ATAS 2016

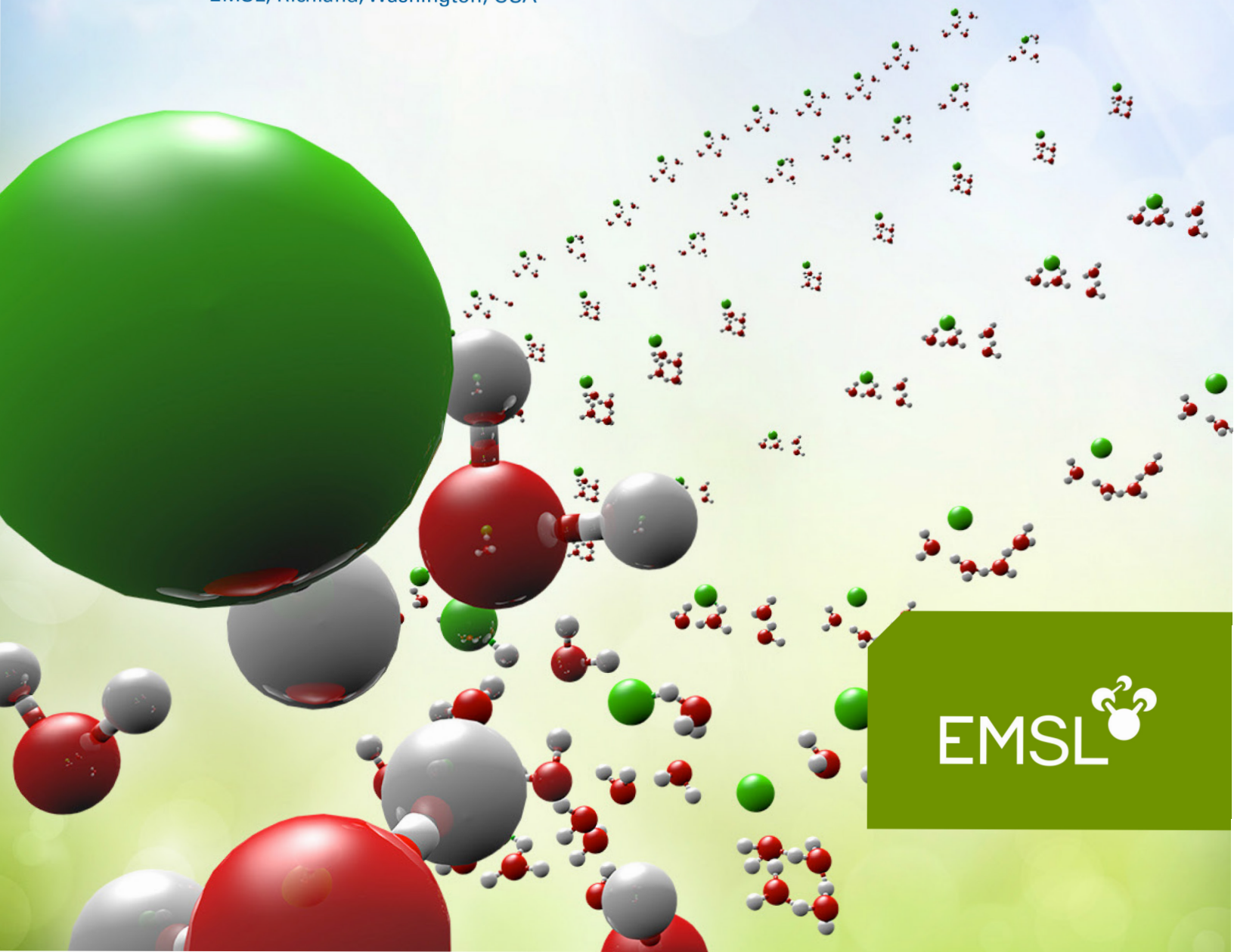
3rd International Workshop on

ADVANCED TECHNIQUES IN ACTINIDE SPECTROSCOPY (ATAS)

Abstract Book

November 7 – 10, 2016

EMSL, Richland, Washington, USA



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3rd International Workshop on Advanced Techniques in Actinide Spectroscopy (ATAS)

Abstract Book

November 7–10, 2016

Prepared for the U.S. Department of Energy's Office of Biological and Environmental Research under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Contact

EMSL, the Environmental Molecular Sciences Laboratory
3335 Innovation Blvd.
Richland, Washington, USA 99354

Nancy Hess nancy.hess@pnnl.gov
Zheming Wang zheming.wang@pnnl.gov
Carolyn Pearce carolyn.pearce@pnnl.gov

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Preface

We are honored to host the third international workshop on Advanced Techniques in Actinide Spectroscopy, ATAS 2016. We are proud to continue the tradition of this important forum to exchange progress and new approaches in experimental and computational studies of actinides.

Experimentation with computation has been the hallmark of impactful science and a long tradition at EMSL, the Environmental Molecular Sciences Laboratory. Close partnership between these two communities has resulted in accelerated advancement in understanding, experimental and technical design, and computational methods. These advancements have led to improved frameworks that codify our understanding of actinide chemistry and allow predictive understanding.

Theoretical interpretation of spectroscopic results has led to significant deepening of our understanding of f-electron chemistry and actinide chemical behavior under varying chemical conditions. Many studies we will learn about at ATAS 2016 provide the scientific foundation for the design and design validation of combined experimental and computational investigations across many different fields from environmental geochemistry, to separations for pretreatment, waste packages and repositories for radioactive waste. These findings enable advancements in both basic and applied studies.

The products of many of these studies have been deployed at the Hanford Site in Washington State. During ATAS 2016 we will have the opportunity to tour both a new international radiological user facility, RadEMSL, as well as the historic B Reactor, the world's first plutonium production reactor.

The workshop would not take place without kind advice and support from the HZDR administration, which is gratefully acknowledged. Finally the organizers thank Pacific Northwest National Laboratory and Bruker for generous funding which makes this workshop possible.

Allison A. Campbell, PhD
Associate Laboratory Director, Earth and Biological Sciences Directorate
Pacific Northwest National Laboratory

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Information

Registration

The registration desk will open at 7:30 a.m. on Monday, November 7th and will be staffed throughout the workshop. Please come to the registration desk if you have any questions.

Instructions to Presenters

Please upload your presentations at the lectern before your session starts. There will be audio visual staff present to assist. Please see the agenda for your time allocation.

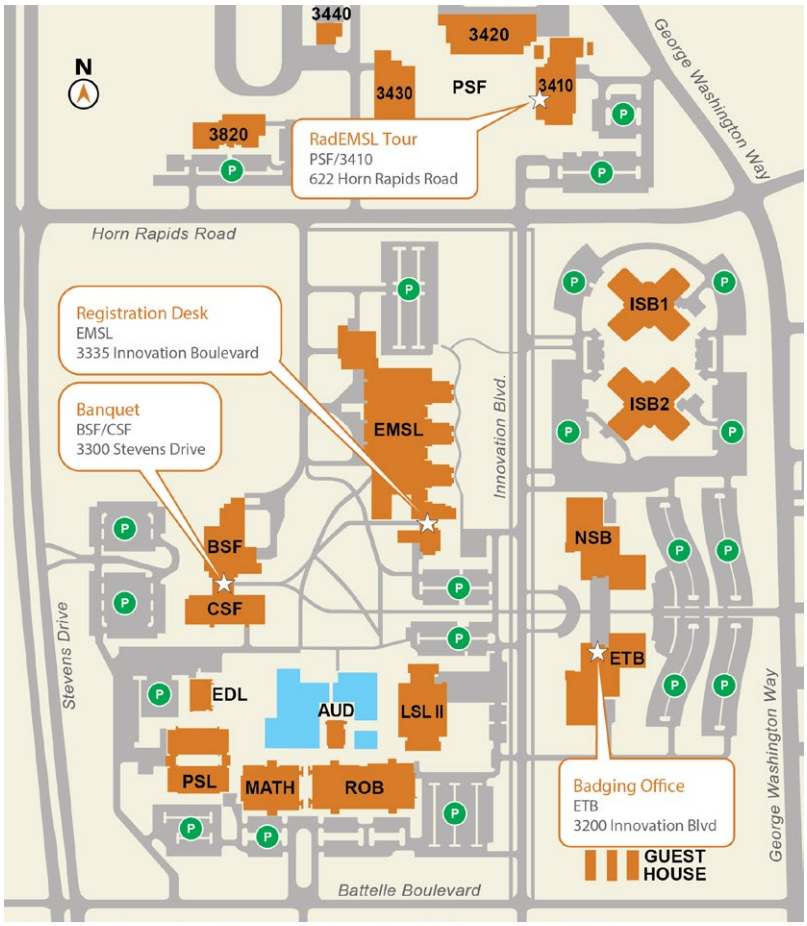
Breakfast, Lunch and Refreshments

Breakfast, lunch and refreshments will be provided throughout the workshop. Refreshments will also be served at the poster session on Monday evening.

Poster Session

The poster session will be held on Monday, November 7th from 5:30 p.m. – 7:30 p.m.
Poster guidelines are as follows:

- The maximum poster dimensions are 40″ × 60″ wide (101 cm × 152 cm)
- Paper or fabric posters recommended. Thumbtacks to secure the poster to the display boards will be provided.



Banquet

A buffet dinner will be served at the banquet on Wednesday, November 9th starting at 6:00 p.m. The banquet will be held at Pacific Northwest National Laboratory in the lobby of the Biological Sciences Facility and Computational Sciences Facility, 3300 Stevens Drive in Richland. This building is located directly west of EMSL, the Environmental Molecular Sciences Laboratory and is less than a 5 minute walk away.

EMSL Tours

Tours of both EMSL and RadEMSL will occur on Tuesday, November 8th. A temporary Department of Energy visitor badge is required to attend this tour (this is separate from your name tag). Please go to the ATAS registration desk if you have any questions.

ATAS Transportation

Please go to the ATAS registration desk or email atas.conference@pnnl.gov if you require transportation from your hotel to/from the workshop.

Wi-Fi Instructions

Complimentary wireless internet, called VisitorLAN, is available. Select **VisitorLAN** from the list of available wireless networks and click Connect. Open a web browser like Chrome or Safari and attempt to browse any web page such as Google. You should then be redirected to the VisitorLAN registration. Read the notice and click **Accept and Register as Guest**. Complete the online form with your information. The PNNL host is **Allison Coyne**. Once registration is complete, please close and restart your web browser.

Agenda

SCIENTIFIC PROGRAM

Monday, November 7, 2016

Time	Topic/Participants	Location
8:30 a.m.	Registration and Badging (FNVA badging starts at 8:30 am in the ETB Badging Office)	EMSL Lobby/ ETB Badging Office
10:00 a.m.	**Welcome and Opening Remarks** Allison Campbell, Associate Laboratory Director, Pacific Northwest National Laboratory	EMSL Auditorium
	Opening Chair: Zheming Wang, Pacific Northwest National Laboratory	EMSL Auditorium
10:30 a.m.	**Actinide Spectroscopy and Quantum Calculations Applied to Understand Uranyl Peroxide Nanoclusters** (Keynote, INVITED) *Peter Burns, University of Notre Dame*	EMSL Auditorium
11:30 a.m.	**A Multiple-Technique Round-Robin Test in Actinide Spectroscopy** *Harald Foerstendorf, Helmholtz-Zentrum Dresden-Rossendorf*	EMSL Auditorium
12:00 p.m.	Lunch	EMSL Auditorium
Session 1	**COMPUTATIONAL CHEMISTRY** (Chair: Ping Yang, Los Alamos National Laboratory)	
1:00 p.m.	**Theoretical Studies of Orbital Mixing in Actinide-Ligand Bonds via Core-Level K-edge XAS** (INVITED) *Enrique Batista, Los Alamos National Laboratory*	EMSL Auditorium
1:30 p.m.	**Quantum Chemical Modeling of Actinide Hydrolysis Complexes** *Sven Kruger, Technical University of Munich*	EMSL Auditorium
1:50 p.m.	**Quantum Chemical Modeling of U(VI) and Np(V) Adsorption on the Solvated (110) Edge Surface of Montmorillonite** *Alena Kremleva, (Presented by Sven Krueger) Technical University of Munich*	EMSL Auditorium
2:10 p.m.	**Fragment Molecular Orbital (FMO) Method for Studying Actinide Interaction with DNAs and Proteins** *Satoru Tsushima, Helmholtz-Zentrum Dresden-Rossendorf*	EMSL Auditorium
2:30 p.m.	Intermission	EMSL 1075/1077
Session 2	**FLUORESCENCE** (Chair: Harald Foerstendorf, Helmholtz-Zentrum Dresden – Rossendorf)	
2:50 p.m.	**Luminescence Spectroscopy of An/Ln in Environmental Systems** (INVITED) *Robin Steudtner, Helmholtz-Zentrum Dresden-Rossendorf*	EMSL Auditorium
3:10 p.m.	**Luminescence Lifetime Measurements of Trivalent f-elements in Mixed Solvent Systems** *Heather Felmy, Washington State University*	EMSL Auditorium

Monday, November 7, 2016 (cont'd)

Time	Topic/Participants	Location
3:30 p.m.	**Spectroscopic Investigation for the Structure of Actinides Sorption on the Solid/Liquid Inter-surface** *Wangsuo Wu, Lanzhou University*	EMSL Auditorium
3:50 p.m.	**TRLFS and ATR-IR Studies on Eu(III) and Am(III) Adsorption on SiO_2 Particles in the Presence of a Small Organic Ligand** *Hee-Kyung Kim, Korea Atomic Energy Institute*	EMSL Auditorium
4:10 p.m.	**Spatially-Resolved Sorption Studies of Eu(III) on Granite Surface with Time-Resolved Laser Fluorescence Microscopy (TRLFM)** *Konrad Zesewitz, Helmholtz-Zentrum Dresden-Rossendorf*	EMSL Auditorium
4:30 p.m.	**Retardation and Release of Uranium on Phlogopite Mica at the Absence and Presence of Humic Acid: A Batch and TRLFS Study** *Duoqiang Pan, Lanzhou University*	EMSL Auditorium
5:30 – 7:30 p.m.	**Poster Session**	EMSL 1075/1077

Tuesday, November 8, 2016

Time	Topic/Participant(s)	Location
7:45 a.m.	Continental Breakfast	EMSL 1075/1077
Session 3	**SOLUTION CHEMISTRY** (Chair: Robert Baker, University of Dublin)	
8:00 a.m.	**Actinide Solution Chemistry and the Processing of Nuclear Materials** (INVITED) *Sue Clark, Pacific Northwest National Laboratory and Washington State University*	EMSL Auditorium
8:30 a.m.	**Detection of Actinides and Lanthanides in Solutions by Chemiluminescence Laser Spectroscopy** *Igor Izosimov, Joint Institute for Nuclear Research*	EMSL Auditorium
8:50 a.m.	**Complexation of Actinides by Branched N-macrocycle DOTA** *Thomas Dumas, CEA (Atomic Energy Comm.)*	EMSL Auditorium
9:10 a.m.	**Electrochemical and Spectroscopic Behavior of Neptunium in Aqueous Nitric Acid** *Dev Chatterjay, Pacific Northwest National Laboratory*	EMSL Auditorium
9:30 a.m.	**Efficient Removal of Radionuclides from Aqueous Solutions Using Carbon Nanomaterials** *Xiangke Wang, North China Electric Power University*	EMSL Auditorium
9:50 a.m.	Intermission	EMSL 1075/1077
10:10 a.m.	TOURS: EMSL and RadEMSL	EMSL and 3410 Building
12:00 p.m.	Lunch	EMSL Auditorium

Tuesday, November 8, 2016 (cont'd)

Time	Topic/Participant(s)	Location
Session 4	**NMR and VIBRATIONAL SPECTROSCOPY** (Chair: Herman Cho, Pacific Northwest National Laboratory)	
1:00 p.m.	**Structure and Ligand Exchange Dynamics in Ternary Uranium(VI)-Peroxide Complexes Studied by NMR Spectroscopy** (INVITED) *Zoltan Szabó, Royal Inst. of Technology (KTH)*	EMSL Auditorium
1:30 p.m.	**Probing the Pu4+ magnetic moment in PuF_4 with ^{19}F NMR spectroscopy** *Cigdem Capan, Washington State University, Tri-Cities*	EMSL Auditorium
1:50 p.m.	**^{31}P Nuclear Magnetic Resonance as a Probe of Plutonium Incorporation and Radiation Damage in Phosphates** *Ian Farnan, University of Cambridge*	EMSL Auditorium
2:10 p.m.	**Raman Scattering Investigations on Actinide Oxides** (INVITED) *Patrick Simon, National Center for Scientific Research*	EMSL Auditorium
2:30 p.m.	**Assignment of Unexpected Raman Spectra of Uranyl Triperoxide Complexes** *Mateusz Dembowski, University of Notre Dame*	EMSL 1075/1077
Session 5	**COMPUTATIONAL CHEMISTRY II** (Chair: Satoru Tsushima, Helmholtz–Zentrum Dresden–Rossendorf)	
2:50 p.m.	**Structures of Plutonium(IV) and Uranium(VI) with *N*,*N*-Dialkyl Amides from Crystallography, X-ray Absorption Spectra, and Theoretical Calculations** *Dominique Guillaumont, Atomic Energy Commission*	EMSL Auditorium
3:10 p.m.	**Quantum Chemical Investigation of Incorporation of Uranium(V) into Magnetite: Combining Multi-Reference *ab initio* Methods and Density Functional Theory** *Robert Polly, Karlsruhe Institute of Technology*	EMSL Auditorium
3:30 p.m.	**Probing the Structure of Uranium Complexes in Molten Salt by Absorption Spectroscopy and DFT Calculation** *Tao Su (presented by Hongtao Liu) – Shanghai Institute of Applied Physics*	EMSL Auditorium
3:50 p.m.	**Unusual Magnetic Properties of Actinide Thiocyanate and Selenocyanate Complexes** *Robert Baker, Trinity College, Dublin*	EMSL Auditorium
4:10 p.m.	**Interplay Between Theory and Spectroscopy in Understanding Interfacial Interactions: A Case Study for CeO_2** *Ping Yang, Los Alamos National Laboratory*	EMSL Auditorium

Wednesday, November 9, 2016

Time	Topic/Participant(s)	Location
7:45 a.m.	Continental Breakfast	EMSL 1075/1077
Session 6	**ENVIRONMENTAL XAS** (Chair: Carolyn Pearce, Pacific Northwest National Laboratory)	

Wednesday, November 9, 2016 (cont'd)

Time	Topic/Participant(s)	Location
8:00 a.m.	**XAFS Spectroscopic Studies of Uranium Speciation at Mineral-Water and Sediment-Water Interfaces** (INVITED) *Jeffrey Catalano, Jeffrey – Washington University St. Louis*	EMSL Auditorium
8:30 a.m.	**The Effect of Iron Oxides and Montmorillonite Clays on the Transformations of Uranium Under Reducing Conditions** *Maxim Boyanov, Institute of Chemical Engineering*	EMSL Auditorium
8:50 a.m.	**Investigations of Plutonium Behavior in Vadose Zone** *Melody Maloubier, Clemson University*	EMSL Auditorium
9:10 a.m.	**Actinides Speciation in Seawater and Uptake by Marine Accumulating Organisms** *Christophe Den Auwer, University Nice Sophia Antipolis*	EMSL Auditorium
9:30 a.m.	**XAFS Investigations of UVI Reduction by Biotic and Abiotic Green Rusts** *Ken Kemner, Argonne National Laboratory*	EMSL Auditorium
9:50 a.m.	Intermission	EMSL 1075/1077
Session 7	**HANFORD** (Chair: Zheming Wang, Pacific Northwest National Laboratory)	
10:10 a.m.	**Migration at the Hanford Site: Understanding and Models Provided by Microscopic Methods and Important Remaining Challenges** (INVITED) *John Zachara, Pacific Northwest National Laboratory*	EMSL Auditorium
11:10 a.m.	Lunch	EMSL 1075/1077
	TOURS	
12:15 p.m.	Load onto bus	EMSL Parking Lot
12:30 – 4:30 p.m.	B Reactor Tour	B Reactor
4:30 – 6:00 p.m.	LIGO – Laser Interferometer Gravitational-Wave Observatory	Hanford Site
6:00 – 8:00 p.m.	Banquet/Announcements	BSF/CSF Lobby

Thursday, November 10, 2016

Time	Topic/Participant(s)	Location
7:45 a.m.	Continental Breakfast	EMSL 1075/1077
Session 8	**XAS** (Chair: Ken Kemner, Argonne National Laboratory)	

Thursday, November 10, 2016 (cont'd)

Time	Topic/Participant(s)	Location
8:00 a.m.	**X-ray Absorption Spectroscopy of Actinium and Comparison with Actinide +3** *Maryline Ferrier, Los Alamos National Laboratory*	EMSL Auditorium
8:20 a.m.	**Actinide and Lanthanide EXAFS Applications for the Nuclear Fuel Cycle** *Vanessa Holfeltz, Pacific Northwest National Laboratory*	EMSL Auditorium
8:40 a.m.	**Coordination Structure of Uranium Complexes in disordered Systems using X-ray Absorption Fine Structure Spectroscopy** *Linjuan Zhang, Shanghai Institute of Applied Physics*	EMSL Auditorium
9:00 a.m.	**XAFS and µ-XRF Investigation of Highly Radioactive Nuclear Waste Samples at KIT/ANKA** *Jorg Rothe, Karlsruhe Institute of Technology*	EMSL Auditorium
9:20 a.m.	**Actinide- and Actinide-Relevant XAS without a Synchrotron** *Gerald Seidler, University of Washington*	EMSL Auditorium
9:40 a.m.	Intermission	EMSL 1075/1077
Session 9	**XPS and Other** (Chair: Christophe Den Auwer, University Nice Sophia Antipolis)	
10:00 a.m.	**XPS Determination of Uranium Oxidation States** (INVITED) *Eugene Ilton, Pacific Northwest National Laboratory*	EMSL Auditorium
10:20 a.m.	**Diffuse Reflectance Spectroscopy of Plutonium Fluorides and Other Pu Solids: Evolution of Spectral Signature in Time as a Built-In Chronometer of the Sample Age and Crystallinity** *Sergey Sinkov, Pacific Northwest National Laboratory*	EMSL Auditorium
10:40 a.m.	**The optical properties of uranium carbide measured by spectroscopic ellipsometry** *Wigbert Siekhaus, Lawrence Livermore National Laboratory*	EMSL Auditorium
11:00 a.m.	**Probing the Electronic Structures of Thorium Oxides Using Anion Photoelectron Velocity Map Imaging** *Hongtao Liu, Shanghai Institute of Applied Physics*	EMSL Auditorium
11:20 a.m.	**Investigation of Europium (III) Acetylacetonate Complexes at Air/Water Interface by Sum Frequency Generation Vibrational Spectroscopy** *Zheming Wang, Pacific Northwest National Laboratory*	EMSL Auditorium
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Actinide spectroscopy and quantum calculations applied to understand uranyl peroxide nanoclusters

P. C. Burns

E-mail: pburns@nd.edu
Center for Sustainable Energy at Notre Dame
Energy Frontier Research Center – Materials Science of Actinides
Department of Civil and Environmental Engineering and Earth Sciences
Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, IN 46556

More than a decade ago we discovered that uranyl peroxide polyhedra self-assemble in aqueous solution under ambient conditions to form an extensive family of nanoscale cage clusters. These contain as many as 124 uranyl polyhedra, and have diameters in the 1.5 to 4 nm range. Since the initial discovery we have extensively applied spectroscopic techniques in combination with quantum chemical calculations and X-ray diffraction and scattering to discover 120 members of this family of nanomaterials, as well as many of their properties. In this presentation I will describe the development of our understanding of this novel system of materials, from the initial discovery to our current understanding, and how actinide spectroscopy (specifically Raman, NMR, and ESI-MS), quantum chemistry (DFT), and molecular dynamics simulations have been used throughout our work. I will close with a brief discussion of selected potential applications of uranyl peroxide cage clusters.

A multiple-technique round-robin test in actinide spectroscopy

H. Foerstendorf,[1,*] K. Müller,[1] S. Tsushima,[1] R. Steudtner,[1] M. U. Kumke,[2,†] G. Lefèvre,[3,†] J. Rothe,[4,†] H. Mason,[5,†] P. Yang[6,†]

* *E-mail*: foersten@hzdr.de

[†] On behalf of the participants of the single clusters of the Round-Robin test.

[1] Helmholtz-Zentrum Dresden – Rossendorf, Institute of Resource Ecology, Dresden, Germany

[2] Institute of Chemistry (Physical Chemistry), University of Potsdam, Potsdam, Germany

[3] PSL Research University, Chimie ParisTech — CNRS, Institut de Recherche de Chimie Paris, Paris, France

[4] Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany

[5] Physical and Life Science Directorate, Lawrence Livermore National Laboratory, Livermore, CA, U.S.A.

[6] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

In the advent of the 2nd International Workshop on Advanced Techniques in Actinide Spectroscopy (ATAS 2014), held in November 2014 at HZDR, an inter-laboratory Round-Robin Test (RRT) was initiated. The main goal of the RRT is the comprehensive molecular analysis of an aqueous complexing system – U(VI)/acetate, which was selected to be independently investigated by different spectroscopic and quantum chemical methods applied by leading laboratories in actinide or geochemical research. Finally, more than 40 scientists hosted at twenty institutions in seven countries were attending this RRT, which was finally subdivided into five clusters. A representative speaker was nominated for each cluster who received the submitted raw data sets as well as the analyzed data (e.g. data transformations, background subtraction, smoothing, deconvolution…). A first reporting of the preliminary results followed by plenum discussions was given by the cluster speakers during special sessions at the ATAS workshop.

The outcome of this RRT can be considered on two levels: First, conformities as well as sources of discrepancies between the results of each cluster have to be evaluated. It was found that consistencies of the raw data by the experimental approaches are widely given. In particular, for complex set-ups such as accelerator based X-Ray absorption spectroscopy, the agreement of the raw data was surprisingly high, whereas data obtained from Luminescence spectroscopy turned out to be strongly related to the chosen acquisition parameters which were quite heterogeneously chosen by the participating experimentalists. More detailed results of the single clusters will be presented.

On the second level, the potentials and limitations of coupling different spectroscopic and, in particular, theoretical approaches for the comprehensive study of actinide molecule complexes are assessed. The additional benefit of the combined approach with respect to the exploration of the aqueous speciation of the U(VI)/acetate system will be elaborated.

Theoretical studies of orbital mixing in actinide-ligand bonds via core-level K-edge XAS

E. R. Batista

E-mail: erb@lanl.gov

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

For the past few years we have put a significant amount of effort into the development of reliable computational methodologies for quantifying the amount of covalent interactions in actinide-ligand bonds. These studies shed lights on the bonding nature and aided the interpretation of ligand core-level spectroscopy measurements by experimental colleagues, and the two efforts together yielded solid evidence of covalent bonding and 5f participation in that interaction. On a more applied side, our studies have been instrumental in elucidating fundamental differences in electronic structure that lead to stronger bonds and selectivity in chemical separations of actinides. In this lecture we will discuss the computational methodologies and the application at prediction of XAS spectra in actinide species. As a corollary we will also discuss the connection between the covalent nature of the bonds and the strength of the bond, which is a concept that has confused the community for a long time. An implicit misunderstanding has been the connection between this evidence of covalent interaction and the relative strength of these bonds. In this presentation we address this issue with quantum mechanical methods to clarify and separate the two concepts. These developments are illustrated in a series of molecular complexes where the bonds are clearly defined and described in “simple” language.

Luminescence spectroscopy of An/Ln in environmental systems

R. Steudtner,[1,*] S. Lehmann,[1] M. Vogel,[1] B. Drobot[1]

* *E-mail:* r.steudtner@hzdr.de

[1] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf e.V., Dresden / Germany

Luminescence spectroscopy is a powerful tool to study the chemistry of f-elements (actinides – An, lanthanides – Ln) in trace concentration. Manifold operating mode, e.g. steady-state, time-resolved, laser-induced, site-selective, cryogenic, etc. were used to investigate the environmental behavior of An/Ln in various geological and biological systems. Hydrolysis is the basis for more complex aquatic systems and thus a deep understanding of those systems is indispensable. In case of U(VI) we demonstrated that a combination of luminescence spectroscopic methods together with state of the art data analysis (parallel factor analysis – PARAFAC) and quantum chemical calculations is a powerful setup to gain information on that system. We were able to extract thermodynamic constants for the mononuclear hydrolysis species using optimized data processing. Furthermore, advanced deconvolution of individual luminescence spectra demonstrates the correlation of luminescence spectroscopy and vibrational spectroscopy. Under reducing conditions expected in the near field of nuclear waste repository the tetravalent uranium should be the major oxidation state. We studied the U(IV) luminescence characteristics in presence of various inorganic ligands (ClO_4^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}). By using cryo-TRLFS at 77 K the speciation analysis limit for U(IV) was determined with $5 \cdot 10^{-6}$ M and this corresponds to uranium concentrations occurring in the environment.

For kinetic studies of geological or biological sorption phenomena, different microscopic or flow-through cell techniques are useable. For online monitoring and characterization of U(VI) sorption species we develop a new technical in situ luminescence spectroscopy setup in comparability to the well established in situ time-resolved ATR FT-IR spectroscopy. In analogy to the in situ ATR FT-IR measurements, the three typical subprocesses (conditioning, sorption, flushing) were observed for the U(VI) sorption on SiO_2. For biological systems we combined microscopy with luminescence spectroscopic measurements for localization, visualization and chemical characterization of An/Ln-complexes. These approach enables us to distinguish between biosorption, intracellular uptake or biomineralization as dominant retention process for An/Ln in biological samples.

Actinide Solution Chemistry and the Processing of Nuclear Materials

S. B. Clark

E-mail: sue.clark@pnnl.gov
Pacific Northwest National Laboratory and Washington State University
Energy and Environment Directorate, 902 Battelle Blvd, Richland, WA 99354

Chemical processing of nuclear materials is required for energy production, medical applications, and military purposes. Much of this processing occurs in solution, making consideration of actinide and fission product solution chemistry of paramount importance. For the f-elements, aqueous solution complexation reactions are sometimes driven by entropy achieved via disruption of the solvation sphere surrounding the lanthanide or actinide cation. As solvent mixtures are altered to include other solvents or diluents, these thermodynamic driving forces change, sometimes in unpredictable ways.

The chemistry of nuclear materials processing is currently an important focus area at the Pacific Northwest National Laboratory (PNNL). In this presentation, an overview of the history of irradiated materials processing at the Hanford Site will be provided, with emphasis on the context of solution speciation, thermodynamics, and spectroscopic analysis. In addition, a modern context for the thermochemistry of the f-elements in relation to analytical tools such as separations and mass spectrometry will be described.

Raman scattering investigations on actinide oxides

P. Simon,[1,*] O. A. Maslova,[1] E. S. Fotso Gueutue,[1] A. Canizarès,[1] M. R. Ammar,[1] G. Guimbretière,[1] P. Desgardin,[1] M. F. Barthe,[1] N. Raimboux,[1] F. Duval,[1] R. Mohun,[2] L. Desgranges,[2] C. Jégou,[3] S. Peuget,[3] M. Magnin,[3] S. Miro,[3] N. Clavier,[4] N. Dacheux,[4] O. Cavani,[5] B. Boizot[5]

* *E-mail:* simon@cnrs-orleans.fr

[1] CEMHTI UPR 3079 CNRS 45071 Orléans Cedex 2, France

[2] CEA/DEN/DEC Cadarache 13108 Saint-Paul lez Durance, France

[3] CEA/DEN/DTCD Marcoule BP 17171, 30207 Bagnols sur Cèze, France

[4] ICSM UMR 5257 CEA/CNRS/UM2/ENSCM, BP 17171, 30207 Bagnols sur Cèze, France

[5] LSI, UMR 7642 CEA/CNRS/Ecole Polytechnique, 91128 Palaiseau, France

Raman scattering is well-known to be an efficient tool for characterizing defects inducing local symmetry lowering and inhomogeneites in crystallized materials. A review of recent results on actinide oxides will be presented here. Raman imaging allows an accurate characterization of uranium oxide ceramics, giving access to specific features of core and grain boundaries, and in particular their behavior under ion beam irradiation [1]. Whatever the type of particles (light or heavy ions, electrons), irradiation induces a triplet of defect lines. Their mechanisms and kinetics of appearance and annealing *vs.* temperature can be followed by *in situ* Raman inside the irradiation facility, an original device that will be shown in details [2]. This triplet looks to originate from a Frenkel pair on the U site, as deduced from Raman and position annihilation spectroscopy on electron-irradiated samples.

These Raman defect lines occur also in PuO_2 and ThO_2 [3], even if for the latter they are masked by strong luminescence processes and revealed only by time-resolved Raman experiments.

All these results help to understand the recent Raman spectra of spent fuels (UO_2-based and MOX) [4], where all the spectral features correspond to those of model irradiated actinide oxides, but with stronger defect lines, consistent with the high doses undergone by these fuels.

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Structure and ligand exchange dynamics in ternary uranium(VI)-peroxide complexes studied by NMR spectroscopy

Z. Szabó[1,*] and I. Grenthe[1]

* *E-mail*: zoltan@kth.se

[1] Royal Institute of Technology (KTH), School of Chemical Sciences and Engineering, Department of Chemistry, S-10044 Stockholm, Sweden.

The uranium(VI)-ion forms a number of compounds that contain coordinated peroxide, O_2^{2-}, e.g. the minerals Studtite and meta-Studtite, $[UO_2(O_2)](H_2O)_4$ and $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$. These may be formed in nature in the reaction of Soddyite ($[(UO_2)_2SiO_4](H_2O)_2$) and Schoepite ($UO_2(OH)_2$) with hydrogen peroxide. Hydrogen peroxide can be formed when spent nuclear fuel is in contact with ground water. Hence, peroxide complexes may contribute both to the dissolution/transformation of UO_2 and to the formation of soluble peroxide species.

Uranium clusters containing peroxides such as $[UO_2(OH)(O_2)^-]_{60}^{60-}$ have been recently discovered and extensively studied [1], but no quantitative chemical information available on their formation. The talk is focused on our recent research of the composition and the ligand exchange dynamics of precursors present in ternary uranium(VI)-peroxide-hydroxide [2,3] and –carbonate [4,5] systems, these can act as building blocks in the cluster formation. Two ternary complexes $[UO_2(OH)(O_2)]-$ and $[(UO_2)_2(OH)(O_2)_2]^-$ have been identified in the uranium(VI)-peroxide-hydroxide system in tetramethylammonium (TMA) nitrate medium [2]. Addition of alkali-ions to this system results in the formation of two new complexes $M[(UO_2)(O_2)(OH)]^{2-}$ and $M[(UO_2)(O_2)(OH)]_4^{3-}$ (M = Li, Na and K) which are in slow chemical exchange with each other on the 17O NMR time-scale [3]. The alkali-ions act as templates, facilitating the formation of strong peroxide bridges between the uranyl units that provide the thermodynamic driving force for these reactions. We have also identified a number of complexes in the ternary uranyl(VI)–peroxide–carbonate systems [4]. We observed the formation of cyclic oligomers, "$[(UO_2)(O_2)(CO_3)]_n$", n=4,5,6, with different stoichiometries depending on the ionic medium used. This suggests that Li^+, Na^+, K^+ and TMA^+-ions act as templates for the formation of uranyl peroxide rings where the uranyl-units are linked by bridged peroxide-ions. The templating effect is due to the coordination of the M^+-ions to the uranyl oxygen atoms. These complexes can be considered as inorganic analogues to crown-ethers. The transformation of the complexes and their ligand exchange dynamics studied by ^{13}C NMR magnetization transfer is also presented.

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XAFS spectroscopic studies of uranium speciation at mineral-water and sediment-water interfaces

J. G. Catalano,[1,*] L. D. Troyer,[1] F. Maillot,[1] D. E. Giammar,[1] V. Mehta,[1] Z. Pan,[1] Z. Wang[2]

* *E-mail*: catalano@wustl.edu

[1] Washington University, St. Louis, MO 63130 USA

[2] Pacific Northwest National Laboratory, Richland, WA 99352, USA

X-ray absorption fine structure (XAFS) spectroscopy provides critical quantitative information on the coordination environment, oxidation state, and species distribution of uranium in environmental samples. This technique has been applied, often in combination with other analytical methods, to answer key questions about geochemical processes controlling uranium fate in both model laboratory systems as well as in the field. In this presentation, XAFS spectroscopy is applied to determine how phosphate addition to subsurface systems affects U(VI) immobilization. Cooperative and competitive interactions between U(VI) and phosphate and the underlying molecular mechanisms are the central focus of these studies.

In laboratory analog experiments, dissolved phosphate enhances macroscopic U(VI) uptake onto the iron oxide goethite at pH 4 but suppresses retention on the solid at pH 6 and 8. In contrast, U(VI) binding to the clay mineral montmorillonite is unaffected by the presence of phosphate. XAFS spectroscopy shows that at pH 4 phosphate forms ternary surface complexes with U(VI) on both minerals. These contrasting macroscopic effects despite similar molecular-scale U(VI) speciation results from difference in phosphate adsorption behavior: it adsorbs extensively to goethite but shows little binding to montmorillonite except when co-adsorbing with U(VI). At higher pH, XAFS spectroscopy and laser induced fluorescence spectroscopy (LIFS) show that U speciation is dominated by carbonate ternary surface complexes. Suppression of U(VI) adsorption on goethite at neutral to alkaline pH is caused by competition for surface sites between negatively charged U(VI)-carbonate complexes and phosphate anions.

Similar experiments investigated the transition from U(VI) adsorption on montmorillonite and goethite to precipitation of U(VI)-phosphate. At alkaline pH conditions there is a nucleation barrier that slows the onset of precipitation until substantial supersaturation is reached. XAFS spectroscopy and LIFS show that intermediate species, such as prenucleation clusters, do not form in this supersaturated region. XAFS spectroscopy demonstrates that U(VI) speciation can be quantitatively described by a mixture of adsorbed and precipitated U(VI) for all conditions examined.

Our work has also investigated U(VI)-phosphate interactions in sediments from contaminated field sites. Phosphate slightly enhances U(VI) adsorption by sediments from the Rifle, CO, field research site. XAFS spectroscopy and LIFS shows that U(VI)-phosphates only precipitate at phosphate and uranium concentrations much higher than observed in the environment and that U binding is dominated by adsorption. Phosphate has a greater effect on U(VI) uptake onto sediments from the Hanford Site 300 Area, substantially enhancing adsorption, likely through precipitation of calcium phosphates, as well as causing precipitation of U(VI)-phosphates. A nucleation barrier is seen, and XAFS spectroscopy and LIFS confirm that this again reflects a transition from adsorbed to precipitated species without an intermediate responsible for the inhibition of precipitation.

Migration at the Hanford Site: understanding and models provided by microscopic methods and important remaining challenges

J. M. Zachara

E-mail: john.zachara@pnnl.gov

Pacific Northwest National Laboratory, Richland, WA

The Hanford Site has significant environmental problems resulting from the release of diverse waste streams and contaminants to the ground, and their subsequent reaction and migration through the vadose zone and underlying groundwater system. Over the past 20 years, research has explored the geochemical and biogeochemical interactions of priority contaminants (including Cr, ^{137}Cs, ^{99}Tc, Pu, ^{90}Sr and U) with Hanford sediments of variable composition and mineralogy using spectroscopic and microscopic methods. Field samples from in-ground contaminant plumes have often been used, considering them as reactive tracer experiments of opportunity. Results of fundamental and applied scientific interest have been obtained. Long in-ground residence times and waste-sediment reaction have produced unexpected speciation states and mineral associations involving surface complexes, solid phases, and poorly defined intra-grain states that have led to new conceptual and numeric models of reaction paths and retardation processes. While many science questions remain, new understanding has, in some cases, directly influenced decision-making by providing insights on in-ground stability, future migration potential, and risk. Occasionally, useful parameters for reactive transport modeling have been determined. Contemporaneous with scientific research, site contractors have excavated enormous volumes of contaminated sediment from the river corridor and central plateau and transported this to a central landfill to reduce in-ground inventories and environmental risk. Active current research is underway in the Columbia River corridor where a number of existing plumes (Cr, ^{90}Sr, and U) discharge to the river, and where others (^{99}Tc) are expected in the future. Potential remediation methods are being explored, and the biogeochemical function of the extended hyporheic zone is under investigation as a last line of natural defense against groundwater contaminants entering the river. As for other Hanford environments such as the central plateau, spectroscopic methods have significant potential to identify reaction mechanisms and products in this important zone as necessary to forecast future behavior.

XPS determination of uranium oxidation states

E. S. Ilton

E-mail: Eugene.Ilton@pnnl.gov

Pacific Northwest National Laboratory, Richland, WA 99352

In this presentation I review different aspects of the XPS spectra that can help one determine U oxidation states and effectively quantify the XPS of complicated mixed-valence U phases. After a discussion of the valence band, the focus turns to the U4f region, where the use of binding energies, satellite structures, and peak shapes is discussed. Binding energies are strongly dependent on bonding environment and consequently are not effective guides for determining U oxidation states unless one has independent information on composition and structure. Likewise, the spin orbit split $4f_{7/2}$ and $4f_{5/2}$ peak shapes do not carry significant information on oxidation states. In contrast, both satellite-primary peak binding energy separations, as well as intensities to a lesser extent, are relatively insensitive to composition/structure within the oxide-hydroxide-hydrate system and can be used to both identify and help quantify U oxidation states in mixed valence phases. The theoretical predictions of the U4f XPS spectra are compared to experiment. Examples using the satellite structure to constrain the interpretation of complex multivalence U phases are given.

Quantum chemical modeling of actinide hydrolysis complexes

I. Chiorescu, S. Krüger,* N. Rösch

* *E-mail*: krueger@ch.tum.de

Department Chemie, TU München, Lichtenbergstr. 4, 85748 Garching, Germany

Actinides in the oxidation states VI and IV are known to exhibit a rather complex hydrolysis, which until now has been studied mainly for U(VI) and Th(IV) [1]. With increasing pH, besides simple mononuclear hydroxides, also multinuclear oxo-hydroxo complexes are formed in aqueous solution. For other actinides in the oxidation states VI and IV as well as for actinides in the oxidation states V and III, only a few hydrolysis species have been characterized and accepted in thermodynamic data bases [1]. Especially the speciation at basic pH is less developed as precipitation and colloid formation hamper experimental investigations. Using a scalar relativistic density functional approach [2,3] in combination with a GGA exchange-correlation functional, we studied various types of actinide complexes formed by hydrolysis under conditions free of carbonate to complement and extend the current knowledge based mainly on experimental efforts. For U(VI) and Np(VI), we compared mononuclear and dimeric hydroxide complexes to trimeric species that dominate at medium pH the hydrolysis of this oxidation state at higher than trace concentrations. Relative stabilities of dimeric and trimeric complexes compared to monomeric compounds essentially confirm the current speciation model and the order of appearance of various hydrolysis species with increasing pH. Varying the charge of trimeric species we compared cyclic and linear isomers as well as various types of bridging and central ligand arrangements, to suggest and characterize preferred species. For monomeric hydroxides of U(VI), Np(V), and Am(III), we searched for the limiting species with increasing pH of these series and we also considered oxo and oxo-hydroxo complexes as alternative species. Compared to anionic hydroxide complexes, commonly expected to be present at higher pH, species with oxo ligands seem to be thermodynamically preferred.

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Quantum chemical modeling of U(VI) and Np(V) adsorption on the solvated (110) edge surface of montmorillonite

A. Kremleva,* S. Krüger, N. Rösch

* *E-mail*: kremleva@theochem.tu-muenchen.de

Department Chemie, TU München, Lichtenbergstr. 4, 85748 Garching, Germany

Adsorption of actinides on mineral surfaces is regarded as the main retardation mechanism against transport of these elements in the environment [1]. In this regard, clays and clay minerals are of special interest as they are common in nature and considered as effective barriers. To model transport and distribution of actinides, a thorough mechanistic understanding of the adsorption phenomena at the atomic level is necessary. Pertinent fundamental questions are the nature of the adsorbed species and the sites they occupy. Quantum chemical calculations offer a complementary approach to the commonly applied spectroscopic methods [1] to shed light on these questions.

We studied the adsorption of uranyl(VI) and neptunyl(V) on the exemplary (110) edge surface of the common 2:1 dioctahedral clay mineral montmorillonite with a density functional method (GGA) using the plane-wave based projector augmented wave

(PAW) approach as implemented in the program VASP [2] and periodic supercell models.

A major problem when modeling adsorption on mineral surfaces is the proper treatment of surface solvation. In our surface models we include a water layer to represent surface solvation. Reliable relative energies of adsorption are only achieved by carefully equilibrating the water overlayer together with the adsorption complex [3]. For that purpose we applied an efficient simulated annealing procedure at low temperature to circumvent a costly fully dynamic approach. This allows a systematic study of various types of adsorption complexes at many sites of a mineral surface. With this advanced approach we determined favorable sites for uranyl(VI) and neptunyl(V) adsorption. Using a charge analysis of the surface sites and estimated surface deprotonation energies [3, 4], we were able to suggest preferred adsorption complexes. Besides the typical five-coordinated bidentate uranyl adsorbate, we also determined uranyl hydroxide species and some adsorption complexes with a reduced coordination number of 4. In contrast to uranyl(VI), neptunyl(V) prefers monodentate adsorption and a coordination number of 4 [4]. For Np(V), we calculated adsorbed monohydroxide species to be rare, in agreement with the known lower hydrolysis constant. The calculated geometry parameters may be helpful for interpreting results of EXAFS experiments.

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Fragment molecular orbital (FMO) method for studying actinide interaction with DNAs and proteins

S. Tsushima,[1,*] T. Ishikawa,[2] S. Tanaka,[3] H. Mori,[4] M. Saeki,[5] T. Nakano,[6] Y. Komeiji,[7] Y. Mochizuki[8]

* *E-mail*: s.tsushima@hzdr.de

[1] Institute of Resource Ecology, Helmholtz–Zentrum Dresden–Rossendorf, Dresden, Germany

[2] Department of Molecular Microbiology and Immunology, Nagasaki University, Nagasaki, Japan

[3] Department of Computational Science, Kobe University, Kobe, Japan

[4] Faculty of Core Research Natural Science Division, Ochanomizu University, Tokyo, Japan

[5] Quantum Beam Science Research Directorate, QST, Tokai, Japan

[6] Division of Medicinal Safety Science, National Institute of Health Sciences, Tokyo, Japan

[7] Biomedical Research Institute, AIST, Tsukuba, Japan

[8] Department of Chemistry, Rikkyo University, Tokyo, Japan

Due to its potential health and environmental impacts, actinide binding to biomolecules has been a subject of intensive investigations. A large number of experimental works have been carried out but our understanding remains mostly in a macroscopic scale. Modeling actinide interaction with large biomolecules using *ab initio* quantum chemical calculations may drastically expand our molecular level knowledge but is challenged by a demand for huge computational resources.

Our strategy to overcome this difficulty is to apply fragment molecular orbital (FMO) method. In FMO, the molecular system of interest is partitioned into small fragments. Each fragment and fragment pair is subject to self-consistent field calculations under environmental electrostatic potentials and the electronic structure of the whole system is reconstituted [1]. This procedure drastically reduces computational cost of Hartree Fock calculations from N^3 to N^2 (or less) and is readily parallelizable. FMO has been extended to MP2 and to DFT to include electron correlation and was successfully applied to the systems such as hydrated DNA (~ 7500 atoms) [2].

Currently we are upgrading the FMO program Abinit-MP [3] to implement 5f elements into the program. We first choose uranyl-bound DNA for a case study. Calculations are performed as follows. UO_2^{2+}-bound d(CGCGAATTCGCG)$_2$ (Dickerson-Drew dodecamer) with 20 Na^+ ions and SPC/E water shell with 10 Å thickness (a total of 15559 atoms in the system) is first thermally equilibrated and subsequently submitted to molecular dynamics (MD) simulation at 300 K for 100 ns interval using AMBER 14 program. Force field parameters for UO_2^{2+} and coordinating water are those developed by Pomogaev et al. [4]. At each 1 ns time step of MD simulation, the structure is extracted and submitted to FMO single point energy calculation at the MP2 level. In FMO, nucleic unit is appropriately divided into sugar, base, and phosphate fragments. Inter-fragment interaction energy analysis is performed to explore the binding affinity of uranyl to DNA and its influence on base pairing.

Binding of Eu^{3+} to Calmodulin and its comparison with Ca^{2+} binding is under investigation.

FMO program Abinit-MP and its graphical user interface BioStationViewer are freely distributed online [5]. This project is funded by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT).

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Luminescence lifetime measurements of trivalent f-elements in mixed solvent systems

H. M. Felmy,[1,*] Z. Wang,[2] S. B. Clark[1,2]

* *Email*: heather.felmy@wsu.edu

[1] Washington State University, Department of Chemistry, Pullman WA 99164-4630

[2] Pacific Northwest National Laboratory, Richland WA 99354

Ion solvation plays an important role in the solution chemistry of the trivalent f-element cations, impacting the thermodynamics of complex formation, chromatographic separations, and the behavior of these cations in reprocessing systems. Luminescence lifetime measurements provide a direct probe of coordinated water molecules for the Eu(III) and Cm(III) cations. This approach was used to probe changes in the primary solvation sphere of these cations in mixed methanol (MeOH)-water and N,N-dimethylformamide (DMF)-water solvents. This ion solvation information, along with thermodynamic data on their complexation with simple carboxylic ligands in these mixed solvent systems, provides a more complete understanding of the role of ion solvation on the behavior of the trivalent lanthanides (Ln(III)) and actinides (An(III)).

The trivalent f-element cations impose significant local order in polar solvents such as water due to their high charge density, resulting in the formation of extended solvation spheres around the cations. The driving force for the complexation of f-element cations with organic ligands is often the entropy gained resulting from desolvation when inner-sphere complexes are formed. While f-element complexation is generally ionic compared to the transition metal ions, the trivalent 5-f cations can exhibit slightly more covalent character compared to the highly ionic 4-f homologs. Differences in An(III) and Ln(III) solvation may also result from small differences in ionic radii. The goal of this project is to explore these differences.

In this study, luminescence lifetime measurements were performed to determine the composition of the inner solvation sphere of the Eu(III) cation in solutions of 0, 10, 30, and 50% (v/v) MeOH-water and DMF-water solvents, and with the addition of 2-hydroxyisobutyric acid (HIBA) and 2-aminoisobutyric acid (AIBA). Potentiometry and calorimetry were also used in order to determine thermodynamic data for Eu(III) complexation with these ligands in these mixed solvent systems.

The results indicate that the addition of MeOH to aqueous systems does little to alter the inner solvation sphere of the Eu(III) cation in solutions up to the 50% (v/v) MeOH-water solvent studied. With the addition of DMF to aqueous solutions, however, there was a greater desolvation of the cation as DMF replaced water molecules in the inner solvation sphere. When HIBA was added to solutions of MeOH-water and DMF-water, further desolvation of the Eu(III) cation was seen as the ligand replaced solvent molecules through complexation. These results were consistent with the formation of inner-sphere complexes between Eu(III) and HIBA. When studying Eu(III) complexation with AIBA, however, there was very little desolvation of the Eu(III) cation indicating the possibility of the formation of a more outer-sphere complex. The next step of this project will be the study of Cm(III) solvation and complexation in mixed solvents for a direct comparison between a trivalent actinide and lanthanide.

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Spectroscopic investigation for the structure of actinides sorption on the solid/liquid inter-surface

W. Wu

E-mail: wuws@lzu.edu.cn

Radiochemistry Laboratory, School of Nuclear Science & Technology, Lanzhou University, Lanzhou 730000, China.

Knowledge of actinides sorption behaviors on solid/liquid inter-surface is of great importance to the study of radionuclide migration in the natural environment. Sorption of UO_2^{2+} on TiO_2 was focused on to introduce the use of various spectroscopic methods in this study. Spectroscopic methods such as laser induced fluorescence spectroscopy (LIFS), extended x-ray absorption fine structure (EXAFS), time-resolved laser fluorescence spectroscopy (TRLFS) were usually employed to the study the surface properties, to give the sorption structural information and to measure the species of actinides on on solid/liquid inter-surface. These measurements thus will have major implications, giving the information of the sorption mechanism of actinides sorption on the atomic/molecule scales. The use of these micro-investigations for actinides sorption on solid/liquid inter-surface is surely of great importance in understanding the species, migration of radionuclides and the performance and safety assessments of geological repository to long-life and high level radioactive waste.

TRLFS and ATR-IR studies on Eu(III) and Am(III) adsorption on SiO_2 particles in the presence of a small organic ligand

H.-K. Kim,* K. K. Park, E. C. Jung, H.-R. Cho, W. Cha

* *Email*: hkim11@kaeri.re.kr

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Korea

Physicochemical interactions of actinides at a water-solid interface are important determinants of the migration rates of radionuclides in groundwater. Naturally abundant organic substances in groundwater can significantly affect the interactions through co-adsorption or competitive binding. Am(III) is one of the major concerned long-lived radionuclides in nuclear waste, but little is known about its interactions with solid phases and organic substances. In order to understand the interactions of Am(III) with metal oxides and the effects of organic ligands on these interactions at the molecular level, we carried out TRLFS and ATR-IR studies on Eu(III) and Am(III) interacting with SiO2 particles in the presence of a small organic ligand, picolinic acid. Eu(III) was employed as a radio-inactive analogue of Am(III).

Batch sorption experiments show that Am(III) sorption behaviors are almost identical to those of Eu(III) on various metal oxide surfaces including SiO_2, Al_2O_3, and TiO_2. In the presence of picolinic acid, the formation of ternary surface complexes of SiO_2-Eu(III)/Am(III)-picolinate is suggested for SiO_2 particles. TRLFS and ATR-IR results indicate inner-sphere bindings of 1-3 picolinate molecules to Eu(III) in a bidendate coordination with a carboxylate and a N donor in solution. Strongly enhanced Eu(III) luminescence was observed upon excitation of picolinates owing to the energy transfer to Eu(III) from the excited picolinates with a much greater absorption coefficient at the UV region. Enhanced luminescence enables the detection of Eu(III) within the nano-molar range, which in turn has enabled studies under neutral to slightly basic conditions without precipitation problems occurring on the surface. Luminescence lifetime measurements show that the adsorption of Eu(III) on a SiO_2 surface in the presence of picolinates takes place by displacing 5-6 inner-sphere bound water molecules, which correspond to one more displaced water molecule compared to those in the absence of picolinates. However, there was no considerable change in spectral shape by the presence of picolinates. These observations suggest that the adsorption geometry of Eu(III) onto a SiO_2 surface is likely retained in the presence of picolinates. Furthermore, the geometry disturbs the bidendate binding of picolinates to the adsorbed Eu(III), allowing only a single binding site for a picolinate molecule in a monodendate coordination. Luminescence characteristics of the surface adsorbed Eu(III)/Am(III)-picolinate species are discussed in detail, including surface property-dependency between amorphous and crystalline (α-quartz).

Spatially-resolved sorption studies of Eu(III) on granite surface with time-resolved laser fluorescence microscopy (TRLFM)

K. Zesewitz* and M. Schmidt

* *Email*: k.zesewitz@hzdr.de

Helmholtz-Zentrum Dresden – Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400 01328, Dresden, Germany

The finding of an appropriate long-term repository for high-level nuclear waste is a highly relevant topic. To that end, the interaction of radionuclides with mineral phases contained in possible host rocks and construction materials must be understood. On a time scale of up to a million years, especially the scenario of a water intrusion into the repository and thus dissolution of radionuclides has to be considered. To investigate the sorption behavior of actinides and lanthanides, time-resolved laser fluorescence spectroscopy (TRLFS) is a widely used method, because of its trace concentration sensitivity and capability to distinguish multiple species in complex systems. On one hand this method gives the spectral information of the emitted fluorescence light, which allows determining the symmetry and the grade of complexation of the sorbed Ln/Ac. On the other hand the lifetimes of the excited electron states provide information about the surrounding quenchers, mainly water. Typically, TRLFS investigations will focus on the interaction of an actinide with one relevant mineral phase. For a real rock formation, e.g. granite, sorption will however be a competitive process involving multiple mineral phases at the same time.

In this study a new method called time-resolved laser fluorescence microscopy (TRLFM) is introduced, which will add a spatial dimension to TRLFS. By doing so, it is possible to separate the multi-phase system into discrete single-phase systems and therefore to make a step beyond model systems by investigating, for example whole natural granite rock with TRLFS. Because of its advantageous fluorescence properties we use europium as an analogue for the trivalent actinides americium and curium. Sorption experiments with Eu(III) on granite under different solution conditions, regarding metal concentration and pH will be presented. These samples are excited by a focused pulsed laser beam at a wavelength of 394 nm, and scanned through the laser's focal point by an XYZ-Stage with a resolution in the micrometer range. The sample is subsequently mapped by Raman-Microscopy to distinguish the different phases and the TRLFM data is then compared to the combination of Raman-data with TRLFS data of the single phases.

First results show that the different sorption behavior of the single phases can be resolved by this method. Lifetimes and emission spectra have been measured for quartz, feldspar and mica phases on granite plates, which evidence that the spatial resolution is sufficient to distinguish mineral grains in natural granite. XRD and XFA are done for the samples to determine all possible constituents. Partial maps of the europium distribution and speciation are presented together with phase identification by Raman microscopy and a comparison to optical microscopy images.

Retardation and release of uranium on phlogopite mica at the absence and presence of humic acid: a batch and TRLFS study

D. Pan,[1,*] Z. Wang,[2] W. Wu[1]

* *E-mail*: panduoqiang@lzu.edu.cn

[1] Radiochemistry Laboratory, School of Nuclear Science & Technology, Lanzhou University, Lanzhou, Gansu 730000, China

[2] Pacific Northwest National Laboratory, Richland, WA 99352, United States

The batch experiments and cryogenic time-resolved laser-induced fluorescence spectroscopy (TRLFS) technique were applied to investigate uranium(VI) sorption/desorption on phlogopite at the absence and presence of humic acid (HA) in this work. The results showed that at the absence of HA, the uranium(VI) sorption on phlogopite was strongly dependent on pH while minimally affected by the ionic strength, multiple inner-sphere surface species (including $\equiv SOUO_2^+$, $\equiv SO(UO_2)_2(OH)_2CO_3^-$ and $\equiv SOUO_2(CO_3)_x^{1-2x}$) were formed with their abundance varying as a function of pH, and a portion of uranium precipitated as uranyl oxyhydroxides at high pH (> 9). The presence of HA made little difference below pH 4 while inhibited uranium(VI) sorption above pH 4, and such effects became much more pronounced by increasing HA concentration from 20 mg/L to 50 mg/L. Fluorescence spectra indicated the formation of ternary surface complex at low pH, uranium-humate complex preferred binding directly on surface rather than via HA. Multiple aqueous uranium-humate complexes were responsible for the suppression of uranium sorption at high pH. The presence of HA enhanced uranium mobility without altering dominant surface species before and after desorption treatment.

Detection of actinides and lanthanides in solutions by chemiluminescence laser spectroscopy

I. N. Izosimov

E-mail: izosimov@jinr.ru

Joint Institute for Nuclear Research, 141980 Dubna, Russia

The use of luminescence methods for detection of lanthanides/actinides in solutions allows the sensitivity to reach [1-3] the limit of detection (*LOD*) up to 10^{-13} M. Pu, Np, and some U compounds do not produce direct luminescence in solutions, but when excited by laser radiation, they can induce chemiluminescence of some chemiluminogen (luminol in our experiments) [1-3]. It is because of its high sensitivity [4] (*LOD* from 10^{-6} M to 10^{-13} M) that chemiluminescence is widely used in many fields such as flow injection analysis, chromatography, biology, medicine, etc. Of some interest was to use advantages of luminescence procedure for selective detection of actinides and lanthanides having no intrinsic luminescence by initiation of chemiluminescence of some agents as an example luminol via excitation of the element to be detected. Chemiluminescence initiation by UV radiation [1] of a nitrogen laser is unselective. Therefore a key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection. Appropriate selectivity can be reached when chemiluminescence is initiated by transitions within *4f*- or *5f*-electron shell of lanthanide or actinide ions, which correspond to visible spectral range. Since the energy of one quantum excitation in visible range is insufficient for initiation of luminol chemiluminescence it was proposed [1-3] to excite lanthanide and actinide ion by multi-quantum absorption of visible light.

Data on luminol chemiluminescence in solutions containing Sm(III), U(IV), and Pu(IV) are presented. Chemiluminescence was initiated by two-quantum excitation of lanthanide or actinide ions in the range of *4f*- or *5f*-electron transitions by the schemes: two step–one color and two step–two color [1-3]. It is shown that appropriate selectivity of lanthanide/actinide detection can be reached when chemiluminescence is initiated by transitions within *4f*- or *5f*-electron shell of lanthanide/actinide ions corresponding to visible spectral range. In this case chemiluminescence of chemiluminogen arises when the ion of *f*-element is excited by multi-quantum absorption of visible light.

The multi-photon scheme of chemiluminescence excitation makes chemiluminescence not only a highly sensitive but also a highly selective tool for the detection of lanthanide/actinide species in solutions.

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Complexation of actinides by branched N-macrocycle DOTA

M. Audras,[1] C. Tamain,[1] L. Berthon,[1] C. Berthon,[1] D. Guillaumont,[1] T. Dumas,[1,*] P. L. Solari,[2] C. Hennig,[3] P. Moisy[1]

* *E-mail*: Thomas.DUMAS@cea.fr

[1] CEA/DEN, DRCP, 30207 Bagnols sur Cèze, France

[2] Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

[3] ESRF, 6 Rue Jules Horowitz, 38000 Grenoble, France

The comprehension of the actinides affinity for interest ligands has been a pivotal issue since the beginning of the nuclear fuel reprocessing. The difference in interaction between N-donors ligands and O-donor ligands is a hint on the selectivity difference between trivalent and tetravalent actinides. The study of molecules featuring both N and O-donor functions may be a way to reach a better understanding. Thus, the poly-amino-carboxylate ligands form an interesting family of f-element cations chelating agents. One specific ligand has been selected for this study: the DOTA macrocycle (1,4,7,10-tetraazacyclododecane-tetra-acetic acid).

DOTA has been widely studied with lanthanides, but few investigations have been carried out with actinides. The main goal of this work is to extend the investigations to the complexing behavior of DOTA with An(III) and An(IV) in aqueous solution.

To achieve this work, our methodology consists in a twofold approach, combining experimental studies with modeling calculations. Americium(III) and plutonium(III) have been selected to represent the An(III) series, while thorium(IV), neptunium(IV) and plutonium(IV) have been chosen to represent the An(IV) series. Besides the laboratory analytical techniques (UV-Vis spectrophotometry, NMR and ESI-MS), the systems have been monitored with X-ray absorption spectroscopy (EXAFS) to identify the ligand complexing sites. Experimental EXAFS spectra are compared to theoretical ones based on hypothetical models obtained thanks to quantum chemistry calculations (DFT) or to single crystal XRD structures when available. Then the best models where used to fit the experimental spectrum with metrical parameter in order to achieve the structural description of the complex.

The experiments proved DOTA can form inersphere complexes involving both carboxylate and amino groups with An(III) similar to what has been observed with Ln(III).

Within the An(IV) series, Np(IV) and Pu(IV) seem to behave either as the An(III) to form inner sphere complexes or soluble hexanuclear species resulting from hydrolysis-complexation competition depending on chemical conditions (i.e. [H^+] and [H_4DOTA]). On the contrary, the complexation of Th(IV) neither end up with the formation of such a (1:1) inner sphere complex involving the DOTA amino groups nor hexanuclear species. Several configurations, such as a (1:2) species only involving the four DOTA carboxylate functions have been observed. This particular behavior is rejecting the use of Th(IV) as a good surrogate for Np(IV) and Pu(IV) in hydrolysis/complexation studies. Finally this study highlights how a polyfunctional ligand like DOTA can be a useful tool to study the fundamental chemistry of actinide complexes. Allowing comparison between competitive chemical reactions with different actinides at different redox states, its strong complexing properties also help to stabilize tetravalent actinides in wide pH range.

Electrochemical and spectroscopic behavior of neptunium in aqueous nitric acid

S. Chatterjee,* A. J. Casella, J. M. Peterson, T. G. Levitskaia, S. A. Bryan

* E-mail: Sayandev.Chatterjee@pnnl.gov

Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

This work is focused on understanding the aqueous solution chemistry of neptunium under conditions relevant to spent nuclear fuel reprocessing. Neptunium can exist in aqueous solutions in a range of oxidation states (+3 to +6). The stability of these oxidation states is dependent on the composition of the solution and acid content. An in-depth understanding of neptunium oxidation states in a range of the acid concentration is critical for the efficient monitoring of neptunium content in a (re)processing flowsheet and the designing of new separation processes. Different oxidation states of neptunium exhibit unique and distinguishable spectral signatures, which can be used to probe relative stabilities of the respective oxidation strengths under given conditions. This work will demonstrate that the oxidation states can be controlled and modulated via the application of a potential. We will describe both the redox and spectroscopic behavior of neptunium as a function of the aqueous nitric acid solution concentration.

Efficient removal of radionuclides from aqueous solutions using carbon nanomaterials

X. Wang,[1,*] C. Chen,[2] J. Li,[2] Y. Sun[2]

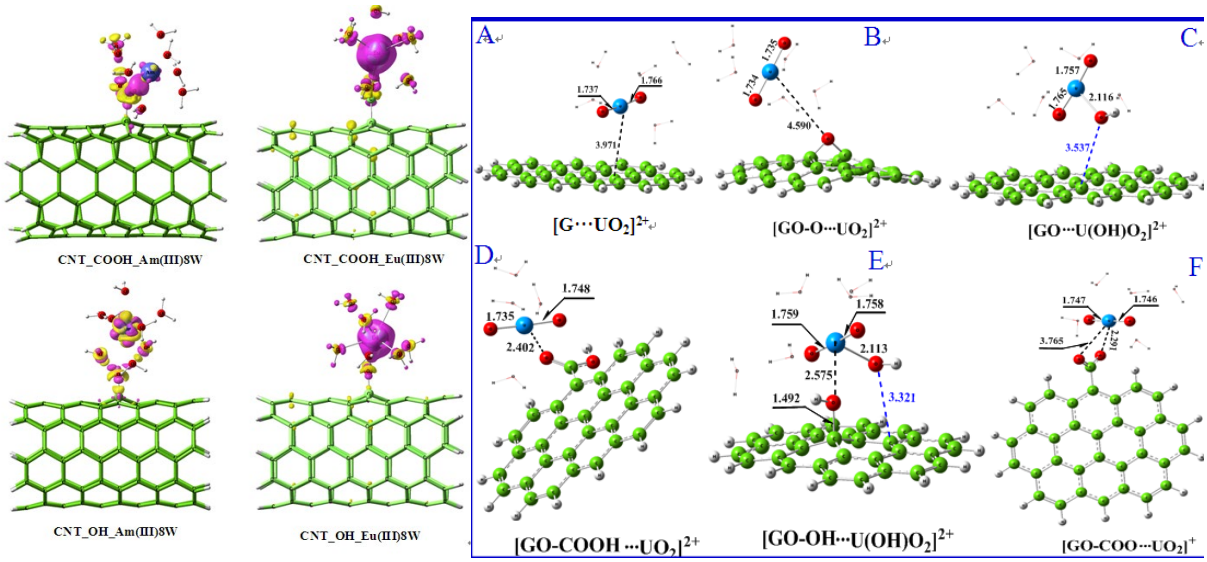
* *E-mail*: xkwang@ncepu.edu.cn

[1] North China Electric Power University, Beijing, 102206, P.R. China

[2] Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, P.R. China

This page presents the surface modification of carbon nanomaterials (carbon nanotubes, graphene oxides) and their application for the efficient and selective removal of radionuclides from aqueous solutions. The interaction mechanism between radionuclides and carbon nanomaterials is studied by batch sorption experiments, surface complexation modeling, spectroscopy analysis and theoretical calculations. The results showed that the carbon nanomaterials have high sorption capacity in the preconcentration of radionuclides from large volume of aqueous solutions, and the surface grafting functional groups could enhance the selectivity of radionulcides from solutions.

The following Figures show the interaction of Eu(III) and Am(III)-243 with carbon nanotubes and the interaction of U(VI) with graphene oxides with different functional groups. From the DFT calculations, the bind energy of radionuclides with different functional groups are quite different. More detailed results and discussion are present in the references.



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Probing the Pu^{4+} magnetic moment in PuF_4 with ^{19}F NMR spectroscopy

C. Capan,[1,*] R. Dempsey,[1] S. Sinkov,[2] B. K. McNamara,[2] H. Cho[3]

* *E-mail*: cigdem.capan@tricity.wsu.edu

[1] Washington State University, 2710 Crimson Way, Richland, Washington 99354, USA

[2] Energy and Environmental Directorate, P.O. Box 999, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

[3] Physical and Computational Sciences Directorate, P.O. Box 999, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

We report the ^{19}F NMR spectra of a powder sample of plutonium tetrafluoride (PuF_4). We have investigated this compound in order to shed light on the relation between electronic configuration and magnetic moment of the Pu^{4+} ions. We have observed a broad resonance that scales with the applied magnetic field and whose lineshape is consistent with dipolar type hyperfine interaction between the F-nuclei and the Pu valence electrons. Surprisingly, the effective moments we derive from fitting the experimental spectra is much larger than the moment of the $5f^4$ electronic configuration that was assigned to this compound based on previous bulk magnetic susceptibility data [1]. We will discuss possible interpretations, including mixed valence states, Pu-Pu interactions, and covalent Pu-F bonding.

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^{31}P nuclear magnetic resonance as a probe of plutonium incorporation and radiation damage in phosphates

I. Farnan,[1,*] K. M. Smye,[1] L. Martel,[2] J. Somers[2]

* *Email*: if203@cam.ac.uk

[1] Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, UK

[2] EC-JRC Institute for Transuranic Elements, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

A series of xenotime (YPO_4) materials were doped with plutonium to test the extent of solid solution and the effect of radiation damage on the structure over several years. A sample of $Y_{0.92}\,^{238}Pu_{0.08}PO_4$ showed the presence of a Pu substituted xenotime phase and a $Pu^{238}P_2O_7$ phase by X-ray diffraction (XRD). The ^{31}P magic-angle spinning nuclear magnetic resonance (MASNMR) spectrum showed peaks for PuP_2O_7 and a number of peaks associated with the ^{31}P resonances of phosphorus atoms coupled to the electronic moment associated with Pu^{3+} substituted into the Y^{3+} sites in the xenotime structure. The binomial intensities of these peaks indicated a random solid solution of plutonium. Examination of the lattice parameter measured by XRD, with reference to the characteristic lattice parameters of the rare earth xenotimes, indicated a substitution of 5.7 mol% Pu, which is probably the limit of solid solution. A Pu-xenotime of composition $Y_{0.96}{}^{238}Pu_{0.04}PO_4$ showed complete solid solution. This is in contrast to cerium surrogate materials that were prepared as a test of the preparation method where <2 mol% of Ce^{3+} could be substituted into the xenotime structure.

A series of ^{31}P MASNMR spectra and X-ray diffraction measurements have been carried out over periods of a few weeks to several years to detect the effect of the ^{238}Pu α-decay on the local and extended structure of the xenotime. The first result observed after 4 weeks was the loss of the reflections due to the $Pu^{238}P_2O_7$ phase in the XRD pattern of the $Y_{0.92}{}^{238}Pu_{0.08}PO_4$ sample. The MASNMR spectra obtained at longer times in both the $Y_{0.92}\,^{238}Pu_{0.08}PO_4$ and $Y_{0.96}\,^{238}Pu_{0.04}PO_4$ samples showed an additional broadened and shifted ^{31}P resonance which is assigned to an amorphised xenotime structure created by α-recoil events. The position (chemical shift) of this resonance is to higher frequency of the Q^0 tetrahedral orthophosphate shift of the crystalline xenotime. Measured shifts of polymerized PO_4 tetrahedra (Q^1, Q^2, Q^3) reported in the literature are all to lower frequency of the crystalline xenotime peak. Thus, the amorphised local structure is assigned to a predominantly Q^0 phosphate arrangement subject to local densification. Ab initio density functional theory calculations of the effect of pressure on the chemical shift of xenotime are consistent with this interpretation in that the shift would be to higher frequency with higher pressure. In separate experiments, amorphisation of the xenotime structure with swift heavy ions (2 GeV Pb) also leads to a similar unpolymerised amorphous local structure, as does the partial amorphisation of ^{10}B doped xenotime by ^{10}B(n,α) in reactor irradiation. It is inferred that the unpolymerised amorphous phase represents the remains of an unpolymerised recoil cascade that is readily recrystallised leading to the low critical amorphisation temperatures of phosphate materials.

Assignment of unexpected Raman spectra of uranyl triperoxide complexes

M. Dembowski,[1,*] V. Bernales,[2] J. Qiu,[3] S. Hickam,[3] G. Gaspar,[3] L. Gagliardi,[2] P. C. Burns[1,3]

* *E-mail*: mdembows@nd.edu

[1] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

[2] Department of Chemistry, University of Minnesota, and Supercomputing Institute, 207 Pleasant St, Se, Minneapolis, Minnesota 55455

[3] Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Indiana 46556

The Na, K, Mg, Ca, and Sr salts of uranyl triperoxide monomers [UTP, $(UO^2(O^2)^3)^{4-}$] exhibit unique Raman signatures. Crystallographically based electronic structure calculations facilitated the assignment of unexpected Raman peaks associated with novel asymmetric and mixed symmetric/asymmetric vibrations of the peroxide ligand $_{v2}(O_2^{2-})$ and $_{v3}(O_2^{2-})$, respectively. ^{18}O isotopic labeling experiments verified assignment of the $_{v3}(UO_2^{2+})$ vibrations bands appearing in the 600 – 800 cm^{-1} region.

Structures of plutonium(IV) and uranium(VI) with *N,N*-dialkyl amides from crystallography, X-ray absorption spectra, and theoretical calculations

D. Guillaumont,[1,*] E. Acher,[1] T. Dumas,[1] C. Tamain[1]

* *E-mail*: dominique.guillaumont@cea.fr

[1] CEA Nuclear Energy Division, RadioChemistry & Processes Department, 30200 Bagnols sur Cèze, France

Understanding the structure of actinide ions in organic solution is of particular interest in the development of effective solvent extraction separations for waste remediation in advanced nuclear fuel cycles. In complex actinide systems, such information is of-ten lacking because of the difficulty to obtain it solely from experimental data. Quantum chemistry calculations, once associated with experimental data, can be an im-portant tool to obtain detailed structural information.

In the present study, we have combined extended X-ray absorption fine structure (EXAFS) with single-crystal X-ray diffraction (XRD) and theoretical calculations to elucidate the structures of plutonium(IV) and uranium(VI) ions with a series of *N,N*-dialkyl amide ligands [1]. The crystal data are used as reference structural models. EXAFS spectra were measured in the solid state and in solution. To help EXAFS analysis, *ab initio* EXAFS spectra were computed from structural parameters and Debye-Waller factors derived from quantum chemistry calculations without using fitting parameters. *N,N*-dialkyl amides with linear and branched alkyl chains were investigated, they are considered are alternative organic ligands to achieve the separa-tion of uranium(VI) and plutonium(IV) from highly concentrated nitric acid solution.

For U(VI), our EXAFS analysis combined with XRD shows that the coordination structure of U(VI) is identical in the solution and in the solid state and is independent of the alkyl chain. For plutonium(IV) complexes, it was not possible to resolve unambiguously plutonium coordination structures in solution from EXAFS measurements and the coordination structure was established from the comparison between experimental and *ab initio* EXAFS spectra. With linear alkyl chain amides, Pu(IV) adopts identical structures in the solid state and in solution while a different coordination structure is found in solution with branched alkyl chain-amides. Finally, it is shown that EXAFS spectra can be well-reproduced from such *ab initio* calculations without using fitting parameters.

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Quantum chemical investigation of incorporation of uranium(V) into magnetite: combining multi reference *ab initio* methods and density functional theory

R. Polly,* B. Schimmelpfennig, I. Pidchenko, T. Vitova, H. Geckeis

* *E-mail*: polly@kit.edu

Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, P.O. 3640, D-76021 Karlsruhe, Germany

Thorough characterization of the chemical states and redox kinetics of uranium in contact with the steel corrosion product magnetite are of substantial importance for understanding uranium transport and retention mechanisms in the near and far fields of nuclear material storage and disposal sites. Uranium has two main environmentally relevant redox states, mobile U(VI) and sparingly soluble U(IV). U(V) is believed to form intermediately and exhibits a poorly understood geochemical behavior. Recent experimental efforts at INE applying high-energy resolution X-ray absorption spectroscopy and EXAFS found that Uranium(V) incorporated in octahedral magnetite sites remains stable over 226 days under ambient conditions as unambiguously shown for the magnetite nanoparticles containing 1000 ppm uranium (submitted to PNAS).

Here we use different methods of theoretical chemistry to tackle this issue and provide additional valuable theoretical information for the interpretation of experimental data.

Magnetite has Fe^{3+} at octahedral and tetrahedral sites and Fe^{2+} at octahedral sites. Fe^{3+} is a high spin case and the occupation of the five d-orbitals in the ligand field is obvious. This is not so clear anymore for Fe^{2+}. What is the occupation pattern for Fe^{2+} and is the ground state a single or a multi reference state? These questions were addressed with complete active space self consistent field (CASSCF) calculations. This is not only of theoretical interest but a major issue in connection of the application of DFT! DFT requires a single reference state. This has to be tested first with proper multi reference methods. Based on these results we performed density functional (DFT+U) calculations on pure Magnetite accounting for the strong on-site Coulomb repulsion of the 3d electrons. We tested this methodology and compared with different available structural information and electric as well as magnetic properties. Furthermore we benchmarked the DFT+U results for pure magnetite with several hybrid functionals and found an excellent agreement for the electric and magnetic properties.

Upon this excellent agreement of out theoretical data with available experimental findings for pure Magnetite we proceeded to calculations of the incorporation of Uranium(V) into Magnetite. Uranium(V) is a $5f^1$ system and hence, theoretical, a fairly easy system, but again we accompanied these DFT calculations with CASSCF calculations identifying the ground state of Uranium(V) in the tetrahedral and octahedral ligand field. For the determination of the changes implied on Magnetite upon the incorporation of Uranium(V) we employed plane wave DFT with periodic boundary conditions. We probed different incorporation and charge compensation schemes of the incorporation of Uranium(V) into Magnetite. Overall we found a very good agreement of our theoretical results with the experimental data provided by Pidchenko and Vitova *et al*.

Probing the structure of uranium complexes in molten salt by absorption spectroscopy and DFT calculation

T. Su,* S. Liu, M. Ge, H. Liu, J. Wang

* *E-mail*: sutao@sinap.ac.cn

Department of Molten Salt Chemistry and Engineering, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Uranium compound, generally used as fuel in the reactor, is one kind of most important chemicals in nuclear field. In that uranium has four valence states, such as U(III), U(IV), U(V), U(VI), complicated compounds can be formed in different solvents which play essential role in the running of reactor and recycling spent nuclear fuels, especially for molten salt reactor (MSR) that is one of six the fourth generation reactors. For example, there had been reports that indicted that the suitable ratio of U(III) and U(IV) in the primary coolant can effectively hinder the corrosion of loops; the U(IV) can react with O^{2-} to form UO_2 precipitate that can induce local overheating of loop to leak; if the oxidation potential were high enough U(VI) with UO_2^{2+} form (denoted as uranyl) would be formed which can be dissolved in molten salt. Previously, many researchers have conducted an amount of investigations on U(III), U(IV) in molten salt, however, less attention was paid on uranyl (UO_2^{2+}). The uranyl is the most stable form of uranium in nature and is usually coordinated by ligands or solvent molecules. Investigations on uranyl complexes and their stabilities are important in understanding the chemical transformation and migration of nuclear wastes, as well as the coordination chemistry. The absorption spectroscopy is one of good methods to probe the structures of compounds. We have figured out the high temperature, anti-corrosion etc. problems to establish the ultraviolet-visible and infrared absorption spectra platform employed to analyze molten salt. A lot of spectra of pure molten salt, for instance, molten nitrate salt (HTS), molten fluoride salt (FLiNaK), have been obtained, as well, some different valences of transition metal ions such as Cr(II), Cr(III), Ni(II), Fe(III) etc. in molten salt have also been observed. In present work, we will use absorption spectroscopy to probe variety of uranyl complexes in molten salt. In addition, density functional theory (DFT) calculations will also be used to predict the absorption spectra of uranyl with expection to supply detailed theoretical interpretation for the experimental results. The next step, the high temperature laser-induce fluorescence experiment will be performed to give more information about structure. A brief description of experimental method will be presented, and especially the setting up of the apparatus of high temperature absorption spectroscopy and the standard method to get the correct data.

Unusual magnetic properties of actinide thiocyanate and selenocyanate complexes

R. J. Baker

E-mail: bakerrj@tcd.ie

School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

The magnetic properties of the actinides are not as well understood as the lanthanides or transition metals due to the fact that spin-orbit and crystal field couplings are approximately the same energy [1]. The magnetic behavior of f^2 U(IV) compounds have been well studied and in most cases the magnetism can be described as a non-degenerate singlet ground-state with Temperature Independent Paramagnetism (TIP) at low temperatures followed by a region of temperature dependent paramagnetism. We have used the $[U(NCS)_8]^{4-}$ ion to probe the influence of the geometry on the magnetic properties in a compound with the same ligand set, as crystal packing dictates the solid-state geometry of this ion [2]. With an Et_4N cation the geometry is cubic, $^nPr_4N$ gives a distorted square antiprism and Cs a perfect square antiprism geometry. The magnetic properties are significantly different at low temperatures and we have used a combination of low temperature crystallography, inelastic neutron scattering, absorption spectroscopy and theoretical methods at the CASPT2 level to rationalise this. Thus, for a square antiprismatic geometry the ground-state is distorted so that a doublet ground-state is observed in contrast to all other U(IV) compounds which has a singlet ground-state. Similar behaviour is observed with $[U(NCSe)_8]^{4-}$ compounds. A bonding picture of the U-NCE (E = S, Se, Te) has been developed on the basis of the experimental and computational results. We have also expanded this investigation to the transuranic compounds where the magnetic properties are even more complex [3].

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Interplay between theory and spectroscopy in understanding interfacial interactions: a case study for CeO_2

P. Yang

E-mail: pyang@lanl.gov

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545

Interfacial chemistry for f-element materials is critical for nuclear waste management and to address the environmental concerns associated with actinides. Cerium is often used as a surrogate for more radioactive actinide elements for thorough characterization using advanced spectroscopic techniques. Herein, we will present recent progress in characterizing interfacial interactions of ligands with CeO_2 in both surface and nanoparticle forms. We will demonstrate how the synergy between theory and experiment has accelerated the progress in this field. The theoretical results are validated by spectroscopic characterizations. A better molecular-level understanding of the interfacial chemistry including coordination, energetics and reaction mechanisms will pave the way to a better strategy for waste management and environment remediation.

The effect of iron oxides and montmorillonite clays on the transformations of uranium under reducing conditions

M. I. Boyanov,[1,2,*] D. E. Latta,[2,3] B. Mishra,[2,4] M. Scherer,[3] E. J. O'Loughlin,[2] K. M. Kemner[2]

* *E-mail*: mboyanov@ice.bas.bg

[1] Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[2] Biosciences Division, Argonne National Laboratory, Argonne, IL 60439

[3] Department of Civil and Environmental Engineering, The University of Iowa, Iowa City, IA 52242

[4] Physics Department, Illinois Institute of Technology, Chicago, Illinois, IL 60616

Uranium (U) is both a legacy and an emergent contaminant—stockpiles resulting from weapons production have accumulated at various sites and new inventories related to nuclear energy production are being generated worldwide. Predicting the consequences of unintended dispersal and designing long-term storage facilities requires a molecular-level understanding of U chemistry in the presence of minerals, bacteria, and dissolved ligands. Factors such as the valence state and the atomic coordination of U ions have significant control on its solubility and its susceptibility to leaching by groundwater. In general, U^{VI} species are more soluble than the U^{IV} species produced in reducing environments; however, the mobility of a particular U valence also depends on speciation, which in many cases cannot be predicted from current thermodynamic data. For instance, we have shown previously that when aqueous U^{VI} ions encounter biological or abiotic reductants the resulting species are often different from the least soluble U^{IV} mineral, uraninite (UO_2).

We are continuing this line of research, focusing on the role of environmental minerals in controlling the speciation of reduced U. Here, we show that reduced clay minerals (SWy-2, NAu-1, NAu-2) are able to transfer electrons to aqueous U^{VI} under the studied conditions (2-100 g/L clay loading, 250 µM U^{VI}, 2 mM bicarbonate, pH 7.2). However, the reaction products depend on the type and the amount of added clay. Using a combination of spectroscopic and imaging techniques (XANES, EXAFS, TEM, EDX) we find that at low clay loadings U^{VI} is reduced to a mixed-valence U^{V}-U^{VI} oxide, whereas higher mineral loadings result in the formation of uraninite. To clarify whether the change in available surface sites or the change in reducing capacity were responsible for this behavior with solids loading we conducted control experiments with redoxinactive SYn-1 clay (Fe-free), in which the two factors could be controlled separately by the addition of a soluble U reductant, AH_2DS. The formation of the mixed-valence U^{V}-U^{VI} oxide was observed only at low AH_2DS concentrations, whereas uraninite was formed at higher AH_2DS concentrations regardless of the clay loading. These results suggest that clay surfaces do not have sufficient high affinity sites for U^{IV} complexation that could prevent uraninite formation and that the formation of the mixed-valence $U^{V}U^{VI}$ oxide is controlled by the reducing capacity in the system. The observed behavior is in contrast to the role of reduced iron oxides (green rusts and magnetite) in U speciation, where we find that U^{IV} is sequestered in a non-uraninite form at high solids loading. These observations suggest that while clays may not have as large a role as iron oxides in the stabilization of non-uraninite U^{IV}, they may have a significant role in buffering the redox conditions for the stabilization of a U^{V}-U^{VI} oxide intermediate. This U^{VI} reduction pathway is currently not considered in reaction models, but may be important in sediments with mildly reducing conditions such as redox boundaries.

Investigations of plutonium behavior in vadose zone

M. Maloubier,[1,*] D. I. Kaplan,[2] P. M. Almond,[2] B. Powell[1]

* *E-mail*: mmaloub@clemson.edu

[1] Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625

[2] Savannah River National Laboratory, Aiken, SC 29808

A wide range of radionuclides have been deposited in the subsurface worldwide due to production, testing, and processing of nuclear weapons. Among these radionuclides, many plutonium isotopes have long half-lives (e.g. ^{239}Pu = 24,130 years) and high radiotoxicity. Thus, understanding the behavior of these actinides in vadose zone in a long-term is a major concern. It is known that transport of actinides in subsurface is influenced by many factors such as oxidation/reduction, sorption, and/or complexation. Laboratory experiments have helped to develop conceptual models of Pu subsurface transport as well as the necessary equilibrium and rate constants. However, there is a need to supplement this data with field scale experiments performed under more representative environmental conditions (longterm aging, wet-dry cycling, specific mineral interactions). To address this question, Clemson University and Savannah River National Laboratory (SRNL) have installed and are currently operating a radionuclide lysimeter testbed at the US Department of Energy Savannah River Site (SRS). Several lysimeters containing sediment from the SRS and a solid well-characterized actinide source in the center are open to natural rainfall. Several sources of Pu with different oxidation states have been placed in lysimeters in triplicate to allow for destructive sampling after 2, 4 and 10 years. To date, lysimeter containing $NH_4PuO_2CO_3$, PuO_2(colloids), $Pu_2(C_2O_4)_3$, and $Pu(C_2O_4)_2$ have been analyzed.

In order to study plutonium vadose zone transport, it is necessary to determine which mineral fractions of the soil are responsible for Pu uptake and to identify Pu speciation within the soil. In this aim, wet chemistry methods and X-ray absorption spectroscopy (XAS), Transmission Electron Microscopy (TEM/EDX), and Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) have been combined to examine the speciation and distribution of the Pu sources. The chemical speciation of Pu within the source materials as well as the surrounding soil into which Pu has migrated were analyzed and compared with the initial sources archived in an inert atmosphere. Comparison with data from previous field lysimeter experiments with Pu sources showed Pu originating from a Pu(VI) and Pu(V) sources were respectively transported significantly further than Pu(IV) sources. After 2 years, little transport of Pu has been observed and greater than 99 % of the Pu appears to have remained within the sources. During the 2.5 years of exposure, the speciation changes observed in the $Pu^{V}NH_4CO_3$(s) lysimeter indicate some reduction to Pu(IV) within the sources leading to the formation of PuO_2.

Actinides speciation in seawater and uptake by marine accumulating organisms

M. Maloubier,[1] M. R. Beccia,[1] M. Y. Dechraoui Bottein,[2] M. Matara Aho,[1,3] H. Michel,[1] S. Minasian,[4] P. Moisy,[5] M. Monfort,[6] D. K. Shuh,[4] P. L. Solari,[7] C. Moulin,[6] C. Den Auwer[1,*]

* *E-mail*: Christophe.Den_auwer@unice.fr

[1] University Nice Sophia Antipolis, Institut de Chimie de Nice UMR7272, 06108 Nice, France

[2] IAEA, Environment Laboratory, 4 Quai Antoine Ier, MC-98000, Monaco

[3] Laboratory of Radiochemistry, University of Helsinki, Finland

[4] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

[5] Commissariat à l'Energie Atomique, DEN/DRCP 30207 Bagnols sur Cèze, France

[6] Commissariat à l'Energie Atomique, DAM/DIF/DASE 91297 Arpajon, France [7]Synchrotron SOLEIL, MARS beam line, 91192 Gif sur Yevette, France

What happens to actinides resulting from nuclear activity in the environment, particularly in sea water, is a social and scientific issue. The magnitude 9.0 Tohokuoki earthquake and subsequent tsunami forced the shutdown of the Fukushima Daiichi Nuclear Power Plant, leading to accidents in three reactors and release of radionuclides into the environment is one of the latest examples. Hence, the need in managing the risk, controlling environmental fate and transport, and preventing human exposure through direct contact and indirectly through the food chain is essential. Among the different environmental matrices, seawater has not been extensively studied although it contains traces of radionuclides from previous atmospheric nuclear tests or accidental releases. It is therefore of crucial importance to attempt to perform direct determination of the physico-chemical species or speciation of these elements in the various compartments of the biosphere and especially in seawater.

We will address in the first part of this presentation the speciation of Th, U, Np, Pu and Am together with Eu (as a non radioactive surrogate) with a combination of Extended X-ray Absorption Fine Structure (EXAFS), Time-Resolved Laser-Induced Fluorescence (TRLIF) and speciation modeling using the JCHESS code. Given the available sensitivities of both TRLIF and EXAFS spectroscopic probes we have decided to work at a doping concentration of [Th, U, Np, Pu, Am, Eu] = $5\ 10^{-5}$ M ($5.\ 10^{-5}$ M was also performed). Our data confirms the role of carbonates in seawater. The bioaccumulation of stable inorganic contaminants (often referred to as "heavy metals") has already been described in occurrence with organisms from all trophic levels such as algae, mussels, fish and sponges. Some studies have also shown that actinides present in seawater can be strongly accumulated by some marine organisms without knowing their speciation. Among these organisms, sponges are immobile active filter feeders and have been identified as hyper accumulators of many heavy metals. We will report in the second part of the presentation on the accumulation mechanism of Eu^{3+} and Am^{3+} in the Mediterranean sponge *Aplysina cavernicola*. Europium(III) was targeted for this study as a representative of the trivalent actinides such as americium or curium, as well as plutonium(III) which is poorly understood but an important chemical form of plutonium under strong reducing conditions.

XAFS investigations of U^{VI} reduction by biotic and abiotic green rusts

S. Yan,[1,2] M. I. Boyanov,[2,3] B. Mishra,[2,4] E. J. O'Loughlin,[2] K. M. Kemner[2,*]

* kemner@anl.gov

[1] School of Earth Sciences, China University of Geosciences, Wuhan, China

[2] Biosciences Division, Argonne National Laboratory, Argonne, IL, USA

[3] Bulgarian Academy of Sciences, Institute of Chemical Engineering, Sofia, Bulgaria

[4] Illinois Institute of Technology, Chicago, IL

Green rusts (GRs) are mixed Fe^{II}-Fe^{III} minerals with high reactivity. They are ubiquitous in anoxic soils, sediments, and groundwater and play an important role in the redox transformation of many organic and inorganic contaminants. GRs can be formed via various biotic and abiotic processes that are likely to affect the relative reactivity of their different forms. Although biotic and abiotic GRs have been shown to reduce U^{VI}, the dynamics of the transformations and the speciation and stability of the resulting U^{IV} phases are poorly understood. We used a combination of carbonate extractions and U L_{III}-edge x-ray absorption fine structure (XAFS) spectroscopy to investigate the products of U^{VI} reduction by biotic and abiotic GRs in mixed batch reactors. The results show that both biotic and abiotic GRs rapidly remove U^{VI} from synthetic groundwater via reduction to U^{IV}. The initial (1h) products in the abiotic GR system are individual U^{IV} atoms associated with the solids. Over time (16-32d) the proportion of nanocrystalline uraninite increases, leading to a dramatic decrease in the extractability of U^{IV} by carbonate. In contrast, the solid- phase U^{IV} atoms in the biogenic GR system remain as relatively extractable, non-uraninite U^{IV} species over the entire reaction period of 32 days. The presence of carbonate and calcium during U^{VI} reduction by GR affected the extractability of U^{IV} in the system with biogenic GR. These data provide new insights into the transformations of U under anoxic conditions in the presence of carbonate and calcium, and have major implications for designing approaches for the remediation of uranium contaminated groundwater.

X-ray absorption spectroscopy of actinium and comparison with actinide +3

M. G. Ferrier,[1,*] E. R. Batista,[1] J. M. Berg,[1] E. R. Birnbaum,[1] J. N. Cross,[1] J. W. Engle,[1] B. W. Stein,[1] S. A. Kozimor[1]

* *E-mail*: mferrier@lanl.gov

[1] Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, USA

The therapeutic potential of alpha emitters (e.g. ^{225}Ac) creates a pressing need to advance fundamental understanding of trivalent actinide coordination chemistry [1]. The risk of working with highly radioactive material, limited availability and scarce spectroscopic features of actinium compared to other lanthanides or actinides make the necessary experiments challenging. Owing to safety concerns with their safe handling. To date, the development of fundamental knowledge in other systems like the separation of minor actinides from lanthanide (Ln) fission products has been also slowed down due by limited access to isotopes of Am and Cm [2].

Recent upgrades and technological improvements at synchrotron facilities provide new opportunities to overcome challenges associated with spectroscopy of low concentrated and highly-radioactive samples. Herein, we will present how we have seized this opportunity to conduct the first XAS studies on actinium. Results will be compared with analogous measurements made on actinides +3 and also with DFT calculations. Experimental and computational results suggested a need to revisit the traditional descriptions of Ac^{III} compared to the minor actinides, e.g. Am^{III} and Cm^{III}. LA-UR-15-22201 and LA-UR-16-20582.

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Actinide and lanthanide EXAFS applications for the nuclear fuel cycle

V. E. Holfeltz,[1,3,*] T. G. Levitskaia,[1] G. B. Hall,[1] E. L. Campbell,[1] S. Lee,[2] A. Paulenova,[3] G. J. Lumetta[1]

* E-mail: vanessa.holfeltz@pnnl.gov

[1] Radiochemical Processing Laboratory, Pacific Northwest National Laboratory, Richland, WA

[2] Advanced Photon Source, Argonne National Laboratory, Lemont, IL

[3] Department of Nuclear Engineering and Radiation Health Physics, Oregon State University, Corvallis, OR

Efficient separation of the trivalent minor actinides (MA) and lanthanides (Ln), as part of a full partitioning and transmutation scheme, is a long-standing challenge in the nuclear fuel reprocessing community. To close the nuclear fuel cycle and optimize repository waste storage, it is necessary to separate the long-lived Am and Cm isotopes in used nuclear fuel from the predominant Ln fission product inventory, as the Ln significantly interfere with the further processing of Am and Cm. Similar chemical properties and coordination behavior make Ln-MA separations extremely difficult. In addition, both Ln and MA (Am and higher) adopt stable trivalent oxidation states in aqueous solutions, further challenging their separation.

Separation of trivalent Ln and MA generally relies on carefully tailoring a solvent extraction system to take advantage of the slight differences in chemistry between the two f-element series. The actinide 5f electron density extends slightly further from the nucleus than the Ln 4f electrons, which allows MA to participate in softer-bonding interactions relative to the Ln. The strategy of many proposed separation schemes is to utilize both hard- and soft-donor ligands, in order to obtain preferential complexation with the Ln or MA. For example, a hard-donor lipophilic ligand used in conjunction with a hydrophilic soft-donor ligand will partition Ln to the lipophilic organic phase and retain MA in the aqueous phase.

Solvent extraction schemes are often further tailored to obtain optimal separation by adjusting extraction conditions (i.e., aqueous phase conditions or extractant concentration/mixture of extractants). However, determination of the structure and exact metal coordination environment of extracted metal complexes in the solvent extraction systems is frequently challenging, and the exact extraction mechanism is not always clear. One focus of our research is the assessment of coordination environment of Ln and MA in the organic phase and its effect on separation efficiency and extraction kinetics. To gain insight to the Actinide Lanthanide SEParation (ALSEP) solvent extraction system, and to identify differences between the organic phase Ln and An complexes, we have performed XAFS on Ln (Eu) and MA (^{243}Am). XAFS data provides structural information by probing the metal center, and is combined with DFT and other theoretical calculations.

Coordination structure of uranium complexes in disordered systems using X-ray absorption fine structure spectroscopy

L. Zhang,* J.-Q. Wang

* *Email*: zhanglinjuan@sinap.ac.cn

Department of Molten Salt Chemistry and Engineering, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Separation uranium from spent nuclear fuel is a key part of advanced nuclear fuel cycle systems, in which high-temperature molten salt is an important reaction and electrolytic media in fuel reprocessing. In addition, extraction of uranium from seawater is expected as a rich supply for long-term nuclear power production, in which development of robust adsorbents with high selectivity is critical to realize the feasibility of uranium extraction. Understanding the coordination structure of uranium in high temperature molten salt and the adsorption mechanism between the functionalized ligand and uranium in aqueous solution benefits to improve the separate and extraction efficiency and thus to guide the electrolysis and distillation technologies as well as the design of adsorbent functionalized group. The fundamental challenges above are closely related with the coordination chemistry of uranium in disordered system: molten salt and aqueous solution.

Due to extreme chemical environment of molten salt, e.g. high temperature, strong corrosion and radioactivity, conventional experimental techniques are disabled, whereas synchrotron radiation (SR) techniques are promising to extracting local coordination environment around uranium. Among SR-based techniques, X-ray absorption fine structure spectroscopy (XAFS) has been widely confirmed as an element– selective and atomic level probe, which can unveil the chemical environment and bonding information in the actinide chemistry. In XAFS technique, EXAFS analysis can describe short-range order surrounding the absorbing atom and provide quantitative structure information such as ligand identity, bond length (R), coordination number (CN), and debye-waller factor (σ^2), while XANES technique is famous to element oxidation state characterization and recently draws great attention for quantification of the degree of 5f orbital participation in U-ligand bonding. In present work, we will discuss our research progress on the coordination environment of uranium complex in molten salts and aqueous solution using XAFS measurement as well as theoretical simulation. Besides, this work also give a brief introduction on our developed in-situ XAFS experimental apparatus, which is appropriate for high temperature melts condition up to 1100°C in vacuum or N_2/Ar atmosphere. In future, we wish make extensive use of in-situ XAFS studies of actinide chemistry and further tackle the problems in the pyrochemical processes for actinide separations from spent nuclear fuel.

XAFS and µ-XRF investigation of highly radioactive nuclear waste samples at KIT/ANKA

K. Dardenne, E. González-Robles, M. Herm, B. Kienzler, V. Metz, N. Müller, J. Rothe*

* *Email:* rothe@kit.edu

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (KIT-INE), PO Box 3640, D-76021 Karlsruhe, Germany

Speciation information on radionuclides such as actinides and long-lived radioactive fission products incorporated into matrices of highly active nuclear waste (HAW) – in particular spent nuclear fuel (SNF) and HAW glass - is mandatory in safety assessment studies, as the chemical and physical state of these elements lastly determines their environmental mobility. The fate of SNF and HAW glass in a future deep bedrock repository (e.g., groundwater induced corrosive degradation and dissolution of the waste forms and the associated release of actinides, fission and activation products) depends mainly on the oxidation state and bonding characteristics of the radionuclides in the individual matrices. Moreover, the expected prolongation of HAW interim storage in actively monitored surface facilities before the advent of final disposal solutions puts a high demand on methods establishing a better understanding how thermal, mechanical and radiological stress alters SNF matrices - with a focus on the possible corrosion and embrittlement of Zircaloy cladding tubes.

To this end, X-ray Absorption Fine Structure Spectroscopy (XAFS) and related techniques are ideally suited as speciation methods for the investigation of such materials, as they are capable to provide *in situ* chemical speciation information (i.e., oxidation states, coordination geometries and short-range structural parameters). X-ray Fluorescence Spectroscopy (XRF) delivers information on the elemental composition of the sample. Those techniques applied with a µ-focus incident beam provide additional spatial resolution of the distribution of elements and chemical species. While XAFS / XRF studies of simulated or radionuclide doped HAW surrogates are numerously reported in the material sciences literature, reports on the investigation of genuine nuclear waste glass or irradiated nuclear fuel and its zircaloy cladding by XAFS are sparse, reflecting the general difficulties to investigate even moderately radioactive samples at most synchrotron radiation laboratories. Research at KIT benefits from the unique situation where a shielded box-line with instrumentation for HAW sample manipulation and analysis operated at INE controlled area laboratories is situated in close proximity to X-ray spectroscopy experimental stations dedicated to radionuclide research - the INE-Beamline and the new ACT station at the ANKA synchrotron radiation source on KIT Campus North. Examples for initial investigations of HAW glass and SNF fragments and fuel cladding tube segments will be discussed in this presentation.

Actinide- and actinide-relevant XAS without a synchrotron

G. T. Seidler,[1,*] A. Ditter,[1] W. Holden,[1] O. Hoidn,[1] S. A. Kozimor,[2] J. Weaver,[3] M. Schweiger[3], C. Pearce,[3] J. McCloy[3,4]

* *E-mail*: seidler@uw.edu

[1] University of Washington, Physics Department, Seattle WA, 98195-1560

[2] Los Alamos National Labs, Los Alamos NM, 87545

[3] Pacific Northwest National Labs, Richland WA, 99352

[4] Washington State University, Pullman WA, 99164-2920

Contemporary research in many branches of fundamental and applied actinide chemistry is strongly influenced by application of x-ray absorption spectroscopy (XAS), including XAFS, x-ray emission spectroscopy (XES), and resonant inelastic x-ray scattering (RIXS). These techniques are almost exclusively performed at synchrotron facilities having outstanding beam flux, brilliance, and time-resolution, in addition to world-class endstation equipment and user support. However, experimental programs at synchrotron user facilities come with notable barriers to progress, including: infrequent access; difficult accommodation for air-sensitive or radioactive samples; high costs for shipping radioactive materials; and limited opportunity for student training.

In this talk we report on an ongoing effort [1-3] aimed at softening or bypassing the above limitations through the development and application of in-house XAS instrumentation using only conventional x-ray tubes. First, a UW-LANL collaboration is optimizing lab-based XES to accelerate progress in actinide coordination chemistry. Two high-resolution (~1-eV or better) XES spectrometers have been built for on-site use at LANL, both a high-powered spectrometer for the 4-12 keV range for actinide M-shell and lanthanide L-shell XES and also a lower-powered instrument for the 2-3 keV range. The latter instrument uses a novel optical geometry to achieve a critical miniaturization: the entire spectrometer can fit into a 30 × 30 × 30 cm^3 volume *inside a glove box*, thus enabling on-demand, synchrotron-quality XES of P or S ligands without sample removal from the controlled atmosphere. The same instrument is expected to function well for Tc. Second, a UW-PNNL collaboration is using the UW's CEI-XANES benchtop XAFS user facility to investigate glass local chemistry and electronic structure for Fe-rich model glasses relevant for long-term storage of low-activity waste. In this project, the key issue is 'routine analytic' XANES that can identify the onset of short-range order upon heat treatment and the onset of crystallization.

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Diffuse reflectance spectroscopy of plutonium fluorides and other Pu solids: evolution of spectral signature in time as a built-in chronometer of the sample age and crystallinity

S. Sinkov,* A. J. Casella, C. Delegard, M. McCoy, L. Sweet, and B. K. McNamara

* *E-mail*: sergey.sinkov@pnnl.gov

Pacific Northwest National Laboratory, Radiochemical Processing Laboratory

A recent review on application of Diffuse Reflectance Spectroscopy (DRS) to Pu solids by Hobart and Boland [1] emphasized a number of useful features that DRS provides for analysis and characterization of Pu compounds. Among them are enhanced signatures of subtle ligand and matrix interactions when translational modes that broaden and smear fine structure components in electronic and vibrational spectra are "frozen out" in the solid state. The authors point out that the DRS offers a rapid and unequivocal identification of oxidation state, compound, and matrix of 5f elements in the solid states especially when the solids possess sharp, well-resolved spectral features in the UV-Vis NIR regions. These researchers reported a number of new results on DRS spectra of Pu solids using a small size cylindrical quartz or plastic cell with a plastic plug to contain samples and an integrating sphere assembly set-up to record the spectra with a high performance and high resolution spectrophotometer. They used a double containment configuration for the DRS sample storage and a single containment in the process of spectral acquisition. Preparation of the Pu samples for DRS in their laboratory took at least two researchers and a number of transfers between radiologically controlled enclosures. Even with reduced cell dimensions the amount of Pu solid had to be maintained at ~ 100 mg to ensure uniform distribution of the material across the scanned area.

In our work we describe a simpler and more robust technique to prepare Pu samples for DRS characterization with amount of Pu material not exceeding 20 mg. Once prepared, the contained samples are suitable for repeated measurement, allowing long-term spectral monitoring to follow radiolytic changes. With this new capability we've focused our efforts on a systematic characterization of a fluoride family of Pu(IV) and Pu(III) compounds and evolution of their spectral signatures with time. Special attention has been given to spectral examination of a large batch of Hanford PuF_4 prepared and sealed in the middle 1960s as a neutron source at the Plutonium Finishing Plant. This sample was opened in 2010 and became available for PNNL researchers in 2014. A number of advanced techniques were used for its extensive characterization to better understand its composition, structure and extent of radiation damage it withstood over its lifetime. Among other things, we compare DRS data for this and similar Pu compounds with extent of the sample crystallinity as measured by XRD.

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The optical properties of uranium carbide measured by spectroscopic ellipsometry

W. J. Siekhaus,* A. J. Nelson, C. K. Saw

* *Email*: siekhaus1@llnl.gov

Lawrence Livermore National Laboratory

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Uranium carbide inclusions are common in metallic uranium, and uranium carbide itself is being considered as a fuel in both gas-cooled, liquid metal cooled, and supercritical water-cooled reactors. To the best of our knowledge, the only study of optical properties deals with high temperature radiance [1]. Here we first characterized a single crystal uranium carbide cube (supplied by Oak Ridge National Laboratory) with sides of a few mm length by X-ray diffraction and X-ray photo-electron spectroscopy and then measured its optical properties with a spectroscopic ellipsometer using a 1 mm diameter light beam at angles of incidence between 65 and 75 degrees with respect to the normal of the (100) planes, and over an energy range from 1.25 to 3.2 eV. The signal strength was low but usable over that energy range, and too low to be useful above 3.2 eV. The measured Δ and Ψ values were converted to the dielectric constants ε1 and ε2, using a general oscillator model [2], and the results of the model fit are shown in Figure 1.

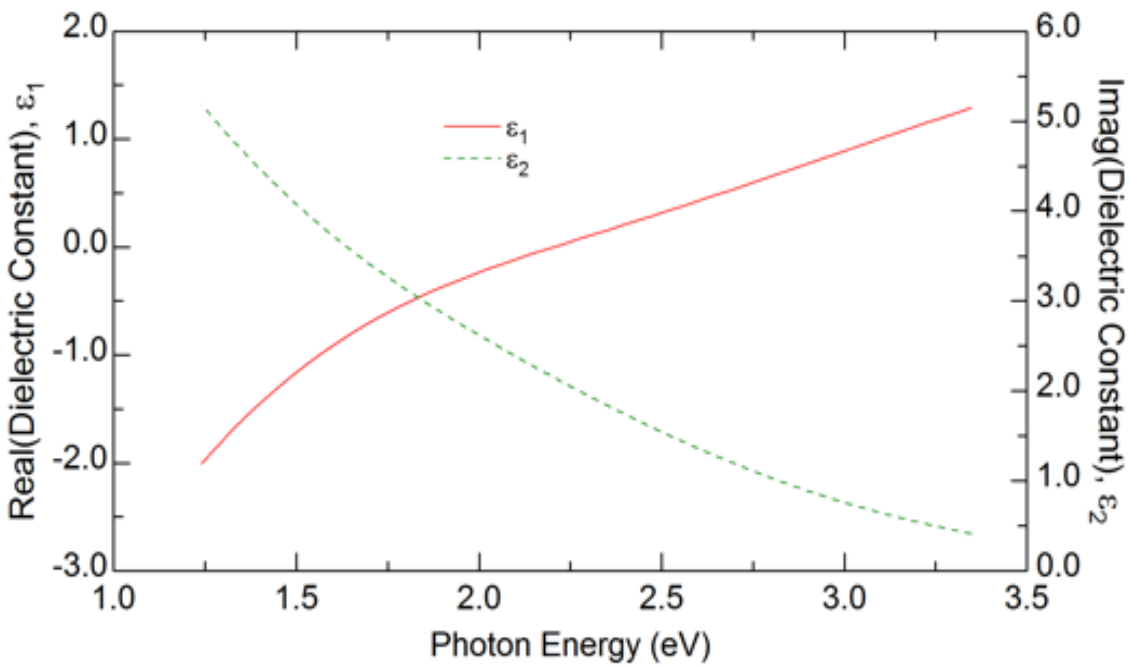

Figure 1. The dielectric constants ε1 and ε2 of uranium carbide.

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Probing the electronic structures of thorium oxides using anion photoelectron velocity map imaging

Y. Li, Z. Fei, X. Xiong, H. Liu*

* *E-mail*: liuhongtao@sinap.ac.cn

Department of Molten Salt Chemistry and Engineering, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Anion photoelectron spectroscopy (PES) is a powerful technique for the study of gas phase molecule and clusters, probing directly the electronic structure of the corresponding neutral species. Recently, the L. S. Wang group reported a series of joint studies on uranium oxides and fluorides by PES and theoretic calculation. However, the resolution of PES is limited to a few meV in the best cases, which is not sufficient to resolve very complicated electronic structures of actinide molecule, even for the simple UO_2. The introduction of velocity-map imaging (VMI) into PES of size-selected anions has made it into a powerful alternative PES method to reveal the electronic fine structures of 5f electrons. The advantage of photoelectron imaging lies at its high detection efficiency while yielding photoelectron angular information at the same time. The ability to detect very low energy electrons makes VMI potentially a much higher resolution method for PES [1].

In this presentation, a newly developed VMI instrument and the application in study actinide molecule will be introduced [1]. The design of cold anion trap combined with VMI was shown significantly eliminate anion vibrational hot band, which allows the electronic fine structure and detail of vibronic coupling for some anion excited state be able to clearly resolved [2,3].

Thorium oxides have been considered as potential nuclear fuels due to their distinctive advantage despite the challenges for applying this material. Thorium is one of the early actinide elements without 5f electron, the ground state configuration of Th atom is $[Rn]6d^27s^2$. Although the chemical property of thorium is making sense in comparing with lanthanide and group IV transition metals. Still, strong relativistic effects lead many unique properties of thorium contained species. Here we applied high resolution anion photoelectron VMI to probe the electronic structure of thorium oxides, and the strong electron correlation effect compared with uranium oxides will be discussed.

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Investigation of europium (III) acetylacetonate complexes at air/water interface by sum frequency generation vibrational spectroscopy

Z. Wang,[1,*] Z. Lu,[1] S. Chen,[2] H.-F. Wang[1]

* *E-mail*: zheming.wang@pnnl.gov

[1] Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99354, USA

[2] Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi, Xinjiang 830011, China

The speciation and molecular orientations at the interfaces of liquid-liquid and liquid-solid play critical roles in actinide chemistry from solvent extraction to spent fuel dissolution and separation. Organic-chelating-agent enhanced extractions have been widely used in separations of lanthanide and/or actinide metal ions from aqueous solutions. The rate-limiting transformations during solvent extraction processes mostly occur at phase boundary rather than in the bulk aqueous or organic phase. So far, there has been little study of the structure and interactions of important interfacial molecules in solvent extraction. It is not known what are the important chemical species at the aqueous-organic interface, what changes have to occur prior to the formation of the interfacial species, how do these chemical processes vary with the polarity of the solvents and the nature of counter ions and ultimately how do these changes affect the separation efficiency and selectivity? Until very recently, few techniques allowed detailed investigation of interactions occurring in the boundary layers between solvents. In this work, Europium (III)-acetylacetonate ($Eu(AcAc)_3$), a model metale-β-diketonate complex, was investigated at air/water interface by sum frequency generation vibrational spectroscopy (SFG-VS), a surface-selective and submonolayer-sensitive nonlinear optical tool. The vibrational spectra of interfacial Eu-AcAc, complexes, most-likely in the form of $Eu(AcAc)_3$ are drastically different from those of the ligand acetylacetone molecules and show dependence on the bulk pH and concentrations. These results provide new insights into the solvent extractions of trivalent lanthanide metal ions and open new avenue to future studies of molecular processes at liquid-liquid interface using SFG-VS.

Extraction of technetium, chromium and iodine from chemically complex waste environments and incorporation into cementitious waste forms

R. M. Asmussen,* C. Pearce, J. J. Neeway, A. R. Lawter, R. E. Clayton and N.P. Qafoku

* *E-mail*: matthew.asmussen@pnnl.gov

Pacific Northwest National Laboratory, Richland, WA 99352

A cementitious waste form (cast stone) has been investigated as an immobilization technology to treat low-activity waste (LAW) in Hanford Site tanks. "Getter" materials were added to selectively sequester risk driving contaminants of concern (COC) from highly alkaline LAW and to lower their diffusivities, thus limiting their release from the waste form. COC present in LAW include the tetrahedral anions pertechnetate (99-TcO_4^-) and chromate ($Cr_2O_7^{2-}$), as well as radioactive iodide (129-I^-). Tin apatite removed >99% of $Cr_2O_7^{2-}$ and 65% of TcO_4^-. Layered potassium metal sulfide (KMS) removed >97% TcO_4^- and < 11% of the Cr, suggesting KMS preferentially removes Tc, although a change in color from yellow to dark green suggested reduction of Cr(VI) to Cr(III). KMS lowered cast stone Tc diffusivities to ~10^{-13} cm^2/s in simulated Hanford vadose zone pore water (VZPW), an order of magnitude lower than without getter. Silver–based I getters efficiently removed soluble I^- from LAW through precipitation of insoluble AgI, but were ineffective in lowering I diffusivity when incorporated into cast stone. A pH effect and competition for Ag from sulfide in cast stone and KMS may result in AgI instability. Single particle digital autoradiography was used to monitor Tc distribution in cast stone before and after leaching, as modelling of COC release from waste forms assumes a homogenously distributed source. Without getters, Tc distribution was uniform initially and concentrated at the cast stone outer wall after leaching. With getters, Tc was present in discrete locations, randomly distributed throughout the cast stone. Tc must first be released from these sites before diffusing through the waste form and this should be considered in future performance assessments. Synchrotron-based x-ray absorption at the Tc K-edge and the Cr L-edge were used to determine oxidation state and local bonding environment of the low concentrations of Tc and Cr associated with the cast stone both before and after leaching. These studies show the importance of combining leaching experiments with solid state investigation into waste form behavior in order to fully understand, model and predict radionuclide and COC release over long periods of time.

Redox behavior of technetium in high ionic strength matrices

S. Chatterjee,[1,*] G. B. Hall,[1] E. D. Walter,[2] N. W. Washton,[2] M. H. Engelhard,[2] Y. Du,[2] T. G. Levitskaia[1]

* *E-mail*: Sayandev.Chatterjee@pnnl.gov

[1] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

[2] Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352

Technetium-99 (Tc-99) is one of the most important contributors of radiotoxicity in longterm nuclear waste storage. One of the DOE-EM current challenges is to meet regulatory requirements for near term Tc-99 disposal due to excess Tc-99 in DOE waste streams. For this, a thorough understanding of the behavior and speciation of Tc is needed. While Tc can exist in a range of oxidation states from +1 to +7, the fully oxidized species, TcO_4^- is considered the most predominant form of Tc, peculiarly under oxic environments. However, recent studies by our group and elsewhere have shown that mildly reductive environments and high ionic strength matrices can make lower oxidation states of Tc accessible. This can be the case of tank waste supernatants in the U.S. DOE Hanford Site. Therefore, elucidation of the mechanism of interconversion between TcO_4^- and the lower oxidation states of Tc at high ionic strength matrices relevant to tank waste is critical for designing strategies for the disposal and removal of Tc from tank waste. Towards this goal, we are studying the electrochemical reduction of TcO_4^- under high ionic strength matrices, and the relative stabilities of the reduced species. Our recent studies have shown significant stabilization of the otherwise exotic Tc(VI), Tc(V) and Tc(IV) oxidation states. This work will look at the redox and spectroscopic behavior of technetium at high ionic strengths, as well as the mechanistic pathway of its reduction to the lower oxidation states through a range of spectroscopic (UV-visible, EPR, NMR, XPS and XAS) and spectroelectrochemical techniques.

Fundamental understanding of technetium-inorganic solid interactions: towards novel composites for sensing, removal and long-term storage of technetium

S. Chatterjee,[1,*] T. G. Levitskaia,[1] M. H. Engelhard,[2] Y. Du,[2] E. D. Walter,[2] T. Varga,[2] M. E. Bowden,[3] B. W. Arey,[1] L. Kovarik[2]

* *E-mail*: Sayandev.Chatterjee@pnnl.gov

[1] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

[2] Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352

Technetium (Tc) is one of the most problematic long-lived contaminants to be addressed at the U.S. DOE Hanford Site because of its complex chemical behavior in the tank waste, limited incorporation during LAW vitrification, and high mobility in subsurface environments. Significant concentrations of ^{99}Tc is observed in the multicomponent liquid matrices such as those related to the contaminated groundwater found in the Hanford area vadose zone, liquid nuclear tank waste, and solution generated during used nuclear fuel reprocessing. Tc transport and discharge from waste sites/sources to ground- and surface water resources creates potential for ecological exposure and significant health risks due to the possibility of its accumulation in several plants and animals resulting in biomagnification of ^{99}Tc in the food chain. This has necessitated an imminent need for ^{99}Tc sequestration and removal from tank waste, soil, watersheds and ground water and long term storage. However, the designing of novel sorbent materials for efficient ^{99}Tc removal is complicated by its ability to exist in a variety of oxidation states and chemical forms with varying mobilities depending upon the environment. In the strongly alkaline oxidative environments it exists mostly as Tc(VII) in the form of pertechnetate TcO_4^-. Reducing conditions, presence of organics and noble metal catalysts promote low oxidation states of Tc, such as Tc(I) tricarbonyl species derived from $[Tc(CO)_3]^+$. Presence of a non-pertechnetate species significantly complicates Tc removal from LAW and its immobilization in the low temperature waste forms. To address this, we have developed novel transition metal based inorganic ion exchange materials that can be applied to tank waste solutions to separate and immobilize all chemical forms of Tc in a one-step process. These materials can be represented by the general formulae $[M_{1-x}^{2+}M_x^{m+}(OH)_2]^{x+}(A^{n-})_{x/n}\bullet yH_2O$ where M^{2+} is a divalent transition metal cation and M^{m+} is a trivalent or tetravalent cation; and A is the interlayer anion (e.g. hydroxide, phosphate, molybdate, tungstate).We have tailored the composition of these materials for the quantitative uptake of TcO_4^- or non-TcO_4^- species from the high nitrate alkaline solutions present in tank waste supernatants and convert them to Tc(IV). Introduction of redox active centers in the composite structure allowed us to maintain the desired +4 oxidation state of Tc and to suppress back oxidation to the highly mobile Tc(VII) upon exposure to the alkaline environments typical for tank waste conditions, preventing its release. This suggests that these materials have potential for both capture as well as a storage medium for Tc. This presentation will focus molecular, structural and electronic properties of these composites, with an effort to identify the Tcsolid matrix interactions which result in uptake. Subsequent distribution and speciation of Tc within the solid matrices will also be discussed using a range of spectroscopic and microscopic techniques FTIR and Raman spectroscopies, X-ray diffraction analysis, scanning and transmission electron microscopies, X-ray photoelectron scattering spectroscopy and UV-visible reflectance spectroscopy.

Luminescence spectra of uranium(VI) – why we observe a spectral shift in cryospectra

G. Geipel,* T. Stumpf

* *E-mail*: g.geipel@hzdr.de

Helmholtz-Zentrum Dresden – Rossendorf, Institute of Resource Ecology, Bautzener Landstr. 400, 01328 Dresden, Germany

It is well known, that uranyl carbonates emits at room temperature only phosphorescence with very short lifetimes {$Ca_2UO_2(CO_3)_3$ ~ 50 ns}[1, 2]. The lifetime of $UO_2(CO_3)_3^{4+}$ in aqueous solution at room temperature was determined to be 9.2 ± 0.05 ns. Freezing these solutions results normally in a strong increase of the luminescence lifetime as well as in a strong increase in the measured intensity. This effect is usually explained by the dynamic quench effect of the carbonate ion as well as the dynamic quench effect of the water molecules in the solvation shell. In addition all spectra of the uranyl carbonates show a hypsochromic shift.

The emission of the uranyl ion is assigned to a triplet state. It is also known that the non-complexed uranyl ion has two phosphorescence emitting levels (20500 and 21270 cm^{-1})[3,4]. The first one is assigned to the direct transition to the lowest vibronic level in the ground state, the second is assigned to the transition of a exited vibronic level to the ground state. The emission peaks at lower wavenumbers correspond to vibronic levels in the ground state and are usually assigned to the transition from the lowest triplet state[5].

We observe for the uranyltricarbonate at room temperature an emission at around 21420 cm^{-1} and at 20610 cm^{-1} which are the two emitting levels in this system. From the higher level also the vibronic levels in the ground state were populated. Under cryogenic conditions we observe that the emission from the higher level disappears. This induces a slight blue shift of the spectrum of about 65 cm^{-1}.

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Synthesis and identification of technetium compounds relevant to tank waste

G. B. Hall,* S. Chatterjee, N. M. Washton, E. D. Walter, A. Anderson, T. G. Levitskaia

* *E-mail*: gabriel.hall@pnnl.gov

Pacific Northwest National Laboratory, Richland, WA 99352

The long half-life, complex chemical behavior in tank waste, limited incorporation in mid- to high temperature immobilization processes, and high mobility in subsurface environments make technetium-99 (Tc) one of the most difficult contaminants to dispose of and/or remediate. Technetium exists predominantly in the liquid tank waste phase as pertechnetate, TcO_4^- (oxidation state +7). However, based on experimentation to-date, a significant fraction of the soluble Tc in tank waste may be present as a non-TcO_4^- species that has not been identified and, based on experimentation to date, cannot be effectively separated from the wastes. It remains uncertain whether alkaline tank conditions even support the formation of proposed low-valent Tc species, i.e., Tc(I) carbonyl compounds. There is no definitive information on the origin of the non-TcO_4^- species, nor is there a comprehensive description of their composition and behavior. The objective of this work is to investigate aspects of the nature and chemistry of the non-TcO_4^- species derived from the Tc(I) carbonyl coordination center, specifically under the conditions typical for the alkaline liquid fraction of the tank waste and to gain better understanding and control over their redox behavior.

Recent research within our group has focused on better understanding of $Tc^I(CO)_3L_3$, and $Tc^I(CO)_2(NO)L_2$ complex species, and potential redox intermediates between Tc^I and Tc^{VII} in order to better understand the speciation of Tc in tank waste through synthesis, characterization, and DFT modeling of experimentally obtained ^{99}Tc NMR, XPS, EXAFS, IR, and EPR spectra.

RadEMSL, an international user facility for the study of radiological environmental samples

N. J. Hess

E-mail: nancy.hess@pnnl.gov

EMSL, Pacific Northwest National Laboratory, Richland WA 99352 USA

RadEMSL, a state-of-the-art laboratory to facilitate application of advanced analytical methods to environmental samples containing radionuclides, has been operational for two years at EMSL, a U.S. DOE Office of Biological and Environmental Research user facility located at Pacific Northwest National Laboratory in Richland, Washington. It supports world-class research in the biological, energy and environmental sciences through integration of computational and experimental capabilities, as well as collaborating among disciplines to yield a strong synergistic scientific environment.

Critical determinants of radionuclide chemical reactivity and mobility are oxidation state, chemical speciation, and formation of surface and solution complexes. Accurate representation of how environmental biogeochemical conditions impact these determinants is key to predictive modelling of radionuclide fate and transport in terrestrial and subsurface ecosystems. Molecular-level characterization of radionuclide containing materials can also be used to trace point of origin in forensic applications. These determinants also impact the chemical behaviour of radionuclides in the nuclear fuel cycle from separations processing to the creation of waste forms and aging under repository conditions. Unfortunately, the application of advanced molecular characterization techniques to radiological samples has often lagged because of the need for dedicated equipment and specialized facilities. Additionally there are fundamental difficulties of observing molecular level processes for radionuclides that are often present in very minor amounts in environmentally contaminated soils and sediments.

RadEMSL provides scientific support and specialized environment where scientists are using advanced imaging and spectroscopic approaches together with NWChem, EMSL's premier computational modelling code, to study radionuclide speciation in environmental samples, nuclear fuel simulants, and in high level nuclear waste storage tanks. The radiological facility consists of approximately 6000 sq ft of contiguous lab space for NMR, EPR, XPS, and fluorescence spectroscopies and EMP, FIB/SEM, SEM, and aberration-corrected TEM imaging to enable investigation of radionuclide systems using multiple experimental and computational vantage points.

Access to RadEMSL is granted through a competitve, peer review process in response to call for proposals. Typcial access is free. The results of several research projects conducted at Rad EMSL that highlight the integration of multiple experimental and computational approaches will be presented.

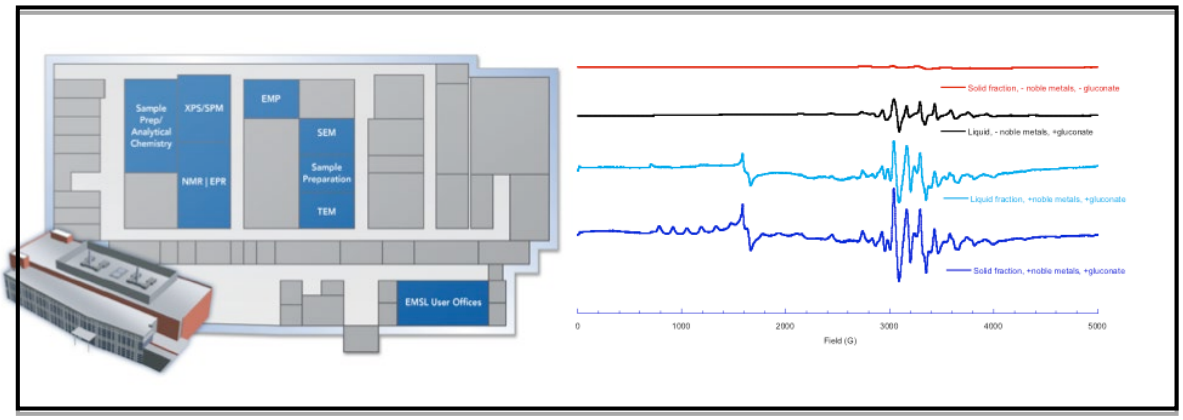

Figure 1. Left panel, RadEMSL layout showing advanced spectroscopy and imaging laboratories. Right panel, cyrogenic EPR of Tc complexes in Hanford waste simulants.

Computational study of semiconducting layered technetium chalcogenide compounds

E. Kim,[1,*] P. F. Weck,[2] F. Poineau,[1] A. Sattelberger,[3] and K. R. Czerwinski[1]

* *E-mail*: kimej@physics.unlv.edu

[1] UNLV

[2] SNL

[3] ANL

Transition-metal dichalcogenides are an important class of inorganic materials exhibiting a wide spectrum of catalytic, electronic, magnetic, and optical properties [1]. Transition-metal dichalcogenides (TMDs) with layered structures (e.g. MoS_2 or WSe_2) are considered attractive for use in next generation nanoscale field-effect transistor (FETs) devices [2-4]. Among TMDs, relatively limited knowledge is available on technetium dichalcogenides. The long-lived β^-–emitting isotope, ^{99}Tc ($t_{1/2} = 2.13 \times 10^5$ years, β^- =294 keV), is produced in sizable amounts from the nuclear fuel cycle (up to 6% yield from the fission of ^{235}U) and constitutes an important challenge for environmental remediation. The immobilization of Tc as Tc–sulfide compounds has been investigated experimentally [5-7]. The Tc–chalcogenide system can be important in the fields of nuclear waste management and nuclear medicine. Here, we discuss the structures and properties of layered technetium dichalcogenides TcX_2 (X = S, Se, Te) investigated using density functional theory [8]. The equilibrium structures of $TcSe_2$ and $TcTe_2$, adopting distorted $Cd(OH)_2$-type unit cells similar to TcS_2, are reported for the first time at the atomic level, along with their electronic properties. In contrast to previous X-ray diffraction analyses, calculations reveal that stoichiometric $TcTe_2$ is not isomorphous to the high-temperature monoclinic phase β–$MoTe_2$. The thermal properties of these TcX_2 compounds have also been predicted using phonon frequencies calculated with density functional perturbation theory [8].

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Spectroelectrochemical analysis of Pu across a range of HNO_3 concentrations

A. M. Lines,* S. Sinkov, A. J. Casella, S. R. Adami, G. J. Lumetta, D. Meier, S. A. Bryan

E-mail: Amanda.Lines@pnnl.gov

Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99354, USA

It is of interest to explore the behavior of Pu over a wide range of HNO_3 concentrations that mimic conditions expected throughout several nuclear materials processing schemes. Acid strength effects several important features including electrochemical response, spectral signature, and speciation of Pu. Spectroelectrochemistry is utilized to explore these systems where applied potential is used to hold Pu in pure or mixed oxidation states while spectra are collected. Both high and low concentrations of Pu were analyzed across a range of HNO_3 concentrations of 1 to 10 M. While Pu concentration did not have any effect on system response aside from increased or decreased intensity of response, HNO_3 concentration significantly impacted electrochemical and spectroscopic signatures. Formal reduction potential and reversibility of couples showed notable shifts and Pu(IV) spectra in particular showed band shifts and changes in molar absorptivity with changing acid concentration. This data has numerous applications including sensor development as well as building calibration sets for advanced monitoring of Pu in solution.

Molecular dynamics study of extractant aggregation phenomena with X-ray spectral simulations

E. Martínez-Baez,* Y. Ghadar, A. E. Clark

* *E-mail*: e.martinezbaez@wsu.edu

Washington State University, Pullman, WA 99164

Recent experimental studies have noted the potential importance of aggregation phenomena within liquid:liquid solvent extraction [1]. Presumably, ampiphilic extractant ligands (of various protonation states) organize with their polar head groups around a central aquo metal cation, or may act to bridge multiple metals – forming extended aggregates of various configurations (spherical, branched, cylindrical). The mechanisms of formation of these aggregates at a water:organic interface are not well understood, nor the affect of the aggregates upon the interfacial structure and dynamics. Herein we describe the results of mixing/de-mixing simulations of tributyl phosphate in nitric acid solutions in contact with hexane. Aggregation has been quantified and spectral simulations of X-ray scattering experiments have been performed.

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The surface reactions of U(VI) on γ-Al_2O_3 *in situ* spectroscopic evaluation of the transition from sorption complexation to surface precipitation

K. Müller,* H. Foerstendorf, A. Rossberg

* *E-mail*: k.mueller@hzdr.de

Helmholtz-Zentrum Dresden – Rossendorf, Institute of Resource Ecology, Dresden,Germany

Aluminates, representing an essential component of clay minerals, play a decisive role in regulating the mobility of contaminants in rock and soil formations, in particular due to their tendency to form coatings on mineral surfaces [1]. In this work, U(VI) sorption on γ-Al_2O_3 is comparatively investigated using in situ vibrational and X-ray absorption spectroscopy. The focus was set to micromolar U(VI) concentrations and a variety of environmentally relevant sorption parameters in order to resolve discrepancies reported earlier [2-4].

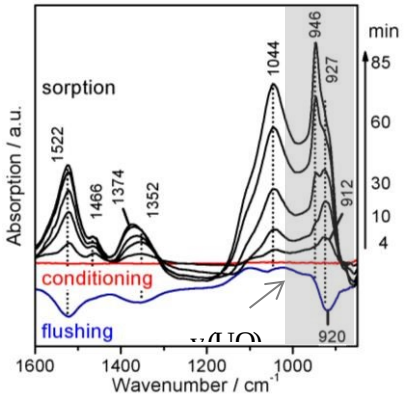

Figure 1. TR ATR FT-IR spectra of U(VI) sorption on γ Al_2O_3.

Time-resolved (TR) IR spectroscopic sorption experiments at the alumina-water interface evidence the formation of three different species as a function of surface loading (c.f. Fig.): a monomeric carbonate complex, an oligomeric surface complex and a surface precipitate. These results are confirmed by IR experiments performed at different flow rates, pH values, ionic strengths, U(VI) concentrations, and in inert gas atmosphere. Results of EXAFS experiments of batch samples are consistent to these findings [5].

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IDREAM: Interfacial Dynamics in Radioactive Environments and Materials

C. Pearce,[1,*] A. Felmy,[1,2] D. Wesolowski,[3] K. Rosso,[1] A. Stack,[3] N. Browning,[1] J. Chun,[1] J. De Yoreo,[1] G. Kimmel,[1] J. LaVerne,[4] K. Page,[3] T. Orlando,[5] X. Li,[6] G. Schenter,[1] A. E. Clark,[2] S. B. Clark[1,2]

* *E-mail*: carolyn.pearce@pnnl.gov

[1] Pacific Northwest National Laboratory

[2] Washington State University

[3] Oak Ridge National Laboratory

[4] University of Notre Dame

[5] Georgia Institute of Technology

[6] University of Washington

Current efforts to treat high level radioactive wastes are slow and costly because processing schemes are limited to narrow conditions based on uncertainties in waste characteristics and behavior during processing. Examples of this behavior include: (i) dilution of waste slurries can sometimes cause precipitation; (ii) sonication of waste slurries can sometimes make colloids larger; (iii) slurry yield stress often does not scale with colloidal size distributions; and (iv) finely divided materials are often more refractory than larger crystalline solids. These uncertainties in waste characteristics will be addressed by PNNL's Energy Frontier Research Center focused on interfacial dynamics in radiation environments and materials (IDREAM), in partnership with Washington State University, Oak Ridge National Laboratory, Georgia Institute of Technology, Notre Dame Radiation Laboratory and University of Washington. The vision of IDREAM is to master molecular–to–mesoscale chemical and physical phenomena at interfaces in complex environments characterized by extremes in alkalinity and low-water activity, and driven far from equilibrium by ionizing radiation. The IDREAM science strategy is presented as four research goals and includes an integrated computational approach at appropriate spatial and temporal scales within and across Research Goals to represent correlations across length and time scales:

- Research Goal 1 (Molecular Speciation) - Understanding solvent dynamics, chemical reactivity, solute organization, and pre-nucleation species in highly alkaline systems of concentrated electrolytes
- Research Goal 2 (Interfacial Structure and Reactivity) - Extend fluid phase dynamics to nucleation, particle growth, and interfacial reactivity in highly alkaline systems of concentrated electrolytes
- Research Goal 3 (Particle Interactions) - Quantify the chemical and physical phenomena leading to hierarchical microstructures of aggregates and other response dynamics that couple across scales to create emergent properties of heterogeneous systems
- Research Goal 4 (Radiolysis and Radiation Effects) - Quantify the role of β and γ radiation in driving molecular speciation and interfacial reactivity far from equilibrium

Mechanisms for simultaneous reduction and immobilization of ^{99}Tc and Cr by $Fe(OH)_2$ mineral transformation

S. Saslow,[1,*] W. Um,[1] C. Pearce,[1] M. H. Engelhard,[1] M. E. Bowden,[1] and W. Lukens[2]

* *E-mail*: sarah.saslow@pnnl.gov

[1] Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA, 99352, USA

[2] Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, CA, 94720 USA

Current remediation plans outlined by the Department of Energy (DOE) for disposal and long term storage of ~1900 kg of technetium-99 (^{99}Tc) at the Hanford Site (Washington State, USA) anticipate a large fraction of ^{99}Tc volatilizing during waste vitrification and being captured in a secondary waste stream. This secondary waste stream faces two major remediation challenges: (i) the reduction of Tc(VII) to less mobile Tc(IV) in the presence of co-mingled redox sensitive chromium, Cr(VI), which is more readily reduced than Tc(VII); and (ii) the immobilization of ^{99}Tc in a stable crystal structure that will inhibit reoxidation and release. In an effort to find a 'silver-bullet' solution to these challenges, this work demonstrates successful use of $Fe(OH)_2$ to simultaneously reduce Tc(VII) in simulated waste streams, even in the presence of Cr(VI), and immobilize the reduced Tc(IV) in magnetite (Fe_3O_4). However, successful incorporation of this remediation approach into nuclear waste processing efforts requires a mechanistic understanding of the reduction/immobilization reaction.

To investigate the mechanisms of Tc(VII)/Cr(VI) reduction and immobilization by $Fe(OH)_2/Fe_3O_4$, X-ray spectroscopies, including X-ray absorption near edge spectroscopy (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS) are used and complemented by X-ray diffraction (XRD), microscopic and trace metal analyses. Initial results from trace metal analyses suggest that reduction of Tc(VII) to Tc(IV) and Cr(VI) to Cr(III) occurs simultaneously; however, complete reduction of Cr(VI) to Cr(III) is achieved earlier than Tc(VII) reduction to Tc(IV). Bulk oxidation state analysis of ^{99}Tc-containing magnetite by XANES confirms that the majority of incorporated ^{99}Tc is present as Tc(IV); however, analysis by XPS suggests that the near surface of these materials may contain a mixture of Tc(VII) and Tc(IV), indicating some level of localized surface reoxidation. In addition, the EXAFS results confirm Tc(IV) incorporation into octahedral sites of the magnetite structure and preliminary results assessing possible ^{99}Tc-Cr and ^{99}Tc-^{99}Tc scattering pathways do not indicate additional substitution of Cr or ^{99}Tc into second shell Fe octahedral sites. XPS analysis of Cr confirms reduction to Cr(III), predominately present as chromite ($FeCr_2O_4$), another identified spinel, and is corroborated by XRD results that show the formation of magnetite-chromite (Fe_3O_4–$FeCr_2O_4$) solid-solutions. Goethite (FeOOH), the expected by-product of the Tc(VII) and Cr(VI) reduction process during which Fe(II) is oxidized to Fe(III), is also present, as detected by XRD and scanning electron microscopy (SEM). This multi-technique approach confirms that Cr(VI) and Tc(VII) are removed simultaneously through mineral transformation and co-precipitation processes facilitated by $Fe(OH)_2$.

On-line speciation of elements through CE-MXRF

I. M. B. Tyssebotn,* A. Fittschen, U. Fittschen

* *E-mail*: imb.tyssebotn@wsu.edu

Department of Chemistry, Washington State University, Pullman, WA

Remediation of contaminated sites and safe nuclear waste disposal requires knowledge of the mobilization of hazardous elements from solid to liquid phase. In order to understand elemental migration, liquid-based separation techniques such as capillary electrophoresis (CE) can be used to study the effects of complexation of metal ions with ligand molecules on the transportation of elements through changes made to the mobile phase. Separation techniques, such as CE, have previously been used for elemental separation and is most commonly coupled with UV-visible spectrometry, a non-destructive on-line detector technique. However, UV-vis does not provide elemental information. To resolve this limitation, mass spectrometry coupled with suitable ionization sources, or optical emission spectroscopy have been used, but these methods require physical access to the mobile phase. Non-destructive on-line detection is feasible by X-ray fluorescence spectrometry (XRF). The viability of this approach has been shown previously using Synchrotron XRF (SR-XRF) and micro-XRF (MXRF) setups. However, application of XRF detection for liquid separation has remained limited because the laboratory XRF, though having elemental sensitivity, was not competitive to UV-vis detection regarding cost and maintenance efficiency, as well as size. Hence, only a few analyses on highly specific applications requiring the most sophisticated instrumentation, like SR-XRF, have been performed. Recently, new developments in XRF low-power tube and electrically cooled detectors have allowed the miniaturization of XRF instrumentation, and made it more cost- and maintenance efficient (e.g. led to commercializing of handheld XRF). Accordingly, an on-line elemental detection in CE can be cost efficiently enabled using XRF instrumentation. Our project aims to set up a micro-XRF detection system for CE separation and evaluate key parameters such as windows, flow, detection limits, precision, and accuracy. Here we present the outline of the set up and first results on the custom built CE instrumentation, as well as static detection limits from a micro-XRF instrument newly build at WSU. Once the laboratory set up is successfully established, it will allow for a sensitive and accurate probing of elements in the liquid phase and provide excellent conditions for the study of dynamic change in oxidation state during elemental migration, which can elucidate information on mobilization of hazardous elements in the environment.

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