress in this domain can be attributed to the limited availability of dedicated facilities permitted to handle radiotoxic materials.

Thin films offer additional degrees of freedom, enabling the utilization of reduced dimensionality and structure modifications that surpass the limits imposed by thermodynamics in bulk systems [1-3]. Furthermore, the ability to combine films of various materials on the nanoscale can give rise to new functionalities, such as the exchange bias effect [4,5] and giant magnetoresistance. The unique ingredient of uranium-based materials—the strong spin-orbit interaction, resulting in a very strong magnetic anisotropy, represents an essential parameter in spin-valve systems. In this talk, we will delve into the achievements in the field of sputter-deposited uranium-based thin films focusing on the magneto-structural correlations and resulting functional properties in bilayers combining selected uranium-based antiferromagnets such as UO_2 and UN with various 3d metals. Specific emphasis will be placed on designing magnetic anisotropy in the layers. The resulting interplay of interactions within and between individual materials (via the proximity effect), emerging at small length scales, renders the phase diagram of uranium-based bilayers and their response to external stimuli very rich.

The research is funded by the Czech Science Foundation (GA ČR) under grant number 22-19416S. The experimental data utilized in this study were generated through access to the Actuslab-PAMEC under the Framework for Access to the Joint Research Centre Physical Research Infrastructures of the European Commission. E.A. Ch.-T. is a recipient of the L'Oréal-UNESCO For Women in Science fellowship.

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Actinide endohedral fullerenes: novel actinide bonding behaviors inside fullerene cages

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Understanding of chemical behavior of actinide elements is essential for the effective management and use of actinide materials. The hollow internal cavity of fullerene buckyballs has been known to be able to encapsulate novel metallic units, especially those otherwise very reactive or virtually impossible to prepare clusters. In this talk, we will present our recent studies of novel actinide endohedral fullerenes, focusing on their unique bonding behaviors. We report the successful synthesis and characterization of $Th_2@C_{80}$.[1] An unprecedented strong covalent Th-Th bond formed between two rarely accessible Th^{3+} ions, stabilized inside a fullerene cage. In addition, Th and Y or Dy were found to form single electron metal-metal bond inside variable fullerene cages.[2] We also report the successful synthesis of uranium-carbon triple bonds in carbide-bridged bimetallic [U≡C−Ce] units encapsulated inside fullerene cages of C_{72} and C_{78}.[3] The molecular structures of $UCCe@C_{2n}$ and the nature of the unprecedented U≡C triple bond were characterized through X-ray crystallography and various spectroscopic analyses, revealing very short uranium-carbon bonds of 1.921(6) and 1.930(6) Å, with the metals existing in their highest oxidation states of +6 and +4 for uranium and cerium, respectively. This work demonstrates exceptional ability of fullerene cages for stabilizing the rare actinide bonding motifs and deepens our fundamental understanding of bonding behavior of the f elements.

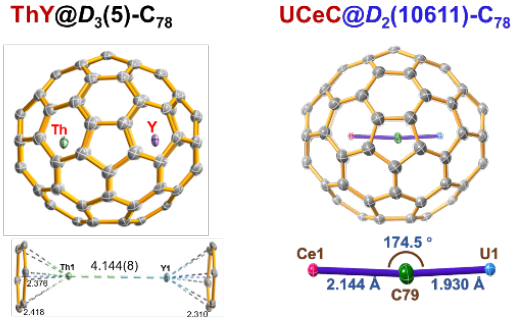

Fig. 1. Molecular structures of $ThY@C_{78}$(left) and $UCeC@C_{78}$(right)

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Radiation Detection Based on Radiochromic and Fluorochromic Thorium-Organic Complexes

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Developing materials that possess colorimetric responses to external stimuli is a promising strategy for addressing the current challenges in radiation dosimetry. However, there's been limited exploration of materials that exhibit color changes specifically in response to ionizing radiation. Herein, the integration of thorium cations and photo-responsive pyridine carboxylate ligands gives rise to a series of thorium clusters or coordination polymers, which display the rather unique radiochromic response and unprecedented fluorochromic behavior in response to ionizing radiation. The intrinsic color or emission color of these materials exhibits gradual transition upon irradiation with accumulated dose, enabling colorimetric dosimetry of ionizing radiation based on a red-green-blue (RGB) concept. Further fabricating these materials into a custom-built optoelectronic device allows for on-site quantification of radiation dose with merits of ease of operation, rapid readout, and cost-effectiveness.

Fig. 1. A new concept of radiation detection based of fluorochromic thorium materials.

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Heat storage potential of the UO_3-H_2O system: study of water sorption and aging

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The world's stock of depleted uranium, mainly made up of U_3O_8 or UF_6, comes from the enrichment stages of natural uranium. One of the nuclear industry's challenges is to recover this by-product material in applications that enable its use on a large scale while avoiding dissemination. At the same time, according to European Commission data, almost 38% of European energy production (from fossil fuels) is used for heating and cooling buildings, while wasted industrial heat could cover 100% of residential and tertiary heating needs. Consequently, as part of the energy transition and with the aim of reducing GHG emissions, one promising solution is to link industry to district heating systems through networks and heat storage systems. The aim of this work is both to recover depleted uranium and to improve the energy efficiency of heating networks through the development of thermal storage systems. An effort to identify uranium-based materials that could be used for heat storage by chemical reaction identified the uranyl oxyhydroxide $[(UO_2)_4O(OH)_6].5H_2O$, often simplified to $UO_3.2H_2O$, as a potential candidate [1]. In the present study, $[(UO_2)_4O(OH)_6].5H_2O$ was synthesized by hydration of amorphous UO_3. The optimum conditions for hydration and dehydration were established for the first time by DVS and subsequently used to investigate the cyclability of the reaction: amorphous-UO_3 ↔ $UO_3.xH_2O$. Thanks to the setting and the use of an automated set-up combined with the study of solids with by means of XRD, TGA, IR, Raman and electron microscopy, the influence of the environment (temperature, hygrometry, hydration time and mode) on the physico-chemical properties of the hydration products (composition, structure, morphology, thermal properties) was evaluated over 10 cycles (Fig. 1). The results show that a succession of water sorption/desorption steps induces particle aggregation and leads to a loss of material performance through reduced hydration kinetics. The end of the study revealed the presence of a new phase in the UO_3-H_2O system. Obtained by long-term hydration of $UO_3.xH_2O$, it is similar to paraschoepite. The rediscovery of this phase raises new questions about phase relationships in the UO_3-H_2O system.

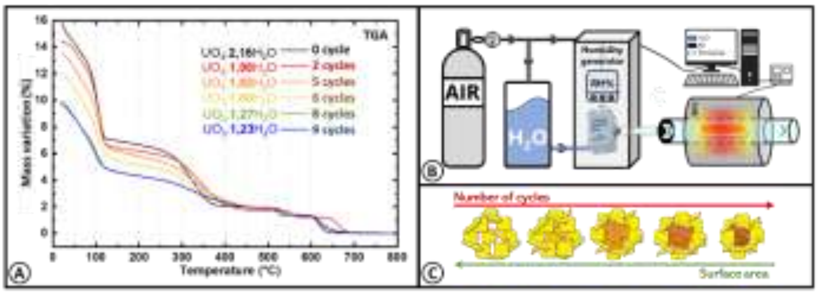

Fig.1. (a) TGA curves with water content through cycles, (b) Dedicated automated set-up, (c) Schematic model of $UO_3.xH_2O$ particle behavior among cycling

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Advancing Nuclear Safeguards: Automated Fission Track Analysis via Synthetic Model Generation and Image Analysis Tools

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The Fission Track Analysis (FTA) method is a cornerstone in nuclear and safeguard investigations. This presentation unveils a pioneering approach that focuses on the automation of FTA through advanced image processing algorithms applied to microscope images. As a critical prelude to our research and development endeavors, our research group has successfully developed an application capable of generating synthetic models of fission tracks. Leveraging trajectory data from the fission products trajectory database, created through GEANT4 simulations, we generate synthetic models of fission tracks. This synthetic bank of images closely resembles light microscope images, providing a controlled and versatile dataset for R&D processes for developing robust image analysis tools. These tools aim to automate the identification of fission track clusters without human intervention, representing a significant leap toward the elimination of manual methods. The preliminary software for image processing demonstrates its efficacy in detecting fission track clusters. Notably, the software logs all fission sites by X-Y coordinates, providing a comprehensive record for analysis. Furthermore, the software calculates the number of tracks, enhancing the efficiency of data interpretation. The automation of Fission Track Analysis not only streamlines the identification process but also serves as a proactive measure to reduce the likelihood of human errors inherent in manual procedures. This is paramount for enhancing the accuracy and reliability of nuclear investigations. We emphasize the seamless integration of GEANT4 simulations into our methodology, ensuring a foundation rooted in accurate trajectory data. This integration bolsters the authenticity and applicability of our synthetic models.

This presentation underscores the pivotal role of synthetic model generation and image analysis tools in automating Fission Track Analysis for nuclear safeguards. Our research strides towards a future where human intervention is minimized, thereby fortifying the precision and efficiency of nuclear investigations. See preliminary results in Fig 1.

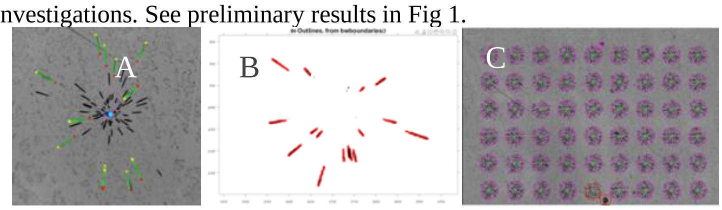

Fig. 1. (A) Synthetic FT Cluster Image Processing For detecting fission sites. (B) Synthetic FT Cluster Image Processing For counting number of tracks and (C) Automatic Recognition of Synthetic FT Batch of Clusters and elimination of artifacts.

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Interactions Between Metals and Eudistomins of Ascidian Origin: A Computational Study

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Ascidians are marine animals which adopt unusual techniques to deter predation. The three main methods are sequestration of unusual metals, high concentrations of sulphuric acid/sulphate ions in tunicate-cells, and the presence of eudistomins. In this study [1], we hypothesize that ascidians sequester metals in their sulphate form, and the complexation of eudistomins with the metals could liberate the sulphate ion. Three representative metal aqua ions were chosen, viz., VO^{2+}, UO_2^{2+}, and Th^{4+} ions; and four simple eudistomins which act as bidentate ligands, viz., Eudistomin-W, Debromoeudistomin-K, Eudistomidin-C, and Eudistomidin-B. By designing 7 model reactions, we tested our hypothesis using Density Functional Theory (DFT) methods PBE-D3, BLYP, and B3LYP. The ΔG values of the model reactions provide strong support for our hypothesis. To verify the hypothesis further, we have calculated the metal-eudistomin interactions with Be, Zn, and Pb. Based on our results we suggest that ascidians may not prefer any particular metal. As these compounds show that they can bind with actinides, it could help in actinide-scavenging from sea/ocean waters. In addition, despite using different DFT functionals we have observed similar ΔG values for each case. With our work, we have successfully used computational tools in our attempt to understand the unique behaviour of ascidians.

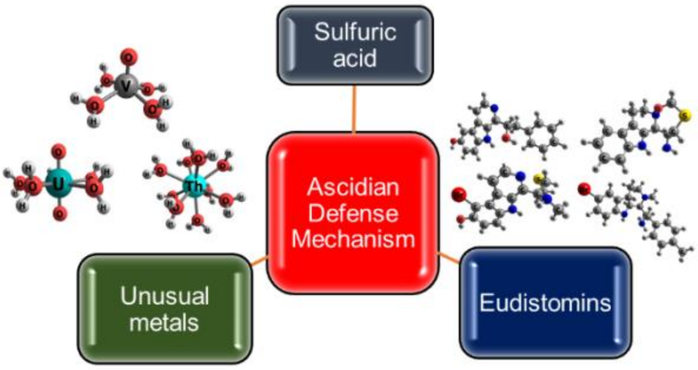

Fig. 1. Possible ascidian defense mechanism

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Atomistic modelling of fission products trapping and mobility properties in actinide oxides

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UO_2 and $(U,Pu)O_2$ actinide oxides are the main current nuclear fuels in Light Water Reactors (LWR). Under irradiation, the fission of uranium and plutonium nuclei produces new elements in these materials. Some of these fission products, especially iodine, caesium and tellurium, may chemically react with one another to form corrosive compounds for the fuel pellets cladding.

To understand and mitigate cladding corrosion, a multiscale simulation approach, which precisely takes into account the speciation and diffusion of volatile fission products, can be implemented. However, critical data are lacking on the behaviour of I, Cs and Te in oxide fuels UO_2, $(U,Pu)O_2$ and Cr-doped UO_2.

We performed electronic structure calculations, using the Hubbard-corrected density functional theory (GGA+U), to determine and compare trapping and migration properties of I, Cs and Te in UO_2 and $(U,Pu)O_2$ crystals. We additionally investigated the preferred oxidation state and location of Cr in UO_2, which is a much debated subject in the literature. As illustrated in Fig. 1, we used the DFT+U relaxed atomic configurations as inputs for the FDMNES code [1], to calculate the XANES spectra of I, Cs, Te and Cr for various trapping sites in UO_2. The comparison of the computed spectra with the experimental ones contributes to the identification of the chemical forms and trapping sites of the various studied species in uranium dioxide.

The use of a Hubbard term (GGA+U) allows us to take into account the strong correlations of actinide 5f electrons. To avoid the metastable states inherent to this method, we use the occupation matrix control (OMC) scheme [2], which also allows us to monitor the valences of each species in the simulation. This particular point makes our approach reliable with respect to the determination of fission products incorporation energies in the various studied defects.

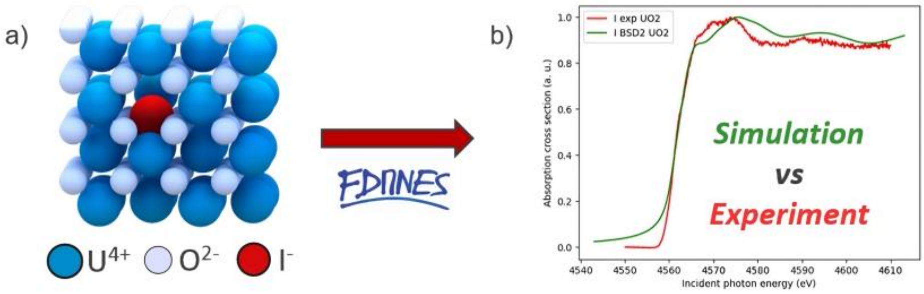

Fig. 1. a) DFT+U calculated atomic structure of an iodine atom in a defect of UO_2.
b) Comparison of the corresponding computed XANES spectrum of iodine L_3 edge with the experiment, measured on an iodine-implanted virgin UO_2 sample [3].

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Laser flash melting of $(UC)_{1-x}(MC)_x$ (M = Ta, Nb, Hf; x = 0.05, 0.15) solid solutions

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Uranium carbide-based materials have recently acquired a renewed interest due to their use as advanced spallation targets to produce medical radioisotopes by the isotope separation on-line (ISOL) method. In ISOL, a beam of high power/high intensity particles, usually protons, hits a spallation target producing radioisotopes by spallation, fission, or fragmentation nuclear reactions. These radioisotopes, which are formed inside the material, are then extracted from the target at high temperature by diffusion, effusion and sublimation/evaporation, being separated on-line by ionization and removed as radioactive ion beams. As a consequence, since a higher temperature during the irradiation process enhances the release kinetics, ISOL target materials should feature a melting point temperature in excess of 2000 °C.

$(UC)_{1-x}(MC)_x$ solid solutions, where M represents a refractory d-metal, are expected to have melting temperatures higher than uranium carbide-based materials due to the very high melting temperatures of the refractory d-metal carbides. However, the data that is available on such alloys is scarce or very old. In this work we present the thermophysical investigation of $(UC)_{1-x}(MC)_x$ solid solutions with M = Ta, Nb, Zr, Hf and $0.05 \leq x \leq 0.2$.

$(UC)_{1-x}(MC)_x$ solid solutions were produced by arc melting the elements under high purity argon atmosphere. The samples were further thermally treated at high temperatures (1800 ºC-2100 ºC) using an electromagnetic induction furnace, and their structure, purity and microstructure were evaluated by X-ray diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS). After confirming the formation of the solid solutions and their homogeneity, the thermophysical properties of the samples, particularly the solidus temperatures, were characterized by laser flash melting. The addition of the refractory metal carbides promoted an increase on the melting temperature of all tested compositions, with a minimum raise of 8 % with 0.05 doping being observed. HfC exhibited the highest melting temperature, exceeding 3100 ºC according to preliminary analysis. These results add pivotal information to the outdated data available for uranium carbide-based materials and highlight the remarkable potential of $(UC)_{1-x}(MC)_x$ solid solutions as spallation targets.

Strong electronic correlations and topology in transuranic-based systems: the case of $NpTe_2$

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Binary chalcogenides are prevalent in nature, boasting diverse applications and showcasing a range of novel behaviors. Take, for instance, UO_2, which not only functions as a nuclear fuel but also exhibits intricate thermal transport, piezomagnetism, and magnetoelastic memory under high magnetic fields. Other $LnCh_2$ compounds (where *Ln* denotes lanthanide and *Ch* represents chalcogenide) display local moment magnetism, charge density wave order, and square net crystalline lattices fostering topological electronic states. Notably, UTe_2 presents an unprecedented electronic phase diagram featuring unconventional superconductivity, immense upper critical fields, potential spin triplet pairing, and a unique field-induced superconducting state. The intriguing array of behaviors prompts further exploration of materials combining 5*f*-elements with chalcogen atoms, an area where knowledge about transuranic actinide variants is limited.

Our motivation led us to investigate the compound NpT_{2-x}. Earlier studies indicated that polycrystalline specimens crystallize in the tetragonal UAs_2-type structure, displaying semimetallic behavior with Curie-Weiss paramagnetism (C-W). Here we report on the single crystal synthesis, magnetic, electrical transport, and thermodynamic properties of the actinide analogue $NpTe_{2-x}$. Single crystal x-ray diffraction and energy dispersive spectroscopy measurements reveal its formation in the layered tetragonal UAs_2-type structure, akin to its lanthanide analogues, complete with similar Te-site vacancies. Magnetic susceptibility measurements unveil anisotropic paramagnetism, with an effective magnetic moment consistent with expectations for tetravalent neptunium. A gradual deviation from C-W behavior at low temperatures may stem from hybridization between the 5*f*- and conduction electron states or crystal electric field splitting of the Hund's rule multiplet ($^4I_{9/2}$). Semimetallic behavior emerges in electrical resistivity measurements, reminiscent of other $Ln\mathrm{Te}_{2-x}$ compounds and 5*f*-electron hybridization gap semiconductors. Finally, heat capacity measurements reveal enhanced mass Fermi liquid behavior at low temperatures, as well as evidence for a possible phase transition. Low temperature transport together with preliminary DFT calculations might suggests the presence of a non-trivial structure in $NpTe_{1.75}$, characteristic of topological systems. During the presentation, we will also discuss recent advancements in micromachining-based experimental approaches for transuranic systems using focused Ion Beam Microscopy.

Experiments in and thermodynamic modelling of the Bi-U-O system

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A thorough understanding of possible chemical and physical interactions in Lead-Cooled Fast Reactor is necessary for the safety assessment of proposed new reactors. Within that framework, the Horizon Europe PASCAL project aims to understand the chemistry that can happen in case of cladding breach. In such a case, the nuclear fuel (UO_2 or $(U,Pu)O_2$) can come into contact with the coolant, which is either liquid lead (Pb) or a eutectic mixture of lead and bismuth (Bi). This gives rise to various chemical systems, including the Bi-U-O system, which has to be understood in a large window of composition and temperature. Several investigations into the Bi-U-O system have already been published [1,2].

Here, we report a preliminary thermodynamic model of the Bi-U-O system and the underlying Bi-O, U-O and Bi-U systems will be discussed. For the model, we make use of a formalism compatible with the TAF-ID international database [3]. The model is built upon existing literature data [1,2] and new experiments aimed to complete some gaps in the understanding of the thermodynamic properties of the compounds and the ternary phase diagram. The standard entropy of $BiUO_4$ at 298.15 K has been obtained low temperature heat capacity measurements using a relaxation technique in a Quantum Design PPMS device. Moreover, differential scanning calorimetry (DSC) measurements are performed in the ternary phase field Bi-U-O.

Acknowledgements:
The experimental data used in this research were generated through access to the ActUsLab-PAMEC under the Framework for access to the Joint Research Centre physical Research Infrastructures of the European Commission (PACIFIED-LFR project, Research Infrastructure Access Agreement N° 36345/01 and DOUBLED project, Research Infrastructure Access Agreement N° 36619/06). The authors also want to acknowledge the PASCAL project for funding (Grant Agreement N°. 945341)

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Additive manufacturing of nanostructured uranium dicarbide/carbon nanocomposites via sol-gel technique

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Uranium and other actinides play an unquestionable role in the development of novel radionuclides for diagnostics and targeted therapy, emerging as a frontrunner in the framework of nuclear physics and for the design and production of innovative radiopharmaceuticals. Moreover, uranyl cations UO_2^{2+} offer an immense variety of applications due to the unique photochemical properties and high photosensitivity of its complexes, giving rise to a sheer diversity of opportunities. The excited state of uranyl cation is indeed accessible under UV and visible light, therefore readily producing chemically reactive radical species UO_2^{2+*} upon light irradiation [1]. As these outstanding features come to the fore, we have developed an innovative synthesis protocol to explore the use of uranyl cations as a photoinitiator system for the development of photocurable sol-gel-based formulations, thus coupling the photochemical reactions of uranyl cations with photopolymerisation processes. Hence, the uranyl motifs allow to activate the acrylate functionalities of a photopolymer in a free-radical photopolymerisation process. Micro-architected components have been successfully fabricated via digital light processing technique upon photocleavage of the double carbon bonds and the 3D printed components were then converted into UC_2/carbon nanocomposite upon carbothermal reduction. To the best of our knowledge, this uranyl-mediated additive manufacturing process constitutes the first application of the synergistic role of uranyl motifs as photoinitiator and uranium source in a photopolymer platform, therefore demonstrating for the first time the possibility to directly pattern uranium-based materials in complex-shaped structures.

Fig. 1. 3D printed UC_2/C nanocomposite as-printed (left) and upon carbothermal reduction (right).

The experimental data used in this research were generated through access to the ActUsLab/PAMEC under the Framework of access to the Joint Research Centre Physical Research Infrastructures of the European Commission (AMNUC, PAMEC Access Agreement N°36345/05).

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Orbital spin-singlet state in U-based heavy fermion superconductors.

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The UTe_2 superconductor is regarded as a heavy fermion mixed-valence system with very peculiar properties within the normal and superconducting states. It shows no signs of magnetic order but strong anisotropy of magnetic and superconducting critical fields. In addition to the clear heavy fermion-like behavior in the normal state, it exhibits a distinctive Schottky-type anomaly at about 12 K and a characteristic excitations gap ~35-40 K. Here we show, by virtue of dynamical mean-field theory calculations with a quasi-atomic treatment of electron correlations, that ab-initio derived crystal-field splitting of the 5f2 ionic configuration yields an agreement with these experimental observations. We analyze the symmetry of magnetic and multipolar moment fluctuations that might lead to the superconducting pairing at low temperatures. We find a close analogy of the normal state of the UTe_2 to that of URu_2Si_2 in the Kondo arrest scenario. We also discuss the situation in famous UGe_2 superconductor that believe to be spin mediated superconductor in close proximity to itinerant magnetism instability. We argue, however, for another, localized spin-orbital singlet state scenario of the magnetic instability in this system. We also propose a model description of the observed magnetic anisotropy in UTe2 that is based on the calculated structure of ground state multiplet and anisotropic exchange interactions in the structural U-U dimer.

Plutonium speciation in presence of boric acid – A spectroscopic and electrochemical characterization

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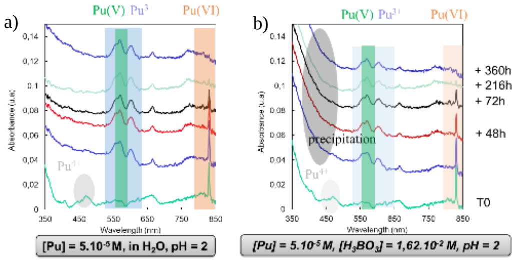
In cases of damage of the zircaloy cladding in a nuclear reactor, a release of small quantities of radionuclides could occur into the primary loop. If such an event occurred, some actinides (mainly U and Pu) could be released in trace concentration. The goal of the research presented here is to improve models for the behavior of plutonium in the chemical condition corresponding to the primary loop solution during cold shutdown. In order to be as representative as possible, the experiments have then to be performed with the lowest plutonium concentration that can be used taking into account the detection limits of the spectroscopic tools at our disposal.
In macroconcentration of plutonium, its chemistry in solution is dominated by the hydrolysis reaction of plutonium +IV which leads to the fast polymerization of Pu and the formation of PuO_2 colloid of nanometer size and its disproportionation reaction to form Pu(VI) and Pu(III) [1]. In the first part of this work, we investigated if this reaction is still predominant for lower concentration of plutonium and in presence of boric acid, which is present in high concentration in the primary loop. These studies were carried out with solutions of Pu(IV) and Pu(III) at different acidities as starting points. Then, the impact of boric acid on the Pu(IV)/Pu(III) redox equilibria was explored by combination of electrolysis experiment and spectroscopy methods.
In the first part, with the use of the UV-vis-NIR spectroscopy, we were able to determine the speciation of the plutonium in water at low concentration and at different acidities. These results were compared to those in presence of boric acid and lead to first interpretation on the boric acid impact on the plutonium speciation. In addition, X-ray absorption measurements were realized on synchrotron to assess lower concentration of plutonium. These measurements used both XANES (X-ray Absorption Near Edge spectroscopy) and EXAFS (Extended X-ray Absorption Fine Structure) spectroscopies, which give information on the oxidation state of plutonium and the structural changes in its first coordination sphere. In the second part, an experimental set-up was used in the ATALANTE facility to perform UV-vis-NIR spectroscopy analysis while performing electrochemistry in the solution. This allowed us to follow the speciation of the plutonium as a function of the potential and to assess the standard potential of the Pu(IV)/Pu(III) couple in water and in presence of boric acid.



[Pu] = 5.10^{-5} M, in H_2O, pH = 2

[Pu] = 5.10^{-5} M, [H_3BO_3] = $1,62.10^{-2}$ M, pH = 2

Figure 1: UV-Vis-NIR spectra of Pu(IV) solution a) in water and b) in boric acid.

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Atomic scale modelling results on the structural and thermal properties of stoichiometric and hypostoichiometric Am-bearing oxides

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One objective of the nuclear industry is to increase its sustainability by increasing the reuse of spent fuel and reducing the amount of final waste and its radiotoxicity. Minor actinides, in particular Americium, are chemical elements produced by neutron capture in nuclear reactors, whose amount in the waste should be reduced. One solution envisaged is to separate them from the rest of the waste and to incorporate them in new fuels to be re-irradiated in reactors [1]. It is therefore necessary to know with great accuracy the properties and behaviour of minor actinide bearing nuclear fuels.

Atomic scale modelling methods are now essential tools to complement experimental characterizations of nuclear fuels and get further insight into the elementary mechanisms governing their behaviour. We will present the results of the combined electronic structure and empirical interatomic potential investigation of properties of the AmO_{2-x} and $(U,Am)O_{2-x}$ americium-bearing oxides as a function of composition and temperature. Structural properties, such as lattice parameter, thermal expansion coefficient and density; thermodynamic properties, i.e., enthalpy increment, specific heat capacity, mixing enthalpy and melting temperature, as well as mechanical properties and diffusion coefficients, will be discussed.

This investigation is included in the PATRICIA project, which has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945077.

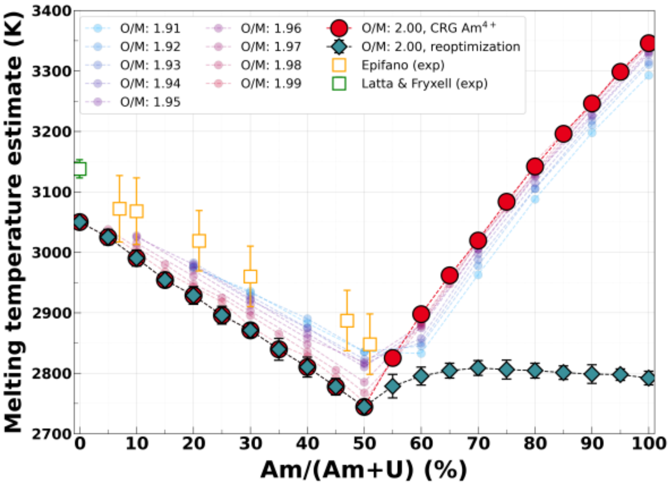

Fig. 1. Estimate of $(U,Am)O_{2-x}$ melting temperature using the Cooper-Rushton-Grimes interatomic potential

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Tuning the band gap in *f*-metal Zintl phases by pressure

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Zintl phases are compound of an electropositive cation and a complex covalently bonded anion. Exploration of the layered compounds with the trigonal structure $CaBe_2Ge_2$ gives us interesting opportunity to compare Eu and U compounds. Eu compounds, as e.g. $EuZn_2P_2$ (T_N = 23 K [1]) described here, exhibit an AF order, and they are narrow-band semiconductors with a pronounced effect of magnetic order on electrical resistivity. We found that application of pressure leads to a gradual gap suppression, completed around p = 17 GPa, and the material becomes semi-metallic. The resistivities are suggestive of an increase of T_N with decreasing volume, suggested by comparison of several EuT_2X_2. However, the maximum in □(T) is higher than T_N, which reaches only 43 K in 9.5 GPa. Hence the resistivity maximum can be attributed to magnetic polarons, stemming for magnetic correlations within the basal planes. Those can be strongly affected by field, as seen in Fig. 1c.

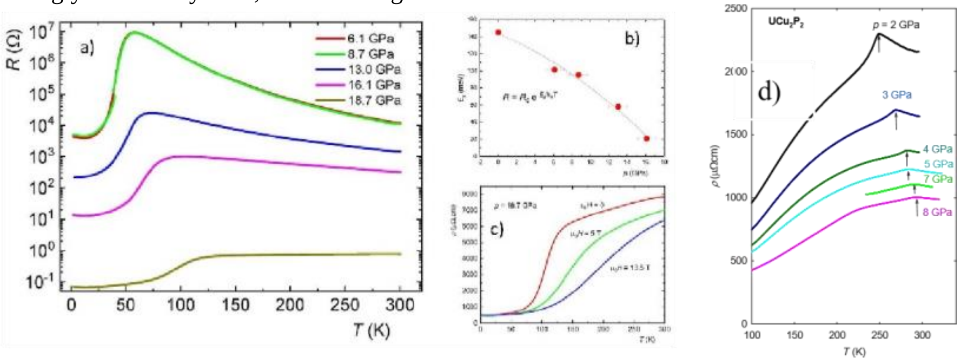

Fig. 1. Pressure variations of electrical resistivity of $EuZn_2P_2$ (a), derived pressure dependence of the width of gap (b) and field variations at p = 18.7 GPa, the highest pressure applied. Fig. (d) shows the increase of T_C with pressure for UCu_2P_2.

Further shrinking of unit cell can be found in UCu_2P_2. It is semi-metal at ambient pressure, while calculations reveal only one-spin states at E_F, i.e. it is also a ferromagnetic half-metal. Its T_C = 216 K [2] increases with pressure with enormous rate, 10 K/GPa. Around p = 8 GPa it reaches room temperature. Its resistivity values keep decreasing to the level usual in metals. The question is what happens then and whether additional volume compression can be achieved by doping.
The work has been supported by the Czech Science Foundation under the grant No. 21-09766S

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Chemistry and speciation of protactinium +IV – a theoretical study

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Protactinium (Z = 91) is an enigmatic element for chemists. Positioned between thorium and uranium in the actinide series of the periodic table, it exhibits unique properties that pose challenges for experimental studies and interpretations. For example, the five valence electrons of its free atom can be distributed in numerous ways across the valence 5f, 6d, 7s, and 7p shells, creating a quantum chaos of states even prior to ionization. In solution, protactinium element is expected to be dominated by its stable +V oxidation state (formally free of valence electrons), with the potential occurrence, under specific reducing conditions, of the unstable +IV state (displaying one unpaired 5f electron in the ground state). The limited experimental data on protactinium compounds in aqueous solutions and the gas phase present a challenge to understand the fundamental chemistry of this element. However, leveraging the available data on Pa +V and Pa +IV, we developed a working hypothesis that guided our research towards obtaining more information on the properties of Pa compounds through quantum chemical calculations. Our recent progress in studying the fundamental chemistry of protactinium has facilitated a better understanding of its enigmatic nature, enabling us to conduct more systematic experimental studies in the future. The synergy between theoretical and experimental studies will likely involve characterizing various Pa +IV compounds under different conditions and analyzing their reactivity, as well as other properties such as chemical composition, stability, and spectroscopic behavior. Through this research, we aim to shed more light on the unique properties of protactinium and contribute to a better understanding of its role in various chemical and physical systems.

This work was supported by the Région des Pays de la Loire (RCT-PaPAn project) and by the French National Research Agency (ANR-21-CE29-0027, LABEX CaPPA/ANR-11-LABX-0005-01 and I-SITE ULNE/ANR-16-IDEX-0004 ULNE)

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Machine Learning Interatomic Potentials for Atomistic Simulations of Nuclear Fuel

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High-accuracy first principles methods such as Density Functional Theory (DFT) are the approaches of choice for atomic scale characterization of nuclear fuel materials. However, due to high computational cost, numerous properties remain out of reach. At larger scales, semi-empirical potentials allow classical molecular dynamics simulations involving billions of atoms and microseconds long but does not always compare well to first principles reference calculations.

In recent years, machine learning has proven to be a reliable tool to develop highly accurate interatomic potentials by learning the potential energy surfaces from reference first principles calculation datasets [1]. Filling the gap between first principles and classical methods, so-called machine learning interatomic potentials maintain first principles accuracy through large-scale simulations at a fragment of its computational cost.

This work presents the development of machine learning interatomic potentials for the U-O system using high dimensional neural networks [2] and spectral neighbor analysis [3]. Active learning methods are paired with state-of-the-art DFT+*U* calculations to generate diverse and representative ensembles of atomic configurations on which the potentials are trained. Those newly developed potentials are then used to perform large-scale molecular dynamics to investigate the thermo-mechanical properties of irradiated UO_2 materials.

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Theory of Valence-to-Core RIXS Measured at the Uranium M_5 edge: UO_2 and UF_4 Compared

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Motivated by a recent experimental study [1], we model the valence-to-core resonant inelastic x-ray scattering (RIXS) measured at the uranium M_5 edge in insulating compounds UO_2 and UF_4. To do so, we employ the Kramers–Heuisenberg formula in conjunction with the Anderson impurity model extracted from the corresponding LDA+DMFT electronic-structure calculations [2]. We find that the spectral feature experimentally observed at an energy loss of roughly 10 eV reflects the charge-transfer excitations from the uranium 5f shell to the ligand 2p states, in agreement with other closely related investigations [3]. We analyze how the intensity of this feature depends on the strength of the metal–ligand hybridization and discuss whether there is a direct link between the energy loss, at which this feature is observed, and the band gap as argued in [1].

This work was supported by the Czech Science Foundation under the grant No. 21-09766S.

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Parametric study of uranyl speciation and stability in peroxocarbonate media

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In France, potash treatment of liquid or gaseous effluents, or tailings coming from the front end of the nuclear fuel cycle, leads to the formation of uranium containing precipitates. These materials are mostly sludges where uranium is found in the form of potassium diuranate ($K_2U_2O_7$) among other impurities. These sludges, named KDU in reference to the uranium form, represent a significant source of valuable uranium currently stored for further reprocessing and valorization of the uranium. An innovative and eco-friendly way to reprocess these materials is their dissolution in peroxocarbonates media which leads mainly to two uranyl complexes $[UO_2(O_2)(CO_3)_2]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ according to the reactions (1) and (2) [1]. This work aims to study the speciation of uranyl complexes and the stability of UO_2^{+} in peroxocarbonates media, depending on the experimental parameters (nature of cation and initial pH).

$$UO_2^{2+} + yCO_3^{2-} + xO_2^{2-} \rightarrow [UO_2(O_2)_x(CO_3)_y]^{2-2x-2y} \qquad (1)$$

$$UO_2^{2+} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} \qquad (2)$$

In the first part of this work, UO_2F_2 was used as uranium precursor. The concentration of uranium was fixed at 50 g/L and the $[CO_3^{2-}]/[U]$ and $[H_2O_2]/[U]$ molar ratio was chosen equals to 4. The cation was varied by changing the carbonate counter-ion (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$). The initial pH was adjusted with nitric acid and hydroxide to obtain pH of 8, 9 and 10. The speciation and stability of the species was followed in time by Raman spectroscopy. Using similar conditions but exploring other pH, the study was extended to KDU precursors: a laboratory synthesized KDU, free from impurities, and industrial KDU sludges. It was found that both pH and counter-ion have great impact on the speciation and the stability of the uranyl complexes. Around a pH equal to 8 or in NH_4^+ media, $[UO_2(CO_3)_3]^{4-}$ is mainly formed whatever the precursor. Around a pH of 11 or using Na^+, $[UO_2(O_2)(CO_3)_2]^{4-}$ is largely formed and is stable in time. Finally, although that in NH_4^+ media, only carbonates are stable, the maximum uranium concentration is reach with this counter-ion, which therefore appears to be the most promising.

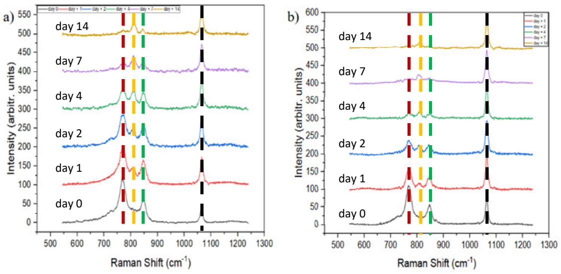

Fig. 1. Evolution of uranyl speciation in a) Na_2CO_3-H_2O_2, b) K_2CO_3-H_2O_2 (🟥 $[UO_2(O_2)(CO_3)_2]^{4-}$; 🟨 $[UO_2(CO_3)_3]^{4-}$; 🟩 $[UO_2(O_2)_2]^{2-}$; ⬛ CO_3^{2-})

Reference

[1] K.W. Kim *et al.*, *Environmental Science & Technology* **43(7)**, 2355–2361 (2009).

Ultrafiltration separation of Am(VI)-polyoxometalate from lanthanides

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Oxidization of Am(III) to Am(VI) producing AmO_2^{2+} ions is recently thought to be a promising solution to facilitate the partitioning of americium from lanthanides, however, the rapid reduction of Am(VI) back to Am(III) by radiolysis products and organic reagents required for the traditional separation protocols including solvent and solid extractions hampers practical redox-based separations. We recently reported a nanoscale polyoxometalate (POM) cluster with a vacancy site compatible with the selective coordination of hexavalent actinides (^{238}U, ^{237}Np, ^{242}Pu and ^{243}Am) over trivalent lanthanides in nitric acid media[1]. Such precise and strong coordination by a large cluster not only stabilizes Am(VI) to an unmatched level but also efficiently discriminates americium and lanthanides with a large size difference between their coexisting chemical species (Fig. 1). When combined with an industrial ultrafiltration technique, these efforts give rise to a new separation method.

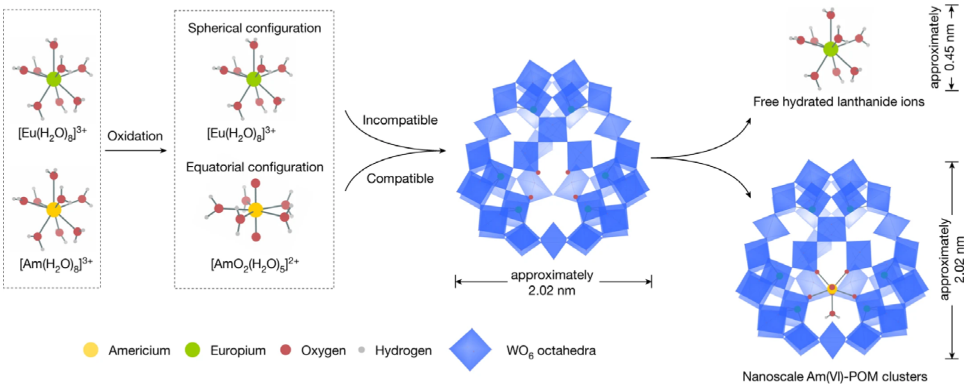

Fig. 1. Schematic illustration of the frame of the ultrafiltration separation of nanoscale Am(VI)-POM clusters from lanthanides

References

[1] H. Zhang et al., *Nature*, 482-487, 616, (2023).

APAWlib: New fully-relativistic projector augmented wave datasets for actinides

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The projector augmented wave (PAW) method is a generalization that incorporates the key ideas from both the ultrasoft pseudopotentials (USPP) method and the linearized augmented plane wave (LAPW) method. To perform electronic structure calculations utilizing the PAW method, reliable and efficient PAW datasets for the elements that involved are imperative. Currently, there are a number of PAW datasets that cover a large part of the periodic table. However, the PAW datasets designed for the actinides remain scarce. The available PAW datasets (from Th to Cm) included in the VASP code are relatively hard, requiring large cutoff energies. Furthermore, they are challenging to achieve convergence, especially for the transuranium elements. In this work, we present new fully-relativistic PAW datasets for the actinides (from Ac to Lr), namely APAWlib. The datasets were generated in the abinit and UPF formats by using the Atompaw4 code. Thus, they are compatible with the common open source *ab initio* software packages, such as Abinit and Quantum ESPRESSO. For generations of the PAW datasets, the 6*s* and 6*p* semicore orbitals were considered as valence orbitals, the non-linear core correction was applied, the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) scheme was employed to construct smooth pseudo partial waves, and the spin-orbit coupling was included. The performance of the PAW datasets was examined on solid state calculations for the actinides with simple *fcc* structures. The benchmark results suggested that the convergence properties of the PAW datasets have been significantly improved, while their computational accuracies are comparable with those in the VASP code.

Analyzing the two-dimensional (2D) micrographs as three-dimensional (3D) representation of a Lexan fission trucks in the field of nuclear forensics

Rami Babayew[1,2], Shay Dadon[1], Yaacov Yehuda-Zada[1,2], Noam Elgad[1,3], Jan Lorincik[3], Itzhak Orion[2], Aryeh Weiss[4], Galit Katarivas Levy[2], Itzhak Halevy[1,2]

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The Lexan detector produces two-dimensional photographs of fission tracks. The physics behind fission is widely recognized to have 4π symmetry, as illustrated in Fig 1. The width of the tracks is below 0.1µm, which approaches the limit of resolution for light microscopes. In order to emphasize the fission trucks, we employed the etching process, which enlarges the width of the trucks and renders them more noticeable. To etch the lexan, it is immersed in a solution of NaOH 6.5N at a temperature of 70°C for approximately 13 minutes. A new issue has arisen due to deterioration on the lexan surface, resulting in a distorted surface that decreases the signal-to-noise ratio (SNR) of the light microscope images. Minor imperfections on the lexan material are also magnified. The relationship between the width of the trucks and the etching time is illustrated in Fig 2. We are introducing a novel way to boost trucks using fluorescent technology. The detector is submerged in a fluorescent liquid (DHPI) within a low-pressure environment, causing the liquid to fill the narrow 3D truck tubes. Initial findings indicate that it is possible to decrease the etching duration to enhance the visibility of the trucks without causing any harm to the detector surface.

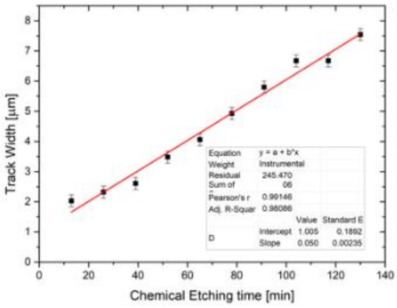

Fig 1: Linear relation between Track Width and chemical etching time.

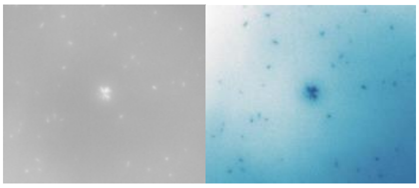

Fig 2: Image data with fluorescence Agent.

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[1] Rami Babayew *et al.*, Simulation Tools for Improvement of the Fission Track Analysis Method for Nuclear Forensics. Journal of Radioanalytical and Nuclear Chemistry(Accepted, December 2023).

[2] Weiss. A. *et al.*, Fission Track Detection Using Automated Microscopy. Journal of Nuclear Engineering and Radiation Science (2017). DOI: 10.1115/1.4036434.

Fundamental investigations of actinide immobilization by incorporation into solid phases relevant for final disposal

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This contribution provides an overview of a current research network funded by the German Federal Ministry of Education and Research (BMBF), entitled “Fundamental investigations of actinide immobilization by incorporation into solid phases relevant for final disposal” – AcE. The AcE project aims at understanding the incorporation and immobilization of actinides (*An*) in crystalline, repository-relevant solid phases, such as zirconia (ZrO_2) and UO_2, but also in zircon ($ZrSiO_4$), pyrochlores ($Ln_2Zr_2O_7$) and orthophosphates of the monazite type ($LnPO_4$), which may find use as host matrices for the immobilization and safe disposal of high-level waste streams.

Recent studies by the AcE-project consortium, addressing the structure, properties, and the radiation tolerance of monazites and Zr(IV)-based solid phases containing actinides or their surrogates from the lanthanide series will be presented. Material synthesis strategies in the AcE project have aimed at generating single-phase solid solutions in the form of polycrystalline powders, dense ceramics, and single crystals. Structural studies using powder X-ray diffraction at ambient conditions, but also at high temperatures and pressures have been complemented with a wide range of microscopic and spectroscopic techniques to address differences between the host- and dopant environments in the solid matrices at ambient and extreme conditions. The radiation tolerance of the synthetic solid phases have been investigated by combining external heavy-ion irradiation of inactive Ln-doped materials and *in situ* self-irradiation of ^{241}Am-doped Zr(IV)-phases with monoclinic, cubic defect fluorite and pyrochlore structures. The latter experiments have been conducted in joint efforts with the Joint Research Center in Karlsruhe within the ActUsLab programme.

Uranium-organic hybrid materials for direct X-ray detection

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As the heaviest element in nature, uranium has superior high-energy photon stopping power over other elements. Diversified functional uranium-based radiation detection materials can be modulated based on the plentiful coordination geometry and valence. The recent results show the potential applications of semiconductive uranium-organic hybrid materials for direct X-ray detection.

In the first study, we report the first instance of 0D to 3D polycatenation in an actinide-based metal-organic framework (SCU-14).[1] This emphasizes the unique potential of semiconductive behaviors owing to the special long-range π-π stacking through the whole structure. The experimental results show that the material has an obvious X-ray photoconductivity effect with a high carrier migration ability. In addition, the X-ray detection sensitivity of this material can reach 54.93 $\mu CGy_{air}^{-1}cm^{-2}$, comparable to commercial amorphous selenium detection materials. After long-term X-ray irradiation, its photocurrent hardly changes, proving the stability of the material.

In practical applications, there are specific requirements for the size and quality of the crystals. We further developed and examined the electrical characteristics of large, millimeter-sized crystals of a uranium-based semiconductive metal-organic framework (SCU-15). [2] These high-quality crystals significantly enhanced the performance of single-crystal devices compared to devices using pelleted powder. The single-crystal device exhibited exceptional charge mobility and lifetime product, along with a notable carrier diffusion length, surpassing other MOF detectors.

These two studies represent a leap forward in the development and application of uranium-based MOFs, paving the way for more efficient electronic devices and innovative direct radiation detection materials.

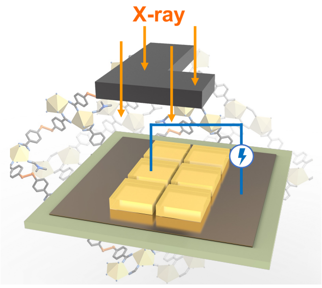

Fig. 1 Schematic drawing of the single crystal X-ray detector based on SCU-15

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[2] L. Cheng; C. Liang; Y. Wang; Y. Wang; S. Wang et al., *Cell Rep. Phys. Sci.* **3.**,101004 (2022).

The Actinide User Laboratory in Karlsruhe

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In line with the vision of the European Research Area (ERA) launched in 2000, the Actinide User Laboratory ("ActUsLab") was initiated in 2001 in the PAMEC laboratory (Properties of Actinide Materials in Extreme Conditions) and was a pioneer Open Access initiative at the Joint Research Centre (JRC), research arm of the European Commission. Supported by the Directorate-General for Research and Innovation (DG RTD) responsible for EU policy on research, science and innovation, ActUsLab gained significant traction and demonstrated impressive success in terms of attracting interest from the scientific community, receiving numerous proposals, generating scientific publications, and contributing to the completion of PhD theses. Therefore, the programme was extended beyond its initial three-year period and finally turned into a long-term activity. In 2018, ActUsLab became an integral part of a newly-established global JRC Open Access framework and further expanded its reach when two additional Research Infrastructures (Fuels and Materials Research (FMR) and Hot Cells (HC-KA)) from JRC Karlsruhe joined forces with the program.

ActUsLab is one of the few civil laboratories in Europe where actinide materials can be safely investigated. The facilities and actinide materials available at ActUsLab are suitable for cutting-edge research in fundamental science and innovative materials (e.g., phase transitions, bonding, exotic phenomena), nuclear safety and security research (e.g., wastes, severe accident research, thermal barriers), as well as non-power applications research (e.g., targets for radio-medical isotopes production, nuclear clock, space exploration).

Fig. 1. Examples of ActUsLab facilities (clockwise from centre-top): Spark plasma sintering device, Laser flash heating, electron microscopy set-ups SEM and TEM in FMR laboratory; XRD, SQUID magnetometer, Surface Science set-up in PAMEC laboratory; Hot cell line for Post irradiation examination and spent nuclear fuel investigations in HC-KA.

Acknowledgements
We are grateful to Ms. Krisztina Varga for administrative support to the programme and to the colleagues of PAMEC, FMR and HC-KA laboratories for scientific and technical support to Users. We also thank the support Units of JRC-Karlsruhe for making the access possible.

Web portal:
https://joint-research-centre.ec.europa.eu/tools-and-laboratories/open-access-jrc-research-infrastructures_en

Nuclear Forensics – Fission Track Analysis – Star Segmentation and Classification using Deep Learning and simulation program

Noam Elgad[1,2], Rami Babayew[1,2], Mark Last[3], Yaacov Yehuda-Zada[1,2], Jan Lorincik[4], Itzhak Orion[2], Erez Gilad[2] Aryeh Weiss[5], Galit Katarivas Levy[2], Itzhak Halevy[2]

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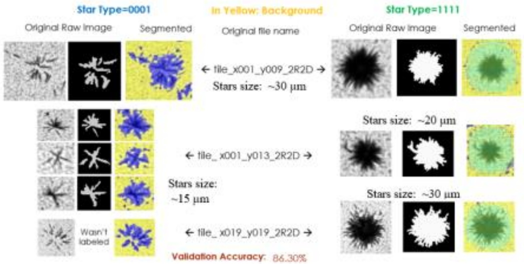
This work proposes a new methodology for identifying and classifying nuclear fission tracks in microscopic images for nuclear forensics purposes, using deep learning techniques. The model we created uses U-Net networks based on an FCN neural network with 5-fold cross-validation. The model was built to identify stars smaller than 60 micrometers and under 200 pixels with less than 10 leaves and no black center. The model achieved an area under the ROC curve of 0.84. In addition, a model was built for larger and richer stars that achieved an area of 0.90 under the ROC curve. Also, preliminary models were built for the purpose of making a diagnosis between roses of different shapes and sizes at the same time. As part of the work, a new star database with 2,750 images was established, the types of stars and the model were characterized, the architecture was defined, training runs and identification through segmentation were completed and various optimization tests were performed. In addition, a focused study was carried out to determine thresholds for background noise filtering and to improve identification and semi-automatic adaptive threshold setting. In order to increase the database, augmentations were performed in 4 different methods: using manual data engineering to define the images, automation was developed to increase the database artificially, the third method included the development of a semi-automatic labeling mechanism and in the fourth, which was implemented as a complementary method, a dedicated simulator was used that was built in parallel work for the purpose of simulation new stars.

Results of segmentation and identification of two types of stars after training shown in Fig.



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Uranium materials reprocessing by means of a new peroxocarbonate route

Leonard Floarea[1], **Gaëlle Milanole**[2], **Mehdi Arab**[2], **Elise Berrier**[1], **Murielle Rivenet**[1]

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In France, a large quantity of valuable uranium materials coming from the front end of the nuclear fuel cycle is stored, awaiting reprocessing and valorization of the uranium. These materials are mostly sludges composed of potassium diuranate, $K_2U_2O_7$. The dissolution of these sludges in a medium containing a mixture of complexing agents, Na_2CO_3 and H_2O_2, is an innovative and eco-friendly way to recover uranium in the form of an uranyl peroxocarbonate, according to the reaction summarized in Eq. 1 (based on *Kim et al.* paper [1]).

$$U_2O_7^{2-} + 2yCO_3^{2-} + 2xO_2^{2-} + 6H_3O^+ \rightarrow 2[UO_2(O_2)_x(CO_3)_y]^{2-2x-2y} + 9H_2O \qquad \text{Eq. 1}$$

The transport, storage and handling of liquid H_2O_2 in industrial quantities being potentially costly and hazardous, this work aims to study a new route involving the use of a solid peroxide reagent in place of liquid H_2O_2 and to compare the properties of the solutions resulting from potassium diuranate dissolution (uranium content, composition).

Potassium diuranate was synthesized and used as reagent in all experiments. The working concentration of uranium was fixed to 50 g/L and measured experimentally by X-ray fluorescence. The dissolution media were prepared either by using the sodium carbonate perhydrate, $Na_2CO_3{\cdot}1{,}5H_2O_2$ (Fig.1.c), or a mixture of Na_2CO_3 and H_2O_2 (molar ratio $[CO_3^{2-}]:[H_2O_2]:[U_{th}] = 4:6:1$). Once the dissolution of potassium diuranate has been achieved (Fig.1.a) the resulting solutions were analyzed by Raman spectroscopy in order to investigate the uranyl speciation. The stability of the complex $[UO_2(O_2)(CO_3)_2]^{4-}$ over time was followed by UV-visible spectrophotometry and by free peroxide ion assay per 0,02M $KMnO_4$ solution during two weeks. It was shown that the solids present different dissolution kinetics, but the same concentration of $[UO_2(O_2)(CO_3)_2]^{4-}$ complex is obtained after one day of reprocessing, regardless of the route used. However, the higher the reaction time, the more stable the sodium carbonate perhydrate route, the decrease of the $[UO_2(O_2)(CO_3)_2]^{4-}$ complex concentration tending to generate another complex: the uranyl tricarbonate, $[UO_2(CO_3)_3]^{4-}$.

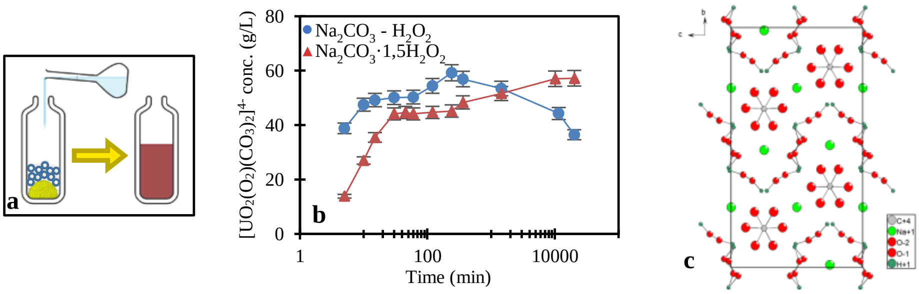

Fig. 1. a) Experimental schematic diagram ; b) Evolution of the concentration of uranyl peroxocarbonate complex as a function of time ; c) $Na_2CO_3{\cdot}1{,}5H_2O_2$ structure

References

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<u>Leonard Floarea</u>[1], Gaëlle Milanole[2], Mehdi Arab[2], Elise Berrier[1], Murielle Rivenet[1]

[1] *Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 59000 Lille, France, e-mail: leonard-gabriel.floarea@centralelille.fr*
[2] *ORANO Tricastin, Direction de La Recherche & Développement, Site du TRICASTIN BP 16, 26701 Pierrelatte, France*

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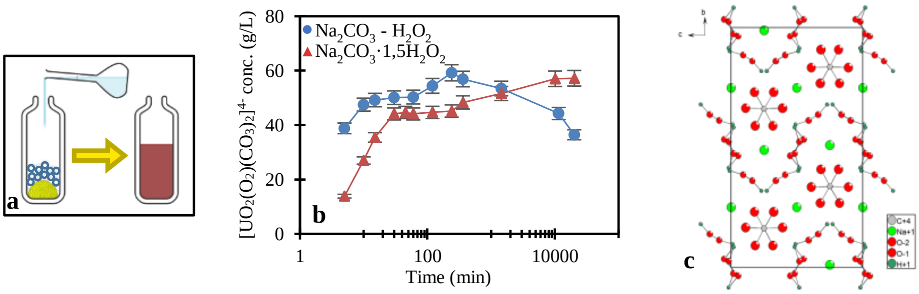

Fig. 1. a) Experimental schematic diagram ; b) Evolution of the concentration of uranyl peroxocarbonate complex as a function of time ; c) $Na_2CO_3{\cdot}1{,}5H_2O_2$ structure

References

[1] K.W. Kim *et al.*, *Environmental Science & Technology* **43(7)**, 2355–2361 (2009).

Solubility Evaluation of the Coprecipitate Uranium / Plutonium Under Hyperalkaline and Reducing Conditions

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Actinides, such as uranium and plutonium, lead to long-term radiotoxicity in deep nuclear waste disposal [1].

This study consist in the investigation of the precipitation of UO_2 and the coprecipitation of thorium (Th) and plutonium (Pu) with UO_2(s) as host phase under hyper-alkaline and reducing conditions that mimic conditions of deep geological repository systems. Our working hypothesis, using both liquid and solid characterization is to evaluate the solubility of the U/Pu coprecipitate and show that coprecipitation can play a critical role in the retention of long life radionuclides.

All the aqueous solutions were prepared with degased Milli-Q water. The HCl and NaOH stock solutions were prepared in a glove box under an argon atmosphere (O2 < 0,5 ppm). The experimental procedure consists (1) in the formation of U(IV) from (UVI) nitrate solution by precipitating schoepite by adding 0.5 M NaOH, then dissolving the precipitate in 1 M HCl solution. The dissolved U(IV) stock solution was obtained by coulometric reduction (-1 mA, 10h) in the glove box. The pH of this solution was kept lower than 1 (pH : 0.7) to ensure the stability of dissolved U(IV). The precipitation of UO_2 from the U(IV) solution was achieved in the glove box by adding NaOH or an alkaline solution to reach a pH of 13. The alkaline solution composition mimics the artificial cement pore water of a fresh cement paste (*e.g.* CEM V/A Rombas, Calcia) including NaOH, KOH, CaO, Na_2SO_4, NaCl.

The reduction process was followed by UV-visible spectrophotometric measurements performed on a Shimadzu UV-mini 1240 spectrophotometer installed outside the glove box and connected by optical glass fibers directly to the glove box (λ = 350 – 900 nm). The U(IV) absorption spectrum was measured during the reduction several times and periodically after the reduction in order to check the stability of U(IV) solution. After precipitation, using both NaOH and the alkaline solution, the concentration of U(IV)in the filtrate was measured by ICP-MS.

The next step consisted in the coprecipitation of U(IV) (0.04 M, pH<1) mixed with Th or Pu (4×10^{-4} M) to obtain the coprecipitation of about 1% of Th and/or Pu with UO_2 (Th(Th+U) and Pu/(Pu+U) at a molar ratio of 0.01). The concentration of U(IV), Th and Pu were measured by ICP-MS and ICP-MS-HR.

Colloidal solid phases of UO_2 and the coprecipates were characterized by LIBD, XRD, and EXAFS. LIBD was used in order to check the absence of colloids formation during the acidic U (VI) reduction and the presence of colloids during solution aging and after the addition of NaOH / cement solution.

The Extended X-ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near-Edge Structure (XANES) spectroscopy measurements were performed on the MARS beamline at the SOLEIL synchrotron facility (Saint-Aubin, France). The different spectra were collected in the fluorescence mode with 13 element Ge detector at low temperature at the plutonium LIII edge (18057 eV) and at the uranium LIII edge (17166 eV).

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Structure, spectroscopic and theoretical analysis of plutonium (III) and americium (III) crown ether inclusion complexes

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Understanding the coordination chemistry of actinides is driven by a broad range of potential applications, including used nuclear fuel reprocessing, environmental remediation, and radiopharmaceutical *etc.* [1]. Herein, we report the synthesis, single crystal structure, solid state UV-vis-NIR spectroscopy, and theoretical calculations on trivalent plutonium crown ether inclusion complex $[(H_3O)(18\text{-crown-}6)][Pu(H_2O)_4(18\text{-crown-}6)](ClO_4)_4\cdot 2(H_2O)$ (donated as Pu^{III}-18C6) and trivalent americium crown ether inclusion complex $[Am(NO_3)_2(18\text{-crown-}6)]_3\cdot[Am(NO_3)_6]$ (donated as Am^{III}-18C6). Single crystal X-ray diffraction reveals that Pu^{III}-18C6 crystallizes in the orthorhombic space group of *Pccn* which is assembled by independent ionic pairs including $[Pu(H_2O)_4(18\text{-crown-}6)]^{3+}$, $[(H_3O)(18\text{-crown-}6)]^{+}$ and perchlorate anions. Am^{III}-18C6 crystallizes in the monoclinic space group of $C2/m$, which is assembled by independent ionic pairs including $[Am(NO_3)_6]^{3-}$, $[Am(NO_3)_2(18C6)]^{+}$and disordered $[Am(NO_3)_2(18C6)]^{+}$. The plutonium atom and americium atom are both fully encapsulated within the cavity of 18-crown-6. The theoretical calculations confirm the presence of weak dative bond (Pu-O and Am-O) between Pu^{III}/Am^{III} ions with 18-crown-6 [2]. This work may deepen the understanding on the host-guest interactions between trivalent transuranium and macrocyclic ligands.

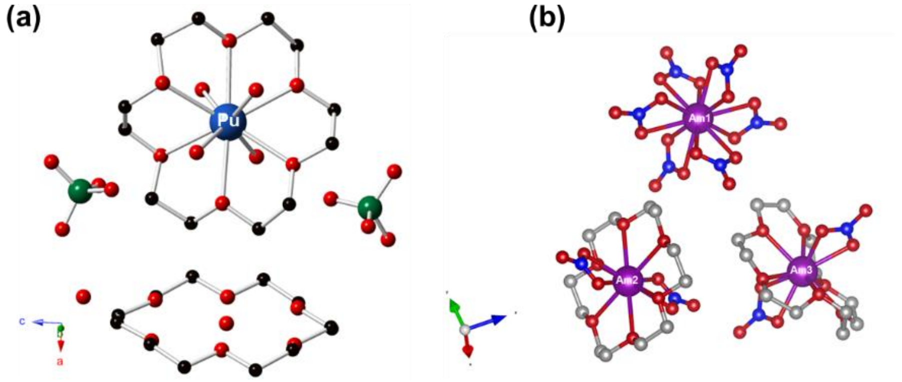

Fig. 1. (a) The molecular structure of Pu^{III}-18C6. Color code: black, carbon; blue, plutonium; green, chloride; red, oxygen; (b) The molecular structure of Am^{III}-18C6. Color code: gray, carbon; purple, americium; blue, nitrogen; red, oxygen. Hydrogen atoms are omitted for the clarity.

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Superconductivity in high-entropy alloy $(NbTa)_{0.67}(MoWTh)_{0.33}$

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High entropy alloys (HEAs) are solid solutions of five or more elements in nearly equimolar ratioa. They are characterized by a well-defined, ordered crystal structure with high chemical disorder, meaing that elements randomly distributed at equivalent crystallographic positions. HEAs crystallize in simple structures, usually bcc and fcc, and are characterized by high configurational entropy during solidification [1]. The alloys are recognized for their exceptional mechanical properties, thermal stability, and corrosion resistance [2–4]. Therefore, they are considered materials with high potential for application, such as high-durability mechanical devices, magnets, or superconductors.

In recent years, there has been considerable interest in high-entropy superconducting alloys, but knowledge of actinide-containing high-entropy alloys is limited. (These alloys are typically made up of tantalum-niobium matrices that are doped with transition metals such as Ti, Zr and Hf). Currently, the study of HEA with uranium is mainly focused on the development of advanced high strength materials. However, a superconducting state has also been discovered in one of the alloys, namely $(TaNb)_{0.31}(TiUHf)_{0.69}$ [5]. To the best of our knowledge, there are no known superconducting HEAs containing thorium.

Motivated by this fact, we conducted a search for the first Th-based superconducting HEA. Here we present the crystal structure and physical properties of a new high-entropy alloy $(NbTa)_{0.67}(MoWTh)_{0.33}$. The alloy is a mixture of bcc and fcc phases and exhibits BCS superconductivity with a critical temperature of approximately 5.6–7.5 K. Additionally, we present the results of a numerical study of the electron structure of the alloy using the DFT formalism. Full version of this contribution has been published elsewhere [6].

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Phase equilibria in the U-Fe-C ternary system at 1100ºC

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The need of accurate thermophysical data for uranium carbide-based materials is a critical issue for their application, e.g., as nuclear fuels or spallation targets. Here is presented an investigation of the ternary uranium-iron-carbon isothermal section at 1100ºC, using powder X-ray diffraction and Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry.

At 1100°C the U-Fe-C system is characterized by the existence of two ternary compounds, $UFeC_2$ and another phase with composition close to 29% U, 32% Fe, 39% C, thirteen 3-phase regions and six 2-phase regions. $UFeC_2$ crystallizes in an original structure type, a distorted variant of the $UCoC_2$-type structure, with space group $P4/n$ and lattice parameters a = 3.503(5) Å and c = 7.405(5) Å. The compound ~29U:32Fe:39C has a crystal structure related to the $Th_{11}Ru_{12}C_{18}$ structure-type (space group $I4\bar{3}m$) with lattice parameter $a \approx 10$ Å. Furthermore, an island of a α-UC_2-based phase with approximate composition 35% U, 4% Fe, 61% C was found in the ternary isothermal section. The presence of this phase, which decomposes in the binary system below 1480°C, indicates the inclusion of Fe in the binary compound and its stabilization effect.

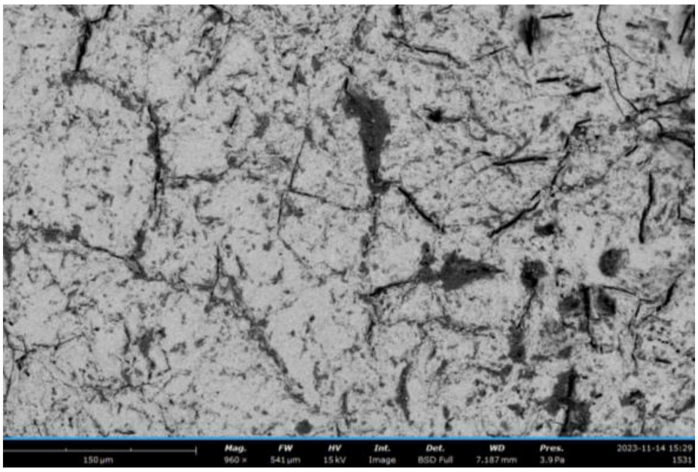

Fig. 1. SEM-BSE image of the 32U:4Fe:64C at.% nominal composition sample (white phase: α-UC_2-based; dark phase: carbon).

Micrometric drilling of (meta-)studtite square platelets formed by pseudomorphic conversion of UO_2 under high-frequency ultrasound

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Research on the oxidative dissolution of spent nuclear fuel under storage conditions due to radiolysis has garnered considerable interest. At the UO_2/water interface, hydrogen peroxide (H_2O_2) is known to be one of the major species formed during water radiolysis, which may contribute to the corrosion of UO_2-based matrices through the formation of uranyl peroxide precipitates. Such species can further promote the dissolution and release of radionuclides into the surroundings.[1-3] Sonochemistry, which pertains to the effect of ultrasound waves on chemical reactions, can be considered as an alternative to simulate the products of water radiolysis under alpha or beta gamma irradiation. The formation of radicals and accumulation of H_2O_2 in aqueous solution are known to be highly dependent on the experimental conditions including the acoustic frequency or power, saturating atmosphere, medium… Additional physical effects are also potentially observed (erosion of solids, enhancement of mass transfer, decrease of diffusion layers..) providing specific effects for the sonicated heterogeneous systems.[4] In this work, the effect of power ultrasound was evaluated on UO_2 samples prepared by the oxalic route and exhibiting a typical square platelet shape (Fig. 1a). The partial or complete conversion of the oxides into (meta-)studtite $[(UO_2(O_2)(H_2O)_2)\text{-}xH_2O]$ was observed under ultrasound in pure water and slightly acidic media under an oxygenated atmosphere.[5] The characterization of the solids after sonication revealed the formation of studtite crystal structures with a preservation of the original platelet morphology (Fig. 1b), suggesting a complex formation mechanism at the interfaces. Interestingly, under specific sonochemical conditions, the platelets showed a reproducible central void (Fig. 1c). The underlying mechanism has been studied.

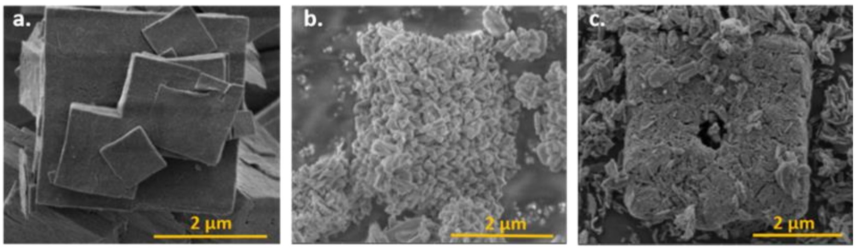

Fig. 1. SEM image of a) UO_2 platelets, b) and c) uranyl peroxide observed after sonication of UO_2 in H_2SO_4 5 10^{-4} M during 6 h at 346 kHz (20 $W.mL^{-1}$, 20°C, Ar/O_2).

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Stable and high-flux adsorptive polyacrylonitrile/hafnium phosphonate nanofibrous membranes for actinide-containing wastewater treatment

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The practical applications of many adsorbents have been impeded by the as-synthesized powder form that is not compatible with continuous actinide removal [1]. Herein, we incorporate hafnium phosphonate (HfP) fine powder into polyacrylonitrile (PAN) via a simple and economical electrospinning technique [2], engendering a stable and hydrophilic nanofibrous membrane (PAN/HfP NFM), which can effectively remove Th(IV) and U(VI) from acidic solutions with a high permeate flux and a considerable breakthrough volume in membrane filtration module [3], and the concentration of actinides in the permeate meet the discharge standards of nuclear wastewater. The resulting NFMs are expected to be utilized in the rapid and continuous treatment of a large volume of actinide-containing wastewater.

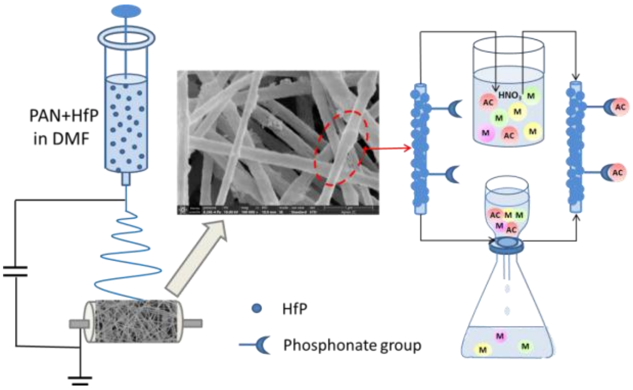

Fig.1. Fabrication and utilization of adsorptive PAN/HfP NFMs

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Electronic Structure and properties of Plutonium Compounds

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In this report, we report a comprehensively quantum-chemical study of the electronic structure and properties of bimetallic X−Pu bonds. First, in the mono-carbonyl compounds, the XPuCO structure alternates from cyclic [PuCBO] to linear [AlCPuO] and [GaCPuO] when atomic radii of the group 13 elements increase. A donor−acceptor model is the best description for bonding interactions between X and Pu, that is donation patterns of CBO → Pu or XC → PuO (X = Al and Ga), and the backdonation patterns of XC ← PuO. Second, the first ethylene dione (OCCO) compounds of plutonium are found in $AlPu(CO)_n$ ($n = 2, 3$). A direct Ga−Pu single bond is first predicted in the series of $GaPu(CO)_n$, where the bonding pattern represents a class of the Pu → CO π back-bonding system. Third, the d-f multiple bond is in sharp contrast with a single bond between plutonium and transition metals.

Removal of plutonium and americium from nitrate solution by precipitation

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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.
Literature [1] 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:

$$\mathrm{Pu^{4+} + 2H_2C_2O_4 + 6\ H_2O \rightarrow Pu(C_2O_4)_2, 6H_2O + 4\ H^+}$$

$$\mathrm{2Am^{3+} + 3H_2C_2O_4 + 10\ H_2O \rightarrow Am_2(C_2O_4)_2, 10H_2O + 6\ H^+}$$

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.

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Enigma of the “U_8Si_8O” phase

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Using U_3Si_2 as a nuclear fuel for research and test reactors requires a thorough knowledge of the U-Si phase diagram to predict reliably the in-use fuel behavior. U_3Si_2 seems to be a perfectly stoichiometric compound. Industrial manufacturers use then slightly over-stoichiometric in silicon compositions, to avoid the presence of residual α-U or U_3Si that affect the irradiation behavior of this fuel. Consequently, a secondary phase with atomic ratio close to 50%U-50%Si is present in the industrial fuel plates [1]. From the binary phase diagram [2], the thermodynamically stable compound is $U_{34}Si_{34.5}$. Nevertheless, our investigations on both laboratory and industrial samples by electron backscattered diffraction (EBSD) revealed the presence of the tetragonal $U_{34}Si_{34.5}$ as well as the orthorhombic “U_8Si_8O” phases in arc-melted samples [3]. The latter was first described as USi [4], but later studies suggested that its stability is achieved only by adding some oxygen in the structure [5]. The presence of light elements (mainly carbon) in metallic uranium may justify the formation of this pseudo-binary phase during the synthesis of Si-rich U_3Si_2. But then, why does this “U_8Si_8X” (X = C, O) phase formation depend on the cooling rate after melting? Why does it decompose upon annealing? And why is it formed irrespective of purity of U metal?

To answer these important questions and to understand the phase equilibria in the U-Si system, experimental and theoretical studies were undertaken. On the one hand, phonon calculations predict instability of the binary “USi” at 0 K, but its stabilization if a small amount of C is added. On the other hand, the quantity of “USi” increases with Si-content in rapidly-cooled arc-melted samples, from 41 to 46 at.% Si, and then drops giving way to $U_{34}Si_{34.5}$, the latter being the only visible phase (aside U_3Si_2) from 48 at.% Si. It should be noted that U_5Si_4 was not been observed, except when C was intentionally added (formation of $U_{20}Si_{16}C_3$).

A summary of results obtained from various samples we synthesized will be presented, including ab-initio phonon calculations, X-ray diffraction and EBSD analyses, and scanning and transmission electron microscopies. In particular, the hypothetical stabilization origin (kinetic vs. thermodynamic phases, epitaxy…) of the “USi” phase will be discussed, highlighting the open questions that remain around that topic.

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Uptake of Th, U, Pu and Eu by granite and biotite gneiss materials under oxidizing and reducing conditions

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Several countries consider deep crystalline formations as candidate host-rocks for high-level radioactive waste (HLW) disposal. Crystalline granite and biotite gneiss are characterized by high strength, structural stability, and low permeability. However, the ingress of groundwater in granite environments may occur through fractures and cracks, and accordingly it is necessary to investigate the solution chemistry and retention properties of radionuclides under such conditions. U and Pu are key actinide elements in the context of HLW disposal. Both actinides are characterized by a redox-sensitive behavior, which strongly defines their chemical behavior as a function of the boundary redox conditions. In the reducing conditions expected to develop after the repository closure, U(IV) and Pu(III/IV) are expected to dominate the aqueous chemistry of uranium and plutonium, respectively. U(VI) prevails under oxidizing conditions, whereas plutonium may be found as +IV, +V, or +VI, depending upon pH and E_h conditions.
The uptake of Th, U, Pu and Eu by granite and biotite gneiss materials was investigated in a series of batch experiments. Experiments were conducted under well-defined redox conditions, *i.e.*, oxidizing (air), mildly reducing (Ar-atmosphere and buffered with hydroquinone, pe + pH ≈ 8–9) and strongly reducing (Ar-atmosphere and buffered with $Na_2S_2O_4$, pe + pH ≈ 0.5–3). Radionuclide concentration, pH and E_h were systematically monitored up to $t \leq 113$ days, after the addition of the radionuclide. Solid phases before and after conducting sorption experiments were characterized by XRD.
Eu shows a moderate sorption, with greater distribution ratios (R_d) determined for biotite gneiss than for granite. This observation is possibly explained by the affinity of biotite for Ln(III)/An(III), and the absence of this mineral phase in the investigated granite material. Strong sorption is observed for Th, as well as for U and Pu in reducing systems where the predominance of the +IV oxidation state is expected. For these three systems, the strength of the uptake follows the order $R_d(Pu(IV)) > R_d(U(IV)) > R_d(Th(IV))$, consistently with the strength of the hydrolysis of the corresponding aquo-ions. Significantly weaker sorption is observed for U and Pu under oxidizing conditions, even though the uptake remains significantly higher in the case of Pu. Thermodynamic calculations conducted for the oxidizing conditions predict the predominance of U(VI) and Pu(V)/Pu(IV), which can thus explain the differences observed in the retention of both radionuclides under oxidizing conditions.
These results contribute to a quantitative description and a better understanding of the retention of redox-sensitive radionuclides in crystalline host-rocks. The importance of combining the use of redox stable probes (*e.g.*, Eu, Th) with redox-sensitive actinides (*e.g.*, U, Pu) is emphasized. These results highlight as well the importance of an accurate knowledge of the redox boundary conditions for a correct prediction of radionuclide retention.

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Impact of the degradation products of UP2W filter aid material on the retention of radionuclides by cement

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UP2W is a filter aid based on polyacrylonitrile (PAN), which is widely used in nuclear power plants as support material for ion exchange resins. Significant amounts of used UP2W are disposed in underground repositories for low and intermediate level waste (L/ILW). The hydrolytic degradation of PAN may result in organic degradation products affecting the mobility of radionuclides in cementitious environments, and thus are of particular interest in the context of nuclear waste disposal. This work aims at investigating the impact of UP2W degradation products on the solubility and sorption of selected radionuclides in cementitious systems under alkaline, reducing conditions as those expected at SFR after repository closure.

Experiments were performed under Ar atmosphere with $O_2 < 2$ ppm. Long-term degradation studies (up to 3 a) involving the original UP2W material were conducted in various NaOH media as well as in $Ca(OH)_2$-buffered solutions with pH = 12.5 at T = 25 and 80 °C in the absence and presence of Fe(0). Supernatant solutions were systematically characterized by organic carbon content measurements (NPOC), various spectroscopic analyses (^{1}H / ^{13}C NMR, IR, UV-vis), and chromatographic analyses (LC-OCD-OND and HPLC-MS). Solubility experiments with $Ca(OH)_2$(cr), β-$Ni(OH)_2$(cr), $Nd(OH)_3$(s) and PuO_2(ncr, hyd) (with ncr and hyd standing for nanocrystalline and hydrated, respectively), as well as sorption experiments with ^{63}Ni, ^{152}Eu and ^{242}Pu were carried out in the absence and presence of selected proxy ligands in porewater solutions corresponding to cement CEM I in the degradation stage II (pH ≈ 12.5, [Ca] ≈ 0.02 M). In experiments involving Pu, reducing conditions were maintained by hydroquinone or Sn(II). Retrieved solid phases from the degradation studies, solubility and sorption experiments were extensively characterized.

Based on ^{1}H NMR and in accordance with other experimental observations, three proxy ligands are proposed to simulate the chemical characteristics of the UP2W degradation products. Glutaric acid (GTA) represents the bulk chain of the generated polymer fragments, whilst α-hydroxyisobutyric acid (HIBA) and 3-hydroxybutyric acid (HBA) simulate the effect of the end groups. These proxy ligands show no significant impact on the solubility of Ca(II), Nd(III) or Pu(IV), whereas a slight increase in the solubility of Ni(II) was observed at $[L]_{tot} > 10^{-2}$ M. This suggests the possible formation of stable ternary Ni-OH-L (or Ni-L-H, with L-H corresponding to a ligand with deprotonated alcohol group) complexes in hyperalkaline systems. The uptake of Ni(II) and Pu(IV) by cement is weakly affected by HIBA, HBA and GTA at $[L]_{tot} > 0.1$ M 10^{-2} M, whereas no effect was observed in the case of Eu(III). Degradation leachates obtained from the degradation experiments induced an evident but modest decrease in the retention of the investigated radionuclides, so Rd values remained high in all cases. These results highlight the relevance of conducting sorption experiments with real degradation leachates in order to properly capture the impact of complex organic materials disposed in L/ILW. This work provides an improved quantitative and mechanistic understanding of the retention properties of radionuclides in cement systems in the presence of UP2W degradation products.

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Hydride-Dehydride process and spheroidization: an alternative route to produce spherical metallic U-6 wt.% Nb powders

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Advances in materials development have enabled new types of nuclear fuels to be considered for nuclear energy. Dispersion-based nuclear fuels are on such type, but the fuel type can bring about a wide range of powder requirements, from powder size distribution, impurity content, internal microstructure, as well as material-efficiency of the powder production process itself. As powder properties are known to be dependent on the production method, developing new production routes is crucial to meeting the growing demand for high-quality powders. At LLNL, we have developed a new process for making size selective spherical U-6 wt.% Nb powders that display different microstructures than similar powders produced by gas atomization [1]. Additionally, the HDH process has the potential for recycling out-of-size powders, minimizing waste generation which is important for nuclear energy. This demonstrates that the HDH process combined with plasma spheroidization is an alternative and low-waste production route for U-6 wt.% Nb powders.

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Spin and Orbital Magnetic Moments of UTe$_2$ induced by the external magnetic field

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Newly discovered superconductivity in the heavy-fermion material UTe2 below 1.7 K [1,2] shows a number of peculiar aspects. Unlike the ferromagnetic superconductors, no magnetic order is observed down to 25 mK. Recent high field XMCD experiments at the uranium $M_{4,5}$ edge [3] reveal the spin and orbital magnetic moments of the 5f -shell.
In this work we consider theoretically the spin and orbital magnetic moments of UTe$_2$ in the external magnetic field. We apply the DFT+U(ED) method [4] based on a combination of DFT with many-body exact diagonalization of the Anderson impurity model. The U-5f-shell Coulomb-U=3.42 eV is obtained making use of the linear-response DFT formulation [5]. The results are shown in Table I. in a comparison with the XMCD data, and simplified DFT+U approach of Ishizuka [6].

Table I. The U atom f-shell n_{5f} occupation, spin M_S, orbital M_L magnetic moments (in μ_B), the ratio R_{LS}= $-M_L/M_S$, and the total magnetic moment, M_{Tot}.

U-atom	***U,J (eV)***	n_{5f}	M_S	M_L	R_{LS}	M_{Tot}
***DFT+U(ED)* [5]**	3.42/0.51	2.70	-0.88	2.24	2.54	1.36
***DFT+U* [6]**	2.91/0.0	2.795	-2.18	3.96	1.81	1.77
***Exp. XMCD* [3]**		2.8	-0.68	1.61	2.37	0.93

The ratio R_{LS} calculated with DFT+U(ED) is in a reasonable quantitative agreement with the XMCD data [3], while magnitudes of M_S and M_L exceed the values obtained from the sum rule analysis. On the contrary, the R_{LS} value obtained with simplified DFT+U of Ishizuka differs substantially from the XMCD data. Both XMCD and DFT+U(ED) support the intermediate valence of uranium with 34% of f^2 and 57% of f^3 configurations as well as itinerant-localized dichotomy in metallic actinide compounds [7].

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Scaling up: syntheses and ceramic production of doped zirconia for irradiation experiments and grazing incidence analysis

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Cubic zirconia (c-ZrO_2) is considered a highly radiation-tolerant material. It is also capable of incorporating a variety of large cations within its crystal structure, making it a promising material as a waste matrix for actinide immobilization. In this study, various syntheses of cerium(IV)-doped zirconia co-doped with Gd(III)/Y(III) were conducted to identify compositions exhibiting a pure cubic structure, with cerium serving as a plutonium analogue. Four compositions were chosen for the production of dense ceramics. The ceramic production of ZrO_2 was conducted with a constant Ce(IV) concentration of 18 mol% and varying Gd/Y concentrations. Purely cubic solid solutions phases were obtained for compositions where the trivalent dopant concentrations exceeded 15 mol% (Fig. 1). The full width at half maximum (FWHM) of the XRD peaks in the dense ceramics increased by a factor of 2 in relation to the starting powder material. Their radiation tolerance was assessed through external ion irradiation experiments. In preparation for these experiments, the ceramic surfaces was polished, and half of the pellet was masked using Al-foil. The non-masked part of the pellet was irradiated with 14 MeV Au^{4+} ions to simulate the recoil of daughter products from alpha decay. Samples were irradiated at two different fluences, 10^{14} ions/cm^2 (A1) and 10^{15} ions/cm^2 (A2). Subsequent to irradiation, analyses were conducted with scanning electron microscopy (SEM) and synchrotron X-ray diffraction in grazing incidence mode (GI-XRD).

The cubic ceramic phases demonstrated excellent radiation tolerance, displaying no significant radiation damage of the structure and maintaining their cubic crystal structure even after irradiation at the highest fluence, A2 (Fig.2). However, diffraction peak broadening following irradiation is visible, suggesting that irradiation has induced microstructural changes to the samples (Fig. 2, right). A non-systematic shift of the Bragg peaks towards lower angles is observed in the irradiated part, particularly pronounced for fluence A2, indicating an expansion of the lattice. No amorphous contributions could be observed in the diffractograms. These observations demonstrate the high radiation tolerance of the ZrO_2 crystal structure, and corroborate their use as waste forms for high-level actinide-bearing waste.

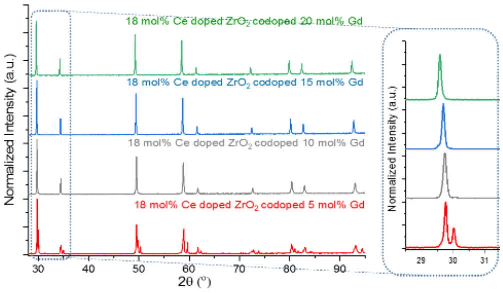

Fig. 1. XRD diffractograms of zirconia doped with 18 mol% Ce, co-doped with 5, 10, 15 or 20 mol% Gd

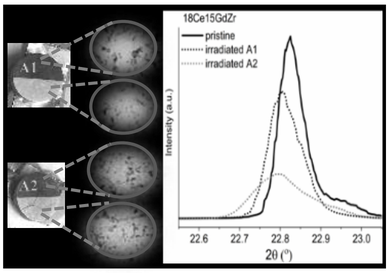

Fig. 2. Left: Photo of the pellets after the irradiation experiments. Middle: SEM images of the pristine and irradiated pellets. Right: GI-XRD diffractograms.

Two Methods for Passivating Plasma-Spheroidized Uranium Alloy Powders to Prevent Spontaneous Combustion in Air

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Abstract: Advances in materials processing have enabled new types of nuclear fuels, including dispersion-based fuel cells. However, safely handling and storing uranium-based powders can be difficult, as metal powders have the potential to spontaneously combust in air. Therefore, it is paramount to examine how to handle material that is potentially pyrophoric, and how to effectively reduce the pyrophoricity of these materials. At LLNL, we have investigated two methods of passivating plasma-spheroidized U-6 wt.% Nb powder: first, by introducing oxygen during plasma spheroidization; and second, by introducing oxygen long after the spheroidized powder has been collected. We compare the benefits and drawbacks of these two methods, including their safety, efficiency, and the quality of powder produced.

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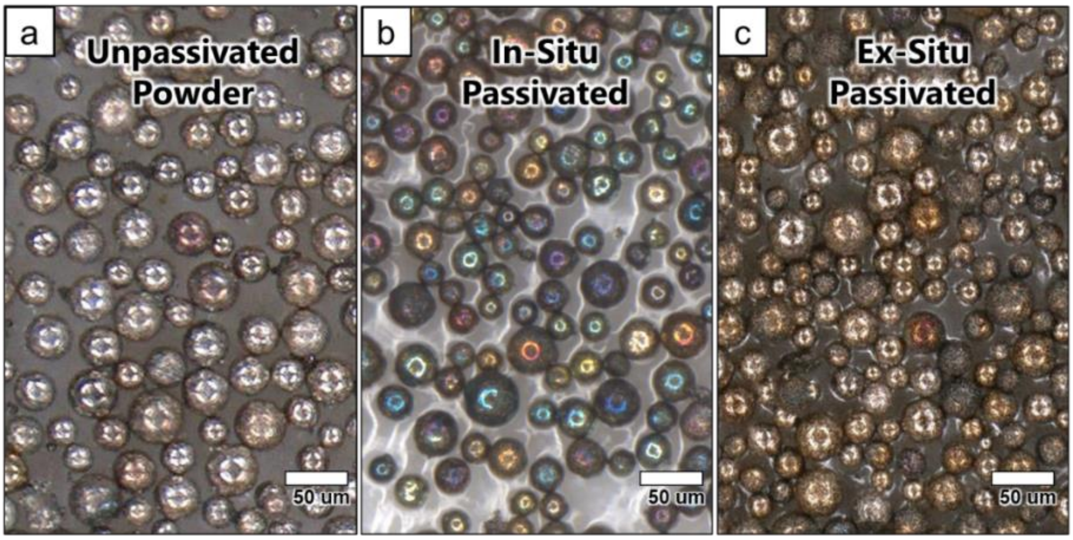

Fig. 1. Effect of passivation method on U-6 wt%. Nb powder oxide layer thickness, observed by color

Atomic scale calculation of thermophysical properties of molten salt reactor fuel via DFT and PIM MD simulations: inclusion of Americium

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In recent years, interest in molten salt reactors has been growing due to their intrinsic safety, facilitation of certain operation and management tasks and their potential for actinide conversion. More in detail, this technology would be able to increase the technology capability of Americium and other minor actinides conversion. In this research field, a highly important aspect for determining design parameters knows as accurately as possible the properties of the fuel itself (density, heat capacity, viscosity, conductivity, expansion, etc.). In MSR, still, this need is even more accentuated due the strong correlation between neutronics, thermo-hydraulics and chemistry. The principal cause of these features is the liquid phase of the fuel, a different concept compared to the most traditional actinides oxides. However, due to challenging conditions encountered in experiments, such as corrosion, high temperatures, and, specifically, in the case of actinides: radioactivity, numerical determination of these properties appears important and necessary for this purpose.

To study salt mixtures based on actinide chlorides like NaCl-$PuCl_3$, NaCl-$(Pu/Am)Cl_3$, and NaCl-$MgCl_2$-$(Pu/AmCl_3)$, atomic-scale simulation techniques such as Molecular Dynamics (MD) are employed. This technique permits to compute crucial properties of the material thanks to statistical mechanics formalism. Yet, to effectively calculate the properties, it is necessary to use a type of interatomic potential suitable for ionic melts, such as the so-called PIM potential [1], whose parameters can be fitted using force-matching methods based on Density Functional Theory (DFT) results. Moreover, it is important to not forget the difficulties encountered when dealing with actinides at atomic scale. This is due to mainly to their complex electronic structure that requires complex modelling procedures. With this method, the parametrisation of the interatomic potential is done minimising the error between the reference DFT forces and the ones predicted from the PIM model.

The strategies and techniques used to include americium to the PIM potential are presented in this work. This is carried out in order to investigate actinide chlorides XCl3 (X=U, Pu, and Am) /NaCl binary systems. Moreover, a comparison between available experimental results and simulations plus the chosen parameters for DFT simulations using the CP2K code [2] (PW cut-off, basis set etc.) are shown, in addition to preliminary MD results on binary systems.

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The chemistry of protactinium solutions: the road to resilience

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There is currently renewed interest in protactinium because of its potential application in various fields outside civil nuclear power (thorium fuel reactors, accumulation of ^{231}Pa in uranium mine tailings): determination of the ^{231}Pa/^{230}Th ratio in oceanography and the ^{231}Pa/^{235}U ratio in nuclear forensics or geochronology, irradiation of ^{231}Pa or ^{232}Th to produce ^{230}U for medical purposes (targeted alpha therapy). Whatever the application, a better understanding of the chemical properties of this singular actinide is required[1].

Protactinium(V) differs from the other pentavalent actinides at the beginning of the series in the absence of a di-oxo bond in its condensed phase compounds: only the presence of a short monooxo bond has been demonstrated experimentally in oxalic and sulphuric media. However, the mono-oxo bond is not so stable and can vanish upon complexation, which is the case in presence of fluoride[2]. This particularity remains poorly understood at present. The current structural data on Pa(V) complexes are rather scarce, especially for predicting the presence or not of this mono-oxo bond. In fact, experimental difficulties occur when isolating significant amount of this actinide, and Pa(V) has a remarkable propensity towards hydrolysis and polymerization. We present here the experimental approach adopted to study the complexation of Pa(V) in aqueous solution, illustrating it with a few examples. Complexation constants are deduced from liquid-liquid extraction experiments combined with gamma spectrometry. In this case, the element is at the ultra-trace scale, which means that polymerization phenomena are not involved, but only average complex compositions are obtained. The thermodynamic study is completed by an infrared and x-ray absorption spectroscopic study with the Pa at millimolar scale in the presence of a strong complexing agent and/or high acidity to limit hydrolysis and colloid formation. The experimental data are then adjusted thanks to theoretical calculations. [3]

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Electronic Structure of Actinide Oxide Nanoparticles

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The unique properties of actinide oxide nanoparticles make them versatile materials with potential applications in various fields such as energy, environment, medicine, and nanotechnology. Actinides generally exhibit a wide range of oxidation states, leading to variations in their electronic configurations and chemical behavior [1]. Understanding the electronic structure of actinides is crucial for understanding how electrons drive chemical reactions and influence fundamental properties like reactivity, bonding, and local structure. We will present the results obtained on CeO_2 [2–4], ThO_2 [5,6], UO_2 [7], and PuO_2 [8–11] nanoparticles by utilizing element-selective synchrotron-based X-ray absorption spectroscopy (XAS) in high-energy resolution fluorescence detection (HERFD) mode [12] at the An M_4 and An/Ln L_3 edges, in combination with electronic structure calculations.

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Preparation and Structural Characterization of an Original Peroxide Complex of Pu(IV)

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Forecasting the behavior of radionuclides within the geosphere or deep underground storage facilities necessitates a comprehensive grasp of the species that may arise when actinide (An) related materials interact with groundwater. A critical facet of An chemistry involves the radiolytic generation of hydrogen peroxide (H_2O_2), which can exert notable influence on the environmental dispersal of An by modifying the initial structure of the compounds and/or generate highly stable nanoscale species.[1] While peroxo-based hexavalent actinides (An) have been extensively investigated through the synthesis of uranyl cage clusters and mineral compounds, the literature description of tetravalent An peroxides is surprisingly lacking and limited to only a few Pu and Th compounds.[2-4] The interactions between H_2O_2 and Pu have been already described during the Manhattan project for several purposes (ex: oxidation state adjustment, purification, precipitation).[5] The stoichiometric addition of H_2O_2 to acidic Pu(IV) solutions was reported to generate the so-called "brown peroxo complex" which transitions to the "red peroxo complex" when increasing the concentration of H_2O_2. $[Pu_2(O_2)(OH)]^{5+}$ and $[Pu_2(O_2)_2]^{4+}$ have been respectively proposed as structures.[6] For higher amounts of H_2O_2, the precipitation of a green solid that may vary in composition and structure was described.[7] Until now, the precise structures for these complexes and solid precipitates have remained elusive and only postulated.

This presentation will discuss the recent preparation and structural characterization of an original water-soluble peroxo complex of Pu(IV). The latter was prepared by dilution of an acidic Pu(IV) solution aliquot into a large volume of an aqueous solution of concentrated H_2O_2 at pH= 1-2. Such a procedure resulted in the formation of a stable green solution devoid of any precipitate. Laboratory and synchrotron characterizations allowed acquiring structural information about this compound. Both the solution and solid precipitated from a saturated solution evidenced structural similarities that allowed us to propose a relevant structure for which the simulated EXAFS spectra perfectly matched with the experimental one.

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Curie temperature in uranium hydrides

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Recently, the increase of the Curie temperatures of transition metal doped α- and β-UH_3 was clearly showed [1], see Fig. 1. At the same time, it was analyzed that in the α-UH3, where the uranium is occupying one Wyckoff position (2*a*), the spin and orbital moments are collinear and along [111] crystal direction. In the β-UH_3 the uranium has two Wyckoff positions (2a and 6c), where the former one is again collinear along [111] direction, but the latter was determined to be slightly canted, *i.e.* non-collinear [2]. This leads surprisingly to the large differences in orbital contributions to the total moment between these two uranium sites. In this contribution using the density functional calculations [3] we determine the change of orbital and spin moments on uranium atoms as well as the phase stability of the transition metal (Tm, Tm=Zr, Mo, Ti, Pt) doped systems. Next, we demonstrate the effective charge transfer among U, H, and Tm atoms for pristine as well as doped β-UH_3 phases. This will affect the magnetic exchange interactions (J_{ij}'s) and therefore the Curie temperature (T_C). It is this correlation, *i.e.* J_{ij}s, T_C and the electronic structure of the doped systems that serves as the main subject of this contribution.

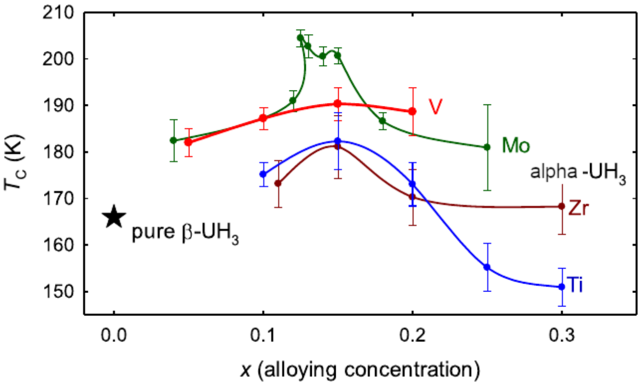

Fig. 1. The Curie temperature of transition metal doped α- and β-UH_3, courtesy of [1]

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Investigating the oxidation of epitaxial $(U_xTh_{1-x})O_2$ thin films

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Exposure of UO_2 to elevated temperatures in air will cause oxidation at the interface. There are several oxidative phases which make up this phase diagram, from UO_{2+x}, U_4O_9, U_3O_7, U_3O_8 and finally UO_3. This phase transition presents challenges for the effective interim and long-term storage of spent nuclear fuel, due to an initial volume contraction in the oxide lattice, followed by expansion as oxidation progresses. The crystallographic phase transition of UO_2 to U_3O_8, known as a topotactic transition, has been observed by J. Wasik and E. Lawrence Bright [1-3], occurring from the (0 0 2) face of cubic UO_2 matching with the (0 3 1) plane of orthorhombic U_3O_8. Therefore, it is possible to observe the mechanism of this transformation whilst maintaining crystallinity.

In this work, we analyse the effect of ThO_2 on the topotactic phase transformation of UO_2 to U_3O_8. Thoria is stable in a +4 oxidation state, making it insoluble and unable to form higher oxide species. Therefore, it is likely to reduce the overall oxidation rate in a U-Th mixed oxide system. A series of epitaxial [0 0 1] oriented $(U_xTh_{1-x})O_2$ thin films were fabricated using reactive DC magnetron sputtering, as part of the FaRMS facility at the University of Bristol, and were characterized using x-ray diffraction (XRD) and x-ray reflectivity (XRR). Oxidation experiments were carried out at the European synchrotron radiation facility (ESRF) ID 11 beam line. Samples were heated in-situ in air up to approximately 390°C, with structural changes and phase transformations measured using high resolution in-plane XRD. Experimental data was collected as 2D mappings of still XRD images, which were converted into reciprocal space maps (RSM). This technique allowed very high spatial resolution, enabling access to a large number of off-specular Bragg reflections. X-ray photoelectron spectroscopy (XPS) was also carried out on the films following heating, to provide post experimental chemical characterisation.

Results indicated a significant reduction in oxidation, with a $(U_{0.9}Th_{0.1})O_2$ sample showing no structural or chemical change over the course the experiment. Additionally, whilst lower ThO_2 content samples, $(U_{0.95}Th_{0.05})O_2$ and $(U_{0.97}Th_{0.03})O_2$, were partially oxidised to U_3O_8 there was a clear reduction in overall oxidation rate. The findings of this study aim to contribute to the advancement of research into the use of $(U_xTh_{1-x})O_2$ as an alternative nuclear fuel, as well as improving understanding into the longer term reactivity and spent fuel behavior at the back-end of the nuclear fuel cycle.

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Superconductivity and quantum criticality in actinide-iridium systems

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One century after the discovery of superconductivity, new properties and new materials are still emerging and actinides are key players in this field such asfor instance, the surprising coexistence of superconductivity with ferromagnetic order, observed only in uranium compounds: UGe_2 [1] and UIr [2] under pressure and URhGe [3] and UCoGe [4] at ambient pressure. Another remarkable discovery of this new century is the observation of superconductivity in transuranium compounds: $NpPd_5Al_2$ [5], $PuCoGa_5$ [6], $PuRhGa_5$ [7], $PuCoIn_5$ [8], $PuRhIn_5$ [9] and $AmCoGa_5$ [10]. These are illustrative cases of some unique properties of actinides that contribute to major advances in condensed matter science as well as to a better knowledge of so-called nuclear materials.

In order to probe the properties of neighboring systems of these compounds close to quantum critical points, we have investigated the transuranium analogues of UIr, a noncentrosymmetric pressure-induced ferromagnetic superconductor, on one hand, and the iridium and neptunium-iridium analogues of $PuCoGa_5$ and $PuRhGa_5$, the actinide superconductors with the highest critical temperatures, on the other hand. NpIr does not show any hint of any phase transition down to temperatures of 0.55 K and under pressures up to 17.3 GPa [11] but exhibits a large effective mass of the quasiparticles. PuIr does not display any anomaly in its magnetic susceptibility, specific heat or resistivity. On the contrary, $NpIrGa_5$ shows the occurrence of antiferromagnetic ordering at $T_N \approx 9.2$ K, but no evidence of superconductivity down to 2K. In $PuIrGa_5$, the residual resistivity strongly decreases under pressure (up to 9.5 GPa), but no superconducting transition is induced in this material, down to 1.4 K [12] and no magnetic transition is detected in the investigated temperature range.

It was shown that isoelectronic substitution of one of the elements in $PuCoGa_5$ is less destructive than other chemical substitutions (see e.g. [13]). In this work we will introduce quantitative values in the Doniach diagram of isolectronic 1:1:5 compounds, supporting the existence of 2 superconducting domes.

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Partial views on chemical bonding: Application to actinide molecular and solid-state systems

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Computational chemistry may be used to determine observables and also to derive non-observable quantities such as atomic charges, atomic spin densities, effective bond orders [1] and delocalization indices [2]. All these quantities are bond descriptors and somewhat related to the concept of ‘covalency’, an integrand part of the ‘chemical bonding’ folklore. Those covalency signatures may not fully correlate with bond distances [1], simply because other bonding mechanisms may be at play. However, it is also clear that the concept of chemical bonding needs no introduction here and neither do its interest for rationalizing molecular and solid-state system properties. Therefore, I will assume that there *is* an interest in determining chemical bonding indicators in general and also more specifically in the field of actinides.

In this presentation, I will try to propose a brief overview of chemical bonding indicators and also of the computational chemistry methodologies that can be necessary to properly determine these indicators in systems subject to both relativistic effects and electron correlation [3]. Though some concepts may be introduced by main-group element examples, I will also discuss extra complications that may arise in the field of actinides and present some new results on actinide molecular and solid-state systems. By essence, this presentation aims at being partly subjective; however, I will also attempt to trigger a consensus toward the general message that care should be given to start from an appropriate level of theory, choose a combination of properly defined bonding indicators, and not overinterpret the results.

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Nuclear Fuel and Pu Redox Studies from The Glenn T. Seaborg Institute at Idaho National Laboratory (U.S.A.)

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The Glenn T. Seaborg Institute at Idaho National Laboratory (INL-GTSI) focuses on advancing fundamental research in the actinide sciences by providing unique opportunities to early career scientists and engineers to gain experience studying the actinide elements and their associated systems. The INL-GTSI is built from three focus areas that are based on the expertise and supporting infrastructure at INL and include solid state chemistry and physics, solution phase chemistry and physics, and forensic and isotope science. INL is the lead Laboratory for nuclear energy research and development in the U. S. and the research on nuclear fuels performed under the INL-GTSI gives good examples of solid state studies. Uranium-Molybdenum (U-Mo) alloys are leading fuel candidates for conversion of high performance research and test reactors to low-enriched fuels. During irradiation, generated fission gas accumulates into bubbles and self-organizes into a gas bubble superlattice (GBS) that effectively stores fission gases and inhibits fuel swelling. A study on the early self-organizing behavior of the GBS shows that not only grain boundaries but the interfaces between the U-Mo matrix and uranium carbide (UC) impurities are important to GBS formation.[1] In solution, understanding the complex redox behavior of plutonium in aqueous environments is critical for establishing optimized nuclear waste reprocessing solvent systems and storage tank environments. INL-GTSI researchers have produced an experimentally validated multi-scale model of the gamma radiation induced behavior of plutonium ions in concentrated aqueous HNO3 solutions.[2] Here, gamma radiation effected only minimal steady state changes in the redox distribution of the plutonium oxidation states. The redox cycling between Pu(IV) and Pu(III) is demonstrated to be mediated by the •OH/NO3• radical oxidation of Pu(III) and the H2O2/HNO3 driven reduction of Pu(IV).

The INL-GTSI offers young researchers the unique chance to work directly with actinide bearing materials in a U. S. National Laboratory environment. Further topical areas of interest to the INL-GTSI include, but are not limited to, fundamental actinide properties, structure/property (electronic, magnetic, thermal) relations, actinide quantum criticality, f-electron interactions, electron correlations, computational studies, new phases, defect effects, interface interactions, isotope production and separation, forensic analytical chemistry, structure and dynamic properties of actinides in non-aqueous media, separations chemistry and kinetics for advanced nuclear fuel cycles, radiation effects, and innovative and advanced ligand design for complexation of the actinides.

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Absence of Induced Ferromagnetism in Epitaxial Uranium Dioxide Thin Films

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Recently, Sharma et al. [1] (Adv. Sci. 9, 2203473 (2022)) claimed that thin films (≈ 20 nm) of UO_2 deposited on perovskite substrates exhibit strongly enhanced paramagnetism (called “induced ferromagnetism" by the authors). Moments of up to 3 μ_B/U atom were claimed in magnetic fields of 6 T. We have reproduced such films and, after characterisation, have examined them with X-ray circular magnetic dichroism (XMCD) at the uranium M edges, a technique that is element specific. We do not confirm the published results. We find a small increase, as compared to the bulk, in the magnetic susceptibility of UO_2 in such films, but the magnetisation versus field curves, measured by XMCD, are linear with field and there is no indication of any ferromagnetism. The absence of any anomaly around 30 K (the antiferromagnetic ordering temperature of bulk UO_2) in the XMCD signal suggests the films do not order magnetically [2].

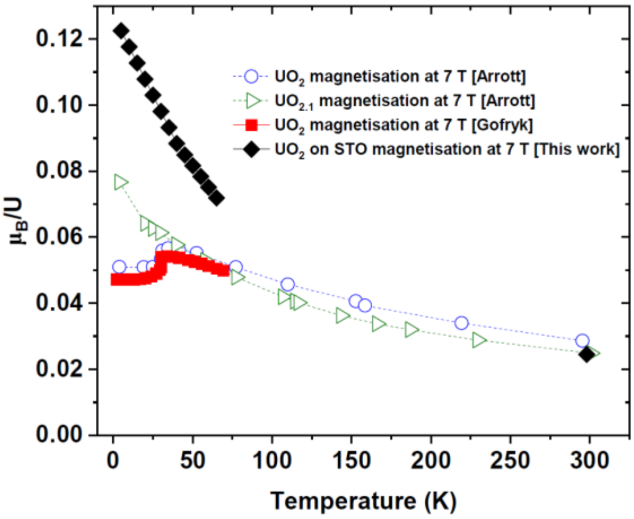

Fig. 1. Moment induced on U atom as a function of temperature at H = 7 T of UO_2 samples. Solid symbols are from stoichiometric UO_2 single crystals. Black diamonds from this work. Red squares from Ref. [3] Open symbols from polycrystalline materials. Open blue from stoichiometric $UO_{2.0}$ and open green triangles from $UO_{2.1}$, both from Arrott & Goldman [4].

Effect of ligands on Pa^{5+} and PaO^{3+} relative stabilities: A computational study

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The physical and chemical properties of solvated actinide complexes, including their speciation, bond nature with the surrounding environment, and thermodynamics and spectroscopic properties, hold significant implications for societal and industrial applications. The coordination of the actinides with ligands [1] affect these properties. Researchers, both experimental and theoretical, are interested in the coordination and properties exhibited by the f-elements with ligands.

Among the actinides, protactinium (Z=91) keeps on being specific because, depending on its oxidation state it can behave as ''f element" (Pa(VI)) or "d element" (Pa(V)). In solution, Pa(V) is dominating because Pa(IV) is unstable and can be directly oxidized to Pa(V) unless a strong reducing agent is present [2]. Pa(V) can exist in solution as Pa^{5+} and in some specific solutions it will form PaO^{3+} [3], but apparently it does not form the actinyl moiety PaO_2^+ which is not the case of their heavier neighbor elements, uranium, neptunium and plutonium.

In this work, with the use of the state-of-the-art quantum calculations, we investigate the two possible forms of Pa(V), namely PaO^{3+} and Pa^{5+} and the influence of coordinated ligands in order to determine the suitable experimental conditions to tune their relative stability. For that we consider two different stoichiometrically equivalent complexes $PaO(OH)_2(X)(H_2O)$ and $Pa(OH)_4(X)$ where X=OH^- , F^- (see Fig. 1), Cl^-, Br^-, I^-, NO_3^-, NCS^-, $C_2O_4^{2-}$ and SO_4^{2-} and compare their relative stabilities.[4]

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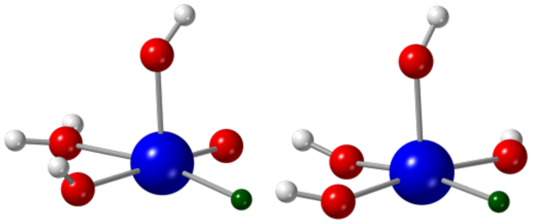

Fig. 1. Perspectives $PaO(OH)_2(F)(H_2O)$ and $Pa(OH)_4(F)$ in water (protactinium in navy blue, oxygen in red, hydrogen in white and fluoride in dark green).

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Searching for new arsenides

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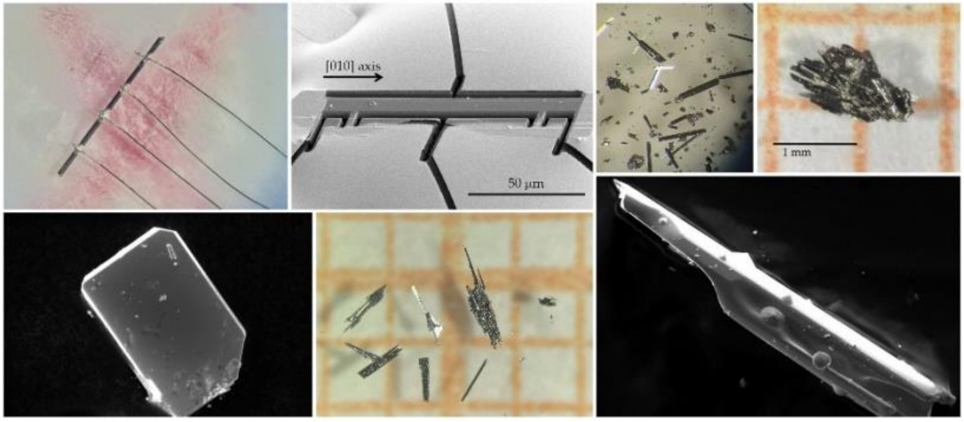
As new classes of superconducting materials emerge, puzzles of high-temperature superconductivity continue to be one of the pressing issues in condensed matter physics and solid-state chemistry. In particular, iron-arsenic superconductors still pose many open questions.[1] Given chemical similarities between *f*-elements and alkali/alkali earths, we can stipulate the formation of *f*-electron-based compounds with the architecture of iron-arsenides. And while these compounds are not likely to be high-T_c superconductors, we can use their small energy scale for an easy tuning from one ground state to another.

Surprisingly, only a handful of stoichiometries has been discovered among the lanthanide/actinide-iron-arsenic compounds[2,3] which is perhaps a result of synthesis complications imposed by toxicity, reactivity, and high vapor pressure of constituent elements. In this talk, I will discuss new compounds[4,5] that we have discovered within the U-Fe-As, Sm-Fe-As, Yb-Fe-As and Pr-Fe-As ternaries. All of the new arsenides were synthesized in single crystalline form, with some examples shown below.



I will discuss the interesting properties these new compounds show – negative thermal expansion, room temperature giant magnetoresistance, magnetic order above room temperature, complex magnetic configurations, as well as enhanced effective electron mass. I will then describe how these properties can be understood by relating the crystal structure of these novel materials to well-known pnictides.

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Coordination chemistry of Neptunium(V) and/or (VI) in organic phase in liquid-liquid extraction processes

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Liquid-liquid extraction processes are hydrometallurgical processes used in the nuclear fuel reprocessing cycle. The behavior of Neptunium (present in irradiated nuclear fuel) in liquid-liquid extraction processes is relatively poorly described, as its speciation in the organic phase is not perfectly known. It can be stabilized at various oxidation states (IV, V and VI) and can also form several types of complex in organic solution: inner-sphere complexes (with the extractant directly coordinated to the neptunium cation), outer-sphere complexes (with the extractant in the second sphere of the neptunium cation) [1]. The stoichiometry of the complex can also vary according to the extraction chemical conditions. In addition to monomeric complexes, Neptunium can also form more sophisticated polynuclear cation-cation complexes (CCI) [2, 3]. Although largely underestimated in actinide speciation, these polynuclear species actually have a major influence on actinide chemistry and reactivity. This is why there has been renewed interest in studying these species for several years.

In order to better understand the behavior of neptunium during its extraction in the organic phase, a coordination chemistry and speciation study, based on single-crystal XRD analyses and spectroscopic tools (IR, Raman, UV-vis) was carried out with diglycolamide (TEDGA). DFT calculations were also carried out to help interpret the experimental data on the one hand, and to deepen the description of the species obtained on the other. The data acquired throughout this study has enabled us to better describe the behavior of Neptunium during liquid-liquid extraction.

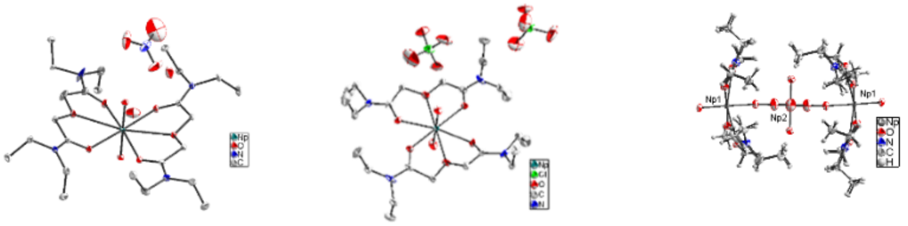

Fig. 1. Crystallographic structures of $[Np^{V}O_2(TEDGA)_2].NO_3$, $[Np^{VI}O_2(TEDGA)_2].2ClO_4$ and $[Np^{V}O_2(TEDGA)_2]_2\ [Np^{VI}O_2(NO_3)_2].2NO_3$

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Anisotropic Resonant Scattering at the uranium M_4 edge: Insights into U_2N_3

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The observation of anisotropic resonant x-ray scattering (ARS) opens new perspectives for describing the bonding in actinide materials. The method relies on intensity appearing at the resonant energy at Bragg reflections that are either forbidden or very weak. One can think of these reflections as arising from an almost exact cancellation of the spherical components of the charge densities (principally arising from the electrons in the radon core), so that the remaining aspherical contributions are observed. We have detected such intensity at the U M_4-edge in semi-metallic U_2N_3 epitaxial films [1].

ARS (also called Anisotropic Tensor of Susceptibility) has been practiced for many years in the case of the *K*-edge of transition metal systems [2]. However, the *K* edge has both dipole $2s \rightarrow 4p$ (E1), as well as quadrupolar $2s \rightarrow 3d$ (E2) channels, with ~equal strength. *L*-edges are more restrictive, but have low energies making diffraction experiments difficult. In certain cases, 2*p*-3*d* hybridization or orbital ordering may be clearly identified [2,3]. In the 5*f* series the situation is different, the *M*-edge E1 ($3d \rightarrow 5f$) transition is strong, with E2 ($3d \rightarrow 6g$ or 7*s*) being very weak, meaning that the transition to states which contribute to the bonding dominates. Additionally, the wavelength of 3.3 Å allows a number of Bragg reflections to be accessed. These unique properties give ARS a promising place for the study of bonding in 5*f* systems.

We will present the results of ARS measurements on a 200 nm single crystal U_2N_3 film using the I16 beamline at Diamond Light Source. U_2N_3 has a *bcc* bixbyite structure (Space group #206). There are two types of uranium in the unit cell: U1 sits at 8b position, with coordinates (¼,¼,¼) which is an inversion center and the second uranium, U2, sits at position 24d with coordinates (*x*,0,¼) where *x* ~ –0.02 and there is no inversion center at this site. This non-zero value of *x* gives rise to weak Bragg reflections. Examining the energy dependence of these reflections, shown in Fig. 1, we will show that the charge densities on the U1 and U2 sites differ, and that an aspherical distribution must be present around the U2 site.

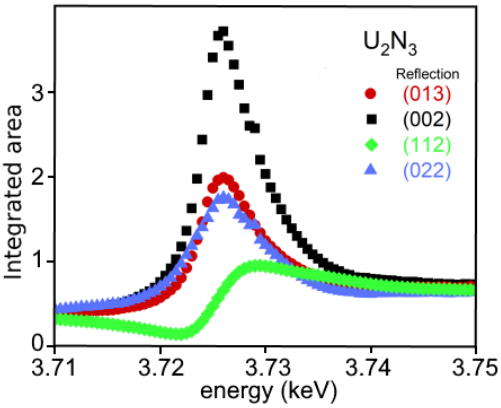

Figure 1: Energy scans of various reflections from U_2N_3. (013), (002), and (022) sense the *f''* term of the scattering factor from the E1 resonance at M_4. (112) shows a standard charge profile.

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Complex magnetic behaviours in $U_6TE_4Al_{43}$ (TE = V, Nb, Ta, Cr, Mo, W) with isolated U-dumbells

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The hexagonal $Ho_6Mo_4Al_{43}$ structure-type is characterized by the formation of dimers of magnetic *f*-element with *f-f* distance of about 3.4-3.5 Å, separated the ones from the others by more than 5 Å in all directions. Accordingly, competing magnetic interactions and frustration may occur between strong intra-dimer coupling and much weaker inter-dimer ones.

If rare earth-based members of this family have been intensively studied these last years, only few reports are available on uranium isostructural aluminides, despite the discovery of 6 of them more 30 years ago [1]. Polycrystalline samples of $U_6Nb_4Al_{43}$ undergo at least two magnetic transitions with a broad maximum at about 12 K and a Brillouin-like anomaly at 7 K, hinting at a ferromagnetic contribution [2]. Opposite, single crystals of $U_6W_4Al_{43}$ remain paramagnetic in the whole temperature domain, with a broad bump on the $\chi(T)$ curve measured perpendicular to the *c*-axis, usually seen in spin-fluctuation systems [3]. This difference of magnetic behavior and the lack of data in this isostructural family motivated its investigation.

The synthesis of pure polycrystalline samples turned out to be difficult due to the peritectoid formation of many 6-4-43 phases. Nevertheless, the paramagnetic nature of the secondary phases (UAl_3 and UTE_2Al_{20} [4]) implies that the transitions observed for each compound (TE = V, Cr, Mo) are intrinsic to the $U_6TE_4Al_{43}$ phases. Moreover, we benefited from the small temperature region where $U_6Nb_4Al_{43}$ is in equilibrium with Al to grow mm-sized single crystals using the Al-flux method (also for $U_6Ta_4Al_{43}$). The presence of at least 2 magnetic transitions at 7 and 12 K is confirmed by magnetic and specific heat measurements, yet with quite different character.

A summary of the main results of our investigation will be presented, starting from the 6-4-43 phase formation, to the crystallographic and physical properties of the different compounds.

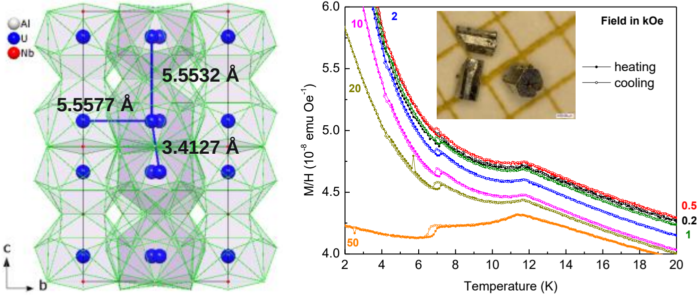

Fig. 1. Crystal structure (left) and magnetization perpendicular to the *c*-axis (right) of $U_6Nb_4Al_{43}$ single crystals grown by the Al-flux method.

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Investigation of HERFD-XANES sensitivity at the U L_3-edge to extract uranyl bond lengths

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X-ray spectroscopies offer valuable insights into the electronic structure of actinide compounds, especially when coupled with electronic structure calculations [1]. We report here the sensitivity of the high-energy-resolution fluorescence detected X-ray absorption near-edge structure (HERFD-XANES) method at the U L_3 edge [2,3] to investigate the local environment of U^{VI} and extract the uranyl bond distances. The theoretical interpretation of the uranyl structure is investigated by combining experimental data and calculations based on density functional theory. XANES calculations were performed using the finite difference method for near-edge structure (FDMNES) code. Our analysis indicates that shifts in the post-edge spectral features at the U L_3-edge are correlated to the uranyl polyhedron distances of the axial and equatorial oxygens, in good agreement with results published by Hunault *et al.* [4]. A comparison of distances determined using the well-known EXAFS approach suggests that HERFD-XANES, together with electronic structure calculations, might offer an alternative route. Additionally, to gain a broader perspective, we created an extensive dataset of uranyl structures and XANES calculations. This dataset is intended to be used to train machine learning models for routinely extracting uranyl bond lengths during synchrotron experiments. We present the project's road map, which aims to make the most use of the experimental data to obtain structural information.

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Spent nuclear fuel treatment by fluidized bed precipitation

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The nuclear industry has long been committed to limiting waste and the consumption of raw materials, by reusing plutonium, a fissile material coming from UOX (UO_2) fuel processing, in MOX (Mixed Oxide UO_2-PuO_2) fuels. In the current industrial process, the used UOX fuels are dissolved in nitric acid. The valuable materials, uranium and plutonium, are extracted from solution, then plutonium is separated from uranium and precipitated as oxalate in a vortex reactor, before calcination as oxide. The implementation of recycling to MOX fuels would increase raw material savings and reduce the radiotoxicity of waste over the long term, however it involves an increase of the annual flow of plutonium to be processed. As the current precipitation process in vortex reactor, is not the most optimized for processing larger quantities of plutonium, the exploration of new processes is encouraged. The choice fell on the fluidized bed process. In the course of this study, a fluidized-bed precipitation plant (semi-pilot) was designed and implemented to study the precipitation of neodymium oxalate, used as an inactive simulant of plutonium oxalate (Fig. 1), with the aim of producing powders with controlled properties, with good flowability, narrow particle size distribution and reduced number of fine particles. To this aim, a study was carried out over a few hours to investigate precipitation and the influence of reactor geometry and phase flow, hydrodynamic conditions and operating protocols as important factors in controlling the quality of the precipitates formed.

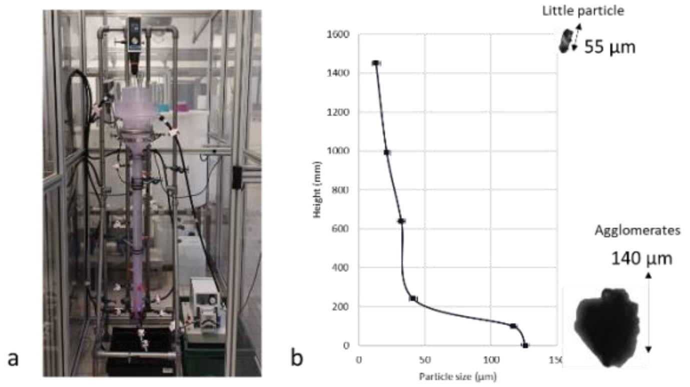

Fig. 1 : Photograph of the fluidized bed (a) and particle size distribution along the column (b)

After 24 hours, mass setting and clogging were observed. The presence of agitation helped to limit mass settling in the column and allow a continuous production over several hours. At the end of the first 24 hours under agitation, sampling revealed the distribution of particles along the reactor and their shape. While only the finest, needle-shaped particles are present at the top, as they are carried along by the fluid, the largest particles (spherical agglomerates) remain at the bottom of the reactor. The properties of the agglomerates, drawn off at the bottom of the reactor, will determine the effectiveness of the fluidized bed as an alternative precipitation process.

The influence of aluminium doping on the structure and chemical state of [001] UO_2

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The safe disposal of the United Kingdom's radioactive waste in a geological disposal facility (GDF) is a high-priority [1]. Due to the complex nature of spent nuclear fuel (SNF), experimental studies on the mechanisms that govern the corrosion of SNF are inherently challenging [2]. A range of doped-UO_2 fuel type exist in interim storage within the current inventory of SNF including Al_2O_3 and Cr_2O_3 doped UO_2. The in-reactor behaviour of these doped fuel types has been previously demonstrated for advanced technology fuel purposes [3]. If fuel is to be stored in a GDF, it is imperative that the corrosive behaviour of these compounds is well understood and predicted for long-term storage [4]. In this regard, thin films offer a significant advantage when investigating corrosion behaviours, as these systems provide idealised surfaces on which single parameter studies can be conducted. By varying the growth parameters, stoichiometry, grain size, and crystallographic orientation can be controlled. Therefore, allowing the doped-fuel within interim storage to be replicated [5].

Here we present an investigation into the structural and chemical state of epitaxial [001]-UO_2 thin films doped with aluminium. Using DC magnetron sputtering, the U-Al-O system has been investigated by doping UO_2 with 1, 2, and 3 wt % of aluminium. Using x-ray diffraction and x-ray spectroscopy techniques at the Facility for Radioactive Materials Surfaces (FaRMS), we have probed the structural and chemical influence of aluminium on these engineered surfaces, making comparisons to pristine UO_2 and U_3O_8.

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Photo- and Radio-luminescences of ThF_4 in UV and visible ranges

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Exciting a nucleus typically requires a relatively large energy probe. Almost 50 years ago it was deduced that the first excited state of the ^{229}Th isotope could be found in the energy domain of lowest atomic transitions. The ensuing possibility to interrogate the ^{229}Th nuclear transition using highly monochromatic lasers suggested feasibility of a nuclear clock [1,2] that would improve the precision of time-keeping by up to two orders of magnitude [3]. The first direct observation of the ^{229}Th isomer (^{229m}Th) provided an excitation energy of 8.3 eV, but its lifetime was only 7 μs due to the Internal Conversion (IC) decay. For suppressing IC, it is enough to embed ^{229}Th atoms in an insulating crystal with a bandgap higher than the de-excitation energy [4]. In the framework of GRaDeTh229 EU project we proposed an experiment to search for the excitation and γ-decay of ^{229m}Th in a novel ThF_4 matrix [5]. However, before implementing ^{229}Th doping the main sources of photon emitting background in ThF_4 film had to be established. To this end, commercial crystalline thin films ThF_4 were tested at the JRC of Karlsruhe using a specifically designed apparatus.

Photo- and radio-luminescences of two different thin ThF_4 films have been measured in UV and visible ranges. The two samples had different thicknesses of 200 and 300 nm and different substrates made of Si and ZnSe. In UV range both luminescences are small normalized to the tested ThF_4 volume. Also, visible luminescences from ThF_4 are relatively small, but environmental background of photo-luminescence in visible range has to be improved. The obtained results allow to propose the thin ThF_4 crystal as the target for the ^{229m}Th gamma decay search and as an operating medium for the future solid state nuclear clock. Moreover, the apparatus developed at JRC of Karlsruhe is ready for the direct ^{229m}Th excitation and gamma decay measurements. The measurements clearly indicate that usage of a small and thin ThF_4 film allows to reduce backgrounds, while the signal may be kept at the same level increasing the ^{229}Th enrichment. The results on photo- and radio-luminescence measurements in ThF_4 will be presented together with prospective of direct ^{229m}Th excitation test.

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Towards deciphering the nucleation and growth stages of colloidal PuO_2 nanoparticles in aqueous solution

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A better understanding of the structural and physico-chemical properties of colloidal nanoparticles of plutonium oxide (PuO_2) is of interest not only for elucidating their environmental migration patterns but also for the potential development of advanced nuclear fuels.[1,2] Colloidal suspensions resulting from the hydrolysis of Pu(IV) are now described as crystalline PuO_2 nanoparticles measuring approximately 2 nm in diameter and exhibiting a structural disorder associated to a surface effect.[3] Although a Pu(IV) hexameric cluster has been recently identified as a reaction intermediate during the formation of these nanoparticles, questions remain regarding their general formation mechanism.[4] In this context, small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS, including XANES/EXAFS) available at synchrotron SOLEIL/MARS beamline appear particularly relevant for characterizing both the morphology and atomic environment variations occurring during the nucleation and growth stages of PuO_2 colloidal nanoparticles. To monitor the hydrolysis of Pu on the facility, a heating module (Figure 1), meeting the specifications of the installation for handling radioactive samples at controlled temperatures, has been developed. The kinetic monitoring of Pu(IV) hydrolysis will then be achieved through the thermal decomposition of a complexing agent stabilizing Pu(IV). Preliminary investigations have demonstrated the feasibility of the chemical approach, where the degradation of a Pu(IV) peroxide complexe at approximately 80°C, followed by the formation of Pu(IV) colloids, have been confirmed by UV-Vis absorption spectroscopy.

This presentation will present the progress on this project by discussing the steps that were necessary for the development of the heating module as well as the preliminary results obtained with Pu and Zr.

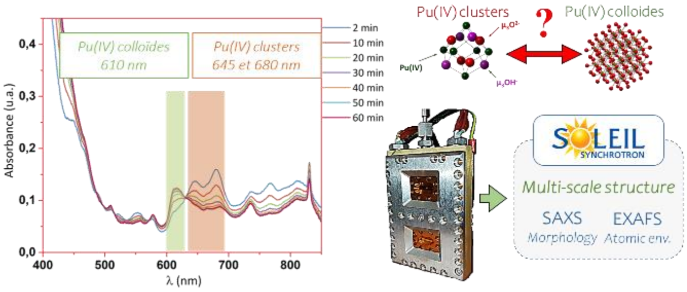

Figure 1: Probing the nucleation and growth of PuO_2 nanoparticles in aqueous solution using sample-holder heating module

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Polyepitaxial grain matching in UO_2 reveals a topotactic phase transition in the uranium oxides

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The way that oxides (and for that matter, nitrides, carbides and many other compounds) transform between stoichiometric phases, is a hugely complex, but important materials problem, where the crystallographic phase transformations are far from obvious. This submission focusses on the oxidation of UO_2 to U_3O_8, but the findings we present here could have consequences for a large number of other crystal systems.

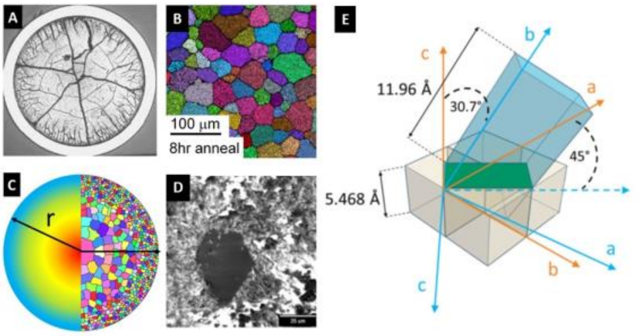

Fig. 1. Panel A shows an example UO_2 fuel pellet structure, which is recreated in schematic form to show grain sizes in panel C, B shows an EBSD reconstruction of an engineered film of UO_2. Panel D shows an in-situ SEM image after oxidation, where the only intact area left was from an originally [001]-oriented UO_2 grain. Panel E shows the relationship between the (001)-UO_2 and (130)-U_3O_8 planes.

We will discuss a novel synthesis route to engineering grains in polycrystalline systems, reducing a 3D structure to a lateral 2D morphology, constant in the growth direction, which we term ‘polyepitaxy’ of UO_2 (see figure 1, A-C). By observing the oxidation of these polyepitaxial UO_2 samples (figure 1, panel D), we have deduced a unique relationship between the (001) UO_2 plane and the (130) plane of U_3O_8 (figure 1, panel E). There is a fully reversible ‘topotactic’ transformation along the UO_2 [001] axis, which solves a long-standing debate in the oxidation process and could shed light, more generally, on the mechanism of transformations between stoichiometric phases. The synthesis of polyepitaxial films could provide a route to uncovering more topotactic phase transitions in other classes of materials.

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Influence of the crystal structure and nature of the ligands on the valence of uranium in chalcogenides compounds

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Thanks to its 5*f* orbitals, uranium benefits from several valence states, from U^{3+} to U^{6+}, in inorganic compounds and possesses a wide crystal-chemistry. The radial expansion of these orbitals leads to energetically close crystal field (dominating in the case of 3*d* elements) and spin-orbit (dominating in the case of 4*f* rare earths) interactions, and subsequent rich and exotic physical properties [1] (e.g. coexistence of superconductivity and ferromagnetism). Associated with a chalcogen element (Q = S, Se, Te), uranium forms inorganic compounds characterized by various crystallographic structures leading to unique uranium polyhedral structures [2] with e.g. the presence of $(S^2)^{2-}$ dimers.

However, due to the limited number of known uranium chalcogenides, practically no experimental information on the nature of the U-Q bond is available in the literature. As a consequence, understanding the localization of 5*f* electrons of actinides in solid-state, a great challenge for theoretical physicists, remain limited to the study of oxides [3] and intermetallic materials.

To increase the field of investigation, some binary uranium chalcogenides (S, Se, Te) have been characterized and studied by HERFD-XANES and RIXS spectroscopies at the U M_4 edge. These preliminary measurements enabled us to determine the oxidation states of uranium for these binary compounds. Moreover, in the case of sulfide compounds, the study has been extended to ternary compounds from U-M-S systems (M = 3*d* metal) [4] with the aim to investigate their physical properties and to have a more general understanding of the chemistry of such class of materials.

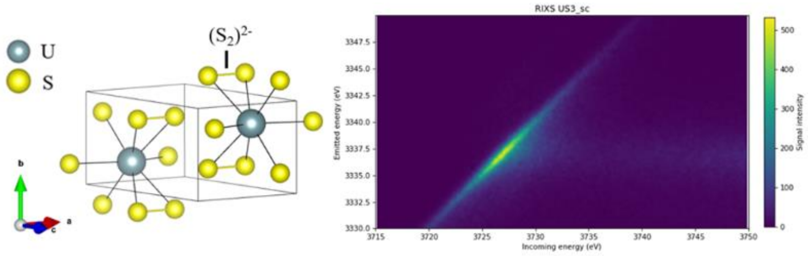

Fig. 1. Crystal structure and U 3*d*4*f* RIXS map of US_3 $(P2_1/m)$

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