

The logo features the text 'ATAS - AnXAS' in blue, with '2024' in yellow. A stylized orange waveform is on the left, and a blue waveform is on the right.

# ATAS - AnXAS 2024

6<sup>th</sup> International  
Workshop on Advanced  
Techniques in Actinide  
Spectroscopy

10<sup>th</sup> International Workshop on  
Speciation, Techniques, and  
Facilities for Radioactive Materials  
at Synchrotron Light Sources



## **ATAS - AnXAS 2024 – 2<sup>nd</sup> Joint Workshop**

KIT Campus North, Karlsruhe, Germany

October 7 – 11, 2024

### **Proceedings**

INE SCIENTIFIC WORKING DOCUMENTS 08

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*ATAS - AnXAS 2024 participants during the excursion at Technik Museum Speyer (photo by P. Müller, KIT-INE)*

## Preface

The international ATAS - AnXAS workshop – organized by the Institute for Nuclear Waste Disposal (KIT-INE) – was held in 2024 at Karlsruhe Institute of Technology in the FTU Auditorium, KIT Campus North, from October 7 to 11. ATAS - AnXAS 2024 has been the second joint workshop since merging the formerly separate ATAS and ActinideXAS series in 2022. Both workshops date back to original initiatives by Helmholtz-Zentrum Dresden-Rossendorf (HZDR). ActinideXAS was launched in 1998 at the ESRF in Grenoble (France) to focus on work at emerging dedicated synchrotron labs licensed to handle radionuclide materials at beamlines. The follow-up events took place at LBNL (USA), FZK (Germany), SOLEIL (France), SPring-8 (Japan), PSI (Switzerland), and Oxford University (UK). The series of ATAS workshops started in 2012 at HZDR in Dresden (Germany) in the context of a comprehensive round robin test comparing actinide speciation methods at labs around the world – followed by events at HZDR, PNNL (USA) and Nice (France). ATAS extended the scope to other advanced, not solely synchrotron-based speciation methods, with an additional emphasis on quantum chemistry. The first joint workshop was held in 2022 – again at the ESRF in Grenoble – feeling the strong need to catch up with personal exchange between experts and novices in the fields of actinide science, radionuclide speciation, spectroscopy and theory after the forced break due to the pandemic. As from the beginning the audiences of both ATAS and ActinideXAS had been largely overlapping, the scientific advisory boards decided to keep the format as a five-day joint workshop for Karlsruhe 2024 and as well for the 3<sup>rd</sup> joint event envisaged to be held at Lawrence Berkeley National Lab at the beginning of 2027.

ATAS - ANXAS 2024 attracted a total of 94 participants from 10 countries: Germany, France, United States, United Kingdom, Republic of Korea, Finland, Japan, Switzerland, Canada and China. The meeting featured 14 topical sessions structured by five invited plenary talks – one scheduled to open each day – 15 invited keynote lectures and 40 contributed oral presentations. These lectures were covering a broad range of radionuclide speciation methods and application fields (from radio-toxicology and medicine to the characterization of nuclear waste forms), where the unabatedly growing impact of

high-resolution X-ray fluorescence detection studies was remarkable. As well noteworthy was the high degree of maturity reached by computational chemistry tools in support of 5f element spectroscopies, e.g., to disentangle the wealth of transition features in resonant inelastic X-ray scattering. The conference program was complemented by an evening poster session held at the premises of the KIT Light Source – the local synchrotron radiation facility operated at the Karlsruhe Research Accelerator (KARA). Preceding the presentation and intense discussion of a total of 22 poster contributions was an introduction into the dual mission of KARA by accelerator physicist Bastian Härer of IBPT (KIT Institute for Beam Physics and Technology): as light source for KIT users and their cooperation partners as well as accelerator technology test facility. The poster session was completed by the possibility to visit 5 beamline stations (SUL-X, CAT-ACT, X-SPEC, NANO, IMAGE) operated by KIT institutes IPS, IKFT and INE.

A visit of the popular Technik Museum Speyer in the nearby Palatinate region was organized as workshop excursion, reached by a 40 minute bus ride from the conference venue. The evening started with a reception and a self-guided tour of the space flight exhibition – with a special section focusing on the benefits of space technology for our everyday life – and was concluded by a buffet dinner in the “Pfälzer Weindorf” on-site the museum’s vast exhibition area. An instructive as well as entertaining dinner talk was given by David L. Clark from Los Alamos National Lab, USA, titled "Historical perspectives on the development of actinide XAS".

Three young participants of ATAS - AnXAS 2024 in their early career phase as PhD students have been selected to receive an award for their work presented as poster or oral contribution.

Awards for the two best posters (voted for by all participants of the poster session):

- **Emily Reynolds** (KIT-INE, Germany) – “Development and Application of a Microfluidic Set-Up for In-Situ Studies of Formation Kinetics of La- and U-Complexes Using High Resolution Spectroscopic Methods”
- **Nathan M. Alcock** (University of Manchester, UK) – “Determination of actinide central-field covalency with resonant inelastic X-ray scattering (RIXS)”

Award for the best young scientist oral presentation (selected by the scientific advisory board):

- **Janik Lohmann** (Universität Mainz, Germany) – “Investigation of gluconate complexation with trivalent Eu, Pu and Am using CE-ICP-MS”

All awards have been kindly sponsored by RSC Advances.

Susanne Fanghänel & Jörg Rothe

Eggenstein-Leopoldshafen, October 2024

Monday (07 October 2024)

## Conference Program

10:30	<b>Registration</b>	
12:00	<b>Lunch</b>	
14:00	<b>Welcome</b>	
<b>Session 1</b>	<b>Spectromicroscopy</b>	
14:20	Application of synchrotron-based microbeam techniques for studying the reactive transport of actinides in clay rock <u>T. Reich (Plenary)</u> (Germany)	<b>S1-T1</b>
15:00	Chemical tomography of Np and Pu diffusion in Opalinus Clay <u>M. Breckheimer, S. Amayri, D. Ferreira Sanchez, D. Grolimund, M. G. Makowska, T. Reich</u> (Germany)	<b>S1-T2</b>
15:20	Chemical imaging and applications using high energy resolution fluorescence detection for the actinides <u>S. M. Webb, N. P. Edwards</u> (USA)	<b>S1-T3</b>
15:40	Quantifying F-Orbital Overlap with Ligand K-edge XAS <u>S. G. Minasian, J. A. Branson, C. H. Booth, Michael A. Boreen, J. Arnold, J. Autschbach, E. R. Batista, J. A. Bradley, A. S. Ditter, O. S. Gunther, J. Kasper, S. A. Kozimor, W. W. Lukens, D. R. Russo, D.-C. Sergentu, D. K. Shuh, Patrick W. Smith, P. Yang</u> (USA)	<b>S1-T4</b>
16:00	Coffee break	
<b>Session 2</b>	<b>Spectromicroscopy / Radiotoxicology</b>	
16:20	AI-assisted lab-on-a-chip experiments: Setting new frontiers in radio-geochemistry <u>J. Poonoosamy, A. Kaspor, C. Schreinemachers, N. I. Prasianakis, E. Curti, G. Deissmann, P. Kowalski, S. V. Churakov, D. Bosbach</u> ( <b>Keynote</b> ) (Germany)	<b>S2-T1</b>
16:50	Uranium and Plutonium interaction with calcium-binding sites of proteins <u>S. Sauge-Merle, L. Daronnat, R. Pardoux, M.-R. Beccia, E. Faux, N. Brémond, N. Boubals, P. Guilbaud, T. Dumas, D. Lemaire, P. Moisy, D. Moreno Martinez, V. Hoffeltz, J. Pansier, C. Berthon, P. Lorenzo Solari, J. Aupiais, L. Berthon, C. Berthomieu</u> ( <b>Keynote</b> ) (France)	<b>S2-T2</b>
17:20	Spectromicroscopic characterization of lanthanide-contaminated mammalian cells <u>B. Schacherl, A. Selvam, J. A. Branson, T. Arino, D. M. Jorgens, M. Kang, J. Wang, A. Ditter, R. J. Abergel, S. G. Minasian</u> (USA)	<b>S2-T3</b>
17:40	Impact of Eu(III) on rat kidney cells in the absence and presence of the decorporation agents DTPA and 3,4,3-LI(1,2-HOPO) <u>C. Senwitz, A. Heller, B. Drobot, M. Vogel, T. Stumpf</u> (Germany)	<b>S2-T4</b>
18:00	Combining in vitro cell culture and luminescence spectroscopy: A powerful tool for studying An(III) impact on and speciation in cells <u>A. Heller, C. Senwitz, B. Drobot, T. Stumpf, S. Taut, M. Acker</u> (Germany)	<b>S2-T5</b>
18:20	End of day 1	

## Tuesday (08 October 2024)

### Session 3 Speciation beyond X-rays

09:00	Speciation of lanthanides and actinides by time-resolved laser fluorescence spectroscopy - Developments from the 1990s to the present day (in honor of J. I. Kim) <u>P. J. Panak (Plenary)</u> (Germany)	S3-T1
09:40	Are actinyl good paramagnetic probe for structural studies by NMR spectroscopy? <u>C. Berthon, H. Bolvin</u> (France)	S3-T2
10:00	Influence of chelating agents on lanthanide and actinide speciation in artificial bodyfluids <u>A. Barkleit, S. Friedrich, D. Butscher, J. Kretzschmar, B. Drobot, R. Steudtner, T. Stumpf</u> (Germany)	S3-T3
10:20	Investigation of gluconate complexation with trivalent Eu, Pu and Am using CE-ICP-MS <u>J. Lohmann, S. Zenker, N. Blum, A. Wiebe, M. Kumke, T. Reich</u> (Germany)	S3-T4
10:40	Coffee break	

### Session 4 Actinide electronic structure / Radioecology

11:00	An entropic approach to multiconfigurational ground states <u>M. Beaux (Keynote)</u> (USA)	S4-T1
11:30	Unravelling the actinides 5f enigma with X-Ray emission spectroscopy <u>J. G. Tobin</u> (USA)	S4-T2
11:50	Speciation and imaging in radioecology <u>J. Aupiais, M. R. Beccia, C. Den Auwer, A. Jeanson, M. Maloubier, M. Monfort, C. Moulin, B. Reeves, P. L. Solari, R. Stefanelli, D. Suhard</u> (France)	S4-T3
12:10	In vivo speciation and molecular mechanisms of the uptake of radioactive metal ions by <i>A. nodosum</i> <u>M. Zerbini, P. L. Solari, F. Orange, A. Jeanson, C. Leblanc, M. Metian, C. Den Auwer, M. R. Beccia</u> (France)	S4-T4
12:30	Lunch break	

## Tuesday (08 October 2024)

### Session 5 Actinide complex stability / Synchrotron facility reports

14:00	Theoretical studies of the coordination structures, stabilities and electronic spectra of Cm <sup>3+</sup> species at the mineral-water interface <i>J. Su, Z.-Q. Chu, R.-Y. Zhu (Keynote) (China)</i>	S5-T1
14:30	Molecular electrochemistry of actinides: Redox and reactivity of Uranium, Neptunium, and Plutonium complexes <i>J. Blakemore (Keynote) (USA)</i>	S5-T2
15:00	Coffee break	
15:20	Probing actinide chemistry and structure with X-rays at the SOLEIL synchrotron: MARS and the other beamlines <i>M. O. J. Y. Hunault, T. G. Burrow, P. Piau, W. Breton, D. Menut, P.-L. Solari (France)</i>	S5-T3
15:40	Combining multiple chemical and physical imaging techniques for comprehensive insight into radioactive specimens at the microXAS beamline and future microXAS 2.0. <i>M. Makowska, D. Grolimund, D. Ferreira Sanchez, B. Meyer, M. Birri, A. Diaz, R. Bruetsch, J. Bertsch, C. Schneider, G. Kuri, L. I. Duarte, S. Bhattacharya, O. Yetik, M. Pouchon (Switzerland)</i>	S5-T4
16:00	Soft X-ray emission and resonant inelastic X-ray scattering for actinide research <i>L. Weinhardt, C. Wansorra, R. Steininger, H. Ramanantoanina, T. S. Neill, R. S. K. Ekanayake, A. Seibert, T. Gouder, N. Palina, J. Rothe, D. Hauschild, T. Vitova, C. Heske (Germany/USA)</i>	S5-T5
16:20	Synchrotron based hard X-ray spectroscopy for radionuclide research at the KIT light source <i>K. Dardenne, J. Göttlicher, T. Prüssmann, J. Rothe, R. Steininger, T. Vitova (Germany)</i>	S5-T6
16:40	<b>Transfer to KARA</b>	
17:00	<b>Introduction to KARA</b> <i>B. Härer (Germany)</i>	
17:45	<b>Poster session with refreshments</b>	
20:00	<b>End of day 2</b>	

## Tuesday (08 October 2024)

### Poster Presentations

- P-1 Development and application of a microfluidic set-up for in-situ studies of formation kinetics of La- and U-complexes using high resolution spectroscopic methods  
*E. Reynolds, R. S. K. Ekanayake, B. Schacherl, C. Kim, X. Gaona, H. Kaufmann-Heimeshoff, R. Steininger, J. Göttlicher, T. Prüssmann, H. Geckeis, T. Vitova (Germany)*
- P-2 Relativistic quantum chemical investigation of actinide covalency measured by electron paramagnetic resonance spectroscopy  
*M. S. Oakley, L. Birnoschi, E. J. L. McInnes, N. F. Chilton (UK)*
- P-3 Experimental characterization and theoretical modelling of X-ray absorption spectra of Protactinium(V) complexes  
*T. Shaaban, C. Le Naour, H. Oher, T. Aubert, P. L. Solari, T. Burrow, M. Hunault, A. S. P. Gomes, F. Réal, V. Vallet, M. Maloubier (France)*
- P-4 Developing Uranium L3 HERFD-XANES and RIXS to investigate Uranium biogeochemical processes  
*C. Waters, T. S. Neill, K. Morris, N. M. Alcock, M. L. Baker, J. F. W. Mosselmans, K. Ignatyev, S. Shaw (UK)*
- P-5 Using experimental actinide chemistry to solve technical challenges in spent fuel and nuclear material management within the nuclear decommissioning authority group  
*E. M. B. MacCormick, C. R. T. Smylie, R. Bernard, H. M. Steele, R. M. Orr, E. K. Gibson, J. H. Farnaby (UK)*
- P-6 Solubility, speciation and thermodynamics of PuCO<sub>3</sub>OH(cr) in carbonate containing NaCl solutions  
*P. Müller, D. Fellhauer, D. Schild, K. Dardenne, J. Rothe, M. Altmaier, X. Gaona, H. Geckeis (Germany)*
- P-7 Solubility, redox speciation and sorption of Sn in cement systems  
*N. Huber, X. Gaona, K. Dardenne, T. Prüssmann, M. Altmaier, H. Geckeis (Germany)*
- P-8 Spectroelectrochemical coupling to study Tc speciation in solution  
*N. Mayordomo, A. Bureika, J. Kretzschmar, K. Müller (Germany)*
- P-9 Deciphering crystal-field excitations with HR-RIXS  
*M. S. Huzan, N. M. Alcock, M. A. Dunstan, K. S. Pedersen, M. L. Baker (UK)*
- P-10 Determination of actinide central-field covalency with 3d4f resonant inelastic X-ray scattering (RIXS)  
*N. M. Alcock, M. S. Huzan, T. G. Burrow, M. L. Baker (UK)*
- P-11 Spectroscopic investigations on the behavior of irradiated light water reactor fuels during prolonged dry interim storage and final disposal  
*K. Dardenne, M. Herm, T. König, Y. Lin, V. Metz, T. Pruessmann, J. Rothe, D. Schild, A. Walschburger, H. Geckeis (Germany)*
- P-12 Monitoring the formation of ternary surface complexes and surface precipitates of U(VI) on zirconia by vibrational spectroscopy  
*H. Foerstendorf, I. Jessat, K. Heim, N. Jordan (Germany)*
- P-13 Investigation of Thorium-based generator concepts – improvements, labeling and speciation  
*K. Maurer, B. Schacherl, M. Schäfer, Y. Remde, Ha. Taş, F. Geyer, A. Fried, S. Happel, M. Benešová-Schäfer, T. Vitova, H. Geckeis (Germany)*



## Tuesday (08 October 2024)

- P-14 A compact X-ray emission spectrometer at the SUL-X beamline of the KIT synchrotron radiation source: Implications for lanthanide and actinide research  
*J. Goettlicher, T. Spangenberg, T. Pruessmann, B. Schacherl, R. S. K. Ekanayake, E. M. Reynolds, H. Kaufmann-Heimeshoff, C. Y. Reitz, H. Ramanantoanina, T. Vitova, R. Steininger (Germany)*
- P-15 On the Sr coordination, Sr K-edge absorption spectra, and solubility product constants of Sr-bearing calcite  
*A. S. Kim, A. S. Son, B. S. P. Hyun, A. K. D. Kwon (Korea)*
- P-16 Ab-initio Pourbaix diagrams for U-H-O system  
*A. S. Son, B. S. P. Hyun, A. K. D. Kwon (Korea)*
- P-17 The actinide chamber at the X-SPEC beamline  
*R. S. K. Ekanayake, N. Palina, H. Ramanantoanina, M. Blankenship, C. Vollmer, C. Wansorra, R. Steininger, D. Hauschild, C. Heske, L. Weinhardt, T. Vitova (Germany)*
- P-18 Soft and hard x-ray spectroscopy with a novel calorimetric superconducting quantum sensor  
*M. Blankenship, K. Bitsch, R. Steininger, C. Wansorra, D. Hauschild, N. Arldt, C. Sandrell, F. Adam, M. Müller, T. Vitova, S. Kempf, L. Weinhardt, C. Heske (Germany)*
- P-19 Spectroscopic study of the Pu(III)-ISA complex in weak acidic conditions  
*S. Cho, U. H. Yoon, H. Cho, K. Jeong, H.-K. Kim, H.-R. Cho (Korea)*
- P-20 Complexation of U(VI) with N-donor ligands studied by high energy resolution X-ray spectroscopy and computations  
*C. Reitz, X. Zhang, C. Vollmer, K. Dardenne, T. Prüßmann, T. Sittel, P. Panak, T. Vitova (Germany)*
- P-21 Electroanalytical and spectroscopic investigations of redox chemistry in heterobimetallic Uranyl crown ether complexes  
*A. Ervin, R. Golwankar, M. Makos, E. Mikeska, H. Kaufmann-Heimeshoff, T. Vitova, V.-A. Glezakou, J. Blakemore (USA)*
- P-22 Complexation of Cm(III) with silicates at variable ionic strengths and pH values  
*S. Özyagan, T. Sittel, P. J. Panak (Germany)*

## Wednesday (09 October 2024)

### Session 6 Design of radiopharmaceutical and separation agents

- 09:00 Targeted radionuclide therapy: the promise and challenges of short-lived alpha-emitting actinides  
*A. Rigby, A. G. Cosby, J. J. Woods, J. N. Wacker, T. Arino, J. V. Alvarenga Vasquez, K. E. Martin, R. K. Strong, R. J. Abergel (Plenary) (USA)* **S6-T1**
- 09:40 Computational ligand design for targeted alpha therapy  
*C. Li, I. Carbo-Bague, C. F. Ramogida, G. Schreckenbach (Canada)* **S6-T2**
- 10:00 Interaction of Ac<sup>3+</sup>-based radiopharmaceutical with Somatostatin receptor revealed by molecular dynamics simulations  
*S. Tsushima (Germany)* **S6-T3**
- 10:20 Polypyridyl extractant design for actinide separation  
*X. Zhang, S. L. Adelman, B. T. Arko, C. R. De Silva, J. Su, S. A. Kozimor, V. Mocko, J. C. Shafer, B. W. Stein, G. Schreckenbach, E. R. Batista, P. Yang (USA/Canada)* **S6-T4**
- 10:40 Coffee break

### Session 7 Data analysis and method development

- 11:00 Using our artificial intelligence tools for analysis of materials characterization data pertaining to nuclear systems: Corrosion and radiation damage  
*J. Terry (Keynote) (USA)* **S7-T1**
- 11:30 Fully automated procedure for XANES and EXAFS processing based on IgorPro  
*S. Mangold (Germany)* **S7-T2**
- 11:50 Exploring f-electron systems through HERFD and RIXS  
*K. O. Kvashnina (France/Germany)* **S7-T3**
- 12:10 New high-resolution X-ray spectroscopic tools for investigating 5f electrons in actinide compounds  
*H. Kaufmann-Heimeshoff, B. Schacherl, M. Tagliavini, J. Göttlicher, M. Mazzanti, K. Popa, O. Walter, T. Prüssmann, C. Vollmer, A. Beck, R. S. K. Ekanayake, J. A. Branson, T. Neill, D. Fellhauer, C. Reitz, D. Schild, D. Brager, C. Cahill, C. Windorff, T. Sittel, H. Ramanantonina, M. Haverkort, T. Vitova (Germany)* **S7-T4**
- 12:30 Lunch break

## Wednesday (09 October 2024)

### Session 8 High resolution X-ray spectroscopy: theory and application

- 14:00 Origins of actinyl XAS features: Application to  $\text{NpO}_2^{2+}$   
*P. S. Bagus, C. J. Nelin, B. Schacherl, T. Vitova (Keynote) (USA)* **S8-T1**
- 14:30 A practical computational tool for actinide coordination chemistry (LFDFT): study of M4,5-edge core-to-core and valence-band resonant inelastic x-ray scattering  
*H. Ramanantoanina, C. Celis-Barros, T. Vitova (Keynote) (Germany)* **S8-T2**
- 15:00 HERFD-XANES vs conventional XANES. The implications of cutting through the RIXS plane  
*L. Amidani (France/Germany)* **S8-T3**
- 15:20 U M4,5 edge XANES of Uranyl: Potential energy curves of core-excited states and applications to x-ray spectroscopy  
*R. Polly, P. S. Bagus (Germany)* **S8-T4**
- 15:40 New generation HPGe detector technologies for synchrotron applications  
*P. Quirin, N. Brocard, M. Ginz, G. Ilie, J.-B. Legras, V. Marian, J. Masseron (France)* **S8-T5**
- 16:00 Coffee break

### Session 9 Nuclear waste forms and debris materials

- 16:20 Real-time tracking of oxidation states of  $\text{UO}_2$  nano particulate electrode using HR-XANES at Uranium M4 edge and a microfluidic technique  
*J. Yao, B. Schacherl, B. K. McNamara, V. Christian, E. S. Ilton, H. Jaeyoung, S. Schenk, E. C. Buck, H. Ramanantoanina, T. Vitova (Keynote) (USA)* **S9-T1**
- 16:50 Application of X-ray absorption spectroscopy in support of Pu disposition strategy  
*L. R. Blackburn, A. A. Friskney, L. T. Townsend, C. L. Corkhill (Keynote) (UK)* **S9-T2**
- 17:20 X-ray absorption spectroscopy (XAS) study on Technetium incorporation within iron oxides, waste glass, and grout waste forms  
*G. Wang, S. A. Saslow, M. R. Asmussen (USA)* **S9-T3**
- 17:40 Dissolution behavior of simulated debris in the presence of malonic acid  
*R. Tonna, Y. Okamoto, T. Kobayashi, T. Sasaki (Japan)* **S9-T4**
- 18:00 X-ray analysis for radioactive particulates from Fukushima-Daiichi nuclear power plant using synchrotron radiation at SPring-8  
*T. Kobayashi, M. Kobata, H. Tanida, S. Fujimori, Y. Takeda, T. Tsuji, T. Fukuda, G. Shibata, I. Kawasaki, R. Doi, Y. Okamoto, T. Okane, T. Yaita, Y. Satou, S. Suzuki, K. Maeda (Japan)* **S9-T5**
- 18:20 End of day 3

## Thursday (10 October 2024)

### Session 10 Quantum theory supporting spectroscopy of 5f-element compounds

09:00	Chemical bonding and electronic structure enabled by 5f-electrons <i>P. Yang (Plenary) (USA)</i>	S10-T1
09:40	Determination of actinide central-field covalency with 3d4f resonant inelastic X-ray scattering <i>M. L. Baker (UK)</i>	S10-T2
10:00	Sensitivity to cis- versus trans- actinide-ligand covalency in M4-edge Resonant Inelastic X-ray Scattering <i>T. G. Burrow, N. M. Alcock, M. S. Huzan, M. O. J. Y. Hunault, M. L. Baker (UK/France)</i>	S10-T3
10:20	Quantum chemical studies of binary and ternary U(VI) hydroxo silicate complexes <i>I. Chiorescu, S. Krüger (Germany)</i>	S10-T4
10:40	Coffee break	

### Session 11 Actinide coordination chemistry

11:00	Exploring actinide free radical interactions with electron paramagnetic resonance spectroscopy and density functional theory calculations <i>T. Z. Forbes, H. Rajapaksha, S. J. Kruse, S. K. Scherrer (Keynote) (USA)</i>	S11-T1
11:30	The coordination chemistry of U <sup>4+</sup> in aqueous solutions: Challenges and insights from spectroscopy and theory <i>G. Raposo-Hernández, R. R. Pappalardo, F. Réal, V. Vallet, E. Sánchez Marcos (France)</i>	S11-T2
11:50	Complexation of Protactinium(V) with chlorides in aqueous solution: Thermodynamic and structural insights <i>M. Maloubier, T. Shaaban, T. Aubert, V. Vallet, F. Réal, B. Siberchicot, C. Le Naour (France)</i>	S11-T3
12:10	Re-evaluation of the Pu(IV)-acetate speciation diagram taking into account polynuclear species <i>G. Chupin, C. Tamain, T. Dumas, P. L. Solari, P. Moisy, D. Guillaumont (France)</i>	S11-T4
12:30	Lunch break	

## Thursday (10 October 2024)

### Session 12 Spent nuclear fuel and waste conditioning

14:00	The application of neutron and synchrotron methods to the chemical and structural characterization of disordered systems of relevance to radioactive materials challenges <i>D. T. Bowron (Keynote) (UK)</i>	<b>S12-T1</b>
14:30	XAS studies on nuclear fuels: from simulated to spent fuels characterizations <i>V. Klosek, M. Rochedy, W. Tomczak, C. Le Gall, E. Geiger, L. Balice, S. Gobert, F. Audubert, M. O. J. Y Hunault, D. Menut, P. L. Solari (Keynote) (France)</i>	<b>S12-T2</b>
15:00	Multi-scale investigation of fission product speciation in $U_{1-y}Pu_yO_{2-x}$ SIMMOx using synchrotron techniques <i>R. Caprani, P. Martin, D. Prieur, J. Martinez, F. Lebreton, K. Kvashnina, E. F. Bazarkina, N. Clavier (Germany/France)</i>	<b>S12-T3</b>
15:20	Actinide immobilization by incorporation into ceramic phases <i>C. Hennig, V. Svitlyk, S. Weiss, L. Braga Ferreira dos Santos, J. Niessen, S. E. Gilson, J. Marquardt, T. Lender, S. Richter, G. L. Murphy, N. Huittinen (Germany)</i>	<b>S12-T4</b>
15:40	Coffee break	
16:15	<b>Transfer to Speyer</b>	
17:30	<b>Reception and visit of space exhibition hall</b>	
19:15	<b>Conference dinner</b>  Historical perspectives on the development of actinide XAS <i>D. L. Clark (Dinner talk) (USA)</i>	
22:00	<b>End of day 4</b>	

## Friday (11 October 2024)

### Session 13 Radionuclide geochemistry

- 09:00 Incorporation of some f-block elements in ancient and synthetic Fe oxides  
*E. S. Ilton, S. T. Mergelsberg, E. J. Bylaska (Plenary) (USA)* **S13-T1**
- 09:40 Understanding the varying mechanisms of radionuclide immobilization by alternative bentonite materials. Combined sorption, EXAFS and luminescence spectroscopy studies  
*G. F. Vettese, X. Li, L. Sirén, K. Silenius, M. Siitari-Kauppi, N. Huittinen, L. B. F. dos Santos, S. Shams Aldin Azzam, A. Rossberg, R. Bes, M. Niskanen, T. Peltola, G. T. W. Law (Finland)* **S13-T2**
- 10:00 Effect of citrate on aqueous U(VI) speciation and U(VI) retention on Ca-bentonite  
*C. Sieber, J. Kretzschmar, B. Drobot, K. Schmeide, T. Stumpf (Germany)* **S13-T3**
- 10:20 Insights into U(VI) reduction during bio-stimulation of microbes in U mine water  
*A. M. Newman-Portela, K. Kvashnina, E. Bazarkina, A. Roßberg, F. Bok, A. Kassahun, J. Raff, M. L. Merroun, E. Krawczyk-Bärsch (Germany)* **S13-T4**
- 10:40 Coffee break

### Session 14 Speciation of actinide materials: from nuclear legacies to fundamental science

- 11:00 Applications of X-ray absorption spectroscopy to the UK's nuclear legacy challenges  
*T. S. Neill, S. Shaw, C. Waters, E. Howard, R. Margreiter, J. F. W. Mosselmans, L. Abrahamsen-Mills, F. Schofield, C. Foster, K. Ignatyev, K. Morris (Keynote) (UK)* **S14-T1**
- 11:30 Investigation of actinide-transition metal bonding  
*R. Gericke, D. Grödler, P. Kaden, M. Patzschke, R. Polly, K. Kvashnina (Keynote) (Germany)* **S14-T2**
- 12:00 Poster and young scientist awards, closing remarks
- 12:30 Lunch break
- 14:00 End of conference

# **Oral Presentations**

## Application of synchrotron-based microbeam techniques for studying the reactive transport of actinides in clay rock

T. Reich

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Since the first Workshop on Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources, Actinide-XAS-98, the applications of modern synchrotron-based techniques for providing molecular scale information on radionuclides in areas such as environmental actinide chemistry and materials sciences have increased significantly. Parallel to the development of established and new X-ray techniques, several synchrotron laboratories have implemented procedures and facilities for studying radioactive materials.

These advances will be illustrated by examples, where the reactive transport of Np and Pu in Opalinus Clay rock was investigated using a combination of synchrotron-based microbeam techniques including  $\mu$ XRF,  $\mu$ XRD,  $\mu$ XAFS and tomography. The experiments at the SLS microXAS Beamline at PSI enabled the observation of redox transformations of the actinides during sorption and diffusion and the identification of reactive mineral phases. In addition, spatially resolved in-diffusion profiles of Np and Pu were obtained. Recently, the microstructure of pristine Opalinus Clay and its influence on the three-dimensional transport patterns of Np and Pu in the clay rock were measured by scanning  $\mu$ XRF-CT and  $\mu$ XRD-CT. The advanced experimental capabilities of the mentioned microbeam techniques allowed to obtain unprecedented information on the reactive transport of redox-sensitive radionuclides in heterogeneous porous media.

### Acknowledgements

Many collaborators have been involved in this study. I would like to acknowledge, S. Amayri (JGU), J. Börner (JGU), M. Breckheimer (JGU), D. Ferreira Sanchez (PSI), D. R. Fröhlich (JGU), D. Grolimund (PSI), U. Kaplan (JGU) and M. G. Makowska (PSI).

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## Chemical tomography of Np and Pu diffusion in Opalinus Clay

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The safety case for a deep geological repository for high-level radioactive waste (HLW) requires a profound understanding of the geochemical and transport processes governing the fate of the potentially mobilized waste inventory. In a multi-barrier concept argillaceous rock is considered as a potential host rock, with Opalinus Clay (OPA, Mont Terri rock laboratory, St-Ursanne, Switzerland) serving as a reference material for a natural clay rock. OPA exhibits characteristic properties of a sedimentary rock such as structural and compositional heterogeneities in a range of length scales [1].

Previous studies, utilizing multimodal chemical imaging at the microXAS beamline (Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland), revealed an influence of the heterogeneous OPA microstructure on the transport, immobilization and redox state of the relevant HLW radionuclides Np and Pu [2-5]. Extending this analytical imaging technique to chemical tomography gives access to volumetric information within the material and, consequently, allows further reducing an invasive sample preparation. This multimodal approach utilizes the different modalities of X-ray attenuation (computed tomography,  $\mu$ CT), fluorescence ( $\mu$ XRF-CT), diffraction ( $\mu$ XRD-CT) and absorption ( $\mu$ XANES), gaining volumetric information of the microstructure, elemental and mineral phase distribution as well as the chemical speciation of the probed radionuclide.

We applied chemical tomography to study the diffusion of Np and Pu in OPA. Based on an experimental approach utilizing small cylindrical samples of intact OPA [6], the experiment was adapted to chemical tomography, further reducing the sample dimensions ( $\varnothing$  1.0 mm) and considering the intrinsic bedding and swelling pressure of the clay rock. These samples were subjected to in-diffusion experiments under aerobic conditions in synthetic OPA pore water media (pH 7.6) with micromolar concentrations of  $^{237}\text{Np(V)}$  and  $^{242}\text{Pu(V)}$ , resp., with a duration of 20 days.

Measurements of selected samples at the microXAS beamline gave access to relevant information regarding the reactive transport of Np and Pu in OPA. Two-dimensional transport patterns resp. in-diffusion profiles of the studied radionuclides in OPA were accessible, serving as a potential data source for reactive transport modelling. The influence of the heterogeneous microstructure could not only be observed in heterogeneous transport patterns, but also in likewise heterogeneous radionuclide distributions within the OPA matrix by means of chemical tomograms. A reduction to tetravalent, less mobile species of the radionuclides could also be observed. The results of this study contribute to an enhanced understanding of the reactive transport of Np and Pu in OPA, relevant for the safety case of a deep geological repository.

### Acknowledgements

Funding from the German Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV) under contract number 02E11860A and from the European Union's Horizon 2020 project EURAD (WP FU-TuRE), EC Grant agreement no. 847593, is acknowledged. O. X. Leupin (Nagra, Switzerland) and D. Jaeggi (swisstopo, Mont Terri Project, Switzerland) are acknowledged for providing OPA samples.

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## **Chemical Imaging and Applications Using High Energy Resolution Fluorescence Detection for the Actinides**

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Microscale synchrotron radiation-based x-ray fluorescence (SR-XRF) chemical analyses can provide a unique capability for chemical signature recognition and classification capabilities for actinide micro-particle analysis. SR-XRF is well suited to forensic type analyses of small particles because it is rapid, non-destructive, highly sensitive, has good spatial resolution, and can provide chemical information on the elements that are present when combined with x-ray absorption spectroscopy (XAS). The combination of spatially resolved distribution and chemical information, often known as chemical imaging, effectively provides a “chemical morphology” of the sample of interest and can show how chemical states are distributed within and among a series of particles. This type of measurement is critical for understanding particle origin and history, as the spectroscopy, and its spatial distribution, can provide unique and complementary chemical signatures that may not be elucidated with other forms of measurement.

However, the conventional XAS capability in the near edge region as commonly implemented is often inadequate for systems that require high sensitivity or require a higher detail of spectroscopic information. This can be overcome with the combination of traditional micro SR-XRF and XAS, integrated with a high energy resolution fluorescence detector (HERFD) crystal analyzer. This has been recently implemented at BL 6-2b at SSRL and applied in the determination of the micron-scale oxidation state of uranium in particles. A discussion of the image and data processing techniques that can be applied using spatially resolved HERFD to obtain chemical and structural information, as well as the distribution of phases across different particles at the micro-scale, will also be presented.

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## Quantifying F-Orbital Overlap with Ligand K-edge XAS

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Controlling the outcome of chemical processes involving actinides requires quantitative models of molecular structure and bonding. However, many previous experiments have shown that the relationship between chemical behavior and bonding is not straightforward. Actinide bonding is confounded by numerous variables that are hard to control. In addition, because the 5f-orbitals are contracted and actinide–ligand overlap is small (particularly for heavier actinides), changes in chemical behavior that result from differences in bonding can be hard to observe.

To understand the possible link between 5f-orbital mixing and actinide chemical behavior, we conducted F K-edge X-ray absorption spectroscopy (XAS) studies of the hexafluorides,  $\text{AnF}_6^{2-}$  ( $\text{An} = \text{U}, \text{Np}, \text{Pu}$ ). Acquiring quantitative F K-edge XAS results was enabled by using the scanning transmission X-ray microscope (STXM) on the Advanced Light Source Molecular Environmental Science (ALS-MES) beamline 11.0.2. By measuring data on small crystallites, we were able to overcome challenges such as surface contamination and saturation that can typically plague measurements with weakly penetrating incident radiation. The F K-edge data were referenced using recent results on  $\text{F}_2$  and  $\text{CeF}_6^{2-}$  [1, 2]. Although the  $\text{AnF}_6^{2-}$  are structurally similar, the extent of  $\text{An}-\text{F}$  bonding varies significantly as 5f-orbital energies and occupancies change with the identity of the actinide. For example, comparisons between  $\text{UF}_6^{2-}$  ( $5f^2$ ),  $\text{NpF}_6^{2-}$  ( $5f^3$ ), and  $\text{PuF}_6^{2-}$  ( $5f^4$ ) show how decreasing 5f-orbital energies may result in increased  $\text{An}$  5f and F 2p orbital mixing.

With the F K-edge XAS results in hand, we were able to derive quantitative comparisons to recent chlorine K-edge XAS studies on molecular actinide hexachlorides,  $\text{AnCl}_6^{2-}$  ( $\text{An} = \text{Th}$  to  $\text{Am}$ ) [3, 4]. Because values for the F and Cl valence orbital ionization potentials are known precisely, these comparisons provide an opportunity to control for changes in orbital energy and show if covalency is affected by overlap. Interpretations of the F K-edge XAS are facilitated by electronic structure calculations, and the percentage of F 2p character determined experimentally will be related to theoretical values determined from the Mulliken population analyses provided by electronic structure calculations by Batista and Yang (LANL). Efforts to advance computational methodology for f-elements benefit greatly from these spectroscopic studies at the ALS, because the technique provides high energy resolution, feature-rich spectra while also probing interactions with both the f- and d-orbitals.

This work and the Advanced Light Source was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy at LBNL (contract DE-AC02-05CH11231).

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## AI-assisted lab-on-a-chip experiments: Setting new frontiers in radio-geochemistry

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Co-precipitation of radionuclides in host phases is considered as a relevant retention mechanism in some scenarios of safety cases for deep geological repositories for radioactive wastes. Ba and Ra released from the radioactive waste will react with porewater containing sulphate, triggering the formation of (Ba,Ra)SO<sub>4</sub> or even (Ba,Sr,Ra)SO<sub>4</sub> solid solutions. In the specific case of <sup>226</sup>Ra, the solid solution with BaSO<sub>4</sub> irreversibly binds the contaminant in a stable phase, whose mixing behaviour and thermodynamic properties are well described in the literature. However, for a rigorous assessment of the fate of <sup>226</sup>Ra in the subsurface with reactive transport modelling, a conceptual approach describing transport-induced crystallization of solid solutions in tightly confined porous media is required, considering the effects of kinetics<sup>1</sup>. However, to our knowledge the crystallization kinetics of (Ba,Ra)SO<sub>4</sub> have not been determined so far. <sup>226</sup>Ra (half-life: 1600 years) decays to form gaseous <sup>222</sup>Rn and a series of other short-lived  $\alpha$ -emitting isotopes. Decades after the pioneering work of Marie Curie, Doerner, and Hoskins, the utilization of <sup>226</sup>Ra in contemporary research remains constrained to trace amounts (<10<sup>-8</sup> M) due to its high radioactivity (3.7 × 10<sup>10</sup> Bq g<sup>-1</sup>). What if lab-on-a-chip technology would create new opportunities, enabling work with highly radioactive elements beyond trace amounts to gain new insights and fill knowledge gaps? With the main objective of providing an integrated experimental and theoretical approach to predict transport-induced precipitation of radium-bearing solid solutions in tightly confined porous media or fractured crystalline rocks, we devised a series of investigations to (i) determine whether nucleation is inhibited in confinement<sup>2</sup>, (ii) decipher crystallization processes of solid solutions leading to oscillatory zoning<sup>3</sup>, and (iii) establish the crystallization kinetics of (Ba,Ra)SO<sub>4</sub><sup>4</sup>. The methodology used in this work combines AI-assisted lab-on-a-chip experiments and reactive transport modeling on pore- and continuum-scale. The lessons learned from these studies mark the first building blocks towards an automated radio-geochemical lab-on-chip.

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## Uranium and Plutonium interaction with calcium-binding sites of proteins

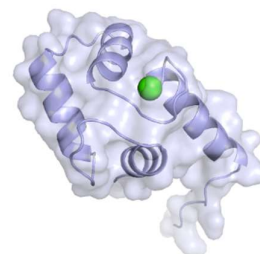
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Uranium and plutonium exhibit both chemical and radiological toxicity. While their physiological impact and the target organs are well-documented, the molecular mechanisms of cellular uptake and transport to these organs remain unclear. As alpha emitters, plutonium and uranium exert short-range effects that are closely dependent on these molecular processes. It is believed that proteins play critical roles in these mechanisms, motivating the study of uranium and plutonium interactions with proteins.

Studies on the structure-property relationships between uranium and proteins or peptides have identified determinants of the affinity of these interactions, such as the presence of phosphoryl groups [1, 2]. Studies on the interactions between plutonium and proteins and associated stability constants are few in number. Publications have revisited Pu interaction with the blood iron carrier transferrin [3], or with the iron-storage protein ferritin [4]. Interestingly, a Pu affinity constant similar to that for transferrin was measured for the blood plasma protein fetuin, which binds small clusters of calcium phosphate [5] and Ca-binding proteins were highlighted as possible Pu(IV) targets in a metalloproteomic approach [6].

We investigate the binding properties of U(VI) and Pu(IV) to calproteins using engineered variants of the calcium binding sites of the N-terminal domain of calmodulin as template (Figure 1). Combining site-directed mutagenesis of the metal-binding loop with fluorescence, ITC, CE-ICP-MS, native-mode ESI-MS, UV-Vis, FTIR, XAS, and EXAFS analysis establishes structure-property relationships.



**Figure 1** : Structural model of an engineered variant of calmodulin N-terminal domain with Ca(II) bound at site I, obtained using AlphaFold3 (10)

For U(VI) we show that the structure of the active site has an effect as large or larger than that of introducing strong phosphoryl ligands on uranyl affinity [1, 7, 8]. For Pu, we show that the metal binding site has a strong effect on both Pu speciation and affinity [9]. At low protein and Pu(VI) concentrations, formation of 1:1 complexes is observed,

with different affinities correlated with the charge of the metal binding site. The most stable complex has an affinity constant close to those reported with transferrin. At higher protein-Pu concentrations, Pu(IV) reduction or stabilization of a hexanuclear Pu(IV) complex have also been observed. Formation of the hexanuclear Pu(IV) complex is correlated with the presence of water molecules in the Pu coordination sphere as proposed by MD simulations of the protein-Pu(IV) complex in solution [9]. These data shed light on the molecular mechanisms of uranium and plutonium interactions with proteins.

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## Spectromicroscopic characterization of lanthanide-contaminated mammalian cells

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In the event of an accidental release of radiological/nuclear material, actinides (An) and lanthanide (Ln) fission products pose severe health risks due to both radiological and chemical toxicities. The toxicity of these metal ions is governed by their mechanisms of uptake, oxidation state and speciation, intracellular distribution and interactions with various macromolecules. It also depends on their physiochemical properties and ligand preferences. While biokinetic, toxicological, and epidemiological data are abundant, little is known about their toxicity mechanisms at the molecular level and how metal sensing is translated into appropriate cellular responses.<sup>1,2</sup>

In this work, we seek to elucidate the fundamental properties governing Ln homeostasis in mammalian cells. Using spatially resolved X-ray absorption spectroscopy (XAS), we can examine the localization and chemical speciation of Lns upon cellular uptake. Scanning transmission X-ray microscopy (STXM) and ptychography are employed as they are ideal techniques to probe mammalian cells under diverse conditions with high spatial resolution. Cerium was chosen as a representative Ln ion because it can access multiple redox states. Therefore, it can be viewed as a homologue for redox active Ans such as Pu.

We probed lung cancer cells (A549) that were contacted with Ce-containing media with concentrations ranging from 0.25 mM to 4 mM for 24h. To elucidate membrane associated Ce washing procedures with either PBS or 3x2min with EDTA solution (10 $\mu$ M) were performed. Several different sample preparation methods to maintain the structural and chemical integrity of the cells during measurement were tested and compared. Therefore, each set of samples was either 1) cryo-preserved by rapidly plunge-frozen in liquid ethane; 2) chemically fixed using glutaraldehyde and air dried; or 3) chemically fixed, ethanol dehydrated, resin embedded, and then sliced to different thicknesses (100 nm - 700 nm) using an ultramicrotome with sections collected onto SiN windows and TEM grids. Spectroscopic data collection was carried out using the cryo-STXM capabilities of the Soft X-ray Spectromicroscopy (SM) beamline at the Canadian Light Source (CLS)<sup>3</sup> and the Cosmic beamline (7.0.1.2.) at the Advanced Light Source (ALS).<sup>4</sup> Alongside Ce detection derived at the M<sub>4,5</sub> edges, the feasibility of evaluating chemical speciation at the O and P K-edges was investigated.

Ce localization and spectroscopic information of different sample preparation methods were compared and revealed complementary information. Membrane associated and internalized Ce in and on several organelles was resolved. Similar spectra hinting at a limited effect of the chemical fixatives on the oxidation state Ce in the samples. The spectroscopic speciation was set in context with chemical solution analysis. Elemental maps and signatures at the O and P K-edges are discussed in the context of different organelles and inorganic compounds. These data are critical for understanding toxicity mechanisms associated with Ln and An, which will be discussed.

Spectroscopy experiments were supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Heavy Element Chemistry Program at the Lawrence Berkeley National Laboratory (LBNL) under contract DE-AC02-05CH11231. Sample preparation was supported by grants from the Department of Defense (W81XWH-21-1-0984) and the National Institute of Allergy and Infectious Diseases or the National Institutes of Health (1P01AI165380-01), through the Alliance for Radiological Exposures and Mitigation Science, at LBNL, under contract no. DE-AC02-05CH11231. Part of the research described was performed at the Canadian Light Source, a national research facility of the University of Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the University of Saskatchewan. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

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## Impact of Eu(III) on rat kidney cells in the absence and presence of the decorporation agents DTPA and 3,4,3-LI(1,2-HOPO)

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Radionuclides (RN) pose a potential health risk when they enter the human organism. Upon accidental RN incorporation, decorporation agents (DA) are applied to enhance RN excretion and to reduce chemo- and radiotoxic effects. Although renal RN excretion is one major elimination pathway, *in vitro* investigations on interactions of these elements with kidney cells are still scarce.

In the present study, we investigated the interactions of Eu(III) with normal rat kidney cells (NRK-52E) in the absence and presence of the DA DTPA and 3,4,3-LI(1,2-HOPO) [1]. Eu(III) represents the non-radioactive lanthanide (Ln) analogue of the actinide Am(III) and possesses excellent luminescence properties, which allow for sophisticated speciation studies *in vitro*.

In exposure studies, cells were incubated with up to 1 mM Eu(III) +/- DA for 7 and 24 h, respectively. Afterwards, cell viability as well as intracellular Eu(III) bioaccumulation were measured. Furthermore, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was applied to analyze Eu(III) speciation in cell culture medium and washed cells. To visualize the spatial Eu(III) distribution inside exposed cells, luminescence spectroscopic mapping was conducted using chemical microscopy [2].

Eu(III) shows time- and concentration-dependent cytotoxic effects on the kidney cells. The speciation analyzes reveal protein and phosphate binding motives for extracellular Eu(III) in the cell culture medium, whereas intracellular metal ions seem to be exclusively phosphate-bound. Chemical microscopy suggests Eu(III) deposition in granular vesicles close to the nucleus (*e.g.* lysosomes).

Upon 24 h incubation, both DA exhibit protective effects and reduce Eu(III) cytotoxicity at concentrations up to 500  $\mu$ M for DTPA and 1 mM for HOPO. However, higher DA concentrations cause significant chemotoxic impacts on the kidney cells.

In cell culture medium, the affinity of both DA towards Eu(III) is high. However, different effects on cellular Eu(III) uptake are visible: DTPA reduces Eu(III) accumulation, probably due to the formation of a cell-impermeable DA-metal complex. In contrast, 3,4,3-LI(1,2-HOPO) seems to form a cell-permeable complex, resulting in increased metal uptake and, thus, elevated intracellular Eu(III) concentrations. However, this only applies to steady state *in vitro* conditions, which do not allow elimination of complexed Eu(III) and may favor an intra-extracellular Eu(III) equilibrium. Nevertheless, the achieved results contribute to a better understanding of cellular DA dynamics and elucidate Eu(III) complexation in cell culture medium and cells.

### Acknowledgements:

This work is part of the German joint project "Speciation and transfer of radionuclides in the human organism with special consideration of decorporation agents (RADEKOR)" and was funded by the German Federal Ministry of Education and Research (BMBF, 02NUK057B).

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## Combining *in vitro* cell culture and luminescence spectroscopy: A powerful tool for studying An(III) impact on and speciation in cells

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In general, due to their radio- and chemotoxicity, radionuclides (RN) pose a potential health risk if they enter the food chain and are ingested by humans. For RN like trivalent actinides, renal excretion is the major elimination pathway. It is, therefore, essential to understand the RN speciation in biological fluids on a molecular scale and RN interactions with mammalian renal cells *in vitro* on a cellular level, respectively. Concerning the non-radioactive lanthanide analog Eu(III), these questions were recently addressed by us and data for Eu(III) cytotoxicity on renal cells as well as its extra- and intracellular speciation were reported [1]. Equivalent data for Am(III) or Cm(III) are currently not available.

Therefore, we investigated the impact of <sup>243</sup>Am(III) onto the viability of normal rat kidney cells (NRK-52E) and its intracellular accumulation using *in vitro* cell culture bioassays and gamma counting. Morphological alterations were followed using fluorescence microscopy after selective staining of cellular compartments. Using time-resolved laser-induced fluorescence spectroscopy (TRLFS) combined with parallel factor analysis (PARAFAC), Am(III) speciation was determined in cell culture medium and in lysates of exposed and washed cells.

In a second step, the influence of diethylenetriaminepentaacetic acid (DTPA) and 3,4,3-LI(1,2-HOPO) (HOPO) on the Am(III) cytotoxicity and uptake was assessed. In order to minimize the health risk in case of RN incorporation, strong chelators, also called decorporation agents (DA), are administered as soon as possible to increase RN excretion. At present, DTPA is the only approved and commercially available DA for trivalent actinides. HOPO is being developed and in clinical trials as an superior alternative to DTPA. Therefore, the Am(III) speciation was also determined in presence of DA in the cell culture medium as well as in cell lysates. Exposure studies were performed for 7 and 24 h, respectively, with up to 0.8 mM Am(III) and metal-to-ligand-ratios (M:L) from 1:0.5 to 1:3 for both DA.

Am(III) alone exhibits a strong cytotoxic effect on the kidney cells which is time- and concentration-dependent. Intracellular Am(III) increases with RN concentration and is ~0.5% of the applied amount. At micromolar Am(III) concentrations, the simultaneous application of DTPA has no significant effect on the cell viability and the amount of intracellular Am(III) after 24 h exposure. In contrast, upon simultaneous HOPO application, the cell viability is significantly decreasing with increasing M:L and the amount of intracellular Am(III) after 24 h exposure is drastically increasing. This contrary effect of the DA is even more pronounced at millimolar Am(III) concentration after 7 h exposure.

In cell culture medium, Am(III) fluorescence is quenched. However, TRLF spectra of complexes formed with DTPA and HOPO are measureable and AmDTPA<sup>2-</sup> as well as AmHOPO<sup>-</sup> were confirmed. In lysates of exposed and washed cells, no TRLF spectrum was measured in the case of <sup>243</sup>Am(III) w/o and with DTPA. In contrast, a good spectrum was measured in the case of Am(III) + HOPO corresponding to AmHOPO<sup>-</sup>. Hence, results from *in vivo* cell culture and TRLF + PARAFAC are consistent and contribute to a better understanding of the effect of DA after RN incorporation at the molecular level.

Finally, the combination of *in vitro* cell culture bioassays and luminescence spectroscopy is a powerful tool to study An(III) interactions with mammalian cells on both a cellular and molecular level.

### Acknowledgements:

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## Speciation of Lanthanides and Actinides by Time-resolved Laser Fluorescence Spectroscopy - Developments from the 1990s to the present day

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This presentation is held in honor of Prof. J. I. Kim, who passed away on 03.12.2023. He was a great luminary in the field of nuclear chemistry. His scientific results on actinide chemistry and radionuclide behavior under the conditions of a nuclear waste repository using innovative speciation methods are still held in high international esteem today. One of his most important achievements was the introduction of time-resolved laser fluorescence spectroscopy (TRLFS) in the 1990s by his coworkers at the Technical University of Munich. At this time, the first spectroscopic speciation studies on hydrolysis, carbonate and humic acid complexation of Cm(III) were performed. With this method, a new tool for determining stability constants of the main geochemical reactions of trivalent actinides in natural systems has been established. In the following years, TRLFS was extended to other areas of actinide research, comprising the complexation of actinides with inorganic, organic and bioligands.

This presentation provides an overview of the development of TRLFS from its beginnings in the 1990s to the present day. Examples from the first investigations at the Technical University Munich are shown. Due to technical improvements over the course of time, TRLFS is now an even more sensitive speciation method that can be successfully used to characterize lanthanide and actinide complexes. It provides important information on the stoichiometry, structure and bonding properties of actinide and lanthanide complexes, in particular in combination with other speciation methods such as NMR and X-ray absorption spectroscopy. Some selected examples from new fields of actinide research are presented to demonstrate the versatile applicability of this speciation method.

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## Are Actinyl good paramagnetic probe for structural studies by NMR spectroscopy?

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Whatever the field of research (nuclear fuel reprocessing, nuclear medicine, dismantling, dissemination of radioelements in environment, etc.) getting structural information are of main importance to get a better insight at molecular scale of the actinide species involved.

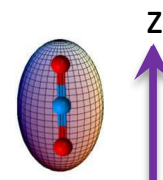
The NMR spectroscopy can provide information on molecular conformations in actinide-ligand complexes because most of actinide are paramagnetic cations and they induce significant paramagnetic shifts (called AIS) like the lanthanide cations (LIS). Thanks to Bleaney's equation<sup>1</sup> developed in the 80's, paramagnetic induced shifts rationalized experimental values of the lanthanide series.

However, the 5*f* electrons behave differently from their 4*f* homologue and specific constants<sup>2</sup> defined for the lanthanide in Bleaney's equation are not reliable for the An series. One of the main explanation is that 5*f* orbitals are more sensitive to ligand fields and thus they are not constant anymore. Another point is that actinide cations exist in solutions at different oxidation states conversely to the Ln(III).

The larger 5*f* orbital compared to the 4*f* one, may explain a greater electronic delocalization on the ligand and then a greater contact interaction in the paramagnetic induced shift than with the lanthanide. This is the case for the spheric actinide cations (cation at oxidation states III and IV) but not observed for molecular cations like the actinyl (cations at oxidation state V and VI).

In this presentation, we will see that the AIS of actinyl complexes are only driven by dipolar interactions based on <sup>1</sup>H and <sup>13</sup>C spectra analyses of actinide complexes with the dipicolinic acid (DPA)<sup>3</sup> and tetraethylidiglycolamide (TEDGA)<sup>4</sup> ligands as an example.

The actinide at oxidation state V and VI undergo the ligand field from the "yl" oxygens providing an axial symmetry. This native axial magnetic susceptibility ( $\Delta\chi_{ax} = \chi_z - \bar{\chi}$ ) of the actinyl cation induces a significant dipolar contribution in the paramagnetic shifts. Furthermore, this symmetry is not disturbed by the ligand field of the DPA or TEDGA in the coordination plan. Thus,  $\Delta\chi_{ax}$  can be considered as constant for NMR conformational studies. Since  $\Delta\chi_{ax} > 0$  ( $\chi_z > \bar{\chi}$ , in another words, the prolate shape of the magnetic susceptibility tensor) the sign of the induced paramagnetic shifts only depend on the geometrical factors G which are negative for all nuclei laying into the coordination plan.



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## Influence of chelating agents on lanthanide and actinide speciation in artificial bodyfluids

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When radionuclides (RN) enter the food chain and are ingested by humans, they pose a potential health risk due to their radio- and chemotoxicity. In order to accurately assess the health risk after oral ingestion and to apply effective decontamination methods, it is essential to understand the processes of (bio)chemistry and speciation of RN at the molecular level. To minimize the health risk, chelating agents, which are usually strong complexants, are used after the accidental incorporation of RN for decorporation, that means to increase RN excretion. To date, however, only the aminopolycarboxylate diethylenetriamine-penta-acetic acid (DTPA) is approved and used commercially, although it is only effective for trivalent actinides. Alternative potential decorporation agents such as the hydroxypyridinone 3,4,3-(LI-1,2-HOPO) (HOPO) are being developed [1], but are not yet ready for commercial use.

We experimentally investigated the speciation of trivalent lanthanides and actinides (Ln(III)/An(III)) as well as hexavalent uranium (U(VI)) in model fluids of the digestive tract in the absence and presence of chelating agents. The artificial biofluids saliva, gastric juice, pancreatic juice, and bile were synthesized according to the international Unified Bioaccessibility Method (UBM) of the Bioaccessibility Research Group of Europe (BARGE) [2]. As chelating agents we used DTPA and alternative aminocarboxylates like ethylene diamine tetraacetic acid (EDTA) or ethyleneglycol tetraacetic acid (EGTA) [3], as well as some promising new chelators like HOPO [1] and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), which was formerly used as a pharmaceutical. The solutions were spiked with Eu(III) as a non-radioactive analogue for An(III) as well as with the actinides Cm(III) and U(VI). Samples were analyzed multi-spectroscopically, mainly using time-resolved laser-induced luminescence spectroscopy (TRLFS) combined with parallel factor analysis (PARAFAC) as well as nuclear magnetic resonance (NMR) spectroscopy.

Speciation studies for Eu(III) and Cm(III) in artificial biofluids resulted in variable coordination spheres with carbonate, phosphate, and also some proteins such as  $\alpha$ -amylase or mucin, depending on the composition of the biofluid [4]. The complexation of U(VI) is mainly dominated by carbonate. The influence of the complexants on the speciation of metal ions in the biofluids varied. For Eu(III), for example, HOPO displaced bioligands just as strongly as DTPA. HEDP was found to be not suitable for trivalent actinides as it forms insoluble complexes at physiologically relevant pH [5]. For U(VI), both HOPO and HEDP were equally capable of displacing the very strong bioligand carbonate from the coordination sphere.

The results of this work contribute to a better understanding of the effect of decorporation agents after RN incorporation at the molecular level and support making them more effective in the future.

### Acknowledgements:

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## Investigation of gluconate complexation with trivalent Eu, Pu and Am using CE-ICP-MS

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Organic molecules like gluconate (Glu) can enter a nuclear waste repository as degradation products or cement additives and thereby affect the migration behavior of radionuclides [1].

The complexation of lanthanides with gluconate has already been investigated in literature [2]. However, little data on the complexation of trivalent actinides with gluconate can be found [3]. Most experiments were conducted at concentrations significantly above those expected in case of leakage in the nuclear waste repository. In order to close these data gaps, we studied the complexation of trivalent Eu, Pu, Am with gluconate at trace level concentrations, i.e.  $\sim 1 \mu\text{M}$  Eu and  $\sim 0.1 \mu\text{M}$  An, using capillary electrophoresis coupled to inductively coupled plasma mass spectrometry CE-ICP-MS.

In order to first gain a good understanding of the system, comparative investigations were carried out on the Eu(III)-Glu system using time resolved laser induced fluorescence spectroscopy TR-LFS and CE-ICP-MS. The TR-LFS provided the number of Eu-Glu species present in solution at pH 4 and their relative concentrations, while CE-ICP-MS provided information about the charge of the complexes and thus about their stoichiometry. The measured electrophoretic mobilities are proportional to the mean charge in solution. The trend in mobility with increasing gluconate concentration allows for complex formation constants to be determined. By combining both methods, it was possible to better quantify the Eu(III)-Glu-system.

CE-ICP-MS was then used to check whether the results for Eu(III) hold up for the actinides Am(III) and Pu(III). A good agreement was observed between the complexation behavior of Eu(III) with Glu and both trivalent actinides.

At pH 4 binary complexes with up to four gluconate ligands could be measured, depending on the metal ion. At pH 10 the hydrolysis of the lanthanide/actinides has a significant influence on the speciation. In this pH range, negatively charged complexes as described in the literature [2] were observed and interpreted as ternary Eu(III)/An(III)-OH-Glu complexes.

Using CE-ICP-MS at low concentrations allowed experiments in absence of polynuclear complexes and stoichiometric effects on the complexation. As a result, the formation of complexes with more Glu ligands than previously described was observed. CE-ICP-MS can be used to analyze the speciation of actinides which are otherwise difficult to investigate with other experimental methods.

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## An Entropic Approach to Multiconfigurational Ground States

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For most of the elements in the periodic table, the number of possible electron permutations for an isolated neutral atom in its ground state is limited by the Russell Saunders (LS) coupling that gives rise to Hund’s rule. However, as we march through the periodic table in order of atomic number, the complexity of electronic structure progressively increases as each consecutive period introduces more orbitals with more crowded energy level profiles and more complex electron interactions. With this complexity comes a greater predominance of jj-coupling over LS-coupling and a breakdown of Hund’s rule in limiting electron degrees of freedom.

Of all the elements in the periodic table, plutonium (Pu) is often regarded as the most complex. [1] Janoschek, et al. described the ground state of Pu as being “governed by valence fluctuations, that is, a quantum mechanical superposition of localized and itinerant electronic configurations.” [2] However, a casual online search of Pu’s ground state yields a simple configuration of  $[Rn]7s^25f^6$ , which does not do justice to its complex multiconfigurational ground state as described by Janoschek, et al. By representing Pu’s ground state more generally as

$$[Rn]7s^{2+\gamma_{s,Pu}}5f^{6+\gamma_{f,Pu}}6d^{0+\gamma_{d,Pu}}7p^{0+\gamma_{p,Pu}}$$

where  $\gamma_{s,Pu}$ ,  $\gamma_{f,Pu}$ ,  $\gamma_{d,Pu}$ , and  $\gamma_{p,Pu}$  represent potentially non-integer deviations from the integer occupancies of their respective orbitals, a combinatorial approach can be applied to the allowable permutations

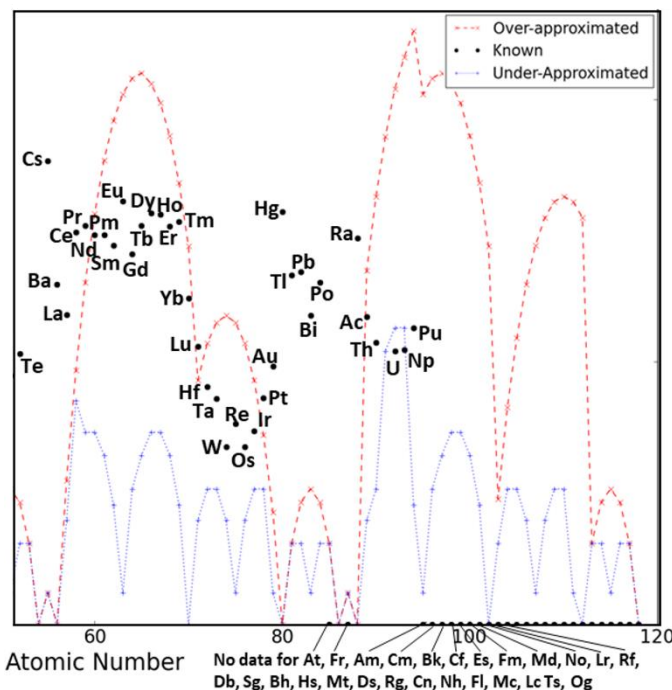


Figure 1. Known standard molar entropies of the elements plotted against the over- (red) and under- (blue) approximations for electronic structure entropies.

of quantum electronic configurations as a means of describing the electron degrees of freedom. This approach enables a classical statistical mechanics methodology to be applied to the discrete number of quantum states for conceptualizing and investigating multiconfigurational ground states. Specifically, an over-approximation (with Hund’s rule relaxed) [3] and an under-approximation (with Hund’s rule enforced) of electronic structure entropy has been established and compared to known molar entropies for the elements (figure 1). Pu will be highlighted to demonstrate how this approach can be used to narrow down the set of possible localized and itinerant electronic configurations that can reasonably contribute to the quantum mechanical superposition of Pu’s multiconfigurational ground state, as well as to estimate the non-integer orbital occupancies of its  $7s$ -,  $5f$ -,  $6d$ -, and  $7p$ - orbitals.

LA-UR-24-24156

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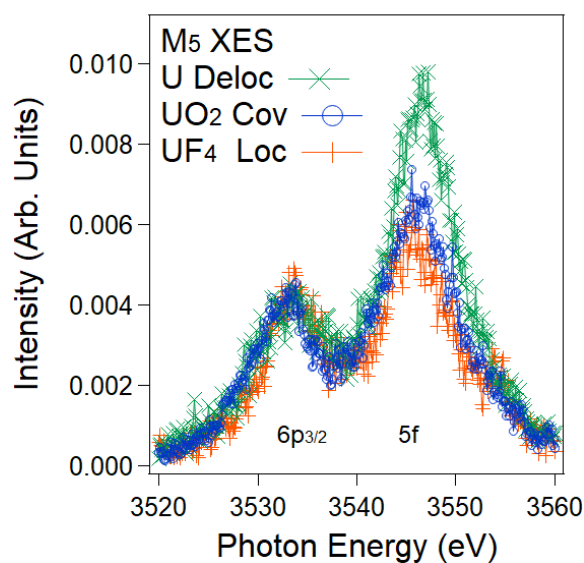
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## Unravelling the Actinides 5f Enigma with X-Ray Emission Spectroscopy

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The advent of new, powerful, highly efficient, multi-component, X-ray monochromators used in the detection of tender x-rays has revolutionized spectroscopic investigations of the 5f electronic structure. All of the new experiments are, in essence, variants of X-ray Emission Spectroscopy (XES), where the improved monochromatized detection plays a key role. In HERFD (High Energy Resolution Fluorescence Detection), the monochromatized XES detection allows the performance of a scattering experiment that devolves into a higher resolution version of X-Ray Absorption Spectroscopy (XAS). It has been shown that the  $M_4$  and  $M_5$  spectra are essentially direct measurements of the j-specific ( $5f_{5/2}$  and  $5f_{7/2}$ ) Unoccupied Density of States (UDOS), which can be directly correlated with the UDOS from Inverse Photoelectron Spectroscopy (IPES) and Bremsstrahlung Isochromat Spectroscopy (BIS). [1,2] Similarly, Resonant XES has been demonstrated to be Raman in nature, with a 5f-5f transition, not a simple charge transfer transition (ligand 2p to actinide 5f). [3,4] Finally, the 5f delocalization in U metal has been quantified with the combined 6p & 5f  $M_{4,5}$  non-resonant XES, which exhibits strong angular momentum coupling effects. [5,6]



*Figure 1 Here are shown the  $M_5$  XES of  $UF_4$  (red +),  $UO_2$  (blue o) and U metal (green x). The horizontal axis is emitted photon energy. Backgrounds have been subtracted and the spectra have been equated at the  $M_5$   $6p_{3/2}$  peak height ( $h\nu \sim 3533$  eV). The  $M_5$  5f peaks are at  $h\nu \sim 3547$  eV. This is non-resonant XES, with the excitation energies slightly above threshold and out of the resonant regime.*

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## Speciation and imaging in radioecology

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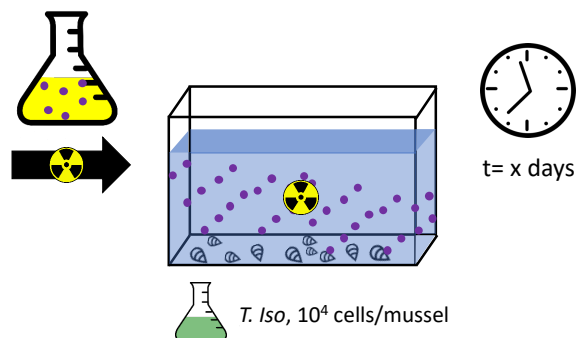
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The mechanisms of dissemination of radionuclides resulting from an accidental release in the environment is a scientific but above all political issue. Hence, the need for managing the risk, for controlling the environmental fate and transport of radionuclides, and for preventing human exposure through direct contamination or more likely indirectly through the food chain is essential. Among the different environmental matrices, oceans and seas represent the largest proportion of the hydrosphere, it covers by itself about 71% of the earth's surface and it is the final repository of pollution (organic and metals). The study of the transfer and accumulation mechanisms of radionuclides in a selected marine ecosystem is a first step to model propagation of radionuclides on larger scales in the hydrosphere. But speciation is poorly described in ecosystems because of their complexity and large dilution factors that preclude direct determination. Therefore, it is required to shift from a purely descriptive radioecology approach to a mechanistic approach and this can be performed with the use of speciation tools and in model (eco)systems.



Our group has been investigating the biochemical processes of uptake of several radionuclides among which <sup>Nat</sup>U and <sup>60</sup>Co by marine species (sponge, sea urchin, mussels) in well-controlled marine (eco)systems. We have explored the speciation of soluble and insoluble species in seawater leading to potentially bioavailable and bio-transferred species [1]. We have addressed this question in semi natural systems by doping natural seawater (see illustration) in order to be able to perform direct

spectroscopic investigation and thus to decipher the molecular speciation [2]. We have also monitored the uptake mechanisms *in vivo* by using sentinel species [3,4]. For instance, the sea urchins *Paracentrotus Lividus* or mussel *Mytilus Galloprovincialis* that we have selected are known as sentinel species for heavy metal accumulation. After a specific contamination procedure, organs have been mapped for radionuclide accumulation using a combination of Transmission Electronic Microscopy (TEM), micro X-ray Fluorescence Spectroscopy ( $\mu$ -XFS) and Secondary Ion Mass Spectrometry (SIMS). Speciation has been defined using X ray Absorption Spectroscopy (XAS).

In conclusion, obtaining space-resolved speciation data calls for methodological compromises. The complexity of the studied subjects itself may be viewed as incompatible with the obtention of fundamental data. Nevertheless, the introduction of modern spectroscopic and spectrometric techniques in environmental sciences pushes the limits of detection and supports an argument for integrated methodologies.

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## ***In vivo* speciation and molecular mechanisms of the uptake of radioactive metal ions by *A. nodosum***

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Since the mid XX<sup>th</sup> century, nuclear activities like accidental releases, mining, and military operations have increased the concentrations of anthropogenic metallic radionuclides in the environment [1]. As recipients of discharged pollutants and covering 70% of the Earth's surface, the oceans and their biotope emerged as a primary focus in environmental monitoring efforts. However, the impact of radioactive metals on marine life remains poorly understood due to the difficulty of studying their biochemistry and metabolic interactions.

We present here a multi-scale investigation aiming at understanding the impact of metallic radionuclides accumulation in the model marine macro-alga *Ascophyllum nodosum*, by describing the related uptake mechanism. We investigated the uptake and the *in vivo* speciation of two actinides : 1) the uranyl ion,  $\text{UO}_2^{2+}$ , chemical analogue of heavier actinides such as plutonyl and neptunyl ( $\text{NpO}_2^{1,2+}/\text{PuO}_2^{1,2+}$ ); 2) stable europium ( $\text{Eu}^{3+}$ ), here used as an analogue of americium ( $\text{Am}^{3+}$ ), generated in nuclear reactors through plutonium decay, which has a too high specific activity to be manipulated at the chosen macro-concentrations.

Contaminations experiments were performed on the *A. nodosum* specimens in closed aquaria through seawater exposure, varying concentrations from macro ( $10^{-5}$  M  $^{\text{nat}}\text{U}$  and  $10^{-7}$  M  $^{153}\text{Eu}$ ) to trace levels ( $10^{-12}$  M  $^{152}\text{Eu}$  and  $^{241}\text{Am}$ ). The bioaccumulation was quantified using ICP-MS and  $\gamma$ -spectroscopy, while elemental distribution and speciation in algal tissues were mapped using a combination of electronic microscopy imaging (SEM), X-ray absorption spectroscopy (XAS), and X-ray fluorescence ( $\mu$ -XRF) at the synchrotron.

Our results show that *A. nodosum* can bioaccumulate uranyl and europium through different active and passive mechanisms. Specifically,  $\text{UO}_2^{2+}$  ion displayed a compartmentalization ability, with higher concentrations in the receptacles, the reproductive part of the algae (Concentration factor:  $\text{CF}_{\text{receptacles, natU}} = 49 \pm 12$ ,  $\text{CF}_{\text{thallus natU}} = 3.1 \pm 0.5$ ). We also observed distinct speciation depending on the compartment, the gender of the alga [2], as well as the presence of bacteria living on algal external surface.

To verify the Eu/Am analogy, we conducted uptake and loss kinetics experiments with both  $^{152}\text{Eu}$  and  $^{241}\text{Am}$  at trace levels, which revealed similar uptake and loss kinetics, suggesting chemical and biological similarities between both cations. This allowed us to extrapolate speciation studies conducted on stable europium to americium. No evidence of elemental compartmentalization was found in this case ( $\text{CF}_{^{153}\text{Eu}} = 1086 \pm 79$ ). Our analysis suggests that alginate, the main polysaccharide in algal tissue, plays a role in Eu/Am uptake through bidentate bridging coordination.

This multiscale strategy and use of complementary spectroscopies can be useful for predicting the risk associated with contamination of living organisms, not only in the case of actinides elements, but can also be extended to other toxic metals and related complexes.

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# Theoretical Studies of the Coordination Structures, Stabilities and Electronic Spectra of Cm<sup>3+</sup> Species at the Mineral-Water Interface

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Accurate interpretation and prediction of actinide coordination chemistry at the mineral-water interface is one of the key scientific issues that need to be urgently addressed in environmental radiochemistry as well as in the safe treatment and disposal of radioactive waste. Various electronic spectroscopic techniques are powerful tools for analyzing the interactions between actinides and minerals in the aqueous environment and revealing the morphology and electronic structure of actinide species. However, due to the complexity of the chemical behaviors of actinides at mineral-water interface, the relevant information derived from experimental spectroscopic data is approximate. And therefore, there is an urgent need for precise simulations at the atomic scale to obtain accurate information. However, due to the strong relativistic and electron correlation effects of actinides, as well as the high complexity of their interactions with mineral surfaces, high-precision theoretical calculations of actinides at mineral-water interface are extremely challenging and rarely reported. In particular, no theoretical studies of the electronic spectra of actinides at the mineral-water interface have been carried out.

In this talk, we will report theoretical investigations of the coordination chemistry of trivalent curium ion at typical mineral-water interfaces by combining ab initio molecular dynamics (AIMD) simulations and static calculations (including static density functional theory calculations and wave function theory calculations).<sup>[1,2]</sup> The coordination structure, thermodynamic and kinetic stability, and electronic spectral properties of Cm<sup>3+</sup> sorption species have been accurately predicted, with the calculation results in good agreement with available experimental results. Besides, the effective computational strategies applicable to studying the interaction between actinide ions and mineral surfaces in the aqueous environment have been proposed.

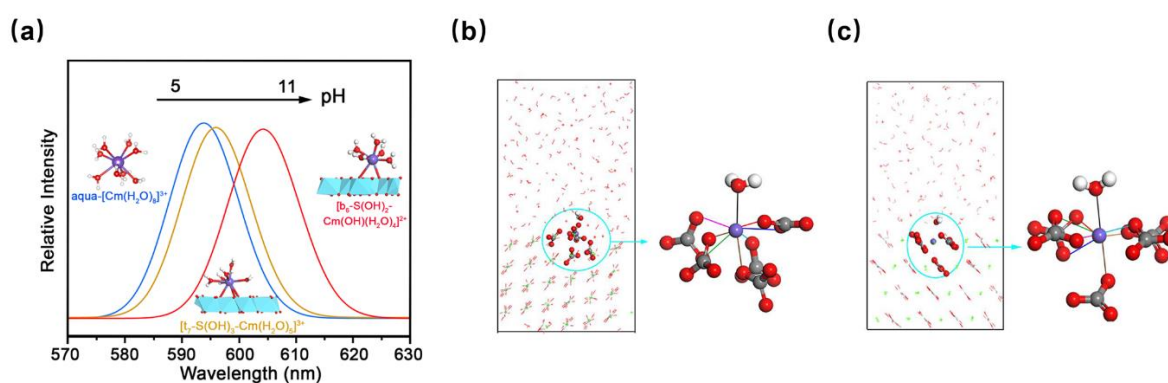


Figure 1. (a) The simulated emission spectra of the Cm<sup>3+</sup> aqua ion and inner-sphere sorption species at the gibbsite-water interface. The configurations of Cm<sup>3+</sup>-incorporated calcite-water system for (b) terrace and (c) stepped surfaces, respectively, from AIMD simulations.

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## Molecular Electrochemistry of Actinides: Redox and Reactivity of Uranium, Neptunium, and Plutonium Complexes

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Redox chemistry strongly influences the reactivity and speciation of the actinides. Particular oxidation states often display unique properties and, therefore, understanding these states and their interconversion can assist with development of new strategies to control their chemical properties. Consequently, electrochemical and electroanalytical methods have a great deal to offer in facilitating studies of actinide-containing systems—from detection of particular species to targeted generation of reactive intermediates of relevance to mechanistic studies. In this presentation, I will share recent examples from my group’s ongoing efforts to apply electrochemical methods to actinide chemistry and develop new chemistries built upon control of redox transformations. In the first part, the nonaqueous redox chemistry of a family of uranium, neptunium, and plutonium complexes<sup>[1]</sup> will be described, highlighting opportunities to study redox processes in nonaqueous media that may not be accessible in conventional aqueous work.<sup>[2]</sup> In the second part, the redox chemistry of crown-ether-ligated uranyl complexes will be described, including ongoing work on spectroelectrochemical studies coupled to various spectroscopies.<sup>[3]</sup> In the third part, the use of electrochemical methods to generate and characterize the chemical behavior of a reactive uranium-containing intermediate will be described, highlighting the opportunity to use electrochemical methods to generate and study the properties of otherwise difficult species.<sup>[4]</sup>

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## Probing actinide chemistry and structure with x-rays at the SOLEIL synchrotron: MARS and the other beamlines

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SOLEIL synchrotron offers a large variety of experimental stations for the study of actinides. The MARS (Multi-Analyses on Radioactive Samples) beamline at the SOLEIL synchrotron (France) is opened to the international community since 2010 and is fully devoted to advanced structural and chemical characterizations of radioactive matter (solid or liquid) using hard X-rays in the 3-35keV energy range [1,2] and has been built thanks to a close partnership with the CEA. Today, the maximum total equivalent activity present at the same time, including the storage on the beamline, is 185 GBq allowing the analysis of nuclear spent fuel [3]. Currently, different types of experiments are available: standard and high-resolution X-ray absorption spectroscopy (XAS), Transmission X-ray diffraction (TXRD), High-Resolution X-ray diffraction (HRXRD), and associated X-ray microbeam techniques ( $\mu$ XRF/ $\mu$ XRD/ $\mu$ XAS). Small Angle and Wide Angle X-ray Scattering (SAXS/WAXS) are also available.[4] In parallel, samples containing actinides with small activities can be studied on the other beamlines at SOLEIL.[5,6]

This contribution presents latest version of the experiment specifications authorized at SOLEIL with radioactive samples and an overview of the most recent achievements on a selection of topics related to the nuclear or radiochemical field at MARS and other beamlines. In particular, the recent developments of sample environments allowing combined experiments will be presented.

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## Combining multiple chemical and physical imaging techniques for comprehensive insight into radioactive specimens at the microXAS beamline and future microXAS 2.0.

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Until October 2023, the microXAS beamline of the Swiss Light Source (SLS) stood out for its flexibility in conducting experiments employing a wide array of techniques, including 2D and 3D imaging with X-ray diffraction- and spectroscopy- contrast. The scanning imaging with submicron resolution was realized by achromatic KB mirror focusing. A unique feature of this beamline was the X-ray beam position stabilization closed-loop system, which allows to maintain the focused beam position even during long term extended energy scans over a wider range of energies.

microXAS is the only beamline of SLS that holds a license for handling radioactive specimens. The installation of the Focused Ion Beam microscope in the Hot Laboratory of PSI has enabled preparation of samples with geometries optimized for scanning chemical imaging with micro-focused beam and at the same time to downsize the samples to significantly lower the activity of the investigated specimens. This development allowed for studies of radioactive samples using the most advanced capabilities of microXAS for 2D and 3D  $\mu$ XRD/ $\mu$ XRF imaging. In this talk, selected examples of such studies will be presented, among others addressing:

- Characterization of the UO<sub>2</sub> fuel pellet-cladding interaction in nuclear spent fuels
- Identification of CRUD deposit phases on a BWR nuclear fuel rod
- Zirconium hydride phase identification and mapping within various types of cladding alloys
- 3D  $\mu$ XRD/XRF imaging of fission gas trapped in pores in high burnup UO<sub>2</sub> fuel combined with 3D ptychographic analysis.

Currently, the Swiss Light Source is undergoing an upgrade to become a 4<sup>th</sup> generation X-ray light source. The transition to such a diffraction limited storage ring (DLSR) and the introduction of a new X-ray undulator source, alongside with new optics, will significantly alter the X-ray beam characteristics of the new microXAS 2.0 beamline. The combination of enhancements will lead to increased flux, enlarged energy range, and improved dynamic focusing capabilities, unlocking new and unique scientific studies of materials and phenomena previously beyond reach. A unique, dynamic transition between pink and monochromatic beams, as well as focused and unfocused beams, will become more readily accessible.

In this presentation we will detail recent examples of studies performed at microXAS before the upgrade as well as the new capabilities of microXAS 2.0.

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## Soft x-ray emission and resonant inelastic x-ray scattering for actinide research

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A detailed understanding of the bonding properties and covalency, in particular involving 5f orbitals, is a central topic in actinide research. This has fueled intensive research efforts using x-ray spectroscopy techniques with their unique sensitivity to the electronic structure. Most of these studies use hard x-rays, exploring the actinide L and M edges. Despite the promise of reduced lifetime broadening and complementary information at the N and O K edges in the soft x-ray range, only some pioneering work can be found in the literature, mainly by Shuh and Butorin (e.g., [1,2]). This is surprising (and likely owed to the experimental complexity), since soft x-ray techniques are necessary to study actinide bonding from the viewpoint of light element ligands.

We have recently begun to exploit the proximity of the newly commissioned X-SPEC beamline [3] at the KIT Light Source and KIT's Institute for Nuclear Waste Disposal (INE) to develop world-wide unique capabilities in soft x-ray spectroscopy of actinide compounds. X-SPEC is a double-undulator beamline, covering soft and hard x-rays from 68 eV up to 16,000 eV. Currently, this allows us to perform soft x-ray absorption (XAS) and emission (XES), resonant inelastic soft x-ray scattering (RIXS), and hard x-ray photoelectron spectroscopy (HAXPES) experiments on samples below the exemption limit. We will present the experimental setup at X-SPEC and discuss soft x-ray spectroscopy results on uranyl halides. With the high-transmission x-ray spectrometer of the X-SPEC beamline, complete soft x-ray RIXS maps can be collected, which are analyzed with the help of spectra calculations based on density functional theory (DFT).

Finally, we will give a preview of further instrumental developments: first upgrading the existing setup and procedures to enable experiments on samples with activities of 100x the exemption limit, and, in a second step, the construction of the dedicated and air-filtered ROXS (Radionuclide materials Observed with soft X-ray Spectroscopy) hutch and experimental station.

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## Synchrotron based hard X-ray spectroscopy for radionuclide research at the KIT Light Source

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Since a first U L<sub>3</sub>-edge transmission XAFS spectrum of a pelletized metaschoepite sample had been recorded on August 19<sup>th</sup>, 2004 during commissioning of the INE-Beamline, X-ray absorption and X-ray emission spectroscopy for speciation investigations of radionuclide materials at KIT (and worldwide) have undergone a tremendous development. Although there are meanwhile more than 50 synchrotron radiation sources operational in the world, facilities with specialized beamline infrastructures and safety protocols allowing for experiments on radioactive samples with activities beyond the exemption limits are still scarce. At the KIT Light Source (KIT Campus North, Karlsruhe, Germany), the Institute for Nuclear Waste Disposal operates two beamline end-stations dedicated to the investigation of radionuclide materials by XAFS and related techniques – the INE-Beamline station (fully operational since fall 2005) and the ACT station of the CAT-ACT wiggler beamline (since 2016) [1-3]. Samples with total activities amounting to 1E+6 times the isotope specific European exemption limits and 200 mg of fissile isotopes <sup>235</sup>U and <sup>239</sup>Pu are feasible at both beamlines. Highly versatile detection systems and sample containments – generally avoiding extensive shielding or sample handling in a glovebox – have been conceived since the initial commissioning of both stations. Those have enabled unique measurements such as tender X-ray XAS (E < 3 keV) of liquid radionuclide samples or in situ studies under non-ambient conditions. Investigations of highly radioactive specimens (e.g., nuclear waste fragments) are feasible regardless of the actual contact dose rate if the radiation field is limited to a few μSv/h at the edge of the experimental table. Nowadays, a clear focus has been placed on high energy resolution X-ray emission techniques [4,5]. This is as well reflected by the commissioning of the reconfigured 5-crystal, Johann-type X-ray emission spectrometer at the ACT station. The so-called NEXT spectrometer (next generation probe of chemical bonding properties of actinides and lanthanides) features variable Rowland circle diameters (0.5 – 1 m) and scattering angles (between 90° standard and 180° backscattering geometry) in addition to a significantly improved enclosure which is keeping all beam paths in He-atmosphere. This instrument is complemented by a recent upgrade of the SUL-X end-station operated by KIT-IPS, now enabling a single analyzer crystal X-ray emission spectrometer mode in Rowland circle geometry inside a vacuum vessel – cf. [6,7] for details. So far, investigations of radionuclides at KIT Light Source at experimental stations without a dedicated safety infrastructure have been restricted to specimens with total activities below the exemption limit. A new protocol has been recently approved and will be implemented in the upcoming months which specifies regulations and conditions under which handling of samples with activities up to (but strictly below) 100 times the exemption limit in a double containment will be enabled at further, non-dedicated end-stations.

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## Targeted radionuclide therapy: the promise and challenges of short-lived alpha-emitting actinides

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Targeted alpha-particle therapy holds tremendous potential as a cancer treatment, since it offers the potential of delivering a highly cytotoxic dose to targeted cells while minimizing damage to the surrounding healthy tissue, due to the short range and high linear energy transfer of alpha particles. While the only available FDA-approved radioimmunoconjugates utilize beta-emitting isotopes, I-131, Y-90, and Lu-177, several actinide isotopes have recently emerged as promising short-lived radionuclides that emit multiple  $\alpha$  particles in their decay chains, dramatically increasing the potential delivered dose. In particular, Ac-225 and Th-227 can act as in vivo alpha-generator radionuclides and are of great interest for new therapeutic applications.

To create a targeted alpha therapeutic, one must assemble 3 basic parts: a targeting moiety, a radionuclide binding molecule, and an appropriate radionuclide such as Ac-225 or Th-227. Though sound in theory, and despite promising therapeutic potential established in pre-clinical and clinical studies, such designs have been slow to emerge. Reasons for this protracted development are many, including limited radioisotope supply, insufficient understanding of isotope biodistribution and biodosimetry, poor retention of alpha-emitting daughter products at the target site, as well as inadequate chelation, one of the major drawbacks.

To seek further development of Ac-225 and Th-227 bioconjugate therapeutics, ongoing efforts aim at addressing all of those limitations. Our approach to clearly delineate the coordination chemistry and biodistribution of these radioisotopes, their short-lived daughter products, resulting dosimetry, mechanisms of induced cellular toxicity, efficacy, and safety will be presented and discussed [1-4].

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## Computational ligand design for targeted alpha therapy

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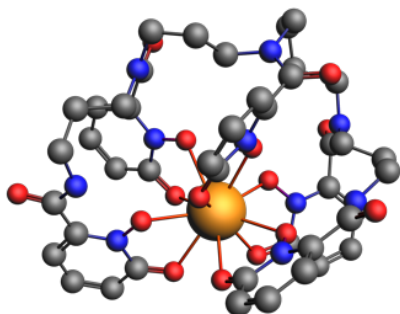
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Targeted alpha therapy (TAT), part of targeted radionuclide therapy (TRT), is a relatively new and highly promising approach to cancer therapy. It relies on bifunctional chelators (BFC) that, on the one hand, specifically target the cancer tissue via covalent attachment to a disease targeting vector, and on the other hand strongly encapsulate the radionuclide. An ideal BFC should be highly selective for the radionuclide of interest.

We have used computational chemistry to support the design of novel multidentate chelators for [<sup>225</sup>Ac]Ac<sup>3+</sup> and other radionuclides such as [<sup>227</sup>Th]Th<sup>4+</sup>. These include:

- 8-coordinate and corresponding, novel 10-coordinate 1-hydroxy-2(1H)-pyridinone (1,2-HOPO) chelators, HOPO-O<sub>8</sub> and HOPO-O<sub>10</sub>. [1]
- A systematic study of the chelating ability of macrocyclic ligands. [2]

We will discuss considerations for the computational study of such systems, including conformational flexibility, solvation effects, relativity, and the judicious use of systematic error cancellation ( $\Delta\Delta G$  approaches). Of fundamental interest in terms of the underlying chemistry of actinium in general is the question of the role (or lack thereof) of the 5f-orbitals in bonding [3, 4] that has been shown to be crucial elsewhere along the actinide series. [5]



Optimized structure of the HOPO-O<sub>10</sub> complex of Ac<sup>3+</sup>.

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## Interaction of Ac<sup>3+</sup>-based Radiopharmaceutical with Somatostatin Receptor Revealed by Molecular Dynamics Simulations

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The use of actinium-based radiopharmaceuticals is on the rise, but the coordination chemistry of trivalent actinium remains poorly understood. The most stable isotope of Ac (<sup>227</sup>Ac) has a short half-life of 21.77 years, making experiments with this element quite ambitious. Computational chemistry is the way forward for exploring actinium chemistry. There have been several attempts to apply combined experimental and theoretical approaches for designing suitable chelators for Ac<sup>3+</sup>-radiopharmaceuticals, including 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetramethylene phosphonic acid (DOTP),<sup>[1]</sup> and 3,4,3,3-(LI-1,2-HOPO).<sup>[2]</sup>

Here, DFT calculations were first performed to compare the binding affinity of Ac<sup>3+</sup> with different chelators. It was revealed that diethylenetriaminepentaacetic acid (DTPA) and “HOPO-O8” are slightly more effective chelators than the widely-used DOTA. DOTP demonstrated the most optimal performance. It is important to pursue the specific high affinity of the chelator towards Ac<sup>3+</sup> to deliver the radionuclide to the target cells. However, it is also imperative to have molecular interactions with the receptor for the recognition of the radiopharmaceuticals. In the next step, molecular dynamics (MD) simulations of somatostatin receptor 2 (SSTR2) overexpressed in neuroendocrine tumors in complex with several different radiopharmaceutical compounds have been performed. Bonding and non-bonding parameters involving actinium have been developed using Metal Center Parameter Builder implemented in *Amber 20* as well as using DFT calculations with B3LYP functionals using *Gaussian16*. MD simulations performed using *GROMACS* program package as depicted in Figure 1.

DOTP, which has been suggested in previous study as an excellent alternative to DOTA,<sup>[1]</sup> was found to perform better than DOTA not only because of better affinity to Ac<sup>3+</sup> but also in terms of the overall higher affinity of Ac<sup>3+</sup>-DOTP-TATE to the receptor compared to the corresponding DOTA complex. Detailed energetic analysis revealed that this is primarily due to electrostatic interactions stemming from high negative charge of DOTP. Further analysis of the secondary structure of the receptor revealed that Ac<sup>3+</sup>-DOTP-TATE perform excellently also in terms of ligand recognition and affect the “toggle switch” for the activation of somatostatin receptor. Furthermore, effect of adding “linker” between the chelator and the peptide part of the radiopharmaceutical have been investigated and it has been revealed that the addition of linker indeed increases the ligand affinity to the receptor.

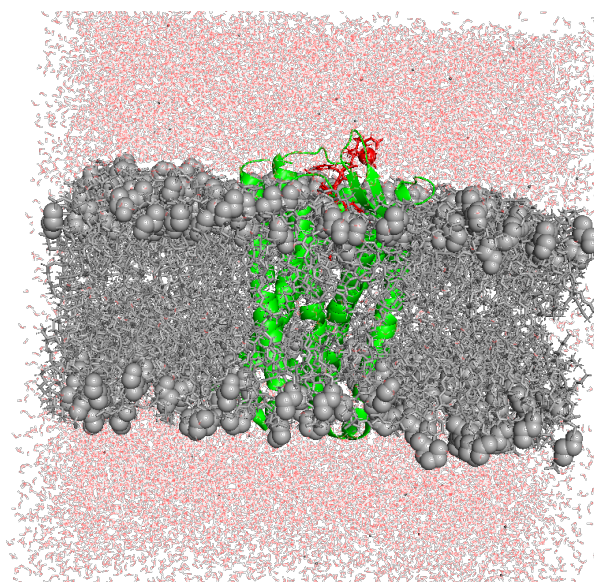


Fig.1. Ac<sup>3+</sup>-DOTA-TATE combined with SSTR2 receptor immersed in lipid bilayer with cytoplasm and extracellular fluid created for MD simulations.

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## Polypyridyl Extractant Design for Actinide Separation

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Advancing the field of chemical separations is important for nearly every area of science and technology.<sup>[1]</sup> Some of the most challenging separations are associated with the americium ion, Am(III), for its extraction in the nuclear fuel cycle, <sup>241</sup>Am production for industrial usage, and environmental cleanup efforts.<sup>[2]</sup> Herein, a series of extractants were studied, using first-principle calculations, to identify the electronic properties that preferentially influence Am(III) binding in separations. The polypyridyl family of extractants was chosen to study as the most used extractant family and because it affords a high degree of functionalization.<sup>[3]</sup> The actinyl ions are used as a structurally simplified surrogate model to quickly screen the most promising candidates that can separate these metal ions. The down selected extractants are then tested for the Am(III)/Eu(III) system.

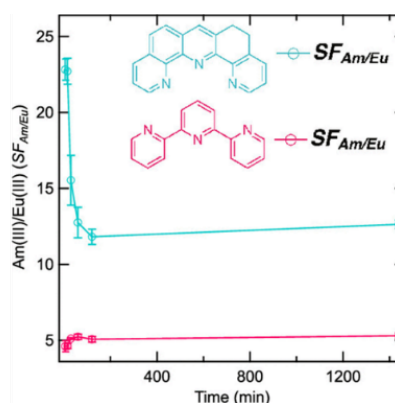
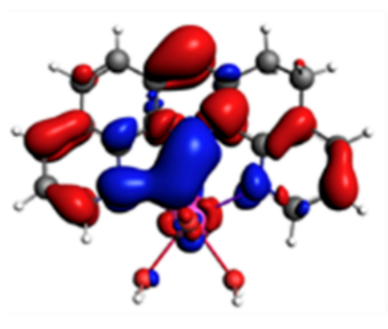


Figure 1: Left: Selected ETS-NOCV<sup>[4]</sup> deformation density (iso-contour 0.0003 a.u.) of center ring  $\pi$  interactions between extractants **13** and  $\text{UO}_2(\text{H}_2\text{O})_2^{2+}$ . Electron density flows from red to blue. Right: A plot showing how distribution coefficients from <sup>241</sup>Am and <sup>155</sup>Eu changes as a function of time (<1 h) during a liquid/liquid separation facilitated by extractant **13**.

Our results showed that  $\pi$  interactions, especially those between the central terpyridine ring and Am(III), play a crucial role for separation. This conclusion is validated by the synthesized 1,2-dihydrodipyrido[4,3-b;5,6-b]acridine (**13**) extractant, a preorganized derivative of the terpyridine extractant(**1**), which we experimentally showed was four times more effective at separating Am(III) from Eu(III) ( $\text{SF}_{\text{Am}/\text{Eu}} \sim 23 \pm 1$ ). These results serve as proof-of-principle in our computational methodology as we would not have predicted *a priori* superiority of **13** over **1** without the in-depth electronic structure analyses. Although we acknowledge a need for more experimental data to test the generality of our predictive capabilities, we are excited by this experimental validation of our computational results and its implications regarding extraction design. Emboldened by these results, we modified substituents on **13** to provide more desirable separation capability. We hope this work<sup>[5]</sup> will stimulate discussion and modeling efforts that advance extractant design principles.

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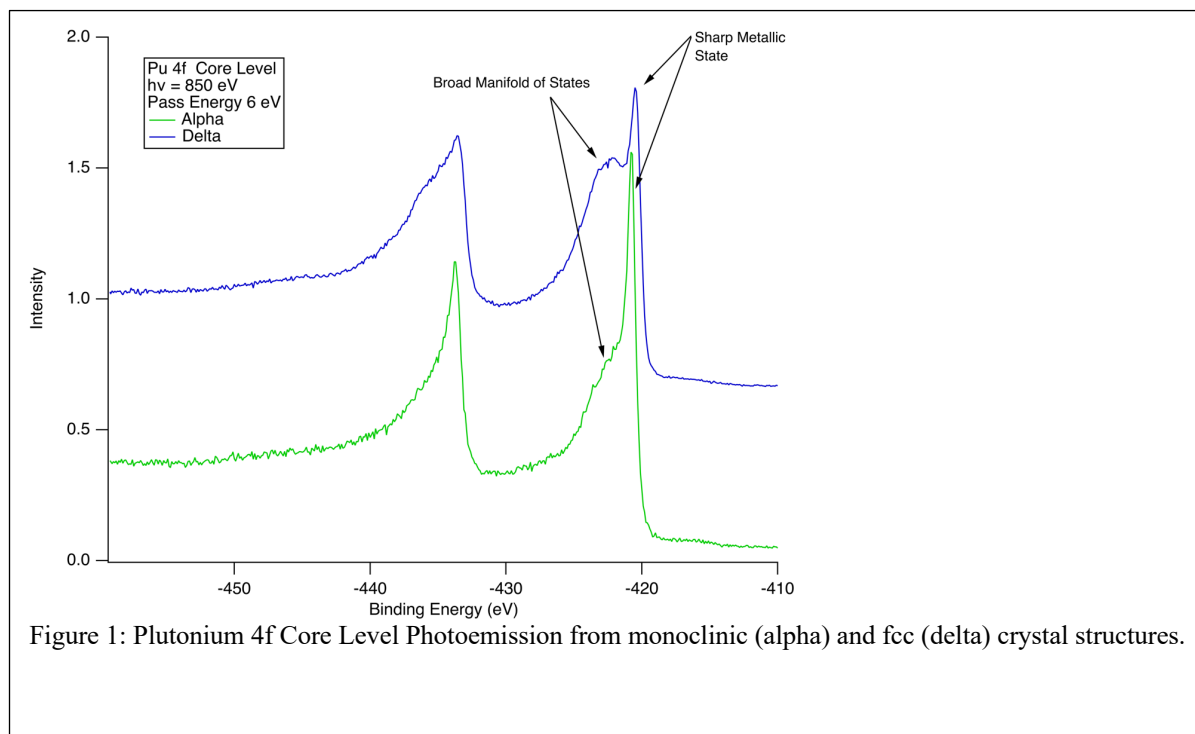
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## Using Our Artificial Intelligence Tools For Analysis of Materials Characterization Data Pertaining To Nuclear Systems: Corrosion and Radiation Damage

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We have developed artificial intelligence (AI) based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS)[1], Nanoindentation, X-ray Emission (XES), and core level photoemission (XPS). Specifically, we use a genetic algorithm to extract the relevant structural parameters through fitting of the measured spectra. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of compounds and specific computational input files that may be present in a given material. The algorithm then attempts to determine the best physically appropriate parameters from these compounds that are present in the experimental measurement. The base analysis package is called Neo and is open source written in Python. I will illustrate the use of this package to studying Pu oxidation and aging (Figure 1); determining metallic fission product interaction in the SiC containment layer of TRISO fuels including high temperature (safety) testing; finally, I will look at the simulated oxidation of TRISO barrier layers with XPS.



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## Fully automated procedure for XANES and EXAFS processing based on IgorPro

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Due to ongoing development at beamlines and synchrotrons, the higher data rate of beamlines can create hundreds or thousands of scans per day. This optimization allows measurement of complex systems from materials science in which a large number of parameters must be varied relative to one another. As a consequence, there is a demand for an automatic and highly reproducible data evaluation. The current available data evaluation programs like Demeter or Larch are not optimized for this. Without optimization of parameters of single spectra's, there are limitations in the XANES background subtraction, E0 calculation for EXAFS and as a result sometimes also in the EXAFS background fit. For XANES an automated solution was shown for Au reference spectra [1]. However, lanthanide and transition metal spectra pose much greater challenges for data evaluation and an automatic EXAFS processing is also needed.

The presented program is based on IgorPro (wavemetrics) to enable the fast development of a prototype including GUI, without caring about versions of the operating system or the programming environment. It is based on EXAFS123 from Scarrow [2]. In contrast to most other EXAFS programs, it does not vary the background spline until X(R) at low R is as small as possible. Additional to a robust edge-position detection a complex fit containing a sigmoidal shaped function with several peaks and a cubic spline is used to model the edge and background. This algorithm is able to produce extremely reproducible XANES spectra without any user interaction. Due to this pre-fit the EXAFS output in the low-k region is significantly improved. The calibration of the spectra is possible with a linear energy shift or a correction based on the angle of the DCM-crystal. All parts are optimized to run with as less as possible user interaction and all intermediate calculation are saved, maintained and can be reloaded without recalculation. All parameters for the data-evaluation are saved and can be easily seen inside the database table. Unlike other programs, it includes the parallel handling of transmission, fluorescence and reference spectra. Therefore, at each step of the data evaluation, a decision can be made as to whether transmission or fluorescence data should be used. Since the processing of hundreds of spectra is possible without restrictions, the individual spectra do not have to be deleted after summation. In addition to standard tools such as the linear combination fitting of several references to a sample spectrum, the calculation of difference spectra and the principal component analysis (PCA), a reference-based estimation of the oxidation states based on the respective edge positions is also available. The PCA is also extremely helpful to checking the for consistency and quality of huge sets of replicate spectra. Additional to an export of XANES, EXAFS and FT also special files for import to Artemis, Larch and EXAFSNeo for EXAFS shell fitting can be written to disc.

The focus of the future development is targeted onto the replacement of last few input-parameters and delivering fully automatic data evaluation. Planned further features are removal of detected glitches and steps to reduce their impact of background subtraction of the EXAFS oscillations. Combined with a live read in of measured data, this will enable automated quality check of the data with included alarm process in cases of insufficient data quality. The process of data evaluation will be demonstrated using battery material spectra containing several transition metals.

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## Exploring f-Electron Systems through HERFD and RIXS

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Understanding the electronic structure of f-electron systems is crucial for comprehending how electrons drive chemical reactions and influence fundamental properties like reactivity, bonding, and local structure. The most direct methods for probing the local and electronic structure of materials are done by X-ray absorption spectroscopy (XAS) or X-ray absorption near-edge structure (XANES) in high energy resolution fluorescence detection (HERFD) mode and resonant inelastic X-ray scattering (RIXS)<sup>1-3</sup>. The experiments are quite complex since they require sophisticated synchrotron radiation sources that can produce highly intense and tunable X-rays. Additionally, the detectors and spectrometers for HERFD-XANES and RIXS must be highly sensitive and capable of resolving small energy differences. The alignment and calibration of the experimental setup need to be extremely precise. There are almost no requirements for sample preparation (data can be collected on liquids, solids and gases; powders, single crystals or amorphous materials). However, data analysis of HERFD-XANES and RIXS process is challenging due to the complexity of the interactions involved. Understanding the electronic excitations involved in RIXS and HERFD-XANES process requires theoretical models and computational tools. Despite the complexity, RIXS and HERFD-XANES are powerful tools for probing electronic structure in f-electron systems (actinides and lanthanides), providing insights that are often not accessible by other spectroscopic methods.

This contribution will provide an overview of the recently performed RIXS and HERFD-XANES studies on actinide and lanthanide-contained materials<sup>4-7</sup> at the Rossendorf Beamline (ROBL) of the European Synchrotron (ESRF) in Grenoble (France)<sup>8,9</sup>. I will show that the experimental data, analysed by electronic structure calculations can provide detailed information about the electronic states and bonding characteristics of atoms within materials, helping researchers to elucidate the relationship between chemical composition, atomic structure, and material properties.

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## New high-resolution X-ray spectroscopic tools for Investigating 5f electrons in actinide compounds

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Due to their complex electronic structure and unusual physical and chemical properties, the actinides (An) are still less understood compared to other elements in the periodic table. In order to achieve a better understanding, advanced spectroscopic tools can be used to provide deep insights into the electronic structure and the role of covalency in actinide bonding. Twenty-one different U, Np, Pu and Am compounds in solid and liquid form were investigated applying An M<sub>4</sub> edge core to core-resonant inelastic X-ray scattering (CC-RIXS) to determine a spectroscopic trend and to develop two spectroscopic tools.[3, 6] The X-ray experiments were performed at the ACT station at the CAT-ACT beamline and the SUL-X beamline at the KIT Light Source (KLS) in Karlsruhe, Germany.[1, 2] The satellite peak in the An M<sub>4</sub> edge CC-RIXS maps originates from the exchange interaction between the 4f core hole and the 5f electrons excited during the An M<sub>4</sub> edge CC-RIXS process as demonstrated by multiplet calculations by means of the full multiplet Quanty code.[4-8] The satellite peak at 90° π scattering geometry provides insight into the number of 5f electrons localized at the investigated actinide atom. Compared to classical tools for determination of the oxidation state, like the chemical shift of the absorption edge of X-ray absorption near edge structure spectra, the satellite peak is not influenced by the delocalized electron density distributed between metal and ligand but mainly by electrons localized on the metal atom. At 90° π scattering geometry, an upward trend was observed from 5f<sup>0</sup> to 5f<sup>4</sup> with a break and following decrease in intensity for 5f<sup>5</sup> and 5f<sup>6</sup> through studying eighteen different U, Np, Pu and Am compounds. At 180° π scattering geometry, the satellite peak shows sensitivity to the metal-ligand bond covalency, as shown by experiments and theoretical ligand field DFT (LFDFT) calculations, investigating a series of uranyl(VI) solid state compounds with small modifications of the chemical environment. This work introduces two new spectroscopic tools for probing the 5f electron configurations as well as the bond covalency of actinides, which can be used to further advance our understanding of the chemical and physical properties of actinide compounds.[7]

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## Origins of Actinyl XAS Features: Application to $\text{NpO}_2^{2+}$

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It is common to describe the X-Ray Adsorption Spectroscopy, XAS, of actinyls with models of isolated molecules. The energies and dipole intensities obtained with quantum mechanical wavefunctions, WFs, for this model are then compared with measurements made in an aqueous environment rather than as an isolated molecule; see, for example, Refs. [1-3]. In addition, for high resolution XAS measurements, HR-XANES [4], the XAS is taken as a slice of the Resonant Inelastic X-Ray Scattering, RIXS map. The departures due to these measurement conditions from the theoretical predictions for an isolated linear actinyl need to be quantified and understood. There are in addition, two other important approximations for the theoretical predictions of the actinyl XAS: Choice of distance between the actinide cation and the O anion. And, choice of the theoretical method used to determine the XAS energies and intensities. This presentation investigates the importance of these four physical and theoretical approximations for the representative case of  $\text{NpO}_2^{2+}$  where the  $M_5 \rightarrow 5f$  and  $M_4 \rightarrow 5f$  excitations are considered.

The WFs for the initial and XAS excited states are fully relativistic *ab initio* Dirac Hartree-Fock and many body configuration interaction solutions.[5] The intensities for the spectra are computed from dipole matrix elements. (1) To study the effect of the environment, the XAS is compared for isolated  $\text{NpO}_2^{2+}$  and for neptunyl in an aqueous environment,  $\text{NpO}_2[\text{H}_2\text{O}]_5^{2+}$ . (2) To study the use of a RIXS slice, the XAS determined by taking a slice of our theoretical RIXS maps will be compared to our direct XAS calculation. Of particular concern here is the broadenings need to match these two plots. (3) The XAS plots are compared for different Np-O distances. And, (4) approximations for the calculation of the WFs are investigated. The particular concern is for the orbitals that must be included in the many-body WFs because of the covalent character of the open shell, dominantly 5f, and closed shell, dominantly O(2p), orbital. This is the first time that a complete study of the various approximations used in the analysis of XAS has been made.

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## A practical computational tool for actinide coordination chemistry (LFDFT): study of M<sub>4,5</sub>-edge core-to-core and valence-band resonant inelastic x-ray scattering

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A great deal of spectroscopic methods have been developed to study actinide coordination chemistry, for example, high-energy resolution x-ray absorption/emission spectroscopy, core-to-core and valence-band resonant inelastic x-ray scattering (RIXS). [1-3] RIXS techniques have been very powerful in deciphering electronic structure effects and helped advancing our understanding of the overall 5f electrons and their ability to participate in a chemical bond. [2] However, investigating actinide M<sub>4,5</sub>-edge RIXS can be made possible hand in hand with theoretical models.

In the last decades, we developed a DFT-based theory for coordination chemistry, the Ligand-Field Density-Functional Theory (LFDFT) model. [4] This presentation reports recent developments in LFDFT, including extended method for modeling actinide M<sub>4,5</sub>-edge core-to-core and valence-band RIXS as well as the treatment of ligand-to-metal charge transfer for simulating covalent binding interactions. We will demonstrate that LFDFT can be used to calculate RIXS maps and to model RIXS spectral profiles from first principles. In a series of applications that are used to benchmark the theoretical model, including uranyl(VI) systems, [5-6] actinide oxides, [7] aqua Pu(III,IV,V,VI) complexes, Am(III) organometallics, etc., we will show that very good agreements with the experimental data can be reached. Furthermore, LFDFT is also proposed to assess the bond covalency of the actinide-ligand interaction.

Acknowledgment: This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (101003292). We would like to acknowledge all collaborators, particularly those involved in the studies referenced under [5-6].

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## HERFD-XANES vs conventional XANES. The implications of cutting through the RIXS plane

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The high-energy-resolution fluorescence detected (HERFD) mode to collect XANES is becoming well known in the actinide field and its use is progressively increasing. In the actinide field, the  $M_{4,5}$  edges are the one that have the greatest advantage in being measured with HERFD over conventional XANES. The partial suppression of the core-hole lifetime broadening reveals spectral features otherwise hidden at the  $M_{4,5}$  edges and it has been demonstrated that the absorption edge position is extremely sensitive to the oxidation state of the actinide ion [1].

Despite HERFD-XANES is often presented as a conventional XANES with higher resolution, these spectra are the product of a more complex physics process and for a correct interpretation of HERFD-XANES it is important to understand it as part of the RIXS process.

This can be shortly resumed in the question: what are the differences between a better resolved XANES and the cut of the RIXS plane along the maximum of the fluorescence intensity?

This talk will be a contribution to start answering this question. I will explore the case of the  $M_{4,5}$  edges of  $\text{ThO}_2$  and uranyl. Theoretical calculations using the Quanty code[2] will be used to look into the specificity of HERFD-XANES compared to conventional XANES. In particular, the role of the two core-holes over a single core-hole in HERFD-XANES and XANES respectively. For  $\text{ThO}_2$  and uranyl, the effects of the local environment on 5f states are substantial[3,4]. With the help of calculations, I will elucidate how spectral features are sensitive to the neighboring atoms and how these effects appear in XANES collected in the conventional or the HERFD mode.

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## U M<sub>4,5</sub> edge XANES of uranyl: Potential energy curves of core-excited states and applications to x-ray spectroscopy

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U M<sub>4,5</sub> edge XANES of uranyl is a very quickly developing field in actinide chemistry to probe the electronic structure of uranyl in different chemical environments [1-5]. We have determined potential energy curves for variation of the U-O distance for the ground and dipole allowed excited states where an electron in the M<sub>4,5</sub> shell is promoted to the empty, nominally U 5f shell. There are major differences between the equilibrium U-O distances for the ground and excited states. This is shown in the schematic figure for the potential energy curves below. We explore the character and the consequences of these differences. In particular, it is shown that the very different shapes of the core-excited states corresponding to the three observed peaks gives rise to different Franck-Condon vibrational broadenings in the three XAS features.

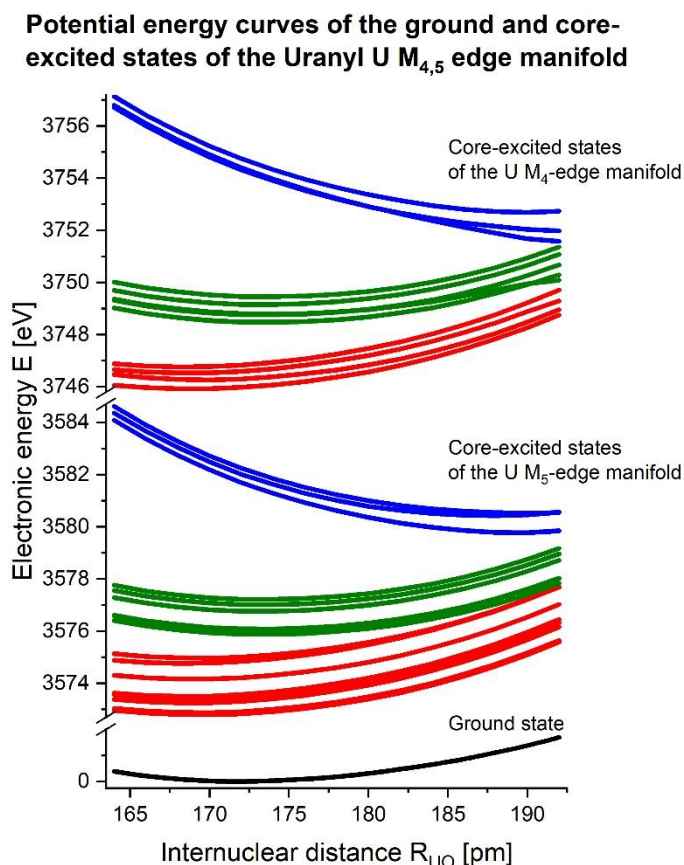


Figure 1: Potential energy curves of ground and core-excited states of Uranyl. The three branches (red, green and blue) of core-excited states in both edges are distinguished by the 5f valence shell occupation (red: 5f  $\delta\phi$  valence occupation, blue: 5f  $\pi^*$  and green: 5f  $\sigma^*$ )

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## **New Generation HPGe Detector Technologies for Synchrotron Applications**

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Over the last few decades, Mirion has been providing advanced High Purity Germanium (HPGe) and Silicon Drift Diode (SDD) detectors as well as instrumentation for world leading research institutes engaged in cutting-edge materials analysis, especially using synchrotron radiation beams, nuclear and fundamental physics research, space science, reactor monitoring, industrial and medical imaging.

The aim of this presentation will be to show the existing building blocks for the development of new HPGe detectors, but above all, the latest major advances.

Among the topics to be presented, particular focus will be placed on:

- New generation pixel HPGe detectors: now available in different layouts, the new generation HPGe pixels detectors are combining the optimized area coverage of monolithic pixelated detectors with the higher count rate performance of discrete, circular-shaped multi-elements detectors.
- Novel fast CMOS electronics that replaced the previous input stage technology, allowing a 5 times faster signal rise time and twice lower degradation between low and high-count rates.
- Customized cryostat configurations: to fit specific room constraints on the beamline.
- Electrical cooling: the previous liquid nitrogen (LN2) dewar configurations are more and more replaced by new, reliable electrical coolers, avoiding the constraints and risks of using LN2. To minimize vibrations or heat dissipation within the hutch, water cooled heat sink (with chiller) are available and especially dedicated for nano focused beamlines.

Recently manufactured detector systems will be presented, with factory and synchrotrons measurements results. Single-element and 4-pixel New Generation prototype detectors were tested in real conditions at Soleil, ESRF and DLS synchrotrons. Relevant experimental data acquired on this occasion will be presented: for example, X-ray fluorescence results on copper and zirconium targets, with up to 5 million counts per second, will demonstrate concretely the advantages of the latest HPGe detector technologies developed for synchrotrons applications.

## Real-time tracking of oxidation states of UO<sub>2</sub> nano particulate electrode using HR-XANES at uranium M<sub>4</sub> edge and a microfluidic technique

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Real-time tracking of the oxidation states of a UO<sub>2</sub> electrode during electrochemical oxidation and reduction was achieved using operando high-resolution X-ray absorption near-edge structure (HR-XANES) spectroscopy at KIT synchrotron beamline in Germany. This was made possible by utilizing a particle-attached microfluidic electrochemical cell (PAMEC) developed by PNNL scientists, and employing KIT's advanced actinide M-edge HR-XANES technique.<sup>1-2</sup> PAMEC is a three-electrode system consisting of a working electrode (WE) made of the materials of interest, platinum (Pt) reference electrode, and Pt counter electrode (Figure 1A).<sup>3</sup> The electrochemical analyzer connected to the PAMEC device controlled the redox process, e.g., applying constant potential on UO<sub>2</sub> electrode to reduce (-1.1 V vs Pt) or oxidize it (0.5V vs Pt), while HR-XANES simultaneously scanned it. Our observations revealed the evolution of U from U(IV) to U(V) and U(VI) during the oxidation process. We were able to demonstrate the reversibility of this process by reducing the same electrode back to pure U(IV), confirmed by HR-XANES (Figures 1B-1C). To our knowledge, this study reports the first in situ and operando measurement of real-time oxidation state changes of UO<sub>2</sub>. The spectra obtained also provided insight into the electronic structure of U(VI) in the UO<sub>2</sub> alteration process. This successful international scientific collaboration showcases the potential of PAMEC for in situ and operando measurements of actinides and highlights its promising broad application for characterizing nuclear materials requiring only micrograms.

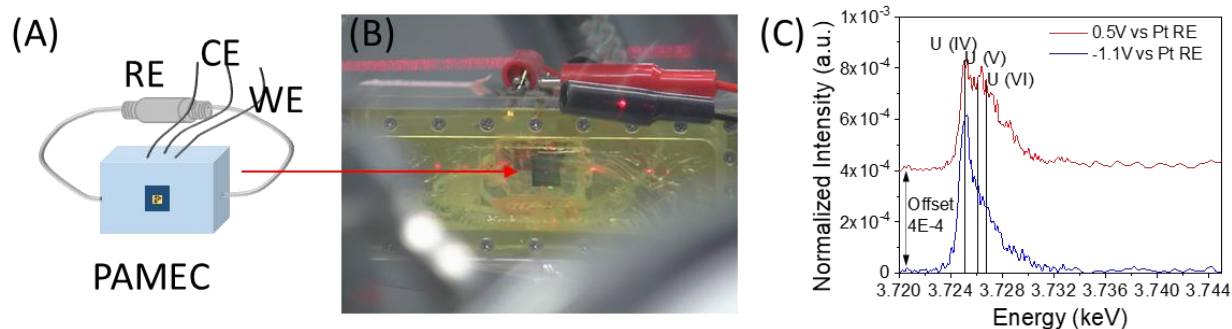


Figure 1. (A) A schematic of PAMEC device with working electrode (WE) wire, counter electrode wire, and reference electrode (RE) wire, (B) the photograph of a PAMEC sealed in a secondary containment and covered by x-ray transparent KAPTON film and mounted on the sample positioning stage of HR-XANES, and (C) the HR-XANES spectra of the U states of the UO<sub>2</sub> electrode incorporated inside PAMEC, showing the real-time tracking of oxidation state changes UO<sub>2</sub> during redox process

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## Application of X-ray absorption spectroscopy in support of Pu disposition strategy

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The ultimate end-point for all UK-owned separated plutonium (Pu) is a geological disposal facility, either in the form of spent mixed oxide (MOX) fuel or immobilised within the structure of a chemically durable ceramic material [1]. Candidate ceramic wasteforms for Pu include titanate ceramics such as zirconolite or a mixed (Pu,U,Gd)O<sub>2-x</sub> disposal MOX with a suitable neutron absorbing additive such as Gd<sup>3+</sup> to prevent against post closure criticality [2]. The zirconolite phase (ideally CaZrTi<sub>2</sub>O<sub>7</sub>) could feasibly act as a disposal matrix for separated PuO<sub>2</sub> through interdiffusion of Pu<sup>3+/4+</sup> cations within specific lattice sites in the zirconolite structure e.g. CaZr<sub>1-x</sub>Pu<sub>x</sub>Ti<sub>2</sub>O<sub>7</sub> facilitated by either high temperature sintering or by hot isostatic pressing (HIP). Controlled parametric studies have demonstrated, for both routes, that it is feasible to incorporate surrogates (namely Ce, U & Th) and neutron absorbing additives (Gd<sup>3+</sup> and/or Hf<sup>4+</sup>) within both the Ca<sup>2+</sup> and Zr<sup>4+</sup> sites, necessitating the addition of a charge modifier, examples of which include Fe<sup>2+/3+</sup>, Al<sup>3+</sup> and Cr<sup>3+</sup> [3]. X-ray absorption spectroscopy is a powerful element-specific tool to probe oxidation states and coordination environments in materials and can therefore be used to underpin solid solution mechanisms for Pu within candidate wasteform phases. This talk will summarise recent advances in wasteform development with a focus on the application of bulk XAS and HERFD techniques to probe solid solution mechanisms and radiation damage behaviour.

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## X-ray Absorption Spectroscopy (XAS) Study on Technetium Incorporation within Iron Oxides, Waste Glass, and Grout Waste Forms

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Technetium-99 (Tc) is a fission product with a long half-life, high mobility in oxidizing conditions that raises many environmental concerns. Tc-99 is present in legacy nuclear wastes at the US Department of Energy (US DOE) Hanford Site where it is destined for immobilization via vitrification or as grout when present in secondary wastes resulting from vitrification. One of the technical challenges with vitrifying these wastes is the high volatility of Tc-99 at vitrification temperatures, which could lead to lower Tc-99 loading in the final glass product. The use of grout waste forms for the solidification of secondary wastes generated by vitrification removes the high temperature challenges, but the stability of Tc-99 due to aging processes such as reoxidation, that could lead to Tc-99 release, presents long-term disposal uncertainty.

This work aims to understand how the local coordination, speciation, and valence state of Tc-99 contribute to improvements in Tc-99 stability in both vitrification and grout waste forms. The volatility of Tc-99 and its long-term stability in waste forms is highly dependent on Tc-99 oxidation state. Published studies have already demonstrated that converting more mobile and volatile Tc(VII) to stable Tc(IV) species improves vitrification retention and long-term grout waste form stability [1-8]. In this vein, this work investigated (1) how combining different reductants and controlling the atmosphere with gas bubbling can be used to reduce Tc(VII) to Tc(IV) and maintain favorable reducing conditions during glass vitrification to improve Tc-99 loading, (2) how incorporating Tc(IV) into iron oxides doped with trace elements (Ni, Zn, Co, and Cr) can improve long-term Tc-99 stability when combined in a grout waste form, and (3) how the geochemical stability of waste forms and phases, e.g., glass, iron oxides, changes when saturated for extended time periods to provide performance metrics under changing disposal environments. In this study, a wide range of inorganic or organic reductants were tested for Tc-99 retention improvement in glass products, and variable ferrous iron (Fe(II))-containing materials were tested as means to further enhance Tc-99 stability in grout waste forms. For each branch of this work, the molecular information provided by X-ray absorption fine structure (XAFS) spectra collected from Tc-99 precursors, intermediates, and end products provided valuable insight into the Tc incorporation mechanism and long-term stability of Tc-99 in the immobilizing phase. This understanding could be used to improve predictive models of Tc-99 behavior in vitrification and long-term grout waste modeling to support the US DOE Hanford cleanup mission.

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# Dissolution behavior of simulated debris in the presence of malonic acid

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## 1. INTRODUCTION

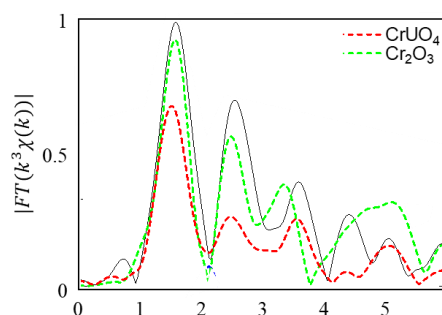
In the accident at the Fukushima Daiichi Nuclear Power Station (1F),  $\text{UO}_2$  fuel reacted with zirconium alloy cladding and stainless steel (SUS) reactor structural materials at high temperatures, forming fuel debris. The debris inside the reactor exists in the coolant water. For planning the safer decommissioning of 1F, it is necessary to understand the chemical properties of the fuel debris and its dissolution behavior in the water mixed with groundwater containing organic matter. Various simulated debris of the  $\text{UO}_2$ -Zr-SUS system has been synthesized under different atmospheric conditions, and the dissolution behavior was evaluated [1]. For instance, the tetravalent zirconium in the  $(\text{U,Zr})\text{O}_2$  solid solutions suppressed the dissolution of uranium. Meanwhile, the uranium in the debris containing  $\text{U}_3\text{O}_8$ ,  $\text{FeUO}_4$ , and others was synthesized under an oxidizing atmosphere and significantly dissolved. In order to understand the dissolution behavior of multi-phase debris in more detail, the dissolution behavior of each single solid phase in the simulated debris has been investigated [2]. However, the impact of organic matter on the dissolution behavior of simulated debris has not been fully understood. This study evaluated the dissolution behavior of some single solid phases in the simulated debris in the presence of malonic acid ( $\text{CH}_2(\text{COOH})_2$ ) through batch immersion tests. Then, the dissolution behavior of multi-phase simulated fuel debris was analyzed.

## 2. EXPERIMENTAL

Mixtures of  $\text{UO}_2$ -Zr-SUS powders were heated for 8 hours at various high temperatures and oxygen potentials, as assumed in 1F accident progression scenarios, to prepare simulated debris. Single-phases of  $\text{UO}_2$ ,  $(\text{U,Zr})\text{O}_2$ ,  $\text{U}_3\text{O}_8$ , and  $\text{FeUO}_4$  were also synthesized as components of the simulated debris. The solid phases were assigned using XRD and SEM-EDX. Furthermore, XAFS analysis was conducted on the  $L_{\text{III}}$  edge of U and the K edges of Zr, Fe, and Cr using the BL-27B beamline at KEK-PF, Japan. The prepared solid phases were immersed in water with malonic acid. After immersion for a given period, the molar concentration of radionuclides in the filtrate was measured using ICP-MS. Additionally, XAFS analysis of the immersion solution was performed. Based on the results, the dissolution behavior of the simulated debris was thermodynamically interpreted.

## 3. RESULTS AND DISCUSSION

For the simulated debris synthesized under 2%  $\text{O}_2$  atmosphere at 1473K, the mixture of  $\text{U}_3\text{O}_8$ ,  $\text{FeUO}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $t\text{-ZrO}_2$  phases was assigned by XRD. EXAFS revealed the chemical coordination environment of each element in the fuel debris, e.g., Cr was solidified in the  $\text{FeUO}_4$  and  $\text{Fe}_2\text{O}_3$  phases (**Fig.1**). The dissolved amount of U at pH 7 increased with malonic acid concentration due to metal complexation. The U concentration was the same as those observed in the immersion of single  $\text{U}_3\text{O}_8$  and  $\text{FeUO}_4$  phases. Meanwhile, a decrease in U concentration was observed without malonic acid, and uranyl ion might be adsorbed to a trivalent iron solid phase. The dissolution behavior of simulated debris prepared under different solution conditions will be discussed using spectroscopic data.



**Fig.1** EXAFS of Cr K-edge of sim-debris heated for 8 hours under 1473 K, Ar+2% $\text{O}_2$  atmosphere

## ACKNOWLEDGEMENT

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## X-ray analysis for radioactive particulates from Fukushima-Daiichi Nuclear Power Plant using synchrotron radiation at SPring-8

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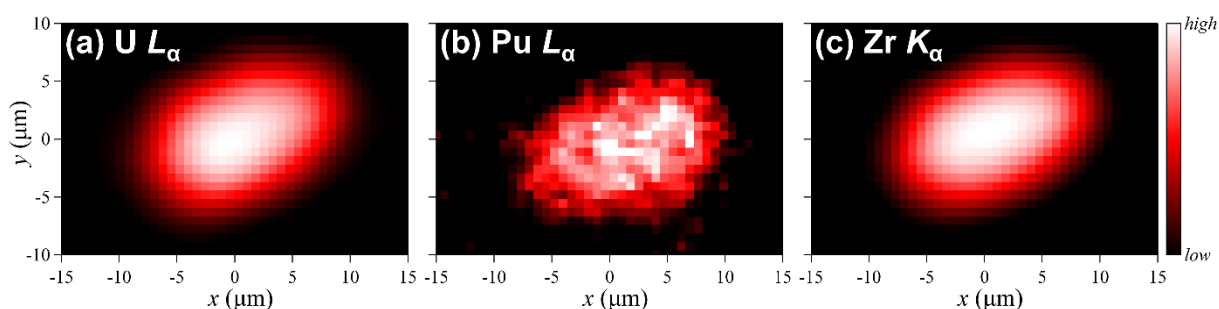
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By the 2011 Tohoku earthquake and tsunami in the northeast area of Japan, Fukushima Daiichi Nuclear Power Plant (1F) lost all electric supplies, and Unit 1, 2, and 3 were seriously damaged. These Units melted down, resulting in a large amount of debris inside their Primary Containment Vessels (PCVs). However, the nature of the debris is not well understood due to the difficulties in collecting samples from inside the PCVs. On the other hand, micron-sized radioactive particulates were collected during an investigation inside the PCVs. These particulates contain important information for understanding the characteristics of the debris.

We performed X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS), and X-ray diffraction (XRD) analyses on the radioactive particulates collected during an investigation inside the 1F Unit 2 PCV using micro-focused synchrotron radiation at BL22XU SPring-8. Figure 1 (a), (b), and (c) show the mappings of a radioactive particulate at U  $L_3$ , Pu  $L_3$ , and Zr  $K$  fluorescence, respectively. The incident photon energy was 20 keV, and the size of the particulate is about 20  $\mu\text{m}$ . We further measured U  $L_3$  and Pu  $L_3$  XAS spectra of the particulate and found that the spectra coincide with those of UO<sub>2</sub> and PuO<sub>2</sub>.

Further analysis of these particles will be presented in the presentation.



**Figure 1** XRF mapping images of micro-sized particulate collected from the inside of 1F Unit2



## Chemical Bonding and Electronic Structure Enabled by 5f-Electrons

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The intricate electronic structure of actinide complexes determines their diverse chemical bonding, reactivity, and spectral properties. The high angular momentum and extended radial distribution of 5f-orbitals facilitate unique bonding interactions that are not observed in other regions of the periodic table. These interactions often result in distinctive spectroscopic signatures, which can be directly measured using valence and core spectral techniques.

Understanding these electronic structures and bonding interactions necessitates the use of advanced quantum chemical techniques. In this talk, I will discuss our recent progress in investigating the novel chemical bonding and spectroscopy of heavy elements across the actinide series, as a function of oxidation state and ligand types. Our close collaboration with experimental teams has highlighted the powerful synergy between theoretical and experimental approaches, significantly enhancing our comprehension of f-orbital participation in chemical bonding.

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## Determination of actinide central-field covalency with 3d4f resonant inelastic X-ray scattering

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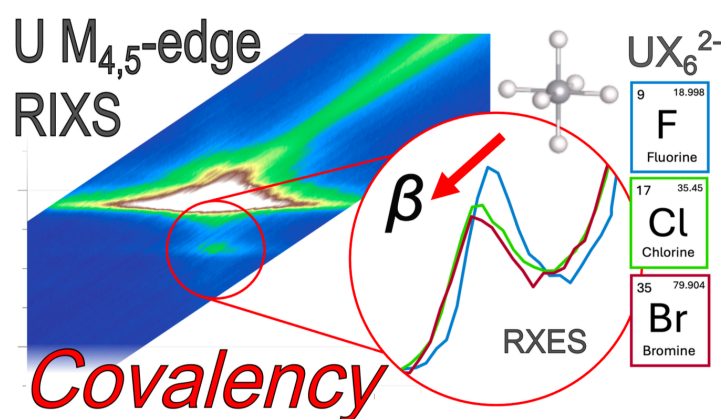
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Understanding the nature of actinide-ligand bonding is a major challenge in actinide chemistry. I will present experimental strategies for addressing this challenge using 3d4f resonant inelastic X-ray scattering (RIXS) to provide experimental insights into electronic structure and bonding. This will include a systematic study of  $[UX_6]^{2-}$  (where X = F, Cl, Br) where spectral satellites are identified with relative energies and intensities that relate to the extent of uranium-ligand bond covalency. By analyzing the spectra in combination with *ab initio* ligand field theory, the satellites are found to carry sensitivity to metal-ligand bonding due to the reduction of 5f inter-electron repulsion and 4f-5f spin-exchange, which is caused by the extent of metal-ligand orbital mixing and the degree of 5f radial expansion, known as central-field covalency.

Compared with other experimental methods, the identified sensitivities of 3d4f RIXS to bonding indicate the method exhibits several advantages for evaluating covalency and testing theoretical descriptions of actinide electronic structure. For instance, 3d4f RIXS does not rely on the actinide's paramagnetic state or the ligand's nuclear spin, and in contrast to ligand K-edge, it is not reliant on absolute transition intensity standards since only relative spectral intensities are required. Based on this ongoing work, we predict the quantification of actinide bonding by 3d4f RIXS to be universal to actinide element identity, ligand element identity, actinide oxidation state and actinide coordination symmetry. Consequently, the method is expected to have the capacity to contribute widely to actinide analytical chemistry and material characterization.



## Sensitivity to cis- versus trans- actinide-ligand Covalency in M<sub>4</sub>-edge Resonant Inelastic X-ray Scattering

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The determination of actinide electronic structure is becoming increasingly more synonymous with high energy resolution fluorescence detected (HERFD) x-ray spectroscopy, with spectra composed of fine structure advantageously obtained from the increased resolution corresponding to final state core-holes with larger lifetimes [1-4]. The fine structure acquired allows for the evaluation of oxidation states and the respective local coordination. HERFD measurements, alone though, provide partial insights, with respect to all phenomena present.

To build upon the foundational information of HERFD spectra, new analysis protocols concerning actinide 3d4f resonant inelastic x-ray scattering (RIXS) measurements, probing the unoccupied 5f orbitals, will be discussed. The proposed protocol accounts for all intensity as a function of the photon-in photon-out inelastic scattering transitions. Interpretation of RIXS spectra measured on model air-sensitive uranium complexes at the MARS beamline of Synchrotron SOLEIL will be presented, along with complementary multiplet theory and density functional theory calculations. This analysis provides comprehensive insights into what can be extracted from actinide 3d4f RIXS data. It will be discussed how RIXS can be used to determine electronic structure, while emphasising how the technique is sensitive to cis-versus trans- covalency, occurring between the actinide 5f orbitals and ligand valence orbitals [1].

Interpretation of the presented RIXS spectra will be discussed considering insights from ligand K-edge x-ray absorption spectroscopy amongst others [5,6].

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## Quantum chemical studies of binary and ternary U(VI) hydroxo silicate complexes

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Orthosilicic acid and its complexes are common in natural surface, ground, and rock pore waters due to the abundance of silicate minerals in the earth's crust. Polymerization and formation of colloids of orthosilicic acid with increasing pH lead to a variety of silicate species in solutions. This results in diverse plausible complexes with metal ions, which makes the silicate speciation and accurate determination of complexation constants of silicate complexes difficult [1]. Silicate complexation is also of importance for the safety of deep geological storage of radioactive waste. Silicate acts as a complexing agent for various cationic radionuclides, including uranium as the most common one. In such waste repositories cement is foreseen both as a construction material and for engineered barriers. Due to the degradation of cement, the pH rises locally, leading to increased silicate concentrations, also due to clay dissolution. We used a density functional (DF) approach to inspect structure and stability of U(VI) silicate complexes. Scalar-relativistic all-electron calculations at the generalized gradient level of exchange-correlation functionals (PBE) have been carried out. Short range solvation effects of the complexes are modelled by explicit aqua ligands of the U(VI) center, while long range effects are accounted for by a polarizable continuum model (PCM) of water.

We studied binary U(VI) silicate complexes of orthosilicic acid as well as of di- and tetrasilicate oligomers to characterize the effect of silicate oligomerization on the complexation. To account for conditions of higher pH, also ternary hydroxo silicate U(VI) complexes  $\text{UO}_2(\text{OH})_x(\text{OSi}(\text{OH})_3)_y^{2-x-y}$  for  $x + y = 2$  and 3 of orthosilicic acid are inspected. In this way a contribution to the characterization of U(VI) silicate complexes at various concentration and pH conditions is provided.

Trends of deprotonation energies of silicic acids are reproduced satisfactorily, although absolute energies of reactions in solution involving charged species are typically overestimated by DF calculations. The deprotonation energies decrease with increasing size of the silicic acid. Also the anionic mechanism of oligomerization [2] is qualitatively confirmed. In line with these trends, decreasing complexation energies for monosilicate complexes with increasing size of the silicate ligand are obtained. While monodeprotonated acids prefer a monodentate coordination, for dideprotonated acids a chelate coordination prevails over bidentate coordination for oligomeric species. Comparison of orthosilicate complexes with hydroxo complexes of same charge show that the silicate ligands bind weaker. Although the deprotonation of orthosilicate is facilitated in the field of the uranyl ion, deprotonation of an aqua ligand is favorable. This leads to a preference of ternary hydroxo monosilicate complexes with monodeprotonated silicate  $\text{OSi}(\text{OH})_3^-$  over binary complexes with dideprotonated silicate  $\text{O}_2\text{Si}(\text{OH})_2^{2-}$  with increasingly negative charge of the complexes at increased pH conditions. Also the composition of ternary hydroxo silicate complexes themselves is affected. For the example of  $\text{UO}_2(\text{OH})(\text{OSi}(\text{OH})_3)^0$  we show that deprotonation of an aqua ligand is preferred over the second deprotonation of silicate. As a result, the anionic ternary species  $\text{UO}_2(\text{OH})_2(\text{OSi}(\text{OH})_3)^-$  is more stable than  $\text{UO}_2(\text{OH})(\text{O}_2\text{Si}(\text{OH})_2)^-$ . This finding supports a combined TRLFS and quantum chemical study suggesting  $\text{UO}_2(\text{OH})_2(\text{OSi}(\text{OH})_3)^-$  at alkaline conditions [3]. A recent speciation model of U(VI) silicate complexation for low silicate concentrations includes  $\text{UO}_2(\text{OSi}(\text{OH})_3)^+$ ,  $\text{UO}_2(\text{OH})_2(\text{OSi}(\text{OH})_3)^-$ , and  $\text{UO}_2(\text{OH})_2(\text{O}_2\text{Si}(\text{OH})_2)^{2-}$  with increasing pH [1,3]. Our results suggest in addition the neutral species  $\text{UO}_2(\text{OH})(\text{OSi}(\text{OH})_3)^0$  and the alternative composition  $\text{UO}_2(\text{OH})_3(\text{OSi}(\text{OH})_3)^{2-}$  for the dianionic one.

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## Exploring Actinide Free Radical Interactions with Electron Paramagnetic Resonance Spectroscopy and Density Functional Theory Calculations.

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The intrinsic radioactivity of actinide elements means that the surrounding is exposed to ionizing radiation and within nuclear fuel, the presence of short-lived fission products leads to the classification of an extreme environment.<sup>[1, 2]</sup> Within this high radiation field, atoms in the surroundings can become excited or ionized to form reactive, free radical species.<sup>[3]</sup> These free radicals can engage with the actinide cation to influence the oxidation state or participate in bonding, but little is known regarding the extent of the interactions and nature of the unpaired spin in these species. In this presentation, interactions between hexavalent actinides, U(VI) and Np(VI), and free radicals (O<sup>•</sup>, NO<sub>3</sub><sup>•</sup>, and Cl<sup>•</sup>) in solid state materials are explored using electron paramagnetic resonance (EPR) spectroscopy. These experimental studies were paired with Density Functional Theory (DFT) calculations to confirm EPR spectral signals and provide an enhanced understanding of spin density associated with the metal and ligands. The importance in modeling the second coordination sphere and chemical surroundings to accurately predict EPR spectral signals using DFT methodology will be discussed.<sup>[4]</sup> In addition, the differences between U(VI) and Np(VI) EPR spectral features will be highlighted through evaluation of actinyl peroxosuperoxo complexes.

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# The Coordination Chemistry of U<sup>4+</sup> in Aqueous Solutions: Challenges and Insights from Spectroscopy and Theory

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The aqueous U<sup>4+</sup> ion is a key species in the chemistry of uranium, with significant implications for nuclear fuel processing, environmental chemistry, and radiochemistry. Indeed, the safety assessment of a future repository, as well as the remediation of various uranium mining and milling legacies, requires a better understanding of cation interactions with potential ions (thermodynamic database, structures, etc.) and its speciation diagram.

At low pH, techniques such as EXAFS and UV-Vis spectroscopy methods are invaluable for investigating the hydrolysis properties and gain insights into the structural properties of U(IV) in solution but do not necessarily agree.

Previous EXAFS studies [1,2,3] report similar distances between U<sup>4+</sup> and its water environment (2.41–2.42 Å) but suggest a wide range of coordination numbers, spanning from 8 up to almost 11, influenced by solvent and concentration variations. This inconsistency introduces significant uncertainty regarding the possible coordination number at low pH and in a diluted solution, which theoretical approaches have not yet fully resolved [4,5,6]. While UV-vis spectroscopy can distinguish U<sup>4+</sup> from the other hydrolyzed species, it does not provide information on coordination numbers [7,8,9].

This study presents a comprehensive examination of the physico-chemical properties of U<sup>4+</sup> in aqueous solution, using a combination of highly accurate relativistic and multiconfigurational quantum calculations with a statistical approach, based on the Wigner sampling method [10,11] or MD snapshots [6]. Quantum-mechanical calculations provide detailed insights into the electronic structure and bonding environment of the U<sup>4+</sup> ion, while statistical analysis addresses the variability and uncertainty in coordination numbers and bond distances reported in experimental studies. By merging these methodologies, we aim to reconcile the discrepancies observed in EXAFS and UV-Vis spectroscopy data, enhancing our understanding of U<sup>4+</sup> chemistry.

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## Complexation of Protactinium(V) with Chlorides in aqueous solution: Thermodynamic and Structural Insights

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Protactinium(V) is a singular actinide with unique chemical properties that differentiate it from other pentavalent actinides, particularly due to the absence of the actinyl moiety in its condensed phase compounds. Instead, Pa(V) exhibits a short mono-oxo bond, experimentally observed in oxalic and sulfuric media. However, this mono-oxo bond is not so stable and can vanish upon complexation, which is the case in presence of fluoride [1]. Additionally, in oxalate and sulfate complexes, the Pa-O bond distance is experimentally observed at 1.75 Å, which contradicts theoretical calculations that predict this distance to be around 1.85 Å [2]. These two phenomena remain poorly understood and highlight the challenges in studying Pa(V). The study of Pa(V) is further complicated by its remarkable propensity for hydrolysis and polymerization even in very acidic conditions, and the difficulty in isolating significant amounts of this actinide, making it difficult to handle and investigate.

In this study, we focus on the complexation of Pa(V) with chloride ions, using X-ray absorption spectroscopy (XAS) to investigate its chemical environment at different hydrochloric acid concentrations. Given the weak ligation properties of chlorides, the presence of the mono-oxo bond in these complexes is expected [3]. Thermodynamic studies have already provided the probable chemical forms of these complexes. However, no direct experimental data on their structures have been collected until now [4].

From our EXAFS data, two structures of Pa(V)-chloride complexes could be determined at 3M HCl and 12M HCl, corroborating the thermodynamic data. Additionally, the EXAFS spectra adjustments with structures obtained by theoretical calculations reveal, for the first time, a Pa-O bond distance around 1.83 Å, aligning more closely with theoretical calculations [1,2,3]. This finding supports the presence of an oxo bond in the Pa(V)-chloride system, advancing our understanding of protactinium chemistry. These results not only reconcile experimental observations with theoretical predictions but also provide a basis for future investigations into the coordination chemistry of Pa(V).

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## RE-EVALUATION OF THE PU(IV)-ACETATE SPECIATION DIAGRAM TAKING INTO ACCOUNT POLYNUCLEAR SPECIES

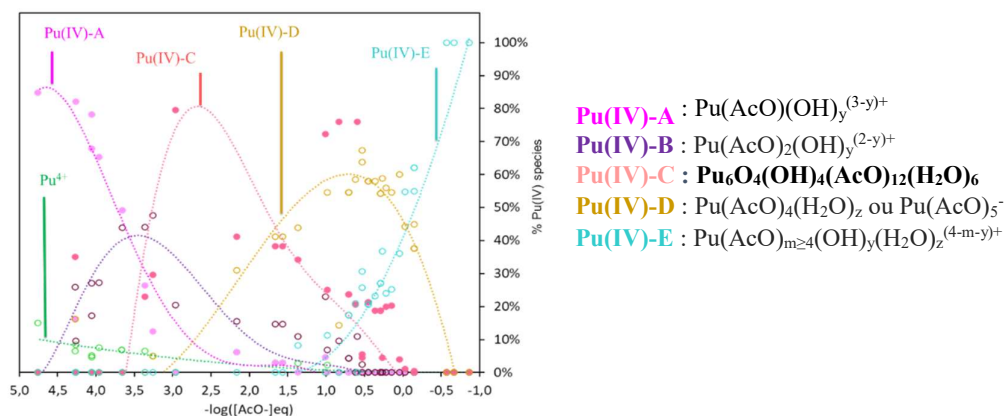
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The speciation of actinides is fundamental to better understand the behavior of these radioelements in condensed phases. Recently, it has been admitted that the competition between hydrolysis and complexation can lead to the formation of polynuclear species (or clusters) with actinide cations connected through oxo (O), hydroxo (OH) or aquo (H<sub>2</sub>O) bridges [1]. These species, stabilized at the surface by organic or inorganic ligands, can appear for not so low acidities and therefore are likely to be formed during the fuel cycle, the geological storage but also in the human body in case of internal contamination. If the structures of the clusters are often described in the solid state, they are much less so in solution as they are not always correctly identified in solution. Therefore they are not taken into account in the main thermodynamic/speciation models.

While working on the Pu(IV)-acetate system, we recently discovered that polynuclear species existed, whereas the literature, which worked under identical chemical conditions, only described monomeric aqueous complexes. Therefore, we undertook a re-evaluation of the speciation diagram of the Pu(IV)-acetate system, which is all the more important because the data in the literature are scarce, incomplete, and sometimes contradictory. To detect all potentially formed plutonium-acetate species, solutions were first characterized by Vis-NIR absorption spectroscopy. Large variations of pH and acetate concentrations were used and six different species were identified: the Pu(IV) aquo cation (Pu<sup>4+</sup>), and five plutonium acetate complexes. Those five acetate complexes were characterized by coupling experimental (Vis-NIR and EXAFS spectroscopies and ESI-MS spectrometry) and quantum chemistry. As a result, Pu<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(AcO)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub> hexameric cluster has been identified: the missing block in the An(IV) series with formate and acetate ligands as hexameric clusters of Th(IV), U(IV) and Np(IV) in solution with formate and acetate were already described in the literature [2, 3, 4]. The four other complexes are monomeric species.



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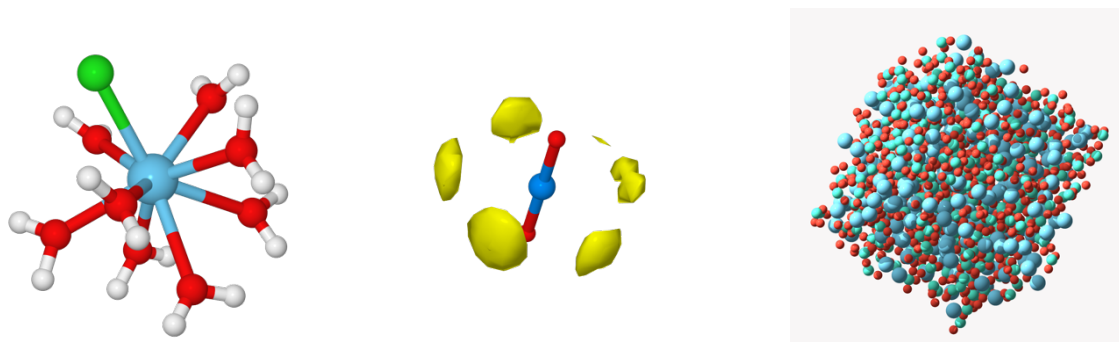


## The application of neutron and synchrotron methods to the chemical and structural characterization of disordered systems of relevance to radioactive materials challenges

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Over the past two decades, the inexorable trends in the exploitation of structurally disordered systems for chemical synthesis and as reaction support media, have highlighted an increasing need for analytical methods that can provide a holistic view of their atomic and molecular structure. Atomistic models driven for consistency with diffraction data [1] have subsequently proven to be a powerful window into this world, and particularly when enhanced via reference to complementary information drawn from other experimental probes such as X-ray absorption spectroscopy. In this presentation I will outline the basis of these methods and illustrate their application to questions in chemical and materials science. Examples will include investigations of chemical speciation and interactions of lanthanides [2] and actinides [3] in aqueous solution, as well as illustrations of how the methods can be applied to the investigation of the structure of glassy materials that are frequently considered for use as radioactive-waste storage media [4].



**Figure 1** Examples of structurally disordered systems characterized by a combination of neutron and X-ray techniques, from left to right (i) The local tri-capped trigonal prism geometry of a  $\text{La}^{3+}$  ion in 1M aqueous solution, where the cation is coordinated by eight water molecules and one chloride anion, (ii) A spatial density map of the equatorial coordination of five water molecules to a uranyl ion, in a 1.0M solution of  $\text{UO}_2\text{Cl}_2$  in water, (iii) A model of a multicomponent silicate glass refined for consistency with neutron total-scattering data.

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## XAS studies on nuclear fuels: from simulated to spent fuels characterizations

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Nuclear fuel undergoes drastic chemical and structural evolutions during irradiation, which affect both its thermal and mechanical properties. Fission of U and Pu during fuel irradiation in nuclear reactors leads to formation of more than 60 different chemical elements, in small or even very small quantities (< or << at.%). Determining the chemical and microstructural roles of the fission products (FPs) in the evolution of nuclear fuel physical properties is of crucial importance to develop reliable long-term predictions of the fuel behavior during reactor operation under normal and accidental conditions as well as for storage and recycling of spent fuel. This speciation is locally influenced by the temperature and the oxygen partial pressure ( $pO_2$ ), which display strong gradients between the center and the periphery of the  $UO_2$  fuel pellet during irradiation.

X-ray absorption spectroscopy (XAS) is the element-specific technique of choice to determine the speciation of an element, even very diluted, in potentially complex samples. However, the accurate determination of nuclear fuel chemistry is a very challenging task. First, fission products in  $UO_2$  create a complex multi-component system, in which a given element can form various phases which may be different depending on the location within the pellet. Secondly, spent nuclear fuel is highly radioactive and requires specific radiological safety devices and protocols to be handled and studied. In some cases, where specific fission products are to be characterized under specific conditions, irradiated nuclear fuels can be replaced by model, low activity materials. For instance, a SIMFUEL is a simulated irradiated nuclear fuel, consisting in natural or depleted, unirradiated  $UO_2$  doped with stable isotopes of fission products introduced as oxides during the sintering process. Volatile or semi-volatile elements, such as Xe, Kr, Cs, I, etc..., can not be incorporated this way, but are rather ion-implanted in  $UO_2$  (or SIMFUEL) pellets.

In recent years, numerous XAS studies have been carried out on such model samples by researchers from the Fuel Research Department (DEC, CEA Cadarache), at SOLEIL, ESRF or KARA synchrotrons, to characterize the chemical states of various FPs, such as Mo, Cs, I, Ba, Zr, etc, in  $UO_2$  as a function of concentrations, temperature and oxygen potential. These “separate effects” experiments aimed at, e.g., feeding thermodynamical databases with experimental data to improve modelling of the pellet – cladding interaction [1], or improving the understanding of the behavior of FPs during a severe accident [2]. They also help developing innovative advanced fuels, e.g. doped with redox buffers. And very recently, for the first time, a massive sample of  $UO_2$  spent nuclear fuel could be characterized by HERFD-XANES on the MARS beamline (SOLEIL synchrotron) to determine the chemical states of Mo and Cs [3]. This first experiment opens up many prospects for future XAS characterizations of spent fuels.

During this presentation, an overview of all these XAS studies on model or spent fuels will be given. In particular, it will show how the numerous separate effects experiments on model fuel samples allowed to pave the way for measurements on spent fuels. The technical and scientific challenges, as well as the required technical and methodological developments will be exposed. Main results will be presented: they constitute important steps towards complete knowledge of the chemical state and structural evolutions of a  $UO_2$  nuclear fuel during irradiation in a pressurized water reactor.

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## Multi-Scale Investigation of Fission Product Speciation in $U_{1-y}Pu_yO_{2-x}$ SIMMOx Using Synchrotron Techniques

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In the context of the nuclear fuel cycle and the management of nuclear waste, Mixed Oxides (MOx) have been developed and are currently employed in Pressurized Water Reactors (PWRs). Understanding the secondary phases formed as by-products of irradiation, primarily composed of Fission Products (FP), is critical for the safety of the fuel in reactors, as well as during fuel reprocessing, where these phases impact dissolution behavior.

To address these challenges, we developed a fabrication route for  $U_{1-y}Pu_yO_{2-x}$  SIMfuel (SIMMOx) to study FP speciation inside MOx fuel. The resulting material is representative of irradiated MOx fuel with a Pu content of 24 wt.% and a burnup of 13 at.%. We designed sample batches with varying FP compositions to perform real separation-of-effect studies. A multi-scale approach was employed to characterize the structural properties, microstructure ( $\mu\text{m}$ -scale), and atomic environments to achieve a comprehensive understanding of FP speciation within irradiated MOx fuel [1], [2].

Our observations revealed the effects of soluble FP (Ce, La, Nd, Y, Sr, Zr) on the (U,Pu,FP)O<sub>2</sub> solid solution, including a slight oxidation of the actinides. Additionally, metallic FP-bearing SIMMOx samples were synthesized to investigate FP-based secondary phases. New insights into FP interactions were obtained, highlighting the partial segregation among metallic FP (Mo, Pd, Rh, Ru) and their crystallographic structures. The addition of Ba was found to induce a speciation shift in several FP and the formation of perovskite inclusions, altering the oxidation state of some FPs like Mo (Figure 1).

Our study demonstrates the effectiveness of SIMMOx as a model material for investigating the properties of irradiated MOx fuel. By coupling various techniques, we provided a detailed description of FP speciation and their impact on MOx fuel properties. This research enhances our understanding of the physico-chemical properties of secondary phases in nuclear fuel.

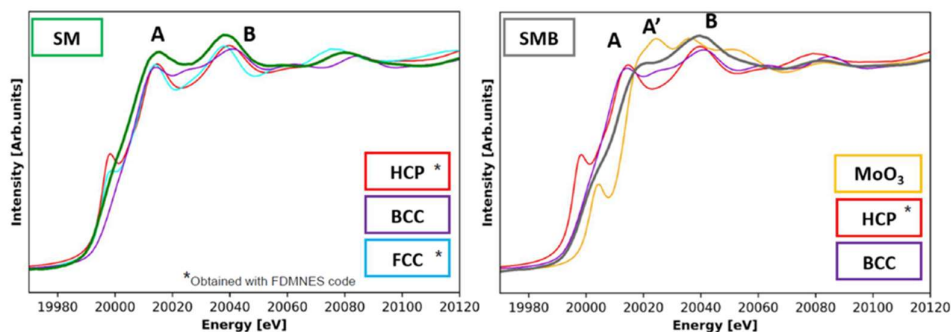


Figure 1: Influence of Ba on the speciation of Mo in Ba-bearing SIMMOX (right)

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## Actinide immobilization by incorporation into ceramic phases

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Various concepts for the final disposal of spent nuclear fuel are under discussion. In addition to the direct disposal of spent fuel, there are reprocessing concepts in which separated spent fuel components such as fission products and actinides require a suitable host matrix. Options for the immobilization of specific radionuclides are vitrification into a glass material or embedding into a ceramic matrix [1]. We have examined various ceramic materials (zirconia, (ZrO<sub>2</sub> and YSZ), zircon (ZrSiO<sub>4</sub>), monazite (LaPO<sub>4</sub>) and pyrochlore (Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>)) with regard to their suitability as host materials for actinides and lanthanides. Th(IV), U(IV), Eu(III) and Ce(IV) were incorporated into the host lattices. The host material must fulfill various requirements. (1) There must be a sufficiently high solubility of actinides and lanthanides in the host lattice without causing phase separation. (2) The host material must have a high temperature stability (up to 1200K) without phase transitions, as this could result in mechanical stresses and fractures which may reduce the resistance to leaching. (3) The material must be able to withstand the pressure in the geological formation and also the pressure that can be generated by He gas due to alpha decay (up to 10 GPa). (4) The structure of the host lattice must be able to withstand the recoil effects of alpha decay. Systematic investigations of these aspects were carried out in the frame of an interdisciplinary project by using synchrotron diffraction techniques available at the Rossendorf Beamline (ROBL) at ESRF. The following is an overview of the main results.

ZrO<sub>2</sub> with low dopant concentrations shows a phase transition from the monoclinic (m-ZrO<sub>2</sub>) to the tetragonal (t-ZrO<sub>2</sub>) phase both at elevated temperatures and upon irradiation, which characterize it as less suitable as a host material. If the t-ZrO<sub>2</sub> and the cubic (c-ZrO<sub>2</sub>) phases are stabilized for ambient conditions, e.g. by doping with yttrium (YSZ) [2], the ceramic becomes resistant in presence of Th(IV) to high temperature and pressure [3]. The structure also maintains its integrity under irradiation [4]. Synthetic monazite shows remarkable amorphization of the structure under irradiation [5], but has the tendency to recrystallize easily [6]. This is also observed in U(IV) and Th(IV) containing natural monazites. A solid solution of Th(IV) pyrochlore results in the formation of Gd<sub>2-x</sub>Th<sub>x</sub>Zr<sub>2</sub>O<sub>7+x/2</sub>. Th(IV) replaces Gd(III) due to the similar ionic radius and thus requires charge compensation. The pyrochlore structure retains its integrity under high temperature and pressure conditions [7]. Zircon, ZrSiO<sub>4</sub>, with incorporated Th(IV), shows excellent stability at high pressure and temperature [8]. However, the synthesis is complicated because a phase separation of (Th,Zr)SiO<sub>4</sub> and ThO<sub>2</sub> easily occurs.

Based on these studies we can classify the suitability of these ceramics as host materials. We have further developed diffraction techniques for the targeted analysis under the above mentioned conditions. This project is fully supported by BMBF grant 02NUK060 (AcE).

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## **Historical perspectives on the development of actinide XAS**

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X-ray synchrotron radiation techniques provide powerful tools to unravel the complexity of actinide chemistry and physics in many applications. These element- and shell-specific techniques probe both the molecular and electronic structure with increasingly high sensitivity and resolution. Electronic structure theory has been central to the interpretation of synchrotron data. In this presentation I will discuss historical developments that established some of the first beamlines and electronic structure codes to study highly radioactive materials at synchrotron facilities.

## Incorporation of some F-block elements in ancient and synthetic Fe oxides

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Extended X-ray absorption fine structure spectroscopy (EXAFS) is a powerful method for determining the local coordination environment of impurities in a host phase. A lack of appropriate standards and/or *a priori* knowledge concerning thermal disorder, coordination numbers, and potential defects renders the traditional shell-by-shell fitting of the EXAFS of impurities uncertain. For example, three studies with nearly identical U L<sub>III</sub> edge EXAFS for U(VI) associated with synthetic hematite offered three different interpretations: 1) all U substituting for Fe in octahedral uranate symmetry, 2.) a nearly 50-50 split between adsorbed uranyl and an incorporated octahedral uranate species, and 3.) all U substituting for Fe in octahedral uranyl symmetry.[1-3] Using *ab initio* molecular dynamics (AIMD) to calculate synthetic EXAFS spectra, we were able to resolve this ambiguity by testing different charge compensation schemes and using linear combination fitting to match the experimental spectra.[4] The AIMD-informed EXAFS results demonstrated that 3 configurations with partially protonated Fe vacancies at corner and face sharing sites were required to best fit the EXAFS. This result was confirmed using STEM-HAADF where the energy of the beam induced the U impurities to become mobile and map out the distribution of nearest neighbor Fe vacancies.[5] We applied the same approach to determine the coordination environment and oxidation state of U associated with 1.6 billion years-old hematite from the Olympic dam ore deposit in Australia.[6] Fitting the experimental spectrum with AIMD synthetic standards showed that U was present as U(V) substituting for Fe(III) in regular structural octahedral sites. Three distinct configurations were required to best fit the data, all involved variably protonated iron vacancies at face-, edge-, and/or corner-sharing sites. The ancient provenance of the hematite attests to the stability of U(V), often considered a short lived intermediate, once incorporated in hematite as well as the suitability of hematite as a waste form for U. Further, the dominant configurations are not necessarily the lowest in energy. We have extended this approach to detailing the coordination environment of HREEs incorporated in Fe(III) (oxyhydroxides). Interest in the potential incorporation of REEs in Fe oxides arises from their association in REE Ion Adsorption Deposits (IADs) and as proxies for the behavior of trivalent actinides. Here we report data that constrains the compatibility of Nd, Dy, Yb, and Lu with the structures of ferrihydrite and goethite across a range of conditions (T and pH) relevant to IADs. Not surprisingly, the compatibility of the HREEs (Yb and Lu) in the Fe oxide structures was higher than for the LREEs (Nd), with Dy showing intermediate behavior. Our most complete data set up to this writing is for Yb: A combination of PDF analysis and AIMD-informed EXAFS details the complex behavior of Yb as FH transitions to goethite, where Yb shifts from 7-fold to 6-fold coordination and a high degree of configurational disorder in goethite. Together with our ongoing characterization of Zn, Ni, and Cu impurities in Fe(III) oxides, we show that configurational disorder is the rule for semi-compatible impurities in Fe(III) (oxyhydr)oxides, not the exception.

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## Understanding the varying mechanisms of radionuclide immobilization by alternative bentonite materials. Combined sorption, EXAFS and luminescence spectroscopy studies.

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Bentonite plays a key role in two components of the engineered barrier system, which is designed to limit radionuclide mobility in geological disposal facilities for high-activity wastes worldwide<sup>[1]</sup>. First, it will be used as a buffer material, it provides mechanical and chemical protection and stability to the waste-containing canister. Second, some countries will use a mixture of crushed rock and bentonite as a closure material required to backfill the central tunnels, vehicle connections, and access tunnels and shafts. Using the Finnish model as an example, the total mass of bentonite required per disposal hole is  $27 \times 10^3$  kg (with 3000 deposition holes there will be  $\sim 81 \times 10^6$  kg) and the estimated total volume of backfill material is almost  $7 - 8.5 \times 10^6$  m<sup>3</sup>[2]. As a natural material, bentonites can vary widely. Indeed, the basic physico-chemical properties of various bentonites have been studied for potential use in spent nuclear fuel disposal in Finland (e.g., [2-4]); however, most experimental work has focused on Wyoming-type high-grade sodium bentonite (POSIVA, 2012 & 2021). Given the operational lifetime of ONKALO®, the volume of buffer required, and potential changes in the global market (*i.e.*, competition from other countries, rising costs, logistics / supply chain issues, and global political instabilities), multiple bentonite types must be considered in order to ‘future-proof’ the disposal concept<sup>[2-5]</sup>.

We present combined physico-chemical data on the chemical interactions between two key, risk-driving radionuclides (U, and Eu as an analogue for trivalent actinides (Pu(III), Am(III) or Cm(III))) and two alternative bentonite materials for use in the Finnish, ONKALO® repository. To distinguish the mechanisms that govern adsorption processes, we completed Extended X-ray Absorption Fine Structure (EXAFS) and luminescence spectroscopy on the radionuclides sorbed to the alternative bentonites. These techniques can discern the complex structures that govern radionuclide–bentonite interactions and elucidate the impacts of alternative bentonites on the radionuclide removal mechanism. Indeed, this study highlights the importance of detailed investigations that describe radionuclide interactions in a quantitative and mechanistic manner. These data provide key information to advise end-users about the varying chemistry of alternative buffer materials and the importance of studying each radionuclide under relevant conditions.

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## Effect of citrate on aqueous U(VI) speciation and U(VI) retention on Ca-bentonite

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In nuclear waste repositories, citric acid may be present due to microbial activity or due to degradation of organic material in the waste. As citrate is able to complex a multitude of lanthanide and actinide ions as readily water soluble complexes and thus increase their mobility, additional investigations are necessary to understand whether the mobility of the radionuclides is affected in case of a water ingress into the repository. Because of the repository's concrete infrastructure, high-pH conditions may form due to leaching. For low-pH systems, interaction of U(VI) with citrate has been studied extensively<sup>[1]</sup>, however complexation data at higher pH is scarce. This study aims to understand the interactions of U(VI) and citrate in alkaline media. Interactions with the geotechnical barrier, in the form of bentonite (potential backfill material) are also investigated.

This study utilizes nuclear magnetic resonance (NMR) spectroscopy, UV-Vis spectroscopy, and time-resolved laser-induced fluorescence spectroscopy (TRLFS) to obtain information on the aqueous U(VI) citrate complexes as well as on U(VI) retention on Ca-bentonite in the presence of citrate. NMR spectroscopy allows for gathering of structural information regarding the ligand. Complementary, TRLFS can show structural information about the complex from the metal ion's perspective. Together with UV-Vis data, these give insight on the complexes' structures. Complexation experiments have been conducted in the pH range 9.0 - 12.4. TRLFS as well as NMR show three distinct species: presumably two trinuclear species of different U: Cit ratio, and a mononuclear uranyl hydroxo citrate complex species. The trinuclear complexes decrease in concentration with increasing pH, where the monomeric complex becomes dominant. For pH > 11.5 and citrate concentration and/or Cit:U ratio sufficiently low ( $\leq 10$  mM) the monomeric citrate complex begins to be displaced by citrate-free uranyl hydroxo species (likely  $\text{UO}_2(\text{OH})_3^-$  and  $\text{UO}_2(\text{OH})_4^{2-}$ ), along with precipitate formation.

U(VI) is well retained on Ca-bentonite over a wide pH range in the absence of complexants<sup>[2]</sup>. Retention in the presence of complexing agents is expected to be reduced<sup>[3]</sup>. Citrate has been found to greatly affect U(VI) mobility if concentration is sufficiently high ( $\geq 10$  mM). U(VI) retention experiments conducted with 50 mM citrate show a decreased retention between pH 9 and 10.5. At pH  $\geq 11.5$ , the U(VI) retention decreases in presence and absence of organic complexants, due to predominant U(VI) hydrolysis.

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## **Insights into U(VI) reduction during bio-stimulation of microbes in U mine water**

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# **Work in progress**

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## Applications of X-ray absorption spectroscopy to the UK's nuclear legacy challenges

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In the UK and globally, nuclear legacy challenges are some of the biggest scientific and engineering challenges of the 21st century. These challenges include the decommissioning of legacy nuclear facilities, such as spent nuclear fuel storage ponds and silos, and the geological disposal of radioactive wastes. These scenarios involve complex chemistries, typically in aqueous systems at neutral and alkaline pH and are often redox-dynamic. Here, the understanding of the chemical speciation of radionuclides, and the implications on radionuclide mobility, are key to underpinning environmental safety cases and proceeding in the most efficient and safe manner. X-ray absorption spectroscopy (XAS) is a powerful tool for investigating radionuclide speciation under a range of environmentally relevant, back-end nuclear fuel cycle environments.

This presentation will cover investigations into radionuclide speciation and behaviour in spent nuclear fuel storage facilities and future radioactive waste disposal conditions. Firstly, understanding radionuclide speciation within legacy facilities at the Sellafield site. These facilities contain radionuclide-bearing colloidal and nanoparticulate phases which may pose challenges to effluent treatment facilities. Our work has highlighted that U speciation is dominated by nano-UO<sub>2</sub> under these conditions,<sup>1-4</sup> and our recent investigations have focused on the role nano-UO<sub>2</sub> plays in controlling the mobility of risk-driving radionuclides (Sr, Tc, Pu and Am) in these facilities. Secondly, speciation of U under high phosphate concentrations in a geological disposal facility was investigated. Magnesium-potassium phosphate cements (MKPCs) are candidate backfill materials for the geological disposal of U-rich wasteforms, due to their reduced alkalinity compared to traditional cements, and phosphate-rich leachates which are anticipated to reduce both U(VI) and U(IV) solubility. Results are presented from interactions of wasteform-relevant U species with MKPCs and MKPC leachates, directly informing geological disposal procedures for U-rich wasteforms. Finally, we present the application of high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) to understanding U in the environment. Understanding changes in U bonding environment and oxidation state are key to predicting the long-term fate of U in nuclear decommissioning and geological disposal. HERFD-XANES approaches at L<sub>3</sub> and M<sub>4,5</sub> edges are promising alternatives to traditional actinide L<sub>3</sub> edge EXAFS for studying speciation of U and other actinides in the environment.<sup>5, 6</sup>

In these case-studies, X-ray absorption spectroscopy, specifically extended X-ray absorption fine structure (EXAFS), XANES and HERFD-XANES at actinide M and L edges and fission product (Tc, Sr) K edges were combined with a suite of analytical techniques (Raman and Infrared spectroscopy, transmission electron microscopy, X-ray diffraction, and aqueous geochemical measurements). This combined, multi-technique analysis facilitates linking radionuclide speciation to behaviour under nuclear legacy relevant conditions.

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## Investigation of Actinide-Transition Metal bonding

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The exploration of the coordination chemistry of actinides significantly lags behind that of transition metals as well as their lanthanide homologues. As such, a fundamental understanding of the binding properties in actinide compounds is still leaving many open questions. Therefore, systematic investigation of various coordination motives around an actinide center can be used as benchmark to evaluate what analytic techniques can reveal about novel actinide-ligand bonding.

In this study, we focus on a square antiprism coordination of only oxygen donor atoms in an actinide series ranging from thorium to plutonium. Installing either one or two transition metals in close proximity to the actinide, leads to an 8+2 coordination at the actinide center. These heterobi- and trimetallic complexes have been investigated using single-crystal X-ray diffraction, NMR, HERFD-XANES, and SQUID magnetometry. The experimental findings were further analyzed with quantum chemical calculations. A comparison with their monometallic counterparts gives new insight into actinide-transition metal bonding.

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# **Poster Presentations**

## Development and Application of a Microfluidic Set-Up for In-Situ Studies of Formation Kinetics of La- and U-Complexes Using High Resolution Spectroscopic Methods

E. Reynolds, R. S. K. Ekanayake, B. Schacherl, C. Kim, X. Gaona, H. Kaufmann-Heimeshoff, R. Steininger, J. Göttlicher, T. Prüssmann, H. Geckeis, T. Vitova,

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In the world of nuclear medicine, interest in targeted tumor therapy has rapidly risen within the last few years.<sup>[1]</sup> For this purpose, radionuclides are often complexed by chelating agents. One such ligand is PSMA-617, a conjugate of DOTA (2,2',2'',2'''-(1,4,7,10-Tetraazacyclododecan-1,4,7,10-tetrayl)tetraacetic acid) and Glu-urea-lysine, which possesses the ability to selectively bind to a surface protein that is overexpressed in prostate tumors.<sup>[2]</sup> In order to observe the complexation of such medically interesting complexes more closely and to relate to the metal-ligand bonding properties, a method is described with which the complexation can be studied in-situ and time resolved using high resolution X-Ray spectroscopy and commercially available microfluidic chips.<sup>[3,4]</sup> Studies were performed at the SUL-X and ACT Beamlines at the KIT Light Source.

For the development of the method, <sup>225</sup>Ac was modelled using the complexation of Lanthanum with the chelating agents DOTA, Ethylenediaminetetraacetic acid (EDTA) and 6-((16-((6-Carboxypyridin-2-yl)methyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)methyl)-4-isothiocyanatopicolinic acid (Macropa). High resolution X-Ray absorption near edge structure (HR-XANES) spectra at the La L<sub>2</sub> edge were measured along the chip channel. Then, kinetic calculations were done with the help of results obtained from a linear combination least squares fit quantitative analyses of the HR-XANES spectra. First investigations were performed, as a preparation for uranyl complexation studies using the set-up, including thermodynamic calculations and HR-XANES of reference substances. With future experiments with samples with higher specific activity in mind, a new design, which offers an extra layer of protection against contamination by including a second containment, was developed.

The authors thankfully acknowledge the financial support of the German Research Association (DFG) via the "4f for Future" project, CRC 1573, A1: 471424360, as well as the ERC Consolidator Grant „THE ACTINIDE BOND“ Nr. 101003292.

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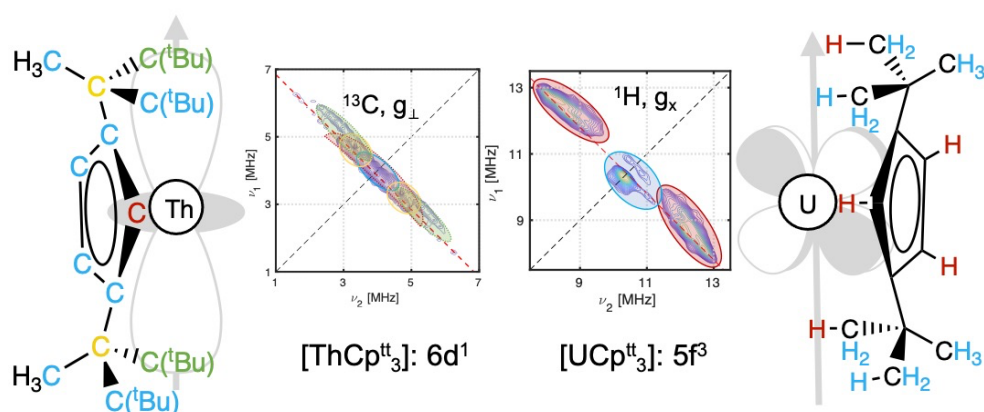
## Relativistic Quantum Chemical Investigation of Actinide Covalency Measured by Electron Paramagnetic Resonance Spectroscopy

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Covalency effects in two actinide complexes  $[\text{AnCp}^{\text{t}}_3]$  ( $\text{An} = \text{Th}, \text{U}$ ) have recently been probed with hyperfine correlated spectroscopy (HYSCORE), which is a direct measure of unpaired spin density on ligands.[1] It was found that a classical point-dipole model was insufficient to reproduce the experimental interactions, and empirical parameters were used to estimate atomic spin densities on the ligands to best represent the experimental spectra. Here, we use a fully *ab-initio* approach to computing hyperfine interactions with relativistic multiconfigurational methods with the HYPERION program, giving excellent agreement with experimental spectra.[2] Our calculated results show that the results for  $[\text{ThCp}^{\text{t}}_3]$  are in good agreement with experimental techniques based on spectral fitting, however the covalency for  $[\text{UCp}^{\text{t}}_3]$  was previously overestimated. We find that this is due to paramagnetic spin-orbit effects that arise from relativistic theoretical descriptions of hyperfine coupling. These results highlight the accuracy of modern computational methods and the need for fully *ab initio* approaches in interpretation of magnetic data for actinides.[3]



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## Experimental Characterization and Theoretical Modelling of X-ray Absorption Spectra of Protactinium(V) Complexes

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The physical and chemical properties of solvated actinide complexes, including their speciation, bond nature with the surrounding environment, and thermodynamic and spectroscopic properties, hold significant implications for societal and industrial applications. Among the actinides, protactinium ( $Z=91$ ) remains unique because, depending on its oxidation state, it can behave as an "f element" (Pa(IV)) or a "d element" (Pa(V)). In solution, Pa(V) dominates because Pa(IV) is unstable and can be directly oxidized to Pa(V) unless a strong reducing agent is present [1]. Pa(V) can exist in solution as  $\text{Pa}^{5+}$ , and in some specific solutions, it will form  $\text{PaO}^{3+}$  [2]. Apparently, it does not form the actinyl moiety  $\text{PaO}_2^+$ , which is not the case for its heavier neighbor elements, uranium, neptunium, and plutonium. To identify the absence or presence of the mono-oxo bond in Pa(V) complexes, one can employ spectroscopic techniques such as X-ray spectroscopies, which have played a crucial role in actinide characterization [3].

An experimental campaign was conducted at the MARS beamline of SOLEIL in February 2024, where different protactinium samples were analyzed using High Energy Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES), Resonant Inelastic X-ray Scattering (RIXS) at the  $L_3$ -edge, and Extended X-ray Absorption Fine Structure (EXAFS) to characterize the electronic structure and obtain structural information. However, the analyzed spectra do reveal intriguing features (see Figure 1). Indeed, while in the past [4], the oxalate ligand seems to favor the formation of the mono-oxo bond, the similarity of the oxalate spectra with the one measured in the fluoride solution, which contains only the  $\text{Pa}^{5+}$  ion, raises question. Thus, to complement this experimental work, we have used another analytical tool: quantum theory.

This work is accompanied by theoretical modeling of the XANES spectra using relativistic Time-Dependent Density Functional Theory (TD-DFT) [4] at the  $L_3$  and  $M_4$  edges of the structural models obtained from the EXAFS fitting. Additionally, these calculations allow us to investigate the nature of transitions which the excitations are occurring.

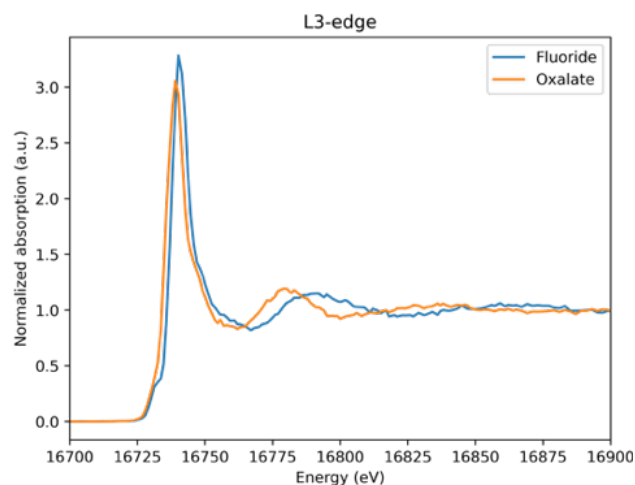


Figure 1: HERFD-XANES  $L_3$  edge spectra of Pa(V) in hydrofluoric and oxalic acids.

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## Developing Uranium L<sub>3</sub> HERFD-XANES and RIXS to investigate uranium biogeochemical processes.

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Variations in the oxidation state and localised uranium (U) coordination environment in solid phases are key controls on U solubility and mobility within natural and engineered environments. Extended X-ray fine absorption structure (EXAFS) at the L<sub>3</sub> edge of U (ca 17 keV) is a widely applied technique for characterising U coordination environment and oxidation state.<sup>1, 2</sup> However, for defining U oxidation state and coordination environment, probing the U standard L<sub>3</sub> -edge EXAFS and XANES has limitations. For example, the technique struggles with oxidation state determination where U(V) is present, and in defining coordination environment within complex matrices where differentiating similar ligand complexes (e.g. phosphate and silicate) is challenging. The current work focuses on extending the X-ray Absorption Spectroscopy toolkit for investigating U biogeochemistry to include HERFD-XANES and resonant inelastic X-ray scattering (RIXS) at U L<sub>3</sub> (17 keV). Specifically, we have applied high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) at the U L<sub>3</sub> -edge to probe changes in electronic structure of U(VI) in environmentally relevant model U-mineral phases and assess the effectiveness of this approach for investigating U(VI) speciation, including the local coordination environment and phase composition.<sup>3, 4</sup>

Here, we present the synthesis and XAS characterisation of a suite of environmentally relevant U(VI) phases. These phases have currently been investigated at the U L<sub>3</sub> -edge using EXAFS, HERFD-XANES and both valence to core (VTC) and core to core (CTC) RIXS, to identify specific sensitivities of these techniques to U speciation. In this work, we present a library of fully-characterised, environmentally relevant U(VI) structures and highlight key diagnostic features in the resultant spectra.

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## Using experimental actinide chemistry to solve technical challenges in spent fuel and nuclear material management within the Nuclear Decommissioning Authority Group

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During the reprocessing of nuclear fuel, uranium and plutonium are separated from waste fission products.<sup>1</sup> This special nuclear material is stored in the form of actinide oxide (AnO<sub>2</sub>, An = U, Pu) powders in sealed packages.<sup>2</sup> Interim AnO<sub>2</sub> storage presents technical challenges. These include adventitious reactions of AnO<sub>2</sub> with atmospheric and other gases, for example radiolysis of water generates H<sub>2</sub>.<sup>3</sup> The chemical composition and the properties of the AnO<sub>2</sub> have also been observed to change during storage.<sup>1</sup> In this work, reactivity studies with atmospheric gases and MO<sub>2</sub> nanoparticles (NPs) (M = U, Th, Ce) aim to establish structure-property relationships to gain a better understanding of this chemistry. The data will contribute to the retreatment and storage solutions needed for the future management of the UK's special nuclear material. Reactivity studies with H<sub>2</sub>, water, and other atmospheric gases will give insight into the absorbed species and the surface chemistry.<sup>4</sup> Structure-property relationships will be investigated using X-ray Absorption Spectroscopy (XAS) and Inelastic Neutron Scattering (INS).

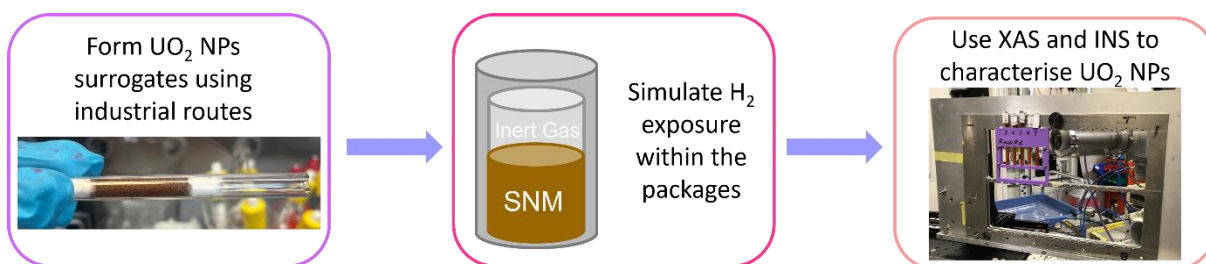


Figure 1: Workflow procedure from forming UO<sub>2</sub> NPs, simulating H<sub>2</sub> exposure, characterising the NPs using XAS and INS

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## Solubility, speciation and thermodynamics of $\text{PuCO}_3\text{OH}(\text{cr})$ in carbonate containing NaCl solutions

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Final disposal of radioactive waste in deep geological repositories is the preferred option in many countries. Ingress of water into a repository may result in the release of radionuclides and thus cause a potential radiological risk. Mobilization and retention of radionuclides are controlled by (geo)chemical processes such as solubility equilibria, complexation, sorption to and incorporation into mineral phases, etc.. Plutonium is the main transuranic element in spent nuclear fuel. Under the reducing conditions of a deep geological repository, +III and +IV are the dominant oxidation states for plutonium. In the absence of complexing ligands, the solubility of plutonium is dominated by hydrolysis reactions. Carbonate is ubiquitous in nature and is a strong ligand for actinides. Carbonate is also considered relevant in the repository environment due to the occurrence of carbonate bearing minerals like calcite ( $\text{CaCO}_3$ ). Solubility and speciation studies in carbonate-containing NaCl solutions have been performed for trivalent plutonium chemical analogs ( $\text{Am}(\text{III})$ ,  $\text{Cm}(\text{III})$ ,  $\text{Ln}(\text{III})$ ), but are missing for  $\text{Pu}(\text{III})$ . Various carbonate-containing solids and complexes are reported for the trivalent plutonium analogs. Of particular interest is  $\text{AnCO}_3\text{OH}(\text{cr})$  which exhibits considerable stability under near neutral pH conditions. The existence of  $\text{PuCO}_3\text{OH}(\text{cr})$  was proven by Hagan [1], but information on stability and solubility were not available so far. In the present work, the synthesis, characterization and solubility of  $\text{PuCO}_3\text{OH}(\text{cr})$  in carbonate containing NaCl solutions is discussed.  $\text{PuCO}_3\text{OH}(\text{cr})$  was obtained as blue fine crystalline solid by equilibration of  $\text{Pu}(\text{OH})_3(\text{am})$  in Na- $\text{HCO}_3$ - $\text{CO}_3$ -Cl solution at  $T = 23\text{ }^\circ\text{C}$  for several months, and characterized by UV/VIS, SEM/EDX and powder XRD. Additionally, Pu L3-edge XANES and EXAFS was performed at the *INE Beamline for Radionuclide Research at the KIT Light Source*. The solubility of  $\text{PuCO}_3\text{OH}(\text{cr})$  in 0.10 - 5.61 m Na-OH- $\text{HCO}_3$ - $\text{CO}_3$ -Cl at  $\text{pH}_m$  5.0 - 8.0 and  $T = 23\text{ }^\circ\text{C}$  was investigated in an Ar glove box with a 1 %  $\text{CO}_2$ . The experimental solubility data show a systematic dependence on  $\text{pH}_m$  and ionic strength, and are overall in good agreement with the chemical and thermodynamic models reported for the plutonium analogs. It is noteworthy, that the solubility of  $\text{PuCO}_3\text{OH}(\text{cr})$  under near-neutral pH conditions is up to 4 orders of magnitude lower than the corresponding solubility of  $\text{Pu}(\text{OH})_3(\text{am})$ , the latter being the solubility controlling  $\text{Pu}(\text{III})$  solid phase in the absence of complexing ligands. Results from ongoing EXAFS evaluation will be discussed in the presentation.

*Acknowledgement: The authors thank the Institute for Beam Physics and Technology (IBPT, KIT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).*

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## Solubility, redox speciation and sorption of Sn in cement systems

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Tin is an important element in nuclear waste disposal, with  $^{126}\text{Sn}$  ( $t_{1/2} = 1.1 \cdot 10^6$  a) being one of the seven long-lived fission products [1]. Other isotopes with shorter half-lives, e.g.,  $^{121\text{m}}\text{Sn}$  ( $t_{1/2} = 55$  a) or  $^{125}\text{Sn}$ -125 ( $t_{1/2} = 0.0264$  a) [2], are also present in the waste and become relevant in the context of low and intermediate level waste (L/ILW). Cementitious materials are widely used in underground and near-surface repositories for L/ILW for conditioning of the waste, as well as backfill-, container- and liner materials. Cement mainly consists of calcium silicate hydrated phases (C-S-H), portlandite ( $\text{Ca}(\text{OH})_2$ ), calcium aluminates types phases (AFt, AFm) and non-hydrated clinker minerals. Cementitious materials buffer the pore water composition in the hyperalkaline pH region ( $10 \leq \text{pH} \leq 13.5$ ) with moderate Ca concentrations ( $10^{-4} \text{ M} \leq [\text{Ca}] \leq 0.02 \text{ M}$ ). C-S-H phases are considered as the main sink of cationic radionuclides and metal ions [2]. Sn is primarily expected in the +IV oxidation state within the stability field of water, although on-going discussions on the uncertainties affecting  $\Delta_r G^\circ(\text{Sn}^{4+})$  and the corresponding impact on the  $E^\circ(\text{Sn}^{4+}/\text{Sn}^{2+})$  may suggest the possible stabilization of Sn(II) in the very reducing conditions expected in underground repositories [1]. In this context, the retention of Sn in cementitious environments and reducing conditions was investigated with a combination of solubility experiments, sorption studies and advanced spectroscopic techniques.

Undersaturation solubility experiments with  $\text{SnO}(\text{cr})$  and  $\text{SnO}_2(\text{cr})$  were performed within  $9 \leq \text{pH}_m \leq 12.8$  and  $0.1 \text{ M} \leq I \leq 3.5 \text{ M}$  in  $\text{NaCl-NaOH}$  and  $\text{CaCl}_2\text{-Ca}(\text{OH})_2$  systems. Solubility results for Sn(II) systems are in good agreement with data available in the literature for  $\text{SnO}(\text{cr})$  and  $\text{Sn}_6\text{O}_4(\text{OH})_4(\text{cr})$ . Solubility data obtained for Sn(IV) are in moderate agreement with recent experimental work by Rai et al. and the calculated solubility limit of  $\text{SnO}_2(\text{cr})$  [1]. Batch sorption experiments resulted in fast and strong uptake of Sn(IV) by C-S-H phases and cement, in line with the sorption behaviour reported for other strongly hydrolysing M(IV) metal ions, e.g., Th(IV) [3] or Pu(IV) [4]. A slightly weaker uptake of Sn by C-S-H phases was observed under very reducing conditions. This behaviour could be explained by (i) the oxidative sorption of Sn, with Sn(IV) prevailing in the solid phase and Sn(II) in the aqueous phase, or (ii) a strong sorption of Sn(II), in line with the strong hydrolysis reported for this +II metal ion [5]. The focus of on-going work targets the mechanistic understanding of Sn retention by cementitious systems. The presence of natural Sn in cementitious materials hints that isotopic exchange may be considered as plausible mechanism for the uptake of radioactive isotopes of Sn in repository systems. XAFS measurements were conducted at the INE-beamline of the Karlsruhe Research Accelerator (KARA) to gain insight on the redox speciation of Sn in cementitious reducing systems. The last results of this on-going work will be presented in this contribution.

*We acknowledge the KIT light source for provision of instruments at their beamlines and we would like to thank the Institute for Beam Physics and Technology (IBPT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).*

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## Spectroelectrochemical coupling to study Tc speciation in solution

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Technetium (Tc) is an inherent radioactive element with isotopes ranging from <sup>85</sup>Tc to <sup>120</sup>Tc [1]. Among them, <sup>99</sup>Tc is the most environmentally relevant since it is a high yield fission product of <sup>235</sup>U and <sup>239</sup>Pu, and the daughter nuclide of metastable Tc-99 (<sup>99m</sup>Tc) – the isotope most commonly used for radiodiagnosis worldwide. <sup>99</sup>Tc is a long-lived beta minus emitter ( $\tau_{1/2} = 2.13 \cdot 10^5$  years) and its aqueous speciation and migration behavior is influenced by the (physico-)chemical conditions (e.g., pH, presence of ligands, redox conditions, etc.). It is known that  $\text{Tc}^{\text{VII}}\text{O}_4^-$  barely interacts with minerals and, thus, its migration in water is high. On the contrary, the mobility of  $\text{Tc}^{\text{IV}}$  is limited since it forms low soluble species (e.g.,  $\text{TcO}_2$  or Tc-sulfides), surface complexes on minerals, and/or it is incorporated into the mineral structures [2]. Deepening our knowledge on Tc mobility is important for the safety assessment of a nuclear waste repository and for radioecology. Thus, several works focused on Tc aqueous speciation based on redox changes and the chemical composition of the solution, e.g., [3–5].

In this work, we have studied the speciation of  $\text{KTc}^{\text{VII}}\text{O}_4$  in carbonate solutions when it is electrochemically reduced at varying pH (8.2 – 10.0), Tc concentration (0.5 – 9.5 mM), carbonate concentration (5 – 1000 mM), and the applied potential.  $\text{Tc}^{\text{VII}}$  reduction was monitored in situ by UV-vis, by using a spectro-electrochemical cell. At –0.85 V a pink solution ( $\lambda_{\text{max}} = 512$  nm) was obtained, corresponding to a  $\text{Tc}^{\text{IV}}$  carbonate species [3], whereas reduction at –0.95 V yields a bluish green solution ( $\lambda_{\text{max}} = 630$  nm), associated with a  $\text{Tc}^{\text{III}}$  carbonate complex [3]. Additionally, the obtained solutions were investigated by ex-situ <sup>99</sup>Tc NMR. The –0.85 V specimen reveals a resonance at ~1600 ppm, characteristic for  $\text{Tc}^{\text{V}}$  [6]. In addition to the  $\text{Tc}^{\text{V}}$  signal mentioned above, the solution obtained at –0.95 V gives a further signal at ~152 ppm, which can be assigned to the chemical shift range of  $\text{Tc}^{\text{III}}$  [6].

These are unprecedented NMR data on aqueous Tc carbonate species, complemented by UV-Vis spectroscopic analysis. They advance the mechanistic understanding of Tc redox behavior, and help to improve safety and risk analyses for nuclear waste management.

Our current focus is on in-situ coupling NMR spectroscopy with electrochemical methods in order to monitor simultaneously the structural changes on redox active (radioactive) pollutants as a function of the redox conditions.

### Acknowledgements:

The authors acknowledge the German Federal Ministry of Education and Research (BMBF) for the financial support of NukSiFutur TecRad young investigator group (02NUK072) [7]).

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## Deciphering crystal-field excitations with HR-RIXS

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Comprehension of actinide electronic structure is notoriously complex owing to the precision required of the individual electrostatic, spin-orbit coupling and crystal-field interactions to describe accurately the 5*f* states. Ligand K-edge XAS [1] and M<sub>4,5</sub>-edge core-to-core RIXS [2-5] prove a quantifiable sensitivity to actinide bonding and covalency trends, however, the inherent core-hole lifetime broadenings of the techniques typically obscure direct evidence of crystal-field excitations.

In this study, high-resolution M<sub>4,5</sub>-edge valence-to-core RIXS is demonstrated to be a quantifiable probe of crystal-field multiplets with direct applicability of accessing the electronic structure and reactivity of molecular moieties *via* the 5*f* orbitals, which previously has been concealed by other experimental techniques. Isostructural molecular model complexes provide a means to establish chemical trends as a function of valence state and element identity. [UX<sub>6</sub>]<sup>2-</sup> where X = F, Cl and Br was selected as a model octahedral complex to explore these chemical trends. *Ab initio* calculations utilising the ligand-field density functional theory (LFDFT) [6] were applied to inform semi-empirical multiplet models to accurately reproduce the experimental measurements.

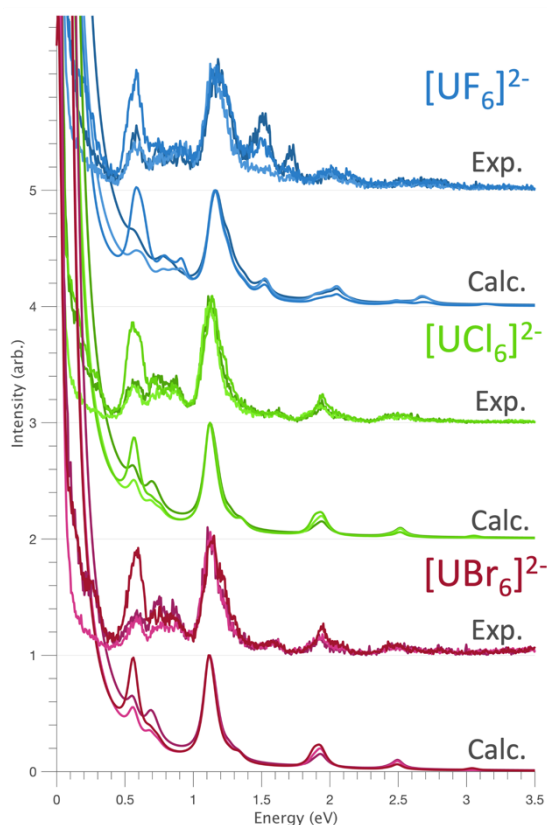
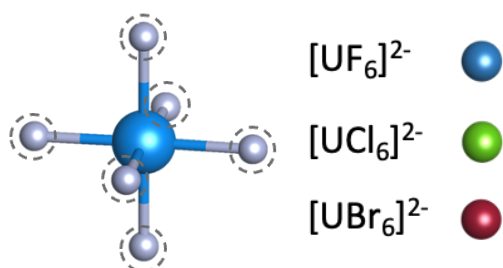


Figure 1: Molecular structure of [UX<sub>6</sub>]<sup>2-</sup> where X = F, Cl and Br studied in this work. M<sub>5</sub>-edge valence-to-core RIXS spectra of the halide series with accompanying multiplet calculations performed at multiple incident energies.

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## Determination of actinide central-field covalency with 3d4f resonant inelastic X-ray scattering (RIXS)

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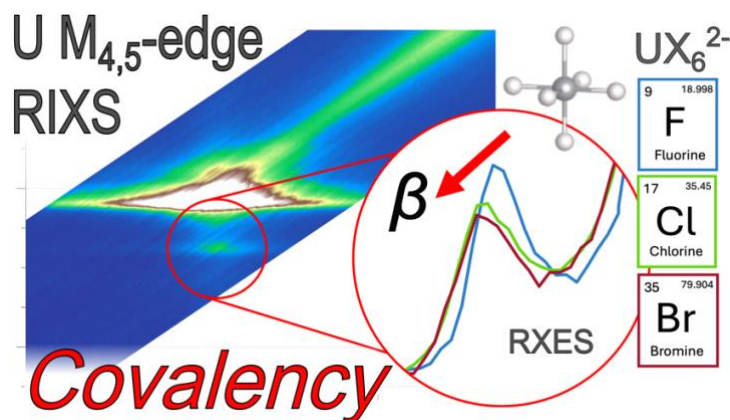
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Understanding the nature of actinide-ligand bonding is of paramount importance to the radiochemistry community for both fundamental chemistry and the implications for nuclear fuel processing and radioactive waste clean-up. However, actinide-ligand bonding interactions are complex and notoriously challenging to predict. Our work addresses this challenge by developing new spectroscopic strategies for evaluating actinide-ligand bonding, using resonant inelastic X-ray scattering (RIXS) techniques.

We present a systematic investigation of uranium(IV) hexahalides,  $[UX_6]^{2-}$ , where X=F, Cl, Br, highlighting the sensitivities of several RIXS techniques to specific aspects of uranium electronic structure and bonding. Specifically, new insights from  $M_{4,5}$ -edge 3d4f RIXS are presented, demonstrating the technique as a probe of uranium(IV)-ligand bond covalency. Measurements are supported by *ab initio* calculations and interpreted using ligand field multiplet theory.

The presented techniques are predicted to be universal to actinide and ligand element identity, actinide oxidation state, and actinide coordination symmetry. Consequently, these methods are expected to contribute widely to actinide analytical chemistry and material characterisation.



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## Spectroscopic investigations on the behaviour of irradiated light water reactor fuels during prolonged dry interim storage and final disposal

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At present, spent nuclear fuel (SNF) assemblies discharged from German nuclear power reactors are stored in dual-purpose casks (DPC) in interim storage facilities and shall be transferred to a geological disposal facility (GDF) after conditioning. The procedure for searching and selecting a site for a GDF is established by the German Site Selection Act which became active in its current iteration in May 2017. Site selection as well as commissioning of a final repository for SNF is presently anticipated for the second half of the 21<sup>st</sup> century. Consequently, the licensed interim storage period of up to forty years for interim storage facilities as well as many loaded DPCs will expire beforehand. Thus, a significant amount of SNF assemblies has to be kept in dry storage conditions for up to 100 years until storage facilities will be cleared and the SNF will be conditioned for emplacement in a GDF. In this process, all safety relevant issues have to be reviewed on basis of the state of the art in science and technology, which might differ from the initial safety demonstrations, expecting only a few decades of dry SNF interim storage. In this context, research at KIT-INE contributes to an improvement of knowledge regarding the behaviour of SNF during dry interim storage as well as the latter deep geological disposal. The long-term integrity of zirconium-based fuel rod claddings (e.g., Zircaloy) is decisive for a safe transport and handling of irradiated SNF assemblies in storage facilities and subsequent conditioning of SNF assemblies from a DPC to a final disposal container, until final emplacement in a GDF.

Already during irradiation, the nuclear fuel pellet and surrounding cladding will undergo changes in its morphological structure and chemical properties. Throughout utilisation in a nuclear reactor, several reactions take place, which alter the initial composition of pristine UO<sub>2</sub> or mixed oxide (U, Pu)O<sub>2</sub> fuel. One of the substantial nuclear reactions is the fission of heavy nuclei (e.g., <sup>235</sup>U, <sup>239</sup>Pu) under emission of neutrons, the generation of fission products and the release of large amounts of energy. In addition, transuranium isotopes, such as neptunium, americium or curium are generated through neutron capture reactions and subsequent  $\beta^-$  decays, starting from <sup>238</sup>U. Moreover, the cladding tubes will incorporate hydrogen originating from the coolant surrounding the fuel rods, forming mainly circumferentially oriented hydrides in the cladding material. As the SNF assembly is transferred from wet to dry storage, hydride precipitates can dissolve during the drying process and potentially precipitate, during subsequent dry interim storage as the SNF further cools down, in radial directions, potentially impacting the integrity of the zirconium-based cladding.

This contribution will give an overview on the current state of spectroscopic investigations performed at KIT-INE concerning aspects of dry interim storage and the subsequent disposal of SNF in a GDF. In order to elucidate the behaviour of irradiated light water reactor fuels, experiments are performed using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) as well as synchrotron-based X-ray absorption spectroscopy (XAS) and grazing incidence X-ray diffraction (GI-XRD). Particular emphasis is given on the occurrence of halogens, e.g., chlorine or iodine, at the fuel-cladding interface, and incorporated hydrogen in the zirconium-based cladding material.

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## Monitoring the formation of ternary surface complexes and surface precipitates of U(VI) on zirconia by vibrational spectroscopy

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The interactions of actinides, such as uranium, with corrosion products in the near-field of a geological repository are of concern regarding its safety assessment. The main corrosion product of the zircaloy cladding material is  $ZrO_2$ , which represents one of the first barriers for interactions with radionuclides in particular during the period of interim storage.[1] Consequently, understanding the molecular interactions between actinides and  $ZrO_2$  under oxidizing conditions is of particular importance in the context of early-failure scenarios for the interim storage of spent nuclear fuel in containers in the vicinity of nuclear power plants.

*In situ* vibrational spectroscopy has been used as a powerful tool for the monitoring of the formation of actinide's surface complexes in an aqueous environment.[2,3] The setup of a flow through experiment allows data acquisition of a stationary  $ZrO_2$  phase during the course of the sorption and desorption reactions in real time, with a sub minute time resolution and under well-defined atmospheric conditions. Hence, we investigated the surface species of U(VI) at the  $ZrO_2$  surface under anoxic and oxic conditions as well as the impact of atmospherically derived carbonate on the surface speciation at neutral pH values. From the frequencies of the bands representing the vibrational modes of the carbonate and uranyl ions, the formation of ternary U(VI)-carbonate surface complexes was deduced. The carbonate ligands were most likely bidentately coordinated to the uranium moiety which in turn was directly bound to the  $ZrO_2$  surface.

The desorption of the ternary surface complex was induced by flushing the solid phase with background electrolyte. The spectra recorded during this reaction step revealed only a poor reversibility of the sorption reaction indicating a predominant inner sphere complexation under the prevailing conditions.

With respect to the circumneutral pH level, spectroscopic investigations are often hampered by the instability of aqueous U(VI) solutions at a concentration level required for an accurate signal-to-noise ratio. This might interfere with the formation of surface precipitates due to the presence of colloids in the aqueous solutions. Here, we conducted a series of *in situ* IR sorption experiments to demonstrate the growing contribution of solid formation beneath ongoing sorption processes using metastable U(VI) solutions. The spectra revealed an increased contribution of surface precipitation in dependence of the age of the solution applied, which was deduced from the spectral changes observed from vibrational modes of both carbonate and uranyl ions.

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## Investigation of thorium-based generator concepts – improvements, labeling and speciation

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Targeted alpha therapy (TAT) is one of the most promising therapeutic approaches in the fight against advanced-staged cancer. For this purpose, radiopharmaceuticals are commonly employed, which traditionally consist of radionuclide, chelating agent, linker entity and targeting molecule. In TAT, both the optimization of existing and the development of novel options of each pharmaceutical fragment remains continuously in demand. In regards to applied radionuclides,  $\alpha$ -emitters, e.g. <sup>225</sup>Ac or <sup>223</sup>Ra are promising candidates, [1] and can be obtained from radionuclide generators [2].

Hence, this work deals with the investigation and optimization of two different radionuclide separation systems: <sup>227</sup>Th/<sup>223</sup>Ra surrogated by <sup>232</sup>Th and <sup>nat</sup>Ba and <sup>229</sup>Th/<sup>225</sup>Ra/<sup>225</sup>Ac surrogated by <sup>232</sup>Th/<sup>nat</sup>Ba/<sup>nat</sup>La. Subsequently, element yields and corresponding purities were evaluated by ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Binding behaviors and elution processes of the three elements were evaluated by X-ray Absorption Near Edge Structure Spectra (XANES) spectroscopic technique on both loading solutions and loaded columns. Additionally, X-ray fluorescence (XRF) maps of the generator columns were recorded to localize the elements during the column elution processes. The experiments were performed at the Synchrotron Laboratory for Environmental Studies (SUL-X) at the KIT Light Source [3].

After the radionuclide's elution, the next important step is represented by its prospective chelation. In this work, we focused on Macropa chelator which is used commonly for <sup>225</sup>Ac complexation. For this purpose, native Macropa and its derivative for more straightforward conjugation were successfully synthesized. Additionally, DOTA was labeled with the radionuclide <sup>177</sup>Lu and five further non-radioactive metals (<sup>nat</sup>La, <sup>nat</sup>Ba, <sup>nat</sup>Lu, <sup>nat</sup>Ga and <sup>nat</sup>Bi). Yields and purities were investigated in correspondence to different peptide backbones or reaction conditions like time, pH and temperature. In addition, the internalization of <sup>177</sup>Lu-labeled DOTA conjugates investigated in corresponding cancer cell lines.

In conclusion the experiments resulted in improved radionuclide elution strategies for radionuclide separation, exemplary chelator synthesis for radionuclides' coordination, pharmaceutical synthesis providing targeted delivery of chelated radionuclides, radiolabeling results and proof-of-concept on functional ability of different radiopharmaceuticals. Through the improvement of the individual components of a radiopharmaceutical a holistic view and multiple avenues for future research were found.

*We acknowledge funding by the Federal Ministry of Education and Research (BMBF) and the Baden-Württemberg Ministry of Science as part of the Excellence Strategy of the German Federal and State Governments. Co-funding of this project was made available through the joint strategic alliance between German Cancer Research Center (DKFZ) and Bayer AG. We thank the Institute for Beam Physics and Technology (IBPT), KIT for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).*

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## A Compact X-ray Emission Spectrometer at the SUL-X Beamline of the KIT Synchrotron Radiation Source: Implications for Lanthanide and Actinide Research

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A compact, one crystal point to point scanning back-scattering X-ray spectrometer in Rowland (Johann)-Geometry with nominal 50 cm radius has been setup in the vacuum-chamber of the experimental station of the SUL-X wiggler beamline at the Synchrotron radiation source of the Karlsruhe Institute of Technology using the existing linear and rotational stages (theta, 2theta, ...).

For the adjustment of the crystal analyzer to Bragg and focusing conditions the theta axis with its xyz-translation stage is used whereas the detector, at present an Avalanche-photodiode, is adjusted via a linear stage and moved with the 2theta circle to keep Bragg conditions.

Due to limited space in the vacuum chamber the Rowland circle is 8° inclined against the beam direction, allowing the incoming beam to bypass below and reach the sample mounted on an additional xyz stage in beam direction behind the analyzers position.

The beam is focused on the sample position with a KB mirror system to about 100x100 μm<sup>2</sup>. Bragg-angles are covered from about 58° to 89° 2theta. At present Si(111), Si(331), Si(220), Si(531), Si(211), Si(100), Si(311), Ge(311), Ge(211), Ge(331) and Ge(110) crystals are available for high resolution X-ray emission spectroscopy (XES) and X-ray absorption near edge structure (HR-XANES) experiments, including higher order reflections covering emission energies at high Bragg angles depending on elemental concentration and emission line probability between about 3.2 and 13.5 keV. Elastic scattering measured at Bragg angles above 80° 2theta results in energy resolution of about 1 eV. An alignment procedure was implemented for optimizing instrumental parameters using two appropriate fluorescence lines close to the minimal and maximal energy of a given crystal by minimizing differences of X-ray fluorescence energies to theoretical values. Across the complete usable energy range of chosen crystal the deviation after calibration is better than 1 eV compared to values listed in PyMca [1].

The vacuum chamber reduces the detector background due to scattered primary photons and prevents the absorption losses in air or He. A transport chamber and a load lock allow the transfer of air sensitive samples from a glovebox to the experimental station and back. Upgrades for sample environment like LN<sub>2</sub> cooling, UV irradiation and a modest heating device are under construction.

Investigations focus so far on the molecular chemistry of rare-earth metals based compounds that are of importance to our high-tech society [2] and on early actinide (An) elements, e.g. U,[3] to clarify the link between covalency and strength of the chemical bond. Resonant inelastic X-ray scattering (RIXS) and HR-XANES methods allow to probe occupied and unoccupied parts of the valence band with high energy resolution in order to gain information also on the chemical bond. Ligands and An materials with tailored properties are needed, e.g., for developing pharmaceutical compounds for target-orientated cancer treatment.

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## On the Sr coordination, Sr K-edge absorption spectra, and solubility product constants of Sr-bearing calcite

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Calcite ( $\text{CaCO}_3$ ) in rock fractures often incorporates metal ions, including strontium (Sr), potentially influencing the mobility of radioactive nuclides in groundwater. However, the fundamental knowledge regarding Sr incorporation, particularly its coordination environment and solubility constant, remains elusive. Strontium carbonate ( $\text{SrCO}_3$ ) exists solely as strontianite (orthorhombic crystal system) with nine-fold coordinated Sr, compared to sixfold-coordinated Ca in calcite. This discrepancy in the coordination structure poses a challenge in understanding Sr-bearing calcite through isomorphic substitution of  $\text{Ca}^{2+}$  by  $\text{Sr}^{2+}$ . As a result, the crystal structure of Sr-bearing calcite is still under debate. Here, we report the crystal structures and thermodynamics of Sr-bearing calcite calculated using density functional theory (DFT). Our DFT simulations predicted mixed coordination numbers of six and seven for Sr in calcite, contrasting the nine-fold coordination in strontianite. Sr K-edge absorption spectra calculated for Sr-bearing calcite, strontianite, and hypothetical trigonal  $\text{SrCO}_3$  also revealed a correlation with the coordination number of Sr. DFT further predicted higher solubility product constants for Sr-bearing calcite compared to Sr-bearing aragonite, with the values increasing with Sr content. This indicates a limited role of calcite in retarding Sr mobility in rock fractures. According to the DFT thermodynamics, the precipitation of Sr-bearing calcite requires unrealistically high concentrations of Sr compared to those typically reported in natural waters. Thus, the occurrence of natural Sr-bearing calcite implies high Sr accumulation in the micro-environment of rock fractures despite lower concentration of Sr in bulk groundwater. The complexity related to Sr-bearing calcite formation has significant implications for geochemical transport modeling of radioactive nuclides. Incorporation of these findings could significantly enhance the reliability of transport models assessing nuclide mobility in geological systems.

## ***Ab-initio* Pourbaix diagrams for U-H-O system**

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Understanding the chemical behavior of radionuclides is essential for assessing the long-term safety of deep geological repositories for radioactive waste. Robust thermodynamic data for radionuclides are fundamental in developing geochemical models to predict their speciation and mobility under varying environmental conditions in repository settings (e.g., temperature, redox potential, pH, and ion concentrations). However, obtaining these experimental data for radionuclide-bearing phases is often challenging due to the inherent risks and limitations associated with radiation hazards and short half-lives. Quantum mechanical calculations can complement the experimental limitation as a reliable theoretical method for obtaining material properties without adjustable parameters. In this presentation, we report density functional theory (DFT) calculation results for uranium solid phases ( $\alpha$ -U, UO<sub>2</sub>,  $\gamma$ -UO<sub>3</sub>, U<sub>3</sub>O<sub>8</sub>, UO<sub>4</sub>·4H<sub>2</sub>O, UO<sub>4</sub>·2H<sub>2</sub>O, and UO<sub>3</sub>·2H<sub>2</sub>O), focusing on the construction of Eh-pH diagrams (Pourbaix diagrams) for the U-H-O system based on the Grand potentials of each phase. We compare our DFT results with available experimental data and discuss the prospects and limitations of current DFT methodology in calculating thermodynamic data of radionuclide phases. *Ab-initio* thermodynamics has the potential to significantly improve geochemical transport modeling of radionuclides, thereby enhancing the safety assessments of geological repositories for radioactive waste.

## The Actinide Chamber at the X-SPEC beamline

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Investigations into the fundamental structural properties of actinides are important for understanding their long-term chemical behavior in both temporary and geological repository conditions, as well as developing radiopharmaceuticals labeled with alpha-emitters for nuclear medical applications. The nature of the 5f states in actinides and their role in chemical bonding are of great interest in actinide chemistry. Well-established and advanced X-ray spectroscopic techniques can be employed to characterize complex actinide systems. In particular, X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) have permitted investigations into the actinide electronic structure, speciation, and local atomic environment using both soft and hard X-rays [1,2]. However, the collection of experimental data from radioactive samples under vacuum conditions, particularly those in liquid or gaseous states, presents challenges and requires safety measures to prevent potential contamination.

The X-SPEC beamline [3], a recently commissioned beamline at the KIT Light Source, offers soft and hard X-ray XAS, XES, and RIXS, as well as soft and hard X-ray photoelectron spectroscopy (HAXPES). We have designed and are currently commissioning a multi-functional chamber, the “Actinide Chamber”, which will be attached to an experimental station (Fig. 1a) at the X-SPEC beamline. This chamber will permit experiments on single crystals and actinide samples in solid, liquid, or gas phase with radioactivity below the European exemption limits. Safety during experiments is enhanced by a dome containing multiple windows with thin (~100 nm) membranes for the incident beam and the fluorescence emitted to the X-ray emission spectrometer (Fig.1b). The sample positioning system can include a heating device or a single-crystal positioning mechanism (Fig.1 c). Additionally, a cell has been developed for conducting soft X-ray spectroscopy experiments on gas-phase radioactive materials, and plans are underway for a flow-through cell designed for liquid radioactive samples. We will discuss the design of the chamber, the cells, and initial measurements.

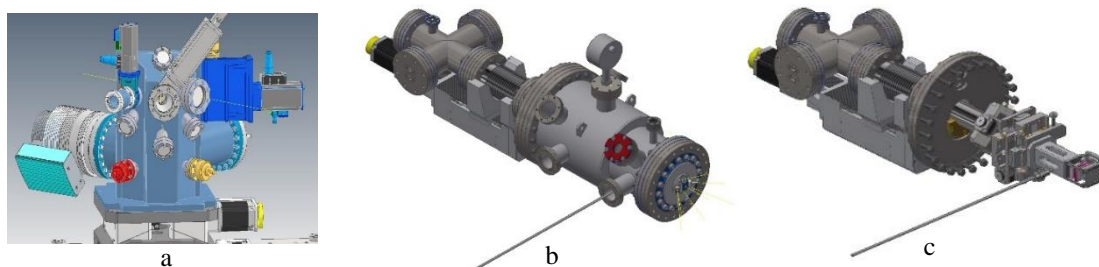


Fig. 1: (a) Experimental station of the X-SPEC beamline, where the “Actinide Chamber” will be attached; (b) the “Actinide chamber” for solid, liquid, and gas phase samples with radioactivity levels below the exemption limit; (c) inside view of the “Actinide Chamber”, including sample positioning and heating components.

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## Soft and hard x-ray spectroscopy with a novel calorimetric superconducting quantum sensor

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X-ray spectroscopy at synchrotron light sources has emerged as one of the most powerful tools available worldwide for the characterization of the chemical, atomic, and electronic properties of materials. While existing x-ray spectrometers provide either excellent energy resolution at low efficiency or moderate energy resolution at high efficiency, magnetic microcalorimeters (MMCs) might be a “gamechanger” as they promise outstanding energy resolution with a  $\Delta E_{\text{FWHM}}$  of 1.25 eV at 5.9 keV [1], a large energy bandwidth, and extremely high detection efficiency. MMCs are ultra-sensitive cryogenic detectors which rely on converting the energy from incident photons into heat. Using an ultra-sensitive thermometer based on the temperature-dependent magnetization of a paramagnetic material in a weak magnetic field, the resulting change in magnetization is sensed with a superconducting quantum interference device (SQUID) [2].

The goal of our activities within the project “Quantum sensor platform for synchrotron x-ray spectroscopy (QUASY)”, is to demonstrate the feasibility of such a x-ray quantum sensor array at multiple synchrotron radiation beamlines (i.e., X-SPEC, CAT-ACT, INE, and SUL-X) at the KIT Light Source using a universal, compact, and modular platform. In this contribution, the current design concept of the platform, which contains x-ray optics and filter foils, will be discussed. We will show first experimental data on the thin filter foils that serve as candidates to block infrared radiation while transmitting x-rays in the soft, tender, and hard x-ray energy regions. If successful, the new instrumentation will not only greatly advance the available experimental techniques, but also allow for the study of samples containing radionuclide materials, with low concentrations, and/or in *in situ* and *operando* environments.

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## Spectroscopic Study of the Pu(III)-ISA Complex in Weak Acidic Conditions

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The safe disposal of radioactive waste is important in the nuclear industry. Understanding the interactions between actinides and organic ligands is crucial for addressing this issue, as these interactions significantly impact the mobility, solubility, and sorption of radionuclides. Plutonium requires careful attention in nuclear waste management, considering its complex chemical behaviors. Isosaccharinic acid (HISA) is of particular interest due to its significant quantity under the alkaline conditions, which are typical of cementitious environments in waste repositories. The formation of actinide complexes with ISA can increase dissolved concentration of actinides [1], potentially leading to environmental contamination. This study focuses on the Pu(III)-ISA complex, determining the formation constant and structure to better understand its chemical behavior in waste disposal scenarios.

Samples were prepared at pH 5, where 1% of Pu(III) is hydrolyzed and 96% of carboxyl group in HISA are deprotonated. Absorption spectra were measured at 25°C in wavelength range from 500 to 700 nm. As the ratio of [ISA] to [Pu(III)] increased, interpretation of spectra for Pu(III)-ISA became complex due to overlap with a broad absorption band of ISA. To analyze the absorption spectrum, second derivative spectroscopy was employed for baseline correction, and Savitzky-Golay smoothing was applied to reduce noise. The Hypspec software was used to deconvolute primary components and determine the formation constant of the Pu(III)-ISA complex. Experimental data confirmed one significant species: PuISA<sup>2+</sup>. The formation constant of PuISA<sup>2+</sup> ( $\text{Pu}^{3+} + \text{ISA}^{-} \rightleftharpoons \text{PuISA}^{2+}$ ) was determined in 1 M NaClO<sub>4</sub> medium. The absorption spectrum of PuISA<sup>2+</sup> species showed typical nephelauxetic effect, such as red shifts and increased intensity at major absorption peaks. These observations align with trends observed in Am(III)-ISA complexes [2]. Additionally, to determine the optimal structure of Pu(III)-ISA, DFT calculations were performed on structures where ISA binds to Pu(III) in both bidentate and tridentate configurations. DFT calculation results will be presented in detail.

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## Complexation of U(VI) with N-donor ligands studied by high energy resolution X-ray spectroscopy and computations

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The degree of involvement of actinide 5f electrons in chemical bonds and trends along the actinide series are still under debate.[1-4] In recent years, experimental techniques such as high-resolution X-ray absorption near-edge structure (HR-XANES) and valence band resonant inelastic X-ray scattering (VB-RIXS) have been developed. These techniques have made significant contributions to the study of the electronic structure of actinides (An), particularly regarding the covalency of the An-ligand bond.[4]

Uranyl(VI) ( $\text{UO}_2^{2+}$ ) solutions with  $\text{UO}_2^{2+}$  to ligand ratios of 1:10/20 were prepared and investigated to evaluate the influence of the N-donor ( $\text{SO}_3$ -Ph-BTP, iPr-BTP, nPr-BTP) or O-based (TODGA,  $\text{NO}_3^-$ ) ligands on the electronic structure of  $\text{UO}_2^{2+}$ . The local coordination of  $\text{UO}_2^{2+}$  was probed by U  $L_3$ -edge extended X-ray absorption fine structure (EXAFS) experimental technique. The influence of ligand binding in the equatorial plane on the covalency of the axial uranyl bond was evaluated by U  $M_4$  edge HR-XANES. U  $M_4$  VB-RIXS was employed to study changes of  $\text{UO}_2^{2+}$ -ligands bond covalency. The X-ray spectroscopic experiments were performed at the ACT station at the CAT-ACT beamline and the INE-Beamline at the KIT Light Source, Karlsruhe, Germany. [5-6] We will illustrate that N-donor ligands bind to  $\text{UO}_2^{2+}$ , which leads to small U(VI) electronic structure variations. Calculations predict reduced bond covalency for TODGA compared to BTP ligands, mainly due to the absence of central oxygen atom  $\pi$  interaction in TODGA. [7]

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## Electroanalytical and Spectroscopic Investigations of Redox Chemistry in Heterobimetallic Uranyl Crown Ether Complexes

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**Abstract:** The redox chemistry of uranium, and particularly of the uranyl ion ( $\text{UO}_2^{2+}$ ), strongly influences speciation properties and reactivity of relevance to separations. More broadly, the development of an understanding of how ligand environment can be tuned to control the reduction potentials of actinide elements represents a strategy for guiding reaction outcomes and improving process efficiency. In this poster presentation, the development of an unusual platinum-based macrocyclic metalloligand for chelation of  $\text{UO}_2^{2+}$  will be described. Coordination of uranyl to the neutral metalloligand results in formation of a dicationic complex in which the  $\text{UO}_2^{2+}$  core is threaded into a crown-ether-like binding site. The U(VI) complex can be prepared in near quantitative yields and was confirmed to be stable both in solution (through nuclear magnetic resonance (NMR) studies) and in the solid state (through single crystal X-ray diffraction (SC-XRD) studies). Most importantly, the electrochemical profile of the complex reveals the most positive U(VI)/U(V) reduction potential yet reported in the literature for the uranyl ion, centered at  $-0.18$  V vs. ferrocenium/ferrocene. The oxidation states of the uranium center in both the U(VI) and U(V) forms have been confirmed through vibrational spectroscopy and near-infrared absorption spectroscopy; the U(VI) and U(V) forms of the complex can be readily interconverted using sensible chemical redox reagents. Moreover, the properties of the two oxidation states have been modeled computationally, affording a view of the electronic properties of these species. Taken together, these findings demonstrate that our metalloligand offers a formally neutral donor set that is capable of chelating uranyl in both the +6 and +5 oxidation states. In this presentation, our latest results will be described as well, including electroanalytical and spectroscopic studies aimed at studying the interconversion of U(VI) and U(V) in this system, as well as spectroelectrochemical work of relevance to advanced characterization methods. We anticipate that an appealing outcome of the ongoing studies will be a detailed view of how crown-ether-like ligands can promote unusual redox chemistry in the actinides.

# Complexation of Cm(III) with silicates at variable ionic strengths and pH values

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Cementitious materials are used for conditioning of different nuclear waste types, as components of waste containers or structural materials at the interface of backfilling and host-rock. In case of water intrusion into the repository, cement degradation processes may occur. Si concentrations in such a scenario can reach concentrations of up to  $10^{-3}$  M. The chemistry of monomeric and polymeric silicates in aqueous solutions is quite versatile. The silicate speciation highly depends on various factors such as the total Si concentration, pH, ionic strength and temperature. In the literature complexation reactions of dissolved silicate with trivalent lanthanide and actinide ions are described. However, these studies are mostly limited to low ionic strengths and acidic to slightly alkaline conditions.<sup>[1-3]</sup> Studies that investigate medium to high ionic strengths, which are present in the pore and formation waters of the clay rock formations in Northern Germany, are scarce in the literature. Moreover, very few data have been gathered for cement-relevant pH values, which determine the geochemical environment of the near-field. For this reason, we initially studied the polymerization of silicates in aqueous solution as a function of the silicate concentration, pH, ionic strength, and time using colorimetric methods. Our investigations show that the formation of polymers occurs predominantly in the pH range of 5 – 10. Additionally, high ionic strengths strongly favor the formation of polymer species. Time-dependent studies also prove that the polymerization is subject to kinetics that are particularly slow at low silicate concentrations. Based on these results, the complexation of Cm(III) with different dissolved silicates was studied using time-resolved laser fluorescence spectroscopy (TRLFS). In summary, the TRLFS data indicate the formation of three Cm(III)-silicate species: a monosilicate species  $[\text{Cm}(\text{H}_3\text{SiO}_4)]^{2+}$  at  $\lambda = 598.5$  nm, a polymeric Cm(III)-silicate species (I) at  $\lambda = 603.2$  nm, and a colloidal Cm(III)-silicate species (II) at  $\lambda = 606.2$  nm. Further studies focused on the speciation of the polymeric and colloidal Cm-silicate species under alkaline pH conditions with varying ionic strengths and background electrolytes. In NaCl systems, the formation of the colloidal species (II) is largely suppressed as the ionic strength increases. From pH = 9.5 onwards, the speciation is dominated by the hydrolysis of Cm(III). In contrast to this, the formation of the polymeric species (I) is suppressed with increasing ionic strength when using  $\text{CaCl}_2$  or  $\text{MgCl}_2$  as background electrolyte. Accordingly,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  appear to stabilize the colloidal Cm silicate species (II), which is also reflected by the fact that no ternary Ca-Cm(III)-OH complexes are formed in alkaline solutions. The results of this work show that due to the polymerization of silicates, which already occurs below the solubility limit of amorphous silica, a variety of complexation reactions with trivalent actinides can take place. TRLFS is an excellent method to identify different complex species and thus providing new insights into the complexation behavior of trivalent actinides in silicate systems under conditions that are relevant in the near field of a nuclear waste disposal.

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