

Actinide Separations

2021

44TH ANNUAL
CONFERENCE



Tuesday–Thursday May 18–20, 2021
pnnl.cvent.com/ASC2021

Times denoted are Pacific Daylight Time

Welcome to the 44th Annual Actinide Separations Conference

Hosted virtually by Pacific Northwest National Laboratory

After postponing the Actinide Separations Conference one year because of the COVID-19 global pandemic, we are pleased to offer this online experience to connect with colleagues and share exciting developments in actinide and separations chemistry.

Who would have guessed two years ago, when we started planning the ASC to be held at PNNL in Washington State, that we would be gathering over Zoom? The silver lining of the virtual conference is that more of us can attend and present this year because of the flexibility offered by the online platform. We also are pleased to hold an interactive virtual poster session on Wednesday afternoon, and hope you'll take time to drop in.

The complexities of actinide and separations chemistry are reflected in the diverse subjects of the technical program. We are looking forward to valuable and informative interchanges on topics such as molten salt chemistry, plutonium processing, critical materials, metal-organic frameworks, solvent extraction, spent nuclear fuel recycling, and medical isotopes.

We encourage you to take this opportunity to learn more about your particular areas of expertise and to explore areas different than your immediate research interests. The success of this conference ultimately is because of the scientists and engineers willing to share information, ask questions, and engage actively in discussion.

We thank PNNL for providing the virtual venue and administrative support. We especially thank you, the participants in the 44th Actinide Separations Conference, for your involvement. We look forward to gathering in person next year.

Conference Chairman

Gregg Lumetta

Conference Coordinator

Becky Ford

Technical Program Chairman

Gabriel Hall

Conference Administrator

Crystal Rosales

Advisory Board Members

Candido Pereira, Argonne National Laboratory

Jack D. Law, Idaho National Laboratory

Kiel Holliday, Lawrence Livermore National Laboratory

Casey Finstad, Los Alamos National Laboratory

Laetitia H. Delmau, Oak Ridge National Laboratory

Gregg J. Lumetta, Pacific Northwest National Laboratory

Tracy Rudisill, Savannah River National Laboratory

Mark P. Jensen, Colorado School of Mines

Mike Simpson, University of Utah

Conference Schedule

Times denoted in Pacific Daylight Time

Tuesday, May 18

8:00 am	Welcome
8:10 am	Tech Session 1 Pyrochemical and Molten Salt 1
10:15 am	Break
10:30 am	Tech Session 2 Plutonium Processing
12:10 pm	Lunch break
13:30 pm	Tech Session 3 Pyrochemical and Molten Salt 2
15:35 pm	Break
15:50 pm	Tech Session 4
17:35 pm	Closing Remarks for Day 1

Wednesday, May 19

7:55 am	Announcements
8:00 am	Tech Session 5 Solvent Extraction 1
10:05 am	Break
10:20 am	Tech Session 6 Solvent Extraction 2
12:00 pm	Lunch break; ASC Board Meeting (closed session)
13:30 pm	Virtual Poster Session opens (special Zoom link)
15:00 pm	Virtual Poster Session closes

Thursday, May 20

7:55 am	Announcements
8:00 am	Tech Session 7 Pyrochemical and Molten Salt 3
9:40 am	Break
9:55 am	Tech Session 8 Medical Isotopes
12:00 pm	Lunch Break
13:30 pm	Tech Session 9
15:35 pm	Break
15:50 pm	Tech Session 10
17:05 pm	Seaborg Award and Closing Remarks
17:35 pm	ASC Conference Concludes

We look forward to seeing you online!
If you have any technical questions,
please contact Gregg Lumetta
(gregg.lumetta@pnnl.gov) or
Gabe Hall (gabriel.hall@pnnl.gov).
Logistical questions can be addressed
to Becky Ford (becky.ford@pnnl.gov)

THE GLENN T. SEABORG

Actinide Separations Award

1984	Glenn T. Seaborg, <i>University of California at Berkeley</i>
1985	Don E. Ferguson, <i>Oak Ridge National Laboratory</i>
1986	Larned B. Asprey, <i>Los Alamos National Laboratory</i>
1987	Wallace W. Schulz, <i>Westinghouse Hanford Company</i>
1988	Lawrence J. Mullins, <i>Los Alamos National Laboratory</i>
1989	Gregory R. Choppin, <i>Florida State University</i>
1990	Donald A. Orth, <i>Westinghouse Savannah River Company</i>
1991	David O. Campbell, <i>Oak Ridge National Laboratory</i>
1992	E. Philip Horwitz, <i>Argonne National Laboratory</i>
1993	Earl J. Wheelwright, <i>Pacific Northwest Laboratory</i>
1994	Leslie Burris, <i>Argonne National Laboratory</i>
1995	Robert R. Penneman, <i>Los Alamos National Laboratory</i>
1996	David G. Karraker, <i>Westinghouse Savannah River Company</i>
1997	Major C. Thompson, <i>Westinghouse Savannah River Company</i>
1998	Walter D. Bond, <i>Oak Ridge National Laboratory</i>
1999	Jack L. Ryan, <i>Pacific Northwest National Laboratory</i>
2000	John L. Swanson, <i>Pacific Northwest National Laboratory</i>
2001	George F. Vandegrift, <i>Argonne National Laboratory</i>
2002	Leonard W. Gray, <i>Lawrence Livermore National Laboratory</i>
2003	Kenneth L. Nash, <i>Argonne National Laboratory</i>
2004	Emory D. Collins, <i>Oak Ridge National Laboratory</i>
2005	Terry A. Todd, <i>Idaho National Laboratory</i>
2006	Renato Chiarizia, <i>Argonne National Laboratory</i>
2007	Leland L. Burger, <i>Pacific Northwest National Laboratory</i>
2008	Gordon D. Jarvinen, <i>Los Alamos National Laboratory</i>
2009	Raymond G. Wymer, <i>Oak Ridge National Laboratory</i>
2011	Darleane C. Hoffman, <i>University of California-Berkeley</i>
2012	Jimmy T. Bell, <i>Oak Ridge National Laboratory</i>
2013	Lane A. Bray, <i>Pacific Northwest National Laboratory</i>
2014	David T. Hobbs, <i>Savannah River National Laboratory</i>
2015	Gregg J. Lumetta, <i>Pacific Northwest National Laboratory</i>
2016	Guillermo (Bill) Del Cul, <i>Oak Ridge National Laboratory</i>
2017	Tracy Rudisill, <i>Savannah River National Laboratory</i>
2018	Jack D. Law, <i>Idaho National Laboratory</i>
2019	Bruce A. Moyer, <i>Oak Ridge National Laboratory</i>

2021 – Mark Jensen

Mark Jensen is Professor of Chemistry and the Jerry and Tina Grandey University Chair in Nuclear Science and Engineering at the Colorado School of Mines. Prior to assuming this position in 2015, he was a staff scientist in the Heavy Elements and Separations Science Group at Argonne National Laboratory.

Mark's interest in actinide science and separations started as an undergraduate student in the ACS/DOE Nuclear Chemistry Summer School, which was followed by a summer internship in the Heavy Elements Chemistry Group at Argonne trying to make a superconducting Pu compound. In 1994 he earned a Ph.D. in inorganic and nuclear chemistry at Florida State University with Greg Choppin, using solvent extraction to study the composition and stability of environmentally relevant actinide and lanthanide complexes. After completing his dissertation, Mark moved to Argonne where he was a post-doctoral research associate mentored by Phil Horwitz and Ken Nash studying a range of separation systems.



Starting as a staff scientist at Argonne in 1995, Mark's research initially focused on understanding separations of trivalent actinides from lanthanides, which led to his first presentation at an Actinide Separations Conference in 1996, *Solvent Extraction Separations of Trivalent Lanthanide and Actinide Ions Using Heterocycle Substituted Methanediphosphonic Acids*, which examined the potential for separation of the size-matched actinide and lanthanide cations Cf^{3+} and Eu^{3+} . The importance of ligand hydration in these complexes sparked an interest in how the particular complexes formed in different separation systems drive selectivity in actinide separations. This led to series of fundamental studies on actinide and lanthanide complexes of sulfur- and nitrogen-containing ligands, including foundational structural studies of Am and Cm extractant complexes and key thermodynamic studies of americium complexes with nitrogen-containing ligands. More recently, his long-standing interest in these separations resurfaced in work on modifications to the ALSEP process to enable separation of Am from Cm and the lanthanides or improve the stripping kinetics.

This interest in the complexes formed in actinide separations created opportunities with colleagues from Argonne as well as domestic and international collaborators for key experiments examining how organic phase complexes evolve with changes in the organic phase caused by phase splitting, substitution of ionic liquids for molecular diluents, sorption on chromatographic supports, or aggregation.

More recently, Mark has been examining ways to co-opt features of metal-binding proteins and peptides to enable novel approaches to separating actinide elements. His work has probed conformationally-switched actinide discrimination, attempted to engineer bacteria to take up actinides, and identified a dozen possible new plutonium-binding proteins, some of which have distinct secondary interactions with receptors suitable for separations. He has shown the conformationally-switched separation of plutonium by the protein transferrin to be delightfully intricate, requiring interactions between two proteins and multiple small molecule ligands that are mediated by ligand-ligand interactions in the outer coordination sphere of the actinide complexes to achieve separation.

Dr. Jensen is the coauthor of 80 peer-reviewed journal papers, 25 peer-reviewed conference papers, and 3 book chapters, and has served as an associate editor of the journal *Solvent Extraction and Ion Exchange* since 2002.

TUESDAY, May 18, 2021

Times denoted in Pacific Daylight Time

8:00 – 8:10

Welcoming Remarks

Jud Virden, Pacific Northwest National Laboratory

Tech Session 1 – Pyrochemical and Molten Salt 1

Session Chair: Marisa Monreal, Los Alamos National Laboratory

8:10 – 8:35

The Development of Vacuum Salt Distillation at AWE

Richard Driscoll, AWE

Dr R J P Driscoll, AWE, Aldermaston, RG7 4PR, UK.

Vacuum salt distillation (VSD) has been investigated as a method for separating metal oxides from chloride salts. It relies upon the relatively high volatility of the salt compared to the oxide: the salt distils at a raised temperature and deposits in a cooler region, leaving the oxide in the feed boat.

To determine appropriate conditions for distillation to occur, several parameters have been investigated, including temperature, pressure, active cooling and use of a baffle. Temperature and pressure were found to have the most significant impact on distillation rate, whereas the use of a baffle was found to affect how the distilled salt deposits in the cold zone.

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8:35 – 9:00

Distillation as an Industrial Separation Alternative for Actinides

Dominik Böhm, University of Szczecin

Dominik Böhm, University of Szczecin, Wielkopolska 15, 70-451, Szczecin, Poland; Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Konrad Czerski, University of Szczecin, Wielkopolska 15, 70-451, Szczecin, Poland; Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Ruth Kaesemann, Fachhochschule Dortmund – University of Applied Sciences and Arts, Sonnenstr. 96-100, 44139 Dortmund, Germany

Armin Huke, Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Jan-Christian Lewitz, Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany; LTZ-Consulting GmbH, Tharandter Str. 12, 01159 Dresden, Germany

Stephan Gottlieb, Fachhochschule Dortmund – University of Applied Sciences and Arts, Sonnenstr. 96-100, 44139 Dortmund, Germany; Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Daniel Weißbach, University of Szczecin, Wielkopolska 15, 70-451, Szczecin, Poland; Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Götz Ruprecht, Institute for Solid-State Nuclear Physics, Leistikowstr.2, 14050 Berlin, Germany

Chlorination and distillation-based separation processes for high purity separation of actinides and reprocessing of used nuclear fuel have been designed and are presented here with simulation results. This separation process also includes, as a pre-processing part, the separation of precious metals, non-chlorinated material and highly volatile components, integrated in several single-stage distillation, condensation and crystallization steps. The subsequent main distillation part, consisting of continuous and subsequent discontinuous distillation columns, allows the high purity separation of actinide chlorides. This part is about modeling, simulation and investigation of the feasibility of the distillation, focused on the separation of UCl_4 , ThCl_4 , NpCl_4 , $\text{PuCl}_3/\text{PuCl}_4$, PaCl_5 , AmCl_3 and CmCl_3 from three free chosen representative molten chloride salt mixtures. For high-purity separation in the ppm range, total reflux distillation columns with five to fourteen theoretical separation stages have been simulated, resulting in column heights from 1.2 m to 5.9 m. Second, for the future, all simulation results are needed for experimental vapor-liquid equilibrium measurements and determination of activity coefficients in a single-stage discontinuous distillation unit set up as a continuous stirred tank evaporator. For the use of appropriate activity coefficient expressions for these vapor-liquid equilibria, a custom modified UNIQUAC model has been developed and presented here, which additionally takes into account the average degree of ionization and the diffusion barriers influenced by the chlorine atoms into which the molecules/ions have to diffuse. All necessary parameters are to be determined from future experiments.

9:00 – 9:25

Purification of Actinides Via Chlorination + Volatilization

Michael Simpson, University of Utah

Parker Okabe, Matt Newton, and Michael F. Simpson, *University of Utah*;
Devin Rappleye, *Brigham Young University*

A two-step pyrochemical process has been proposed for extraction of impurities from a number of different actinides and rare earths. The first step is reaction with H_2 at temperatures up to 423 K to form particles of metal hydrides. The second step is reaction with pure Cl_2 gas at temperatures ranging from 523 to 973 K to form chlorides and simultaneously volatilize impurity metals as chlorides. In this study, cerium was used as the metal to be purified. Added contaminants included U, Fe, Al, Ga, and Ta. It was found that high grade Cl_2 was needed to achieve near complete chlorination which in turn was required to achieve high decontamination factors. A key competitive reaction is formation of metal oxides even at extremely low partial pressures of O_2 in the Cl_2 feed. Uranium decontamination was particularly challenging, probably due to the thermodynamic stability of uranium oxides compared to chlorides. A U decontamination factor of 5 was achieved at 973 K using the highest grade of Cl_2 available fed through a trap to remove O_2 . Cl_2 gas can be conserved in this process by recirculating it through the reactor rather than using a once-through flow process. Very little cerium was lost via volatilization in our experiments (0.8 to 2.8%), indicating that this process can potentially achieve percentage yield values much higher than the competing electrorefining process.

9:25 – 9:50

Options for Chlorination of U Metal to Synthesize UCl_3

David Hamilton, University of Utah

D. Ethan Hamilton, Matthew Newton, and Michael Simpson, *University of Utah*

The molten salt reactor (MSR) is a Gen IV reactor concept that relies on salt as both the fuel and coolant. In this paper, the salt being focused on is a chloride salt mixture with UCl_3 acting as the fissile component. We investigated different routes to produce UCl_3 for inclusion in an MSR fuel salt mixture, as it is not currently commercially available. The first method started with converting the uranium metal into uranium hydride powder via reaction with H_2 at 250° followed by reaction with 5% anhydrous HCl gas to form UCl_3 . The results of reacting HCl with UH_3 are reported at temperatures of 250° , 300° , and 400° . The results show that UCl_3 formation is favored at 250° . Running at higher temperatures results in significant formation of UCl_4 and possibly UO_2 . Also, running the reaction too long can result in formation of UCl_4 . The second method used was to immerse a U metal rod into the base molten mixture (NaCl - CaCl_2) with added FeCl_2 or FeCl_3 . The FeCl_x reacts with the U metal to form UCl_3 and Fe particles. The NiCl - CaCl_2 - UCl_3 salt is poured with a high temperature SmCo magnet below the crucible to keep the Fe particles from leaving the crucible. FeCl_2 was preferred for uranium chlorination as it has a lower vapor pressure than FeCl_3 . Using FeCl_2 and running at 600° limited volatilization and yielded only a 4.2% difference between measured and expected U concentration. Reacting FeCl_3 with U metal and at 850° resulted in 30% lower yield than expected, suggesting either vaporization of FeCl_3 or formation of highly volatile UCl_4 .

9:50 – 10:15

Thermophysical Properties of Liquid Chlorides from 600 – 1600 K: Melt point, Enthalpy of Fusion, and Volumetric Expansion

Matt Jackson, Los Alamos National Laboratory

S.S. Parker, A. Long, Devin Rappleye, S. Vogel, and J.M. Jackson, *Los Alamos National Laboratory: Materials Science and Technology Division*

C. Lhermitte, and M. Monreal, *Los Alamos National Laboratory: Chemistry Division*

Melt point, enthalpy of fusion, and volumetric expansion of single- and multi-component liquid chlorides $\{\text{NaCl}, \text{KCl}, \text{LiCl}, \text{MgCl}_2, \text{CaCl}_2, \text{UCl}_3\}$ were measured experimentally. These properties and materials are relevant in applications such as heat transfer, liquid nuclear fuel, and pyrochemical processing. A novel method for density measurement by neutron radiography was shown to produce high-quality data, consistent with reference literature where available, and allowed measurement of some materials for the first time. This method is especially useful in the characterization of sealed sample crucibles, given the ability of neutrons to penetrate the containment and surrounding furnace material. The results of this study are presented within the context of a comprehensive review of the available published data. The purpose of this review is to integrate measurements of the thermophysical properties of liquid chlorides into empirical descriptions of the relationships between composition, temperature, and thermophysical properties. A model for the prediction of the density of mixtures of liquid chlorides is proposed and demonstrated within a case study of the $\{\text{NaCl} + x \text{ mol\% } \text{UCl}_3\}$ system. LA-UR-21-22826

10:15 – 10:30

Break

Tech Session 2 – Plutonium Processing

Session Chair: Peter Zalupski, Idaho National Laboratory

10:30 – 10:55

Extraction of Plutonium and Neptunium using Monoamide Ligands for ^{238}Pu Production

Lætitia Delmau, Oak Ridge National Laboratory

Lætitia H. Delmau, Robert M. Wham, Luke R. Sadergaski, David W. DePaoli, and Dennis E. Benker, *Radioisotope Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN, 37831-8364, USA*
e-mail: delmaulh@ornl.gov, ph: 865 576 2093

Small-scale solvent extraction tests using neptunium and plutonium have been carried out to determine the feasibility of replacing tri-n-butyl phosphate (TBP) with monoamides during ^{238}Pu production at Oak Ridge National Laboratory. Although TBP is a good extractant for extracting plutonium and neptunium from fission products, it requires removal of phosphorus compounds from the neptunium product subsequently, commonly by large-scale anion exchange. These phosphorus compounds are commonly TBP degradation products, and their presence has been shown to create neptunium cermet issues, such as cracking upon calcination. Results obtained in glovebox tests were promising for both solvent extraction processes found as part as the ^{238}Pu campaign (i.e., plutonium-selective separation and neptunium extraction). As part of the fifth ^{238}Pu production campaign, the solvent extraction process was based on a monoamide, a phosphorus-free molecule originally developed in France in the early 1980s to replace TBP in the Plutonium Uranium Redox EXtraction (PUREX) process. The monoamide diethylhexyl butanamide (DEHBA) was used in two banks of mixer-settlers. The process allowed 2,150 g of neptunium to be separated from the fission products. The higher acidity requirement led to an increase in ^{106}Ru , ^{95}Zr , and ^{95}Nb fission products in the neptunium compared to products obtained using TBP. To alleviate these issues, a different monoamide is being considered for the upcoming campaign.

10:55 – 11:20

Oxidation of DGA resin for trivalent actinide and lanthanide recovery from Mark-18A targets

Nicholas Karay, Savannah River National Laboratory

N.S. Karay, R.A. Pierce, K.P. McCann, and N.W. Spivey, *Savannah River National Laboratory*

SRNL is implementing a separation flowsheet to recover high-value transuranic elements from irradiated Mk-18A targets. The targets contain the world's supply of unseparated Pu-244 along with hundreds of grams of heavy curium. After cladding removal, acid dissolution, and recovery of plutonium by anion exchange, the remaining trivalent actinides, lanthanides and fission products in the anion exchange raffinate can be separated from the waste using diglycolamide (DGA) resin. This presentation features the novel method used to recover these trivalent metals from DGA resin via oxidation and calcination. A series of analytical-scale, bench-scale, and pilot-scale experiments were performed to quantify the operating conditions for resin drying, acid evaporation, resin decomposition, trivalent metal oxidation, calcination, product handling, and off-gas treatment. Experimental results, engineering considerations, equipment design, and future work will be discussed.

11:20 – 11:45

Progress in Converting Research Facilities and Operations into Production Mode for Both Pu-238 and Cf-252

Emory Collins, Oak Ridge National Laboratory

E.D. Collins, R.M. Wham, J.G. Ezold, D.W. DePaoli, D.E. Benker, and L.H. Delmau, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6423

Use of existing research reactors and radiochemical processing facilities is necessary to resume production of ^{238}Pu at the multikilogram level in the United States. Oak Ridge National Laboratory is currently transitioning research and development facilities into production mode, while maintaining biannual multigram and milligram level production of heavy actinides, Am, Cm, Cf, Bk, Es, and other radioisotopes. Scaling up and increasing the efficiency and quality of chemical processing and target fabrication poses significant challenges, but progress has been made in early process development, operations, and waste minimization. Accomplishments and remaining progress needed to meet future tight schedule requirements (Fig. 1) will be described.

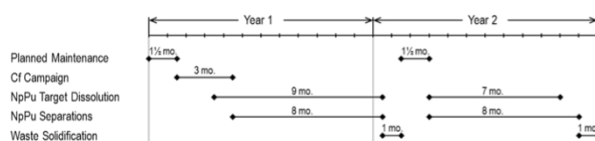


Figure 1. Projected full-scale production schedule for radiochemical processing facility.

11:45 – 12:10

Expanding Aqueous Plutonium Chemistry Capabilities at LLNL

Cyrena Parker, Lawrence Livermore National Laboratory

C.M. Parker, B.D. Smith, K.S. Holliday, J.A. McNeese, and M.C. Bronson, Lawrence Livermore National Lab, Livermore CA 94550 USA, holliday7@llnl.gov

The plutonium facility (Superblock) at LLNL has identified a need for upgrading aqueous plutonium recovery capabilities. A new lab has been renovated and three glovebox lines are being installed, which will not only meet the requirements of LLNL missions, but also provides an opportunity for the forensics community. Because aqueous operations are typically performed to meet product specifications, upsets in minor variables (e.g. acid concentration, oxidant/reductant, etc.) and their corresponding signatures are less explored. The aqueous recovery lab being installed at LLNL features mirror glovebox lines (1 and 3), which result in a high degree of flexibility, while still meeting LLNL missions. Different variables, isotopes, or process conditions can be explored in one line, while maintaining ideal conditions in another. The capabilities being stood up will be a nitric acid based purification process. Standard dissolution, anion exchange, and oxalate precipitation will be employed to recover pure plutonium product. Additionally, hydroxide precipitation will be used to ensure complete recovery of high value plutonium. Line 2, in the middle of the room will serve the other two lines. This will have a salt washing station to eliminate chlorides before introducing salt based residues into the recovery lines. Line 2 will also have solidification of waste solutions and a bag out port capable of sending this solidified waste directly into a drum. Lastly, line 2 will house the vacuum pump that supplies vacuum necessary for the liquid transfer system, which will eliminate the need to bag in and bag out liquids from the glove boxes. Here we present these capabilities in more detail and discuss their possible application to knowledge gaps in the forensics community.

12:10 – 13:30

Lunch break

Tech Session 3 – Pyrochemical and Molten Salt 2

Session Chair: Chao Zhang, Lawrence Livermore National Laboratory

13:30 – 13:55

Reduction and Recovery of Uranium Hexafluoride from 1-Methyl-1-Propylpiperidinium Bis(trifluoromethylsulfonyl)imide

Cassara Higgins, University of Nevada, Las Vegas

Cassara J. Higgins, Katherine I. Lubke, Frederic Poineau, Kenneth R. Czerwinski, David W. Hatchett, *Department of Chemistry and Biochemistry, University of Nevada, Las Vegas, 4505 S. Maryland Pkwy, Las Vegas, Nevada, 89154*

The current method for deconversion of the USA's 700,000 metric tons of depleted uranium hexafluoride (DUF_6) waste involves the mixing of volatilized DUF_6 , steam, H_2 , and N_2 to make uranium oxides and HF gas. The dissolution of solid DUF_6 at depressed temperature into room temperature ionic liquid, 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide ($[\text{MPPi}][\text{TFSI}]$) and recovery of uranium is the focus of the current studies. The spontaneous dissolution occurs with the oxidation of TFSI and reduction of UF_6 . XAFS data of the solution indicates the U(V) oxidation state. Over time a solid precipitate crashes out of solution. TGA analysis indicates that 58% of the mass is lost at temperatures exceeding 114.8°C . PXRD shows the product after TGA is UO_2 . The masses are consistent with the formation of $[\text{MPPi}]_2[\text{UF}_6]$. The addition of deionized water to the solution of UF_6 in $[\text{MPPi}][\text{TFSI}]$ results in instantaneous precipitation. PXRD and TGA data shows the precipitate to be hydrated UF_4 , which is easily converted to U_3O_8 after heating. The recovery rate of uranium is approximately 70% with the remaining uranium in the aqueous phase as UO_2^{2-} .

13:55 – 14:20

Neutron Pair Distribution Function Studies of Actinide-Molten Salts

Sven Vogel, Los Alamos National Laboratory

Sven Vogel, Marisa Monreal, Matt Jackson, *Los Alamos National Laboratory*; Boris Khaykovich, *Massachusetts Institute of Technology*

First demonstrated in the 1960's, the molten salt reactor (MSR) is an advanced nuclear reactor concept currently in development for commercial use; a leading fuel form is one in which actinide chlorides are dissolved in molten alkali/alkaline earth metal chlorides at $450\text{--}850^\circ\text{C}$. Actinide-molten chloride systems are also important to the national weapons production mission, where they have been used for decades in plutonium and high enriched uranium purification processes. Similarly, these materials are used for spent fuel reprocessing, and important step in closing the nuclear fuel cycle. Despite these applications' maturity, there are still gaps in our understanding of the complex systems that actinide-molten salts represent. We have recently embarked on a research project to address the need for an increased understanding of these systems – one that enables prediction of their behavior, a crucial capability that does not currently exist. Our approach is to integrate innovative modeling methods and empirical measurements in order to create a robust predictive capability. Understanding the local structure of actinide-molten chlorides is key to our project, and due to their high-temperature, corrosive, and radioactive nature, there are few established techniques for such studies. We have leveraged our recent experience with developing the required apparatus for using neutron radiography to measure density and viscosity of actinide-molten salts in initiating an effort to use neutron pair distribution function (nPDF) for the study of actinide-molten salt local structure. Our experiences and preliminary results will be presented. **LA-UR-21-23588**

14:20 – 14:45

Reduction of Chlorinated Cerium Back to Metallic Form using Lithium Metal

Mario Gonzalez, University of Utah

Mario Alberto Gonzalez, Sierra G. Freitas and Michael F. Simpson, *University of Utah, Department of Materials Science and Engineering*; Devin Rappleye, *Brigham Young University, Department of Chemical Engineering*; Chao Zhang, *Lawrence Livermore National Laboratory*

A metal purification process based on conversion of impure metals to chlorides via reaction with H_2 and Cl_2 was previously developed by Okabe et al. That process was successfully demonstrated by converting Ce metal and impurities to chloride form. Following conversion, impurity chlorides were volatilized, leaving behind pure $CeCl_3$. The work presented here extends that done by Okabe et al. to include reduction of the purified chloride product ($CeCl_3$) back to metallic form using reductive metals. Mixtures of $CeCl_3$ and Li were heated to $850^\circ C$ while various process parameters including crucible dimension, loading, and hold times were varied. Successful reduction of $CeCl_3$ to cerium metal using lithium metal is reported and a method for recovery of formed cerium ingots is proposed. SEM/EDS analysis of dense metal phases in the recovered ingot confirms the successful production of a dense cerium ingot. SEM/EDS analysis of recovered cerium ingots provides evidence of cerium-oxide formation during reduction when using MgO crucibles. Water is shown to be an effective rinsing media, effectively washing undesired phases in the ingot without increasing oxygen content. The physical form of added Li, crucible dimensions, and mixture hold times above $CeCl_3$ melting temperature have a significant effect on $CeCl_3$ reduction and the formation of a consolidated ingot.

14:45 – 15:10

Effects of Silicon in Pu Pyrochemical Processes

Scott Simpson, Lawrence Livermore National Laboratory

Scott Simpson, David Roberts, and Kiel Holliday, *Lawrence Livermore National Laboratory*

The flowchart of pyrochemical operations consisting of Direct Oxide Reduction (DOR), Molten Salt Extraction (MSE), and Electrowinning (ER) has been a staple for the production and purification of Pu metal for decades. Changes have been made to potentially improve the efficiency of these processes, such as using a different electrolyte medium, altering the mixing setup/speed for improved mass transfer, or varying the current and potential during ER to shorten the timeframe while maintaining a high purity standard of the Pu metal product. Common impurities present in the starting material are Gallium, Chromium, Iron, Nickel, and other elements of Stainless Steel as well as daughter products of Pu decay. Due to a difference in reduction potentials, Pu is readily separated during ER from the unwanted elements in the impure anode. An uncommon impurity of Silicon present in the starting oxide may present several new obstacles to overcome. During DOR, Silicon acts as a deterrent for the reduction of PuO_2 . It also causes a suboptimal separation of Pu during ER. Solutions to these material difficulties are currently being focused on; however, Silicon may present more chemical interactions with Pu that will need to be understood in the future.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344.

15:10 - 15:35

Novel methods in uranium metal production

Bradley Childs, Lawrence Livermore National Laboratory

Bradley C. Childs, Aiden A. Martin, Emily E. Moore, Aurélien Perron, Yaakov Idell, Tae Wook Heo, Kiel S. Holliday, Jason R. Jeffries, *Lawrence Livermore National Laboratory*

Obtaining uranium metal on a gram scale has proven to be difficult using traditional methods. This is due to the extreme thermal environments required to achieve pure material combined with the intricate chemistry involved with precursor material. Success in producing uranium metal from uranium triiodide from a tetra-arc furnace as well as a laser heating system have led to interest in nitrogen bearing uranium compounds as precursor material to produce uranium metal. The precursors of uranium mononitride as well as an ammonium uranium fluoride salt ($(\text{NH}_4)_4\text{UF}_8$) were identified as precursors that would be used. Multiple computational thermodynamic approaches were utilized to identify the extreme temperatures necessary to produce uranium metal from these products. Both precursors were irradiated by a controlled laser under various gaseous environments and in the case of uranium mononitride, yields of up to 96% of uranium metal were produced. The products were confirmed based X-ray diffraction, energy-dispersive X-ray spectroscopy, and density. Residual gas analysis was also conducted in coordination with selective laser melting to identify products lost during the melting process. Further results and characterization will be discussed.

Prepared by LLNL under Contract DE-AC52-07NA27344, LDRD Project 18-SI-001.

15:35 - 15:50

Break

Tech Session 4

Session Chair: Don Wood, Idaho National Laboratory

15:50 - 16:20

The Trouble with Thorium in the Recovery of Rare Earths from Ores

Bruce Moyer, Oak Ridge National Laboratory

Bruce A. Moyer, *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, USA*

Critical materials are so named because of their technological importance, limited ease of substitution, and vulnerability to supply disruption. Rare earths in particular are needed for essential technological applications, including powerful magnets, phosphors for lighting, catalysts, lasers, medical imaging, polishing powders, and others. Despite the existence of numerous deposits around the world, rare earths suffer limited diversification of supply and corresponding supply risk, spurring many nations to pursue new mining. The mineralogy of rare earths is quite varied, but one aspect in common is the co-mineralization of thorium and to a lesser extent uranium. The concentration of thorium in rare earth ores can range widely from less than 0.05% all the way up to 20% for monazite. Even at the lowest concentrations of thorium in ore, though, it is difficult to avoid processing streams that invoke regulatory oversight together with the associated added costs and long delays in obtaining permits. To make matters worse, the market for thorium is close to nil as a potential by-product, and so thorium in effect has negative value as an expensive radioactive mining waste. Opportunity arises, however, in that monazite, rich in rare earths, is abundant in several countries, including the United States. The question arises as to how we may unlock rare earths from the thorium trap. Some options will be discussed in the presentation.

This work is supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

16:20 - 16:45

Metal-Organic Frameworks (MOFs) for Future Nuclear Applications

Ingrid Lehman-Andino, Savannah River National Laboratory

Ingrid Lehman-Andino, Alexandra Hernandez-Jimenez, Jake W. Amoroso, and David P. DiPrete, *Savannah River National Laboratory (SRNL), Aiken SC*; Cecilia C. DiPrete, Corey R. Martinb, Natalia B. Shustovab, *Department of Chemistry and Biochemistry, University of South Carolina (USC), Columbia, SC*

Metal-organic frameworks (MOFs), have been broadly studied due to their crystallinity, porosity, tunability, and structural diversity. These characteristics are also desirable in the context of actinide/lanthanide separation and current radionuclide management and disposal to increase uranium utilization. The separation and capture of long-lived radionuclides from used-nuclear-fuel is recognized as a major technological challenge. This actinide-based MOFs research provide insight on the sequestration of fission products and actinides into a stable MOF matrix. Characterization of precursors, synthesized MOFs, and transmetallation using tetravalent transuranic species, including Pu(IV), will be discussed. Our investigation provides insight into the preparation and long-term behavior in the MOF systems, specifically their incorporation of radioactive elements that are challenging to immobilize. This research supports the expansion of actinide-based MOFs for treatment and immobilization of radioactive wastes.

16:45 - 17:10

Potential Defect Structure Effects in the Volatility Separation of Sub-picogram Quantities of Fission and Activation Products from an Irradiated UO₂ Matrix

Bruce McNamara, Pacific Northwest National Laboratory

Bruce K. McNamara, Bruce D. Pierson, Chuck Soderquist, Samuel S. Morrison, and Edgar Buck, *Pacific Northwest National Laboratory*

The use of fluorination as a rapid separation technique for quantification of trace-mass, short-lived isotopes is illustrated. Single crystal ²³⁸UO₂ was exposed to a 14 MeV neutron source to produce mixed fission and activation products. Selective removal of trace volatile fluorides from non-volatile ones produced two results of interest. A decrease in background produced better detection and quantification of select analytes across the gamma spectrum. Second, at the very low burnup condition described, the volatility behaviors of common isotopes were altered relative to their well-established behaviors in higher burnup metal and metal oxide fuels.

17:10 - 17:35

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

Jen Shafer, ARPA-E

Jenifer Shafer, *Advanced Research Projects Agency-Energy, 1000 Independence Avenue, S.W., Washington, D.C., 20585*

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

17:35 - 17:45

Closing Remarks

Gregg Lumetta, Pacific Northwest National Laboratory

WEDNESDAY, May 19, 2021

Times denoted in Pacific Daylight Time

7:55 – 8:00

Introductory Remarks/Announcements

Gregg Lumetta, Pacific Northwest National Laboratory

Tech Session 5 Solvent Extraction 1

Session Chair: Greg Horne, Idaho National Laboratory

8:00 – 8:25

Head-End Separation of Caesium from Uranium in Spent Nuclear Fuel Recycling using AMP-PAN Composites

Alistair Holdsworth, University of Manchester

Alistair F. Holdsworth, Louise S. Natrajan, Ashley J. Wooles, and Clint A. Sharrad, *University of Manchester, Oxford Road, Manchester, M13 9PL, UK, e-mail: Alistair.Holdsworth@Manchester.ac.uk*; Harry Eccles, Parthiv C. Kavi, Runjie Mao, Gary Bond, and Daniel Rowbotham, *University of Central Lancashire, Fylde Road, Preston, PR1 2HE, UK*

^{90}Sr , ^{106}Ru , ^{134}Cs , and ^{137}Cs are the main sources of radioactive decay heat in spent fuel recycling; directly removing one or more of these, upstream of solvent extraction, would mitigate most operational challenges and safety hazards which arise from solvent radiolysis, and increase capital and operational costs [1], while allowing employment of advanced waste management strategies for increased fuel cycle sustainability. We previously demonstrated that acid- and radiation-resistant [3,4] AMP-PAN (ammonium phosphomolybdate-polyacrylonitrile) composites selectively remove Cs^+ ions from acidic aqueous solutions containing excess polyvalent metal salts (e.g. Ce^{4+}) [1], via ion exchange. Herein, we present the first separation of caesium from the significant excess of uranium found in SNF dissolver liquors via the same method. Capacities, kinetics, isothermal analysis, and dynamic studies are reported. The solid- and solution-phase interactions between uranyl and phosphomolybdate ions, and the implications for advanced recycle strategies are also discussed.

References:

- [1] G. Bond et al, *J. Chromatog. Sep. Tech.*, **10**, 417 (2019)
- [2] A.F. Holdsworth et al, *Preprints* (2020, under peer review)
- [3] A.F. Holdsworth et al, *Clean Tech.*, **1**, 294 (2019)
- [4] A.F. Holdsworth et al, *Separations*, **6**, 23 (2019)

8:25 – 8:50

Demonstration of the ALSEP Process in Centrifugal Contactors using Spiked Simulated Raffinate Solution

Andreas Wilden, Forschungszentrum Jülich GmbH

Andreas Wilden, Giuseppe Modolo, Fabian Kreft, Dimitri Schneider¹ and Zaina Paparigas, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany; Gregg J. Lumetta, Pacific Northwest National Laboratory, Richland, WA 99352, USA; Artem V. Gelis, University of Nevada, Las Vegas, Las Vegas, NV 89154, USA; Jack D. Law, Idaho National Laboratory, Idaho Falls, ID 83415, USA; Andreas Geist, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

An ALSEP process demonstration test for the separation of trivalent actinides from spiked simulated high active raffinate solution was run in a 32-stage 1 cm annular centrifugal contactor setup. The solvent consisted of 0.5 mol L⁻¹ HEH[EHP] and 0.05 mol L⁻¹ T2EHDGA in *n*-dodecane. A flow sheet was calculated with the AMUSE code using single stage distribution data, taking into account the constraint of the available number of 16 centrifugal contactors. The co-extraction of Zr(IV) and Pd(II) was efficiently prevented using 0.05 mol L⁻¹ CDTA as a masking agent. Co-extracted Mo was scrubbed using 0.75 mol L⁻¹ AHA and 0.175 mol L⁻¹ ammonium citrate at pH 3. The separation of An(III) from Ln(III) was achieved using 0.015 mol L⁻¹ DTPA and 0.2 mol L⁻¹ ammonium citrate at pH 2. Finally, Ln(III) were efficiently back extracted using 0.2 mol L⁻¹ TEDGA in 0.5 mol L⁻¹ HNO₃.

A fairly clean An(III) product was obtained with a recovery of 95% Am(III) + Cm(III). The Ln(III) were efficiently stripped by the hydrophilic TEDGA complexant, but the Ln(III) product contained 5% of co-stripped An(III). The carryover of An(III) into the Ln(III) product is attributed to too few actinide stripping stages, which was constrained by the available number of contactors.

The results of the demonstration test will be presented and discussed.

8:50 – 9:15

Effects of Complexants On Solvent Extraction Kinetics In ALSEP

Madeleine Eddy, Colorado School of Mines

Madeleine Eddy, Mark Jensen, Gabriela Picayo, Colorado School of Mines; M. Alex Brown, Argonne National Laboratory

Slow kinetics of metal transfer across the liquid-liquid interface in TALSPEAK-like systems, including the ALSEP process, have impeded industrial scale implementation. Understanding the root cause of this slow transfer rate is imperative to improving next generation solvent extraction systems. By systematically studying the kinetic effects of each individual component in the ALSEP stripping step, we can develop a clearer picture of the rate limiting steps of metal transfer in each direction across the interface. The ALSEP process uses aminopolycarboxylate ligands in conjunction with carboxylic acid buffers to achieve a high aqueous phase selectivity for trivalent actinides over trivalent lanthanides. The specific identity of the aminopolycarboxylate ligand will dictate the type of metal complex being formed and in turn will affect the buffer's role in the system. In this presentation, the differences in kinetic dependence for N-(2-hydroxyethyl)ethylenediaminetetraacetic acid (HEDTA) with citrate and diethylenetriaminepentaacetic acid (DTPA) with malonate ALSEP systems will be further explored – with a focus on the relationships between complexation and kinetics. Microfluidics techniques using Nd and Am, and Nd biphasic spectroscopy have allowed us to directly monitor the metal transfer in the ALSEP stripping step in real time. Preliminary results show that dissociation of the ternary metal-HEDTA-citrate species negatively impacts the kinetics of the system. However, in the DTPA system, the equilibrium complex is a binary metal-DTPA species, whose rates of formation and dissociation have been shown to affect kinetics.

9:15 – 9:40

Novel Preorganized Ligands for Selective Actinide and Lanthanide Separation

Santa Jansone-Popova, Oak Ridge National Laboratory

Santa Jansone-Popova, *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

The multidentate ligands with preorganized binding cavities have an increased binding strength with trivalent f-block elements compared to corresponding non-preorganized counterparts. Furthermore, the innate rigidity and size of the cavity in addition to the ligand's electronic structure provide the means to control the selectivity across the trivalent f-element series by design.¹ We have shown that a phenanthroline-based tetradentate ligand bearing two nitrogen and two amide oxygen donor atoms preferentially binds americium over europium with a separation factor of >200.² However, a structurally similar ligand decorated with electron-donating (alkyl) instead of electron-withdrawing (phenyl) groups extracts both americium and europium from aqueous into non-polar medium with a comparable strength.³ In addition to these findings, the performance of water-soluble phenanthroline-based tetradentate ligands and their ability to capture and release metal ions in liquid-liquid separation setting will be presented.

[1] Healy, M.R.; Ivanov, A.S.; Karslyan, Y.; Bryantsev, V.S.; Moyer, B.A.; Jansone-Popova, S. *Chem. Eur. J.*, **2019**, 25, 6326–6331.

[2] Jansone-Popova, S.; Ivanov, A.S.; Bryantsev, V.S.; Sloop, F.V.; Custelcean, R.; Popovs, I.; Dekarske, M.; Moyer, B.A. *Inorg. Chem.*, **2017**, 56, 5911–5917.

[3] Karslyan, Y.; Sloop, F.V.; Delmau, L.H.; Moyer, B.A.; Popovs, I.; Paulenova, A.; Jansone-Popova, S. *RSC Adv.*, **2019**, 9, 26537–26541.

9:40 – 10:05

From H₅dtpa to H₄octapa: Aminopolycarboxylate Radiometal Chelators for Trivalent Actinide Coordination

Peter Zalupski, Idaho National Laboratory

P. Zalupski, T. Grimes, C. Heathman, and C. Pilgrim, *Idaho National Laboratory*; S. Jansone-Popova, and V. Bryantsev, *Oak Ridge National Laboratory*

The aminopolycarboxylate reagents, when composed of multiple aminoacetate structural building blocks, effectively sequester trivalent f-elements. This contribution highlights recent structure-function relationship studies of trivalent actinide coordination by these chelators. A balance between the soft donor character and total ligand acidity may be modulated as reflected by changes in the An³⁺/Ln³⁺ differentiation. Potentiometric, spectroscopic, and computational studies were supported with radioisotope distribution studies to describe the thermodynamic impact of the structural changes on the protonation, trivalent f-element complexation equilibria, the coordination environment, and An³⁺/Ln³⁺ separation in aqueous acidic mixtures.

10:05 – 10:20

Break

Tech Session 6 – Solvent Extraction 2

Session Chair: Santa Jansone-Popova, Oak Ridge National Laboratory

10:20 – 10:40

Radiolytic Transformation of Acetohydroxamic Acid (AHA) and 1,2-Cyclohexylenedinitrilotetraacetic Acid (CDTA) Under Single-Cycle Conditions

Gregory Horne, Idaho National Laboratory

Gregory P. Horne and Jacy K. Conrad, *Center for Radiation Chemistry Research, Idaho National Laboratory, 1955 N. Freemont Ave., Idaho Falls, 83415, USA*; Stephen P. Mezyk, *Department of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Boulevard, Long Beach California, 90840-9507, USA*; Andreas Wilden, *Forschungszentrum Jülich GmbH, Zentralinstitut für Engineering, Elektronik und Analytik (ZEA-3), 52428 Jülich, Germany*

Historically, the radiation robustness of extractant ligands and the impact of their radiolysis products have been used to evaluate the radiolytic feasibility of solvent system formulations for used nuclear fuel (UNF) reprocessing. However, other key additives (e.g., reducing and hold-back reagents) are employed by these solvent systems. These chemical species have typically been overlooked from a radiolytic perspective, and consequently little is known on how they impact process performance. Therefore, to holistically support the development of advanced, simplified, single-cycle flowsheets for UNF reprocessing, the radiation robustness of two key proposed additives – (i) the complexing reductant acetohydroxamic acid (AHA) and (ii) the hold-back reagent 1,2-cyclohexylenedinitrilotetraacetic acid (CDTA) – have been evaluated under envisioned process conditions using a combination of steady-state gamma and time-resolved pulsed electron irradiation techniques.

10:40 – 11:00

Theoretical Benchmarking of Structure and Selectivity in Ln(III)/An(III) Separation with Phosphinic Acid Ligands

Robert Chapleski, Oak Ridge National Laboratory

Robert C. Chapleski, Jr., Alexander S. Ivanov, and Vyacheslav S. Bryantsev, *Chemical Sciences Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 27831, USA*; Kirk A. Peterson, *Department of Chemistry, Washington State University, Pullman, WA 99164, USA*

Phosphinic acid ligands have shown great experimental and practical promise in the separation of trivalent lanthanides from actinides in spent nuclear fuels. However, theoretical results show method-dependent discrepancies in terms of metal–ligand complex bonding distances and selectivity. To remedy this, we employ several computational methods to investigate a series of $M(H_2PX_2)_3$ complexes, where $M=Am$ or Eu , and $X=O, S, Se, \text{ or } Te$. After first establishing a set of post-Hartree Fock results as benchmarks, we evaluate a set of density functionals and electronic treatments for their accuracy in terms of complex structure and separation reaction energy. Of the functionals tested, we find that those with a high admixture of Hartree–Fock exchange best reproduce benchmark results, showing longer $Am-X$ distances than $Eu-X$, along with increasing selectivity moving down the chalcogen group, when valence f electrons are treated explicitly. Results of natural bonding order analyses provide insight into metal–ligand interactions contributing to differences in selectivity. We anticipate that this work will provide recommendations for more accurate theoretical descriptions of $Ln(III)/An(III)$ separations with phosphinic acid ligands in the future.

This work was supported by the Nuclear Technology Research and Development Program, Office of Nuclear Energy, US Department of Energy.

11:00 – 11:20

Neptunium Speciation and Determination of its Total Concentration in Dissolved Fuel Simulant Solutions by Spectrophotometry

Sergey Sinkov, Pacific Northwest National Laboratory

Sergey I. Sinkov, Gabriel B. Hall, Forrest D. Heller, and Gregg J. Lumetta, *Radiochemical Processing Laboratory, Pacific Northwest National Laboratory, Richland, WA*

A new approach for spectrophotometric determination of neptunium (Np) and plutonium (Pu) in simulated dissolved nuclear fuel solutions has been developed. It is based on a simple chemical modification of the dissolved fuel solution sample by introducing ascorbic acid at molar ratio of approximately 1.5 to 1 with respect to sum of Np and Pu concentrations to convert these redox sensitive transuranic metal cations to tetra- and trivalent states respectively. Once chemical reduction is achieved and the optical absorbance spectrum is recorded, Np is quantified by measuring its top of the peak intensity with maximum at 700 nm (using a 688 to 720 nm spectral window), where Pu(III) has low molar absorptivity. To perform a proper subtraction of the spectral contribution from non-extractable fission and corrosion products, the spectrum of the aqueous raffinate obtained from tri-butyl phosphate based extraction is taken and processed in the same manner. Plutonium in the reduced feed is quantified via top of the peak intensity analysis of its characteristic optical absorbance band at 665 nm using a narrow spectral window limited by 661.3 and 665.9 nm wavelength positions. For these conditions, optical contribution from fission and corrosion products can be eliminated at the data processing step and knowledge of U-, Np- and Pu-depleted aqueous raffinate spectrum becomes unnecessary. For Np determination in the dissolved fuel solution, an alternative spectrophotometric approach is also proposed and tested. It relies on the disproportionation reaction of Pu(IV) after reducing the acidity to low decimolar range by dilution of the feed with water. Plutonium(III) generated by disproportionation of Pu(IV) reduces Np(V) to Np(IV) and total Np is quantified as Np(IV) via its major absorbance band at 981.6 nm. Good correspondence is found between Np and Pu concentrations in the dissolved fuel solution determined spectrophotometrically and by ICP-MS analysis for these transuranic elements.

11:20 – 11:40

Temperature Effects on the Absorption Spectrum of Neptunium(V) in Nitric Acid

Luke Sadergaski, Oak Ridge National Laboratory

Luke R. Sadergaski, Kristian G. Myhre, Gretchen K. Toney, David W. DePaoli, and Lætitia H. Delmau, *Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN, 37830 USA*

The visible/near infrared electronic absorption spectrum of neptunium(V) is comprised of numerous f–f electronic transitions with dynamic temperature dependencies that are not well documented in the literature. Quantifying the concentration of neptunium species in aqueous solutions using spectrophotometry is challenging because of the simultaneous existence in multiple oxidation states, high extinction coefficients, susceptibility to hydrolysis, and the propensity to coordinate with a wide range of ligands. Another challenge that has often been overlooked is the effect of temperature on the absorption spectrum of the pentavalent neptunyl dioxocation (NpO_2^+) in nitric acid (HNO_3), which is the most prevalent species in HNO_3 solutions at concentrations $<5 \text{ M HNO}_3$. Here we present neptunium(V) spectral signatures in 1 M HNO_3 as a function of temperature ($10\text{--}80^\circ\text{C}$) and over a wide range of total neptunium concentration ($1 \text{ mM--}1000 \text{ mM}$). Changes in band intensity, peak positions, and overall shape were characterized using multivariate data analysis. Key findings from 2D correlation spectroscopy and multivariate curve resolution analyses will be discussed.

11:40 – 12:00

Vibrational Sum Frequency Generation Spectroscopy and its Application in Liquid-Liquid Interfacial Chemistry

Zheming Wang, Pacific Northwest National Laboratory

Zheming Wang, Christina A. Louie, and Sue B. Cark, *Pacific Northwest National Laboratory, Richland, WA 99352, Washington State University, Pullman, WA 99164; Washington State University, Pullman, WA 99164*

The speciation and molecular orientations at the interfaces of liquid-liquid and liquid-solid play critical roles in actinide separation processes from solvent extraction to ion exchange to various precipitation and dissolution. 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. Until very recently, few techniques allowed detailed investigation of interactions occurring in the boundary layers between solvents. Recent advances in ultrafast laser and nonlinear spectroscopy techniques, particularly vibrational sum frequency generation spectroscopy (VSFG) makes it possible to probe the speciation and structures of molecules at interfaces with sub-monolayer sensitivity. In this presentation, the current state of the application of VSFG at liquid-liquid interfacial chemistry will be reviewed and examples of the current work on europium (III)-acetylacetonate ($\text{Eu}(\text{AcAc})_3$) at air/water interface and dibutyl-phosphate at liquid-liquid interface will be presented. 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 VSFG.

12:00 – 13:30

Lunch break – ASC Board Meeting (closed session)

13:30 – 15:00

Virtual Poster Session special Zoom link <https://pnnl.zoomgov.com/j/1610892211>
See page 34 for the poster abstracts

ZOOM BREAKOUT ROOM	NAME	AFFILIATION	ABSTRACT TITLE
1	John Ahern	LANL	Rapid Actinide Identification via Luminescence (RAIL) Sensor
2	Gabrielle Ambrosio	LANL	AQCL Production FY 20 and FY21
3	Daria Boglajenko	PNNL	Laboratory-scale X-ray Absorption Spectroscopy for in situ Molten Salt Study
4	Hannah Hallikainen	PNNL	Performance Characterization of a Geiger-Müller Dose Calibrator System
5	Connor Hilton	PNNL	Long-lived actinide measurement of NIST SRM 4350B: Columbia River Sediment
6	Eric Hoar	SRNL	The PreCalc Project: Dynamic Simulation of Plutonium Processing
7	Catherine Riddle	INL	Colorimetric Detection of Actinides (CoDeAc)
8	Ziheng Shen	GIT	Aging mechanisms of silver-functionalized silica aerogel in NO ₂ -containing gas streams
9	Sergey Sinkov	PNNL	Alpha-Induced Degradation of Pu(III) and Pu(IV) Oxalates Probed by Reflectance and Absorbance Spectroscopy
10	Miguel Toro-González	ORNL	Evaluating Polymeric Nanoparticles for Actinide Delivery Using Surrogates

THURSDAY, May 20, 2021

Times denoted in Pacific Daylight Time

7:55 – 8:00

Introductory Remarks/Announcements

Gregg Lumetta, Pacific Northwest National Laboratory

Tech Session 7 - Pyrochemical and Molten Salt 3

Session Chair: Matt Jackson, Los Alamos National Laboratory

8:00 – 8:25

Progress Towards the Electrolytic Reduction of Plutonium Oxide Using a Stirred Cell

Alistair Parkes, AWE

Alistair M Parkes, and Steven M Wilcock, AWE, Aldermaston, Reading, RG7 4PR, U.K

Plutonium is often stored in its less reactive oxide form. In order to close the recycle loop for metallic plutonium operations conversion from the oxide is required. Typically, this reduction is carried out via reaction with calcium in a process referred to as Direct Oxide Reduction (DOR). As with all operations involving plutonium, there are significant drawbacks to undertaking DOR, principal amongst them is the relatively large volume of waste generated during the reduction. Electrochemical Oxide Reduction (EOR) has been proven to be effective at reducing actinide oxides, normally in a configuration with the actinide oxide contained within a basket at the cathode of an electrolytic cell, and offers the potential for decreased waste production.

Investigations are continuing into a stirred oxide bed method to the electrochemical reduction of plutonium oxide in calcium chloride salt. Two approaches are being studied in which the oxide to be reduced is dispersed in the molten salt within a large crucible containing a tungsten cathode and graphite anode. Stirring generates enough turbulence to move the suspended powder into contact with the cathode where the metal oxide is reduced. Alternatively, at higher potentials, dissolved calcium oxide is reduced to calcium which then reacts with suspended oxide particles.

Progress with the two configurations of interest will be described along with data from an initial trial using plutonium dioxide.

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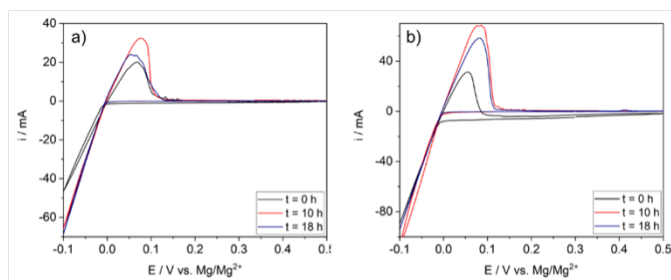
Developing robust reference electrode chemistry for electrochemical corrosion experiments in actinide bearing molten salts

Charles Lhermitte, Los Alamos National Laboratory

Charles R. Lhermitte, S. Scott Parker, J. Matt Jackson, Marisa J. Monreal, *Los Alamos National Laboratory.*

Understanding the redox behavior of actinide species, is key to the development of improved materials for molten salt reactors, as well as for developing new, more efficient techniques for increasing the efficiency of pyrochemical processes. Electrochemical methods play an important role in studying molten salt chemistry, and they provide a powerful means of studying actinides in these systems. One key challenge with performing electrochemistry in molten salts is the lack of a good reference electrode. The most commonly used reference electrodes to date are either a sealed Ag/AgCl electrode, or a Pt wire pseudo-reference. However, Ag/AgCl electrodes are challenging to prepare since they require complicated machining, and Pt pseudo-references suffer from significant potential drift since their potential is determined by their surrounding chemical environment, which can change during the course of an electrochemical experiment.

In this report, we describe the use of the $\text{Mg}^{2+}/0$ couple as a reference in molten MgCl_2 -NaCl. We demonstrate that not only is reference straightforward to prepare and to use, but that the $\text{Mg}^{2+}/0$ redox couple provides a robust and reliable reference potential over a range of melt temperatures (500–675°C). Using cyclic voltammetry (Fig. 1), we show that the Mg reference potential is extremely stable, remaining unchanged over an 18h time period. Finally, we show that this reference chemistry can even be used at high (> 650°C) temperatures, by constructing a molten magnesium reference electrode.



Cyclic voltammograms of a tungsten electrode collected at various times in molten MgCl_2 -NaCl. The reference electrode used was a Mg rod. Scan rate: 100 mV/s.

8:50 - 9:15

High Throughput Electrorefining at Lawrence Livermore National Laboratory

Chao Zhang, Lawrence Livermore National Laboratory

Chao Zhang, David Roberts, Scott Simpson, Kevin Silveira, Jeffrey Ramos, and Kiel Holliday, *Lawrence Livermore National Laboratory*

Electrorefining (ER) has been employed in LLNL for metal purification over several decades. This work includes the redesigning of the ER head and proposals to improve ER efficacy (increase ER current) in light of currently available technologies. The intention of the redesigned ER head is to decrease equipment malfunction to prevent any down time during an electrorefining run. The ER head modifications include incorporating a vertical translator, a slipring, a two-armed cathode ring, and a telescopic shaft to the ER head to replace previous used parts. Improvements to the current ER cell are proposed based on fundamental electrochemistry principles. The improvements are aimed to achieve better mass transports and larger anode surface area through better stirring of the molten metal and salts. Mass transport of metal ions could be improved by increased convection and decreased diffusion layer. A larger anode metal pool vortex resulted from superior stirring could increase anode surface area. These improvements are envisioned to improve efficiency through greater mass transport to shorten run time and more stable equipment that minimizes downtime.

9:15 - 9:40

Electrochemical studies of uranium redox behaviors at phosphate modified electrodes: A prelude to americium redox activity

Xiangyang Hou, Florida International University

Xiangyang Hou, Jeffrey R. McLachlan, Matthew V. Sheridan, and Christopher J. Dares,*
Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199;
Travis S. Grimes, *Idaho National Laboratory, Idaho Falls, ID 83415*

Precise oxidation state control is a challenge in nuclear material reprocessing given the oxidation states of the actinides involved (U, Np, Pu, and Am) range from +3 to +6. Electrochemistry can be used to control oxidation states. We have developed a Ligand Modified Electrode (LME) approach to functionalize the surface towards actinide redox processes. These surface-bound ligands alter the reduction potentials and/or participate in redox events with coordinated metal ions. Phosphate ligands can stabilize high valent metal ions, which is of interest for LMEs to oxidize Am^{3+} to AmO_2^{2+} , where it can be concurrently separated with UO_2^{2+} , NpO_2^{2+} , and PuO_2^{2+} , thereby closing the nuclear fuel cycle using a single-cycle separation process. Am is the lone holdout in this regard. Electrochemical studies involving U (as a surrogate for Am) at phosphate functionalized electrodes will be presented. Both the 1-electron reduction to UO_2^+ **and** the catalyzed 2-electron reduction to U(IV) (as both U^{4+} and UO_2) are observed at -0.2 V. Product composition can be controlled by adjusting the proton concentration. The ligand plays an active role in catalyzing the proton-coupled 2-electron reduction of UO_2^{2+} to U^{4+} . This suggests that the oxidation of Am^{3+} will also include a catalyzed 2-electron oxidation from Am^{4+} to $\text{AmO}_{2.2}^{+}$, ultimately resulting in minimal generation of AmO_2^+ , while the oxidation of Am^{3+} to Am^{4+} will be rate limiting. These expectations are consistent with our results where our phosphate LME quantitatively generates AmO_2^{2+} from Am^{3+} at potentials as low as 1.9 V.

9:40 - 9:55

Break

Tech Session 8 - Medical Isotopes

Session Chair: Gabriel Hall, Pacific Northwest National Laboratory

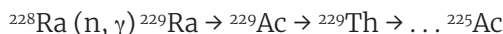
9:55 – 10:20

Evaluation of Molecular Recognition Technology Resin for the Isolation of Radium from Natural Thorium Nitrate Concentrates

Matthew O'Hara, Pacific Northwest National Laboratory

Matthew J. O'Hara, and Hannah R. Hallikainen, *Pacific Northwest National Laboratory, Richland, WA*; Saleem S. Drera, Andrew G. Edwards, and Nicholas J. Veith, *RadTran LLC, Centennial, CO*

Enormous stockpiles of natural thorium exist around the globe, much of it created as a byproduct of rare earth element ore processing operations. Much of this thorium exists in the liquid form as thorium nitrate solution. These thorium solutions approach secular equilibrium with progeny after ~3 decades. The progeny includes two radium isotopes that are recognized to be of value in targeted alpha therapy: ^{228}Ra ($t_{1/2} = 5.75$ y) and ^{224}Ra ($t_{1/2} = 3.63$ d). The former has been proposed as a viable source of ^{225}Ac via the reaction below. The latter is employed as a source nuclide in the $^{212}\text{Pb}/^{212}\text{Bi}$ generator.



A recent collaboration between RadTran and PNNL has focused on a column-based method to isolate Ra from thorium nitrate solution approaching 2 Molar concentration. Under evaluation is a molecular recognition technology (MRT) resin with high Ra selectivity. We will present batch contact and flow-based performance data, as well as empirically-driven computational modeling of Ra/MRT interaction.

10:20 – 10:40

Development of an In-Line Multi-Column Process for the Isolation of ^{224}Ra from ^{228}Th for Use in $^{212}\text{Pb}/^{212}\text{Bi}$ Generators

Lucas Boron-Brenner, Pacific Northwest National Laboratory

L.P. Boron-Brenner, I.S. Miller, J.C. Johnson, D.M. Cain, and M.J. O'Hara, *Pacific Northwest National Laboratory, Richland, WA*

Use of the *in vivo* generator ^{212}Pb ($t_{1/2} = 10.6$ h), which decays to the short lived α -emitter ^{212}Bi ($t_{1/2} = 61$ min), has become an increasingly valued approach to receptor targeted α therapy (TAT). The production of ^{212}Pb can be performed through separation from a long-lived parent in the ^{232}Th ($t_{1/2} = 1.41\text{E}+10$ y) decay chain such as ^{228}Th ($t_{1/2} = 1.91$ y). Generator columns consisting of resin-bound ^{228}Th could be utilized as a direct source of ^{212}Pb , but generator failure by radiolytic damage to the resin over time would result. ^{224}Ra ($t_{1/2} = 3.66$ d), the direct daughter of ^{228}Th , has been shown to be viable alternative as a generator column for the supply of ^{212}Pb . However, due to the significantly shorter half-life, frequent replacement is required in a clinical setting.

For the purpose of producing ^{224}Ra bound generator columns, a rapid (<1 hour) in-line multi-column process was developed to isolate ingrown ^{224}Ra from ^{228}Th and its other progeny. In this presentation, we will demonstrate the following: ^{224}Ra yield is near-quantitative; the ^{224}Ra product has a high decontamination from ^{228}Th and other progeny; near-quantitative recovery of the valuable ^{228}Th stock is possible; waste production is minimal; and dose to the operator is minimal.

10:40 – 11:00

Production, Purification, and Recovery of At-211 at Texas A&M University

Johnathan Burns, Texas A&M University

Jonathan D. Burns, Nuclear Engineering and Science Center, Texas A&M University, College Station, TX 77843, USA; Evgeny E. Tereshatov, Lauren A. McIntosh, Gabriel C. Tabacaru, and Amy L. Vonder Haar, Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA; Kylie N. Lofton, Laura A. McCann, Steven J. Schultz, and Sherry J. Yennello, Cyclotron Institute, Texas A&M University, College Station, TX 77843, USA; Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

Interest in α -emitting radionuclides for applications in Targeted Alpha Therapy (TAT) continues to grow.¹ With its relatively short half-life (~ 7.2 h) and its rather simple decay scheme, At 211 is one of the most advantageous nuclides for this purpose. However, study of astatine chemistry has been limited due to the practical difficulties of having no long-lived isotopes to investigate. The K150 cyclotron at Texas A&M is capable of producing α -particle beams necessary to make At 211 via the Bi 209 ($\alpha, 2n$) reaction and is continuing an effort to establish the capability to routinely produce At 211. The availability of the short-lived species at Texas A&M provides an avenue to achieve systematic analysis of its chemical properties. The aim of this investigation is to perform a fast and efficient recovery of At 211 from a bombarded Bi target. Recent findings from At 211 extraction into a variety of solvents have resulted in new insights into the fundamental properties of At 211. From this enhanced understanding, the behavior of At 211 can be better controlled. This has led to the development of a separation system, based on extraction chromatography, which results in a high yield, high purity At 211 product. Details of the liquid-liquid extraction of At-211 and the separation system being developed will be discussed, with specific interest given to determining the speciation and mechanism of extraction.

(1) Makvandi, M.; Dupis, E.; Engle, J.W.; Nortier, F.M.; Fassbender, M.E.; Simon, S.; Birnbaum, E.R.; Atcher, R.W.; John, K.D.; Rixe, O.; Norenberg, J.P. *Target. Oncol.* **2018**, 13 (2), 189.

11:00 – 11:20

Automating High Pressure Ion Chromatography (HPIC) for Separations Chemistry Use case: Ac-225 separation from Radiolanthanides

Sandra Davern, Oak Ridge National Laboratory

Sandra M. Davern, Kevin Gaddis, Miguel Toro-González, Roy Copping, and Dan Stracener, Radioisotope Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

High pressure ion chromatography is an effective technique for the separation of ionic species, including radioactive lanthanides and actinides. This instrument-driven methodology offers the opportunity to expand automation, increase sample throughput, and minimize waste. Employing remote operation and automation also allows for more effective chromatographic separation and repeatability in sample processing. Production of ²²⁵Ac from accelerator-irradiated thorium targets requires multiple separations chromatography columns performed within hot cells. We have previously established an effective high pressure ion chromatography method to separate ²²⁵Ac from radiolanthanides commonly present from the irradiation of thorium targets. These tracer studies indicate that ²²⁵Ac can be purified of contaminating lanthanides and complexing organic molecules. To further the usefulness of this separation for production, a prototype instrument suitable for a hot cell environment was designed, created, and tested for remote operations. Advances in separations related to the automation of hot cell operations is important to advance research, development, and production of radioisotopes for medicine, industry, and basic research.

11:20 – 11:40

Process for the recovery of Mo-99 from the Accelerator-induced Fission of Uranium

Anna Servis, Argonne National Laboratory

Anna G. Servis, M. Alex Brown, and Peter Tkac, *Argonne National Laboratory*

Technetium-99m (Tc-99m) is the most used diagnostic imaging agent in nuclear medicine. The majority of the world's Tc-99m is generated by the decay of molybdenum-99 (Mo-99), usually produced by uranium-235 fission in a nuclear reactor. One proposed alternative approach to manufacturing Mo-99 involves inducing fission in natural or low enriched uranium targets with an electron accelerator. A new separation process for the recovery of Mo-99 from these irradiated uranium targets has been developed at Argonne National Laboratory. Following dissolution of the target in nitric acid, uranium is recovered for reuse by extraction with tributyl phosphate (TBP). The subsequent isolation of Mo-99 from the remaining fission product mixture is achieved by extraction with di-2-ethyl hexyl phosphoric acid (HDEHP) and stripping with acetohydroxamic acid (AHA). A strong base anion exchange resin column is used as a final purification and concentration step.

11:40 – 12:00

Distribution of U, Pu and Np in a Mo-99 Recovery Process using Sachtopore NP (titania based) Absorbent Material

Edward Kyser, Savannah River National Laboratory

Edward Kyser, *Savannah River National Laboratory*

Savannah River National Laboratory (SRNL) with support from DOE's National Nuclear Security Administration Office of Material Management and Minimization (M3) is helping SHINE Medical Technologies in developing domestic production of Mo-99. SHINE is planning to produce Mo-99 by fission of low enriched uranium-235 (LEU) in a subcritical aqueous solution using accelerator-based neutron generation. The dilute sulfate LEU solution is processed through a titania-based column to recover Mo while the remaining LEU solution is available for recycle. SRNL is providing technical support for the waste form development for the SHINE Mo-99 production process. Current efforts are focused on the retention of U, Pu and Np on the titania column and the amounts to be expected in the waste streams from column washing. A column run with U, Pu, Np and various fission product simulants was performed. Results from gamma analysis of the titania column and ICPMS analyses of the solutions will be presented.

12:00 – 13:30

Lunch break

Tech Session 9

Session Chair: Ingrid Lehman-Andino, Savannah River National Laboratory

13:30 - 13:55

Niowave's Closed Loop Fuel Cycle for Domestic Production of Mo-99 and Other Isotopes

Nathan Johnson, Niowave, Inc.

Nathan Johnson, Terry Grimm, Mitchell Hemesath, Christine Krizmanich, Nicolas Luciani, William Peters, Kristin Shannon, Milan Stika, and Robert Wahlen, *Niowave, Inc., Lansing, MI*, johnson@niowaveinc.com; Allison Cicero, and Artem Gelis, *University of Nevada Las Vegas, Las Vegas, NV*; M. Alex Brown, Peter Kozak, and Peter Tkac, *Argonne National Lab, Lemont, IL*; Eddie Kyser, Mathew Mills, and Tracy Rudisill, *Savannah River National Lab., Aiken, SC*

Niowave is a medical radioisotope company that aims to supply a domestic source of Mo-99 and other therapeutic alpha and beta emitters from uranium and radium. This talk showcases the recent progress across Niowave's closed loop LEU fuel cycle and radiochemistry process for extracting accelerator produced Mo-99 and other isotopes from irradiated LEU. After a seven-day irradiation, LEU fuel is removed from the subcritical reactor and allowed to cool for one day. The LEU fuel is then dissolved while fission gases are captured for sale and abatement. Fission products are then separated from the LEU using a modified UREX process. Mo-99 is extracted from the fission product stream using a novel liquid-liquid extraction process. The Mo-99 is then purified using column chromatography to produce high specific activity Mo-99 that is compatible with existing Tc-99m generators. Additional therapeutic fission products (e.g. I-131, Xe-133, Sr-89, Y-91, Ce-141, Nd-147, Pm-149) are extracted and purified from the fission product stream as well. To close the fuel cycle, the LEU is precipitated and calcined to form an oxide powder. New targets are pressed from this powder and loaded back into the target assembly for further irradiation. All these processes have been demonstrated at Niowave's facilities on a laboratory scale. These radiochemistry processes are now being scaled up to process 10 kgU/week and produce 100 mCi/week of Mo-99 and other isotopes by the end of 2021.

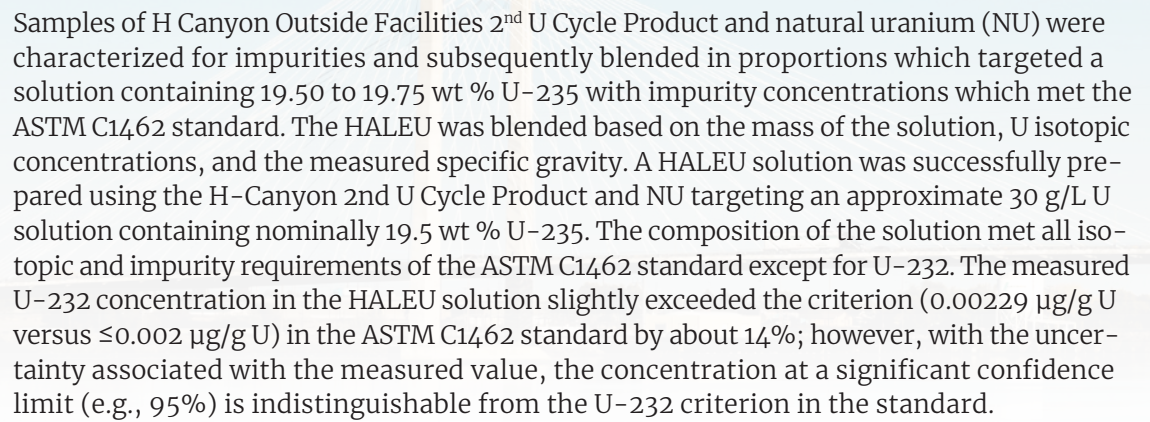
13:55 - 14:20

Demonstration of the Blending of SRS 2nd U Cycle Product with Natural U to Produce a HALEU Solution

Gene Daniel, Savannah River National Laboratory

W.E. Daniel, T.S. Rudisill, *Savannah River National Laboratory*

Continued growth in the demand for high assay low enriched uranium (HALEU) is projected to support the conversion of US high performance research reactors from high to low enrichment and the development and deployment of a new generation of advanced reactors. Current options to meet the growing US need for HALEU include (1) blend-down of excess highly enriched uranium (HEU) from the nuclear weapons program, (2) blend-down of HEU metal from other stockpiles, or (3) recycle of irradiated HEU recovered from spent nuclear fuel (SNF). The recycle of HEU from SNF has been performed at the Savannah River Site (SRS) H Canyon facility for nearly two decades to produce 4.95 wt % U-235 for sale and subsequent use in fuel for Tennessee Valley Authority (TVA) reactors. The SRS H-Canyon facilities could potentially use available 2nd U Cycle product and natural uranium (NU) to produce HALEU that meets the ASTM C1462 specification. The objective of this work was to show that requirements in the ASTM C1462 standard for U metal enriched between 15 and 20% could be met.



Samples of H Canyon Outside Facilities 2nd U Cycle Product and natural uranium (NU) were characterized for impurities and subsequently blended in proportions which targeted a solution containing 19.50 to 19.75 wt % U-235 with impurity concentrations which met the ASTM C1462 standard. The HALEU was blended based on the mass of the solution, U isotopic concentrations, and the measured specific gravity. A HALEU solution was successfully prepared using the H-Canyon 2nd U Cycle Product and NU targeting an approximate 30 g/L U solution containing nominally 19.5 wt % U-235. The composition of the solution met all isotopic and impurity requirements of the ASTM C1462 standard except for U-232. The measured U-232 concentration in the HALEU solution slightly exceeded the criterion (0.00229 µg/g U versus ≤0.002 µg/g U) in the ASTM C1462 standard by about 14%; however, with the uncertainty associated with the measured value, the concentration at a significant confidence limit (e.g., 95%) is indistinguishable from the U-232 criterion in the standard.

14:20 - 14:45

Flowsheet Development for the Dissolution of Aluminum-clad Research Reactor Fuels in the Savannah River Site H Canyon facility

Tracy Rudisill, Savannah River National Laboratory

T.S. Rudisill, W.E. Daniel, and P.M. Almond, *Savannah River National Laboratory*

Spent nuclear fuel (SNF) dissolution flowsheets were developed at the Savannah River National Laboratory for the H-Canyon facility using both unirradiated U-Al and Al alloys as surrogates for irradiated foreign and domestic research reactor fuels. Laboratory experiments demonstrated that the dissolution of Al 1100 provides a bounding estimate for the generation of H₂ compared to the dissolution of U Al alloys or Al-6061. Aluminum-1100 is generally used to fabricate the fissionable component of research reactor fuels and Al-6061 is used for the cladding and structural components. On-line Raman spectroscopy and mass spectrometry were used to continuously monitor offgas during the laboratory experiments. The H₂ generation rate during SNF dissolution was controlled by adjusting the Hg catalyst concentration and the timing of the Hg addition, limiting the total surface area of the fuel exposed to the dissolving solution, and maintaining a continuous purge of the dissolver to dilute the H₂ concentration below the calculated lower flammability limit (LFL). Offgas generation rates from the laboratory experiments were scaled to the H Canyon dissolvers based on the surface area of the dissolved Al alloys and the bounding surface area of the SNF. Flowsheet guidance for the number of fuel bundles which can be charged to a dissolver as a function of the Al concentration in the solution was provided to ensure that the H₂ concentration does not exceed 60% of the LFL during the dissolution.

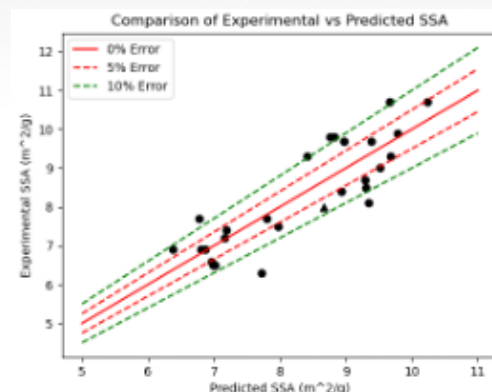
14:45 - 15:10

Advanced Correlations in PuO₂ Processing Data

Eric Hoar, Savannah River National Laboratory

Eric Hoar, Thomas Shehee, and Lindsay E. Roy, *Savannah River National Laboratory*

Decades of work have been devoted to process synthesis and control of PuO₂ due to its importance in a variety of applications from environmental transport and fate, production of nuclear fuels, nuclear forensic analyses, stockpile stewardship, and storage of nuclear wastes. A number of processing conditions have been identified to control the final product properties, including specific surface area (SSA), residual carbon content, absorption of volatile species, morphology, and particle size (PS) distribution. Our interest in this area lies in development of a multi-scale, multi-physics model at a production-level facility to provide a basis for the prediction of specific properties. In order to better correlate process data at the production scale, a simple multivariate model was developed to predict the SSA and PS properties based on a number of production parameters. This model is meant to provide proof of concept for which a more complex data-driven model can be created.



15:10 - 15:35

Demonstrating the Pyrochemical Flowsheet at 200 g

Kiel Holliday, Lawrence Livermore National Laboratory

D. Roberts, D. Rappleye*, J. McNeese, K. Kondrat, and K. Holliday, *Lawrence Livermore National Laboratory*

*D. Rappleye is now at Brigham Young University

The Pu facility at Lawrence Livermore National Laboratory (LLNL) has demonstrated plutonium purification and manufacture at the 200 g scale. While many chemical processes are easily scaled up or down to fit the quantity desired, electrorefining Pu metal is most efficient with batch sizes on the kilogram scale, which is not always ideal outside of production. In scaling down from kilograms to 200 grams, there is a significant volume reduction due to plutonium's density and potential for greater material losses. This reduced volume required a complete overhaul of the electrochemical cell to accommodate the smaller quantity of material while also maintaining containment and effectiveness for the process. To address these challenges, the stirrer was redesigned, the anode serving as the spine of the stirrer, and the size of the cathode and crucible reduced. An initial charge of 200-g of plutonium was prepared for electrorefining by performing molten salt extraction and anode casting. The 187-g casted anode was effectively electrorefined to a 146-g partial ring of Pu metal, an efficiency comparable to the kilogram scale. This material was then alloyed, cast, rolled and annealed to produce homogenous delta phase plutonium for future science experiments. This initial process can be improved upon by combining the molten salt extraction and anode casting steps as well as optimizing the annealing. This reduced scale process provides a key capability and enhanced flexibility in meeting science requirements to support current and future LLNL missions.

15:35 - 15:50

Break

Tech Session 10

Session Chair: Mark Jensen, Colorado School of Mines

15:50 - 16:15

Pyrochemical Operations Overview of SRPPF

Rebecca Carter, Savannah River National Laboratory

Rebecca Carter, Michael DeVore, Kevin McCann, William Holbrook, and Nicholas Bridges, Savannah River National Laboratory

Savannah River National Laboratory (SRNL) is supporting the development of a plutonium pit process line at the proposed Savannah River Plutonium Processing Facility (SRPPF). High purity plutonium metal will be produced through pyrochemical processing methods, including molten salt extraction (MSE), electrorefining (ER), salt scrub (SS), and multicycle direct oxide reduction (MCDOR). The pyrochemical processes are well established from past weapon production efforts at Los Alamos National Laboratory and Rocky Flats Plant. However, there are many difficulties associated with implementation into new nuclear facilities such as designing new equipment. In order to address those challenges, the pyrochemical team at SRNL will conduct surrogate testing at the engineering development laboratory on the next generation pyrochemical processing system. This next generation pyrochemical system is being developed and built for testing starting in September 2021 and will feature significant automation of pyroprocessing operations. The automation features will be incorporated seamlessly with manual operations to maximize efficiency of each unit operation. Early research, using non-radioactive surrogates, will focus on variables related to each pyrochemical process (i.e., operation temperatures, mixing parameters, salt to metal ratios, and material purity).

16:15 - 16:40

Development of Method for Looking at PuO₂ on Benchtop SEM

Forrest Heller, Pacific Northwest National Laboratory

Forrest D. Heller, Ian J. Schwerdt, Jordan F. Corbey, Dallas D. Reilly, Jason M. Lonergan, Matthew K. Edwards, Kyle J. Maloy, and David Meier, Pacific Northwest National Laboratory, P.O. Box 999 Battelle Blvd, Richland, WA United States

The presence of plutonium oxide (PuO₂) powders are most commonly associated with long-term storage, although this material can also be fluorinated and reduced to its metal form. Depending on the processing chemistries, the morphologies of PuO₂ can vary in size, shape, and particle size distribution. To study this phenomena, the Department of Homeland Security's (DHS) National Technical Nuclear Forensics Center (NTNFC) tasked Pacific Northwest National Laboratory (PNNL) to build an R&D platform to study plutonium oxide powders. PNNL generated PuO₂ using the Plutonium (III) Oxalate precipitation method for imaging and morphological analysis using a Scanning Electron Microscope (SEM). The primary challenges for this analysis were to 1) develop a sampling method to generate reproducible SEM sample stubs in a plutonium glove box, 2) create samples with appropriate dispersion and particle density, and 3) safely remove the sample for analysis onto a benchtop SEM. PNNL will present our improved sample preparation methods, and SEM images of PuO₂ will be presented.

16:40 – 17:05

Early Stages of Uranium and Plutonium Oxalate Growth

Karen Kruska, Pacific Northwest National Laboratory

Karen Kruska, Gabriel B. Hall, Shalini Tripathi, Edgar C. Buck, *Energy and Environment Directorate, Pacific Northwest National Laboratory, WA 99354, USA.*

To capture the rapid, early stages of *f*-element oxalate morphologies as a function of the solution formation conditions the particle nucleation and growth, cryo-transmission electron microscopy (TEM) was employed. U and Pu nitrites were reacted with oxalic acid to create the respective oxalates. The reaction was halted by vitrifying the reactants on a TEM grid. This way, the early, meta-stable stages of particles could be investigated. Precipitate sizes and morphologies can be analyzed as a function of reaction time. EFTEM was used for chemical analysis of cryo-samples and post-mortem STEM-EELS was acquired for more detailed chemical analysis of the dried samples. Images after 10 sec show larger particles consisting of agglomerates of smaller particles grown by a particle attachment process. Cryo-TEM reveals the intermediate stages of this non-classical growth process. These results will be discussed as part of the full growth cycle investigated using a combination of optical and electron microscopies.

Seaborg Award and Closing Remarks

17:05 – 17:30

Presentation of Seaborg Award

17:30 – 17:35

Closing Remarks/Announcement of 2022 Actinide Separations Conference

Gregg Lumetta, Pacific Northwest National Laboratory

Poster Abstracts

1 | Rapid Actinide Identification via Luminescence (RAIL) Sensor

John Ahern, Laura Wolfsberg, George Goff, and Franz Freibert, *Los Alamos National Laboratory*

Detection and elemental identification of trace actinides in the diverse plutonium processing feedstock is an essential first step in verifying purity and usability of the oxide including for metal production. Trace actinides such as americium, naturally grow-into aging plutonium sources. Current screening methods for trace actinides are rapid, but are limited in their ability to discriminate actinides and/or quantify ultra-trace amounts. More sensitive methods are expensive and time consuming since samples have to be removed from the glovebox and sent to another group for analysis. There is a need for a sample screening method that is more sensitive than currently used technologies. The Rapid Actinide Identification via Luminescence (RAIL) Sensor will fill this niche as a more sensitive method and reduce the need for costly time-intensive operations such as removing samples from the glovebox line and sending them for analysis. Trace actinides including Np, Am, Cm and U can be detected via sensitized luminescence using the RAIL sensor. The RAIL sensor uses selective organic ligands to amplify the signal from the actinides of interest at concentrations below conventional in-line/mobile screening methods. **LA-UR-21-23564**

2 | AQCL Production FY 20 and FY21

Gabrielle Ambrosio, Dave Kimball, Chris Lopez, and Garret Fulcher, *Associate Laboratory Directorate for Weapons Production: Actinide Operations, Los Alamos National Laboratory, New Mexico 87545, USA*; Joe Romero, and Michael Middlemas, *Associate Laboratory Directorate for Physical Sciences, Los Alamos National Laboratory, New Mexico 87545, USA*

LANL's Aqueous Chloride (AQCL) Process separates and purifies Pu-239 and Am-241 from multiple different waste salts in PF-4. In the beginning of FY 20 AQCL focused on Am oxide production, but paused after an unexpected contaminant was found in the product. SEM analysis showed lanthanum from the feed material to be the source of the product contamination. The team then pivoted to Pu only batches to aid the backlog of waste salts generated from Pyrochemical Metal Production. The shift to the less time consuming Pu batches increased throughput, allowed for inline Solution Assay Instrument (SAI) calibration, and expansion of our Solvent Extraction capability. In FY 21, AQCL also started an Experimental Plan to optimize Am Oxalate precipitations; varying molarity adjustments with DI water versus KOH, and optimizing acid molarity during precipitation. **LA-UR-21-23563**

3 | Laboratory-scale X-ray Absorption Spectroscopy for in situ Molten Salt Study

Boglaenko, D., and Levitskaia, T.G., *Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*; Andersen, A., *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*; Govind, N., *Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*; Seidler, G.T., *Department of Physics, University of Washington, Seattle, Washington 98195, USA*

X-ray absorption fine structure spectroscopy, XAFS, is an element specific technique that delivers structural, electronic and geometric information, and can be applied for any type of material. We employed a laboratory scale X-ray absorption spectrometer for characterization of lanthanide salts before melting (starting materials were $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$) and after melting (predominantly formed compounds were LnOCl , where Ln is Eu, Gd, Tb, and Dy). The melting was conducted in the aerobic environment for the purpose to establish a baseline for Ln compounds formed in the presence of such impurities as oxygen and moisture. Results were complemented with TDDFT calculations, and a good agreement between experiment and theory was found. As a next step, a mini vacuum furnace was installed inside of the laboratory-scale X-ray absorption spectrometer, and first results of an *in situ* molten salt study were obtained and will be presented. This configuration allows for simultaneous collection of X-ray absorption fine structure data and melting of salt mixtures, providing a research capability for the needs of molten salt nuclear technologies.

4 | Performance Characterization of a Geiger–Müller Dose Calibrator System

Hannah R. Hallikainen, and Matthew J. O'Hara, *Pacific Northwest National Laboratory, Richland, WA*;
Daniel M. Jones, and Graham D. Marshall, *GlobalFIA, Fox Island, WA*

Ionization chambers are typically used as dose calibrators, but they are expensive and bulky; a low-cost and compact alternative may be desirable for some applications. A Geiger–Müller (GM) tube-based dose calibrator system has been constructed for use in the support of medical isotope separations. The system is lightweight and easily transported, with a small footprint. It is intended to take accurate activity measurements of samples with minimal user input. At present, it has been shown to be effective for sources ranging from ~ 0.1 – 200 MBq (~ 3 – 5400 μCi). While this system was designed for use in characterizing At-211 cyclotron targets and the isolated product specifically, there may be a wide variety of potential applications for this system, where rapid determination of radio-nuclide activity is desired, and price and space constraints are a consideration. We will present the experimentally determined measurement efficiency values for several nuclides tested on this platform to date, and compare it to a commercially available ionization chamber-based dose calibrator system.

5 | Long-lived Actinide Measurement of NIST SRM 4350B: Columbia River Sediment

Connor Hilton, Kelly McHugh, Steve Shen, Eirik Krogstad, Christopher Brown, *Environmental Signatures Team, Pacific Northwest National Laboratory*

As part of an effort to develop PNNL's 331-mass spectrometry group's analytical capabilities for long-lived actinides, multiple ion exchange chromatography methods were tested to maximize the separation and purification of uranium, plutonium, and americium. The optimal method was applied to a soil aliquot of NIST SRM 4350B (Columbia River Sediment) to determine its concentrations and isotopic compositions of uranium, plutonium, and americium. The sediment was dissolved, processed by column chemistry, and analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Preliminary results indicate that NIST SRM 4350B has 2.0 ± 0.1 $\mu\text{g/g}$ uranium, 0.215 ± 0.003 pg/g Pu, and 0.40 ± 0.02 pg/g ^{241}Am . The measured $^{235}\text{U}/^{238}\text{U}$ ratio is identical to that of natural uranium and the measured $^{240}\text{Pu}/^{239}\text{Pu}$ ratio is 0.101, which is consistent with past studies of Columbia River sediments. Future work will aim to improve the column chemistry methods and adjust the MC-ICP-MS measurement routines to account for isobaric interferences that are not fully removed during sample processing.

6 | The PreCalc Project: Dynamic Simulation of Plutonium Processing

Eric Hoar, and Lindsay E. Roy, *Savannah River National Laboratory*

Studies of PuO_2 and its processing have been performed over many decades due to its role in nuclear fuels and the storage of nuclear wastes. Further studies have been performed to identify models capable of simulating the PuO_2 synthesis process for both process optimization and nuclear forensics applications. It is common for these models to consider one or two aspects of the synthesis procedure for lab-scale synthesis. The PreCalc software combines known and new models for use in modeling plant-scale synthesis. This multi-stage software framework being developed will be able to systematically predict the PuO_2 product characteristics throughout prevalent during the precipitation and calcination processes. The results presented here are meant to provide insight into the current modeling efforts and illustrate the future capabilities to be included in the framework.

7 | Colorimetric Detection of Actinides (CoDeAc)

Catherine Riddle and Rick Demmer, *Idaho National Laboratory, P.O. Box 1625, MS 2114, Idaho Falls, ID 83415*

First responders, military personnel, forensic investigators, and radiological control technicians need simple, rapid, and reliable field equipment to detect radionuclide contamination. When responding to an event, hand-held detectors may provide adequate screening for beta/gamma/neutron emitting radionuclides yet may lack the field sensitivity and adaptability for alpha emitting radiological species like uranium (U) and plutonium (Pu). This research experimentally analyzed new selective colorimetric techniques for actinides, specifically U and Pu, for future use as a visual color change detection system that could be used during a field contamination event as well as everyday maintenance testing at nuclear facilities. Results for showed sensitivity of colorimetric techniques for the detection of U and Pu at parts-per-million (ppm) to parts-per-billion (ppb) levels. Actinide research emphasis was placed on colorimetric indicators, or combinations of indicators, specific for U and Pu and potential environmental interfering ions (iron, nickel, calcium, potassium, etc.). Results for interfering ions, primarily iron, in drinking water showed no interference with the 2-(5-bromo-2-pyridylazo)-5,5-diethylaminophenol (BrPADAP)/1-(2-Pyridylazo)-2-naphthol (PAN) complex with respect to its ability to in U detection. Results for Pu are still be investigated.

8 | Aging mechanisms of silver-functionalized silica aerogel in NO₂-containing gas streams

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Due to its high iodine selectivity and sorption capacity, silver-functionalized silica aerogel (Ag⁰-Aerogel) has considerable potential as a material for the capture of iodine radioisotopes released as byproducts of used nuclear fuel reprocessing. Ag⁰-Aerogel, nonetheless, experiences a steady capacity loss when exposed to other off-gas components. This sorption capacity reduction is known as aging though its underlying mechanisms remain unclear. To investigate aging, we exposed Ag⁰-Aerogel samples to 2% NO₂ in dry air (i.e. a relevant gas stream with a strong aging effect) at 150°C for up to one month. The aged samples were then characterized using Scanning Electron Microscopy, X-ray Diffraction, Fourier-transform infrared spectroscopy, X-ray Photoelectron Spectroscopy and X-ray Absorption Spectroscopy. Our results coherently indicate that aging of Ag⁰-Aerogel in NO₂ involves three major processes: (i) propanethiolate, functional group connecting the silica aerogel backbone and metallic silver (Ag⁰) nanoparticles, is oxidized first to propanesulfonate and then to sulfate ion weakly binding to nanoparticle surface; (ii) Ag⁰ on the nanoparticle is oxidized to Ag⁺ and react with sulfate ions forming silver sulfate molecules; and (iii) silver sulfate molecules migrate off the nanoparticle surfaces and yields silver sulfate crystals. These silver sulfate crystals convert silver into a form that is unfavorable for iodine adsorption. Spectroscopic results reveal that silver oxidation or silver sulfate crystallization is the rate-limiting step. These findings elucidate the mechanisms of aging in Ag⁰-Aerogel, and may be used to guide the development of accurate predictive models.

9 | Alpha-Induced Degradation of Pu(III) and Pu(IV) Oxalates Probed by Reflectance and Absorbance Spectroscopy

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Due to relatively high specific activity of Pu-239, its oxalate compounds undergo gradual degradation with concomitant decomposition of oxalate ligands, loss of crystallinity, and change in visual appearance. Some researchers also reported oxidation state change of Pu ion in initially pure Pu(IV) oxalates, but these findings were not confirmed in subsequent publications. Much less is known about degradation pathways of Pu(III) oxalates. Determination of residual oxalate-to-Pu molar ratio in initially pure Pu(III) (1.5:1) and Pu(IV) (2:1) oxalates is an important characteristic of the degradation process, but historically it was attempted in two studies only with very limited results available at ambient temperature. The earlier proposed approach to measure residual oxalate involves 7 steps and is cumbersome and labor intensive.

In our laboratory we studied a possibility to determine oxalate-to-Pu ratio in a single step procedure which involves dissolution of a small portion of aged plutonium oxalate in a non-oxidizing, weakly complexing inorganic acid (so far we tried HCl). Once the material is fully dissolved, its acidity is adjusted to a low enough level to let remaining oxalate ions interact with Pu(IV), yet maintained at a high enough level of acid concentration to suppress re-precipitation of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. The dissolution is followed by collection of an optical absorbance spectrum which captures these oxalate-based complexation effects with Pu(IV). Quantification of the oxalate-to-Pu ratio is then performed using deconvolution of the spectrum based on molar absorptivities of $(\text{PuC}_2\text{O}_4)_2^{2-}$ and $\text{Pu}(\text{C}_2\text{O}_4)_2^0$ complexes preliminarily refined in a separate experiment at the same acidity. An additional advantage of the proposed approach is direct observation of redox speciation of Pu in the dissolved sample, from which its original speciation in the solid state before dissolution can be inferred and correlated with the reflectance spectrum of the solid sample.

10 | Evaluating Polymeric Nanoparticles for Actinide Delivery Using Surrogates

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Polymeric nanoparticles are promising delivery platforms for a variety of anticancer agents. The utility of polymeric nanoparticles as delivery vehicles for alpha-emitting radioisotopes has yet to be demonstrated. Here we propose using poly(lactic-co-glycolic acid) (PLGA) nanoparticles as an actinide delivery vehicle for targeted radiotherapy. PLGA nanoparticles offer a biodegradable and biocompatible delivery vehicle with the potential to improve targeted delivery and minimize the relocation of actinides and their decay daughters from the tumor site. A double-emulsion method with D- α -tocopherol polyethylene glycol 1000 succinate as emulsifier was used to synthesize PLGA nanoparticles with a mean hydrodynamic diameter of <300 nm. PLGA nanoparticles show high colloidal stability in biologically relevant media over time. The concentration of actinide surrogates within PLGA nanoparticles was assessed after varying different synthesis conditions and determined using inductively coupled plasma mass spectroscopy. Results indicate that the concentration of surrogate ions within PLGA nanoparticles depends on the element being evaluated and its initial concentration. Chelation of surrogate ions with different ligands increased the surrogate concentration within the nanoparticles. The encapsulation of surrogate ions indicates that PLGA nanoparticles are an appropriate test vehicle to evaluate actinide delivery and retention of decay daughters in preclinical settings.

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