46th ACTINIDE SEPARATIONS CONFERENCE
IDAHO FALLS 2023

# 46th Annual
# Actinide Separations Conference

Energy Innovation Laboratory Meeting Center
Idaho Falls, ID

**May 16-18, 2023**

INL Idaho National Laboratory

# WELCOME TO THE 46TH ACTINIDE SEPARATIONS CONFERENCE

Welcome to the 46th Actinide Separations Conference, hosted this year by the Idaho National Laboratory. Four years have passed by since we last had an opportunity to gather in person for this Conference. The unforeseen circumstances of global pandemic forced the cancellation of 2020, and a virtual setting of 2021. Mother nature also challenged us, and the uncertainty of the wildfire forced a virtual gathering of 2022. Finally, the stars aligned, and the meeting of 2023 brings us together again. The Conference features 71 papers on many interesting topics, arranged in 10 sessions, navigating across the fundamental and applied landscapes of actinide chemistry. As we all attempt to return to normal, the plenary session will help us to reflect on the "*Past, Present and Future of Actinide Separations*." We look forward to a valuable and informative technical interchange. Please use this opportunity to network with your colleagues, reminisce on the past experiences of trying times and seek new prospects and collaborations.

*Thank you for coming and we hope you enjoy the Conference!*

| | |
|---|---|
| *Conference Chair* | *Peter Zalupski* |
| *Technical Program Chair* | *Travis Grimes* |
| *Conference Coordinator* | *Michele Oliveira* |

# ACTINIDE SEPARATIONS CONFERENCE ADVISORY BOARD MEMBERS

**Peter R. Zalupski**
Idaho National Laboratory

**Laetitia H. Delmau**
Oak Ridge National Laboratory

**Candido Pereira**
Argonne National Laboratory

**Gregg J. Lumetta**
Pacific Northwest National Laboratory

**Kiel Holliday**
Lawrence Livermore National Laboratory

**Tracy Rudisill**
Savannah River National Laboratory

**Michael Simpson**
University of Utah

**Mark P. Jensen**
Colorado School of Mines

**Casey Finstad**
Los Alamos National Laboratory

# CONFERENCE SCHEDULE

| **Tuesday, May 16** | |
|---|---|
| Registration (open all day) | 7:00 AM |
| Welcome Message | 8:00 AM |
| Plenary Session: The past, present and future of Actinide Separations | 8:15 AM |
| Lunch (on own) | 11:30 AM |
| Session 1: High Temperature Electrochemical Separations | 1:00 PM |
| Session 2: Nuclear Fuel Cycle Solutions | 3:25 PM |
| Poster Session | 6:30 PM |
| **Wednesday, May 17** | |
| Registration (open all day) | 7:30 AM |
| Session 3: Radioisotope Recovery/Purification | 8:30 AM |
| Conference Tour Check-In and Badging | 11:20 AM |
| Conference Tour | 12:00 PM |
| **Thursday, May 18** | |
| Registration (open all day) | 7:00 AM |
| Session 4: High Temperature Non-Electrochemical Separations | 8:00 AM |
| Session 5: Advancements in Molten Salt Measurements | 10:20 AM |
| Session 6: Aqueous and Vapor Phase Actinide Separations | 8:00 AM |
| Lunch (on own) | 12:00 PM |
| Advisory Board Meeting (closed session: Room A110) | 12:00 PM |
| Session 7: Actinide Chemistry Fundamentals | 1:20 PM |
| Session 8: Data Science, High-Throughput and Automation in Actinide Separations | 3:40 PM |
| Conference Banquet* | 6:30 PM |
| Dinner presentation by Marie Holmer | 7:30 PM |
| Seaborg Award Presentation | 8:00 PM |
| Announcement of 47th Actinide Separations Conference | 8:30 PM |

**The Downtown Event Center, The DEC, 480 Park Ave., Idaho Falls. (8-minute walk from Residence Inn)*

# Glenn T. Seaborg Actinide Separations Award

1984 Glenn T. Seaborg, *University of California-Berkeley*

1985 Don E. Ferguson, *Oak Ridge National Laboratory*

1986 Larned B. Asprey, *Los Alamos National Laboratory*

1987 Wallace W. Schulz, *Westinghouse Hanford Company*

1988 Lawrence J. Mullins, *Los Alamos National Laboratory*

1989 Gregory R. Choppin, *Florida State University*

1990 Donald A. Orth, *Westinghouse Savannah River Company*

1991 David O. Campbell, *Oak Ridge National Laboratory*

1992 E. Philip Horwitz, *Argonne National Laboratory*

1993 Earl J. Wheelwright, *Pacific Northwest Laboratory*

1994 Leslie Burris, *Argonne National Laboratory*

1995 Robert R. Penneman, *Los Alamos National Laboratory*

1996 David G. Karraker, *Westinghouse Savannah River Company*

1997 Major C. Thompson, *Westinghouse Savannah River Company*

1998 Walter D. Bond, *Oak Ridge National Laboratory*

1999 Jack L. Ryan, *Pacific Northwest National Laboratory*

2000 John L. Swanson, *Pacific Northwest National Laboratory*

2001 George F. Vandegrift, *Argonne National Laboratory*

2002 Leonard W. Gray, *Lawrence Livermore National Laboratory*

2003 Kenneth L. Nash, *Argonne National Laboratory*

2004 Emory D. Collins, *Oak Ridge National Laboratory*

2005 Terry A. Todd, *Idaho National Laboratory*

2006 Renato Chiarizia, *Argonne National Laboratory*

2007 Leland L. Burger, *Pacific Northwest National Laboratory*

2008 Gordon D. Jarvinen, *Los Alamos National Laboratory*

2009 Raymond G. Wymer, *Oak Ridge National Laboratory*

2011 Darleane C. Hoffman, *University of California-Berkeley*

2012 Jimmy T. Bell, *Oak Ridge National Laboratory*

2013 Lane A. Bray, *Pacific Northwest National Laboratory*

2014 David T. Hobbs, *Savannah River National Laboratory*

2015 Gregg J. Lumetta, *Pacific Northwest National Laboratory*

2016 Guillermo (Bill) Del Cul, *Oak Ridge National Laboratory*

2017 Tracy Rudisill, *Savannah River National Laboratory*

2018 Jack D. Law, *Idaho National Laboratory*

2019 Bruce A. Moyer, *Oak Ridge National Laboratory*

2021 Mark Jensen, Colorado School of Mines

2022 Shelly X. Li, *Idaho National Laboratory*

# 2023 GLENN T. SEABORG ACTINIDE SEPARATIONS AWARD WINNER

### *Edward A. Kyser III*

Dr. Edward (Eddie) Kyser earned his PhD in Chemical Engineering from the University of Missouri – Rolla in 1987 after performing studies on the vapor-liquid equilibrium interactions of light hydrocarbons. He accepted a position at what was then Savannah River Laboratory in the Actinide Technology Division. Initially, he took on existing projects looking at mixing and solids suspension effects on precipitation processes in slab tanks while becoming a student of the process chemistry of the various separations processes used at SRS. Over the first several years of his career his worked on a number of projects ranging from the recycle of highly enriched uranium used in SRS reactors, moderization of the FB-Line Pu239 metal production process, and the direct fabricaiton of Pu238 heat sources pellets. He especially focused on the solvent extraction, ion exchange and precipitation processes run in the SRS canyons and B-Lines.

This was a time of change at the Savannah River Site, with the original contractor, DuPont turning over operation of the site to Westinghouse in 1989. During that time of transition, many of the old guard retired, the Cold War came to an end, and Dr. Kyser became the site subject matter expert on ion exchange, particularly focused on the safe operations of anion exchange processes. He provided laboratory support for the ion exchange processes (both cation and anion) in the FB-Line facility (for Pu239 metal production) and the Pu238 Frame Waste Recovery process (anion) which purified Pu238 for the NASA Cassini and Craft missions. He became the "fireman" who was called when things went wrong, or a new accident was imagined. These events, whether real or imagined, invariably shut down production and Dr. Kyser was the one to provide solutions to get the process back up and running in a short time frame.

One of these involved phosphorous contamination in Pu238 oxide production process. This discovery shut down both H-Canyon and HB-Line due to the tight limit for phosphorous in the Pu238 oxide product. Lacking any viable method to detect P in Pu238 solutions and starting with a method described in the literature using phosphomolybdic acid complexes and a glovebox equipped with fiber optic connections and a UV-Vis spectrometer, he led a small team over a three-week time period to set up this method to screen for phosphorus contamination in Pu238 process solutions at the 100 ppb concentration level and Pu238 production was allowed to resume.

In another instance, an "Earthquake Induced Fire" was postulated in Frame Waste Recovery (H-Canyon Pu238 anion column). In this case, Dr. Kyser developed a technical basis from first principles (and experimental resin reactivity data) that gave the facility a solid technical basis for a 24-hour response time in the event of a serious earthquake rather than a process safety limit of 15 minutes for a flow interruption while processing Pu238.

These types of situations occurred frequently during the 1990's when SRS had two operating canyons. By 2000 Dr. Kyser was focusing his time H-Area processing of Pu and Np through the HB-Line facility, principally the glovebox anion exchange process. He provided the flowsheets for use of the Reillex HPQ resin to process both Pu and Np through the HB-Line facility making extensive use of UV-Vis spectrometry to perform at-line measurements of the Pu/Np concentration. He still was called on to fight the process "fires". He spent more than a couple of midnights in the HB-Line control room when processes had not been performing satisfactorily.

As HB-Line priorities shifted from Pu to Np and starting in 2002, Dr. Kyser turned his focus to getting the Np solution stored in H-Canyon purified and turned into an oxide that could be readily stored and transported. This stockpile of material will provide Pu238 for use in future NASA missions provided by INL and ORNL. This Np was produced in SRS reactors over 30 years as a byproduct of weapons production activities. There were challenges here also. Controlling the reductive washing/selective elution of the Pu238 from the Np237 while loaded on the anion resin was a challenge that we anticipated and pretty much solved in the laboratory prior to the production process. However, when it came to recycling the losses from the HB-Line process through solvent extraction there were problems that Dr. Kyser had to fix on the fly. The flowsheet was based on a historical oxidizing flowsheet (using Ce(IV) to oxidize to Np(VI)). There was no time nor money to allow any significant lab development activities. Due to another issue in the facility causes the solvent extraction process to be paused for over a week and ammonium cerous sulfate precipitation occurred in the canyon solvent extraction equipment when the Ce(VI) was reduced to Ce(III). Dr. Kyser had started to secretly investigate stability of the oxidizing strength of the solution, but at a scale too small to observe the problem that occurred. It was one of a few missed opportunities to avoid large-scale problems. This material had the consistency of peanut butter, and the canyon personnel were fortunate to clean it out of the equipment successfully.

The AFS2 campaign in HB-Line gave Dr Kyser the opportunity to advance the use of UV-Vis spectrometry in the monitoring of anion exchange processes both in the lab and in the production environment. While Dr Kyser had been monitoring laboratory columns with UV-Vis flowcells fitted to glovebox column since the early 1990s, during this time he saw the opportunity to modernize our equipment and software. With the assistance of analytical personnel, we developed the scheme of using a reference spectrometer to correct for lamp and temperature variations and ultimately mapped to a virtual instrument which eliminated the need to perform periodic calibrations of the spectrometer because wavelength and gain checks are constantly being performed between the sample and reference spectrometers using the spectral lines from a Xe arc flash lamp for a reference. Ultimately, we were able to successfully deploy this technology in HB-Line to monitor the process.

Dr. Kyser is probably best known for his work in ion exchange and process valence chemistry, but probably the most satisfying was the UV-Vis spectrometry work monitoring Pu and Np processes. Along the way, he has advised and helped train generations of engineers running SRS processes while standing on the shoulders of the "giants" of the field who preceded him.

# 46TH ACTINIDE SEPARATIONS CONFERENCE BANQUET SPEAKER

### *Marie P. Holmer*

### *"Jeffrey and Goodale: The Openings of a Cutoff on the Oregon Trail"*

Marie has worked for the Cultural Resource Management Office at Idaho National Laboratory since 2014 and currently works as an Archaeological Technician with the program. Her remit includes database development and cultural resource data management, historical research in support of context development for the 1810-1942 period, and work conducted under Section 106 of the National Historic Preservation Act (NHPA). In 2020, she completed a historic context for the Jeffrey-Goodale Cutoff of the Oregon Trail at the INL, where part of the route can be traced, as well as designing public information panels.

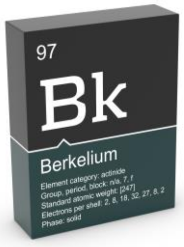
After gaining her undergraduate BS degree in Geology and Archaeology from the University of Birmingham, U.K., she earned a MS in Forensic Archaeology and Crime Scene Investigation from the University of Bradford, also in the U.K., before graduating from Idaho State University in 2015 with a MS in Geographic Information Science. Prior to joining INL, Marie held laboratory positions in environmental chemistry and archaeological science, as well as working with archaeological collections at the Idaho Museum of Natural History during her time at ISU.

She began her work with INL as a GIS technician in the CRMO for the Historic American Landscapes Survey (HALS) of the World War II Arco Naval Proving Ground, a historic landscape within the current boundary of the INL Site, the first HALS to be completed in Idaho (HALS-ID-01). Marie has presented on the history of the Arco Naval Proving Ground, Carey Act Irrigation and Homesteading at INL, and the Jeffrey-Goodale Cutoff of the Oregon Trail.

# CONFERENCE SPONSORSHIP

The conference organizing committee would like to thank **SHINE Technologies** for their sponsorship of this year's Actinide Separations Conference:

Based in Janesville, Wisconsin, SHINE deploys its safe, cost-effective and environmentally friendly fusion technology in a stepwise approach. Its systems are used to inspect industrial components in aerospace, defense, energy and other sectors. SHINE's proprietary medical isotope production processes create non-carrier-added lutetium-177 and will soon create molybdenum-99 via an aqueous subcritical fusion/fission hybrid system. As a next step, SHINE plans to scale its fission product separation and fusion technologies to help solve one of energy's toughest hurdles by recycling spent nuclear fuel and transmuting targeted isotopes. Through a purpose-driven and phased approach, SHINE ultimately aims to generate fusion power to deliver clean, abundant energy that could transform life on Earth.



## SPONSORSHIP LEVEL

# Conference Sponsorship

The conference organizing committee would like to thank **Marshallton Laboratories** for their sponsorship of this year's Actinide Separations Conference:

**MARSHALLTON**

**RESEARCH LABORATORIES INCORPORATED**

Marshallton manufactures specialty chemicals for remediation and recycling in the nuclear energy industry. These include MAXCalix extractant, CS-7SB solvent modifier, and guanidine suppressors, key components for cesium removal. An/Ln partitioning agents and analytical reagents are also available. Marshallton continues to develop new products to meet the growing needs of the nuclear industry. Please contact us about tailoring a new active ingredient or new formulation for your specific application.

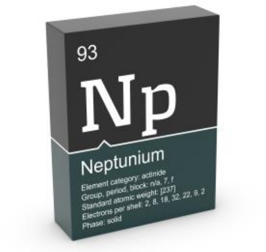
## Sponsorship level

# CONFERENCE SPONSORSHIP

The conference organizing committee would like to thank **Foss Therapy Services** for their sponsorship of this year's Actinide Separations Conference:

Foss Therapy Services, Inc.

Foss Therapy Services Inc. (FTS) offers expertise and leading solutions for your irradiator or radiation device needs. Our irradiator services now include nearly all kinds and makes of gamma irradiation systems. Our service engineers are highly trained and licensed to reload irradiators, perform dose mapping, make repairs, and relocate equipment. We have also manufacture irradiators and offer engineered upgrades to many popular systems that can be performed at your site to improve performance and extend their useful life.

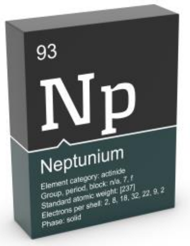


## SPONSORSHIP LEVEL

# CONFERENCE SPONSORSHIP

The conference organizing committee would like to thank **AMETEK Inc.** for their sponsorship of this year's Actinide Separations Conference:

ORTEC is an industry leader in the design and manufacture of ionizing radiation detectors, nuclear instrumentation, analysis software, and integrated systems. Our technologies, products, and services are instrumental in materials analysis for radioisotopic content. Key industry segments include nuclear power, nuclear security and materials safeguard, academia and research, environmental management, and health physics. Our nuclear analysis software and nuclear instrumentation modules can be found in research facilities and educational facilities worldwide. The ORTEC brand is synonymous with offering the latest technology in radiation detector devices. Our hand-held radioisotope identifiers have become a game changer in the nuclear instrumentation industry. We invite you to browse through our website and contact us for all of your radiation detector and nuclear instrumentation needs.



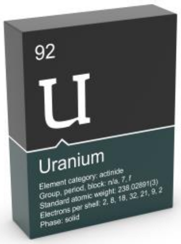
## SPONSORSHIP LEVEL

# CONFERENCE SPONSORSHIP

The conference organizing committee would like to thank **Manufacturing Sciences Corporation** for their sponsorship of this year's Actinide Separations Conference:

MANUFACTURING
SCIENCES
CORPORATION

Manufacturing Sciences Corporation is a high technology metals manufacturing and materials acquisition company with extensive experience in design, metal casting and rolling, fabrication, welding, and precision machining. We are especially experienced and equipped for processing radioactive material in an environmentally sound, safe, and controlled manner. With over 35 years of experience in specialty metal processing, rolling, manufacturing, and acquisition, MSC utilizes its knowledge and expertise to provide our customers with high quality precision products on schedule and within budget. From concept to full production, MSC can lead your project to success with our highly skilled engineering, operations, and management team.

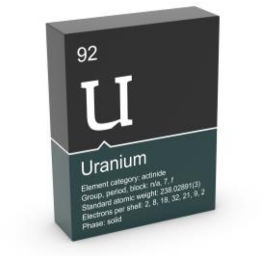


## SPONSORSHIP LEVEL

# CONFERENCE SPONSORSHIP

The conference organizing committee would like to thank **Eichrom Technologies** for their sponsorship of this year's Actinide Separations Conference:

Eichrom Technologies and subsidiaries are world leaders in radiochemistry and radiation protection. Founded in 1990, Eichrom has been at the forefront of new product development and commercialization in the areas of environmental radiochemistry, nuclear medicine, and geochemistry. Eichrom is a world expert in ion Exchange, extraction chromatography and solid phase extraction (SPE): applying chemical separation technology to improve efficiency and lower costs in analytical radiochemistry, isotope geochemistry and nuclear medicine.



## SPONSORSHIP LEVEL

# Conference Sponsorship

The conference organizing committee would like to thank **Eckert & Ziegler Analytics** for their sponsorship of this year's Actinide Separations Conference:

Eckert & Ziegler

Eckert & Ziegler's Isotrak™ business provides high-quality, NIST traceable radioactive calibration sources, solutions, and gases to support laboratory quality management, radiation protection, research, security, and operations across the nuclear industry. Our products are manufactured in three ISO 17025:2017 DAkkS accredited calibration laboratories; Eckert &Ziegler Isotope Products in Valencia, USA, Eckert & Ziegler Analytics in Atlanta, USA and Eckert & Ziegler Nuclitec in Braunschweig, Germany.

As an ISO17043:2010 accredited Proficiency Testing Provider, Isotrak also offers a variety of radiochemical, environmental, health physics and decommissioning proficiency test samples.

The Isotrak product line is continually expanding to meet industry needs including a growing list of matrices used in fit-for purpose reference materials covering decommissioning, NORM and other applications.

Founded in 1997, the Eckert & Ziegler Group is one of the world's largest providers of isotope technology for medical, scientific, and industrial use. The company focuses on applications in cancer therapy, industrial radiometry, and nuclear imaging. The operating business is divided into two segments: Medical and Isotope Products.

# Sponsorship level

May 16, 2023

Plenary Session
EIL A-102

## Actinide Separations Plenary Session
## “The past, present and future of Actinide Separations”

**Tuesday Morning, May 16, 2023**

Session Chair: Peter Zalupski

| | | |
|---|---|---|
| **8:00 AM** | Welcome | Peter Zalupski<br>INL |
| **8:15 AM** | A historical overview of actinide separations at INL | Terry Todd,<br>BGS |
| **8:50 AM** | Actinide Chemistry: A Key Component of Sustainable Nuclear Energy Systems | Monica Regalbuto,<br>INL |
| **9:25 AM** | Morning Break | BREAK |
| **9:45 AM** | Status and Research Needs for Pyrochemical Fuel Cycles | Ken Marsden, INL |
| **10:20 AM** | Oxidative Separation of Am by Multiphoton Excitation and the Radiation Power Generation from Resource Recycle of Radioactive Waste | Tsuyoshi Yaita,<br>JAEA |
| **10:55 AM** | Pilot Facility Development for Aqueous Recycling of Used Nuclear Fuel | Ross Radel,<br>SHINE Technologies |
| **11:30 AM** | Lunch Break (until 1:00 PM) | BREAK |

# A historical overview of actinide separations at INL

Terry Todd

Boston Government Services

The Idaho National Laboratory (INL) and its predecessors (INEL, INEEL, ANL-W) began processing irradiated nuclear fuels in the early 1950s. The INL processed fuel from over 100 different reactors using both aqueous and electrochemical methods. Most of the processing was performed to recover highly-enriched uranium (HEU) from the fuels. Aqueous processing was performed at the Idaho Chemical Processing Plant (later renamed to Idaho Nuclear Technology and Engineering Center) from 1953 until 1991. Electrochemical processing was performed at Argonne National Laboratory- West (later became Materials and Fuels Complex- a part of the consolidated INL contract) from the late 1960s until present day. A description of the processes used, fuels processed and unique attributes of both facilities will be discussed from a historical perspective.

## Actinide chemistry: A key component of sustainable nuclear energy systems

Monica Regalbuto

Idaho National Laboratory

Nuclear energy is set to play a vital role to achieve 2050 net-zero goals. As we move to expand the use of nuclear energy, it is important to address what constitutes a sustainable nuclear energy system. Sustainable energy systems address economic, social, and environmental dimensions. This requires addressing uranium utilization, waste management and proliferation risk. This presentation will cover the important role actinide chemistry plays in addressing front-end and back-end fuel cycle needs to enable the growth of nuclear energy.

# Status and Research Needs for Pyrochemical Fuel Cycles

Ken Marsden

Idaho National Laboratory

Pyrochemical approaches can provide recycling advantages for certain fuel cycle scenarios, particularly for recycling short cooled or high fissile content fuels. Considerable development of pyrochemical fuel cycles has occurred over the last several decades, but opportunities remain for optimization, simplification, and extension to broader feedstocks.

# Oxidative Separation of Am by Multiphoton Excitation and Radiation Power Generation from Resource Recycle of Radioactive Waste

T. Yaita, S. Matsuda, K. Yokoyama, K. Yoshii, T. Fukuda, M. Kobata, T. Shobu

[1]Materials Sciences Research Center, Harima Synchrotron Radiation RI Laboratory/SPring-8
Japan Atomic Energy Agency

We will introduce the initial experiments on power generation from 60 keV γ-ray of Am, conceptual design of a new separation method by oxidation of Am with multiphoton excitation, and future research development in this presentation.

Nuclear power can be considered to be an important energy source that should be utilized for a carbon neutral society. However, a major challenge in sustainable use of nuclear power is the problem of radioactive waste disposal. Especially in a country with a small land country like Japan, recycling of geological disposal sites is a major issue. Needless to say, the handling of high-level liquid waste is an important issue in this regard. In Japan, the use of fast reactors or accelerators for partitioning and transmutation (P&T) has been considered, but Monju, which was the main demonstration fast breeder reactor, has been unfortunately decided to be decommissioned, and P&T will take time to complete the technology.

Therefore, we, the Harima Synchrotron Radiation RI Laboratory of JAEA (SPring-8), started to study the feasibility of radiation power generation as a bridge technology for the management of long-lived α-nuclides such as Am on the ground. This is to examine the possibility of using Am-241 for nuclear power generation as an energy source instead of Pu-238. The γ-ray power generation is not a mainstay of the nuclear battery like thermoelectric conversion, and it is only an attempt to shield the γ-rays and to use it as a partial power source. However, as in the case of superconductivity and magnetic materials developments, if the efficiency is improved by some breakthrough with the participation of many researchers, the shielding material can be lightened, and if a useful amount of power can be extracted, there is even a possibility of establishing a dream technology to recycle energy that has been discarded. In this study, we clarified the characteristics of a component that generates electricity by Schottky junction of Ni to SiC.1) The 60 keV γ-rays of Am can be substituted by synchrotron radiation X-rays, which is also a very easy subject to study.

In particular, separation extractants utilizing the softness of actinides, which are heavy elements, to lanthanides, than  lanthanides, so-called soft donor ligands, have been developed. On the other hand, the use of such chemical processes poses many challenges, such as the various process applicability of the extractant itself and the generation of secondary waste. We have succeeded in oxidation of Am(III) to Am(V) by using the f-f' transition of Am, which is a forbidden transition, as a gate reaction, and by continuously exciting Am to a highly reactive quantum state and reacting with an external environment like solvents.2) Especially the oxidation to Am(V)$O_2^+$ by reaction with nitrate ions existing as a solvent has been clarified by EXAFS using SPring-8. So, this reaction would be estimated to be highly applicable to real processes. Furthermore, since the f-f transition is utilized, Am(V)$O_2^+$ in the solution existing of a wide variety of +3, +4, +6 actinides and +3 lanthanides can also be separated through holdback to the aqueous phase with an oxygen donor extractant acceptable for usage in real process.

1) Fukuda, T., Kobata, M., Shobu, T., Yoshii, K., Kamiya, J., Iwamoto, Y., Makino, T., Yamazaki, Y., Ohshima, T., Shirai, Y., Yaita, T. "Direct energy conversion using Ni/SiC Schottky junction in $^{237}$Np and $^{241}$Am gamma ray regions, *Journal of Applied Physics*, **2022**, *132(24),* 245102.

2) Matsuda, S., Yokoyama, K., Yaita, T., Kobayashi, T., Kaneta, Y., Simonnet, M., Sekiguchi, T., Honda, M., Shimojo, K., Doi, R., Nakashima, N., "Marking actinides for separation: Resonance-enhanced multiphoton charge transfer in actinide complexes", *Science Advances*, **2022**, *8(20),* eabn1991.

# SHINE's Development of an Aqueous UNF Recycling Pilot Facility

Ross Radel, Marek Piechowicz

SHINE Technologies

SHINE Technologies, LLC (SHINE) is leading a venture to address the nation's UNF disposal challenge by developing a game-changing set of interlinked technologies that reduce the environmental impact of nuclear energy generation through the recycling and transmutation of UNF. This approach will reduce the longevity and long-term radiotoxicity of high-level waste, will improve reprocessing economics via value-added isotope extraction, and will advance technologies to enable fusion energy generation. SHINE is leveraging design, construction, and operational experience gained from commercializing its medical isotope (Mo-99) production facility to design an end-to-end UNF processing, recycling, and transmutation system.

As depicted in Figure 1, SHINE is designing a comprehensive U/Pu aqueous co-extraction pilot facility to separate used fuel into U, U/Pu, Np, minor actinides (MA, e.g., Am and Cm), lanthanides, and fission products (FPs). This planned process flow incorporates two aqueous-aqueous separation processes (CoDCon[1,2] and ALSEP[3]). This process flow is a critical step in the larger effort to reduce the volume of high-level waste in storage and includes tangible progress towards implementing a cost-effective transmutation system to burn down the minor actinides.

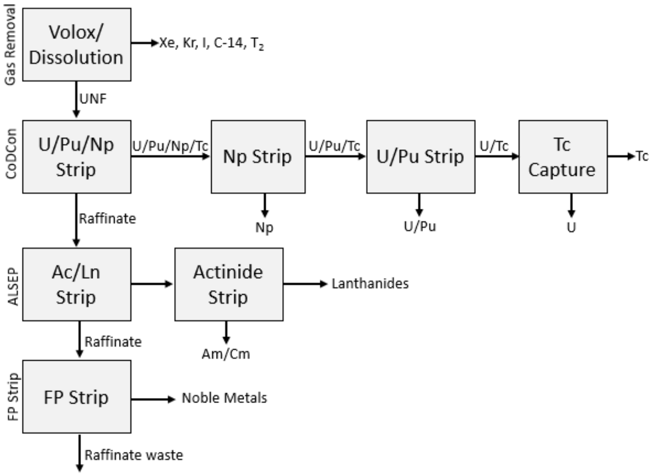


*Fig 1: High-level process flow in SHINE recycling facility*

SHINE is incorporating significant improvements to traditional extraction system design via targeted valuable isotope recovery, removal of key long-lived isotopes for transmutation, improved in-house commercial grade dedicated equipment, and more efficient systems for handling highly radioactive liquid materials, as informed by SHINE's Mo-99 production facility. The synergies between recycling and transmutation technologies enables a holistic solution to the used fuel disposal challenge, and the cost effectiveness of the enhanced liquid-liquid separation system and final disposal forms is key to commercialization. SHINE believes the successful demonstration of this pilot facility will pave a pathway for a permanent, cost effective, and environmentally sustainable solution for recycling used nuclear fuel in the United States and advances a credible, accelerated pathway to commercializing nuclear fusion energy via the use of fusion neutrons for transmutation.

## References

1) Peterson R.A., "Engineering Separations Unit Operations for Nuclear Processing," 2019, Taylor and Francis.
2) Lumetta, G, Allred, J. Asmussen, S. et al., "CoDCon Project: Final Report," 2022, Pacific Northwest Nat. Lab.
3) Gelis, V.A, Kozak, P, Breshears, A.T, Brown, M.A, Launiere, C, Campbell, E.L, Hall, G.B, Levitskaia, T.G, Holfeltz, V.E, Lumetta, G.J. "Closing the Nuclear Fuel Cycle with a Simplified Minor Actinide Lanthanide Separation Process (ALSEP) and Additive Manufacturing," *Sci. Rep.* 2019, 9 (1), 12842.

*Corresponding author e-mail: rossradel@shinefusion.com*

May 16, 2023 Tuesday Afternoon Technical Sessions 1 and 2
EIL A-102

## Technical Session 1: "High Temperature Electrochemical Separations"
## Technical Session 2: "Nuclear Fuel Cycle Solutions"

### Tuesday Afternoon, May 16, 2023

Session 1 Chair: Devin Rappleye, Brigham Young University
Session 2 Chair: Gabe Hall, PNNL

| | **1: High Temperature Electrochemical Separations** | |
|---|---|---|
| **1:00 PM** | First Principles Optimization of Plutonium Electrorefining | Chao Zhang, LLNL |
| **1:25 PM** | Alternating Current Superimposed on Direct Current Bismuth Electrorefining | Greg Chipman, BYU |
| **1:50 PM** | Development of an Electrochemical Oxide Reduction Process for $PuO_2$ | Steven Wilcock, AWE |
| **2:15 PM** | Separation of Uranium from FLiTh Salt | Jinsuo Zhang, Virginia Tech |
| **2:40 PM** | Production and Characterization of Accelerated Aged Alloy | Scott Simpson, LLNL |
| **3:05 PM** | Afternoon Break | BREAK |
| | **2: Nuclear Fuel Cycle Solutions** | |
| **3:25 PM** | Study on Nuclear Fuel Cycle Policy using Dynamic Simulator NMB4.0 | Kenji Takeshita, Tokyo Tech |
| **3:50 PM** | Further optimization of the GANEX flowsheet | Michael Carrott, NNL |
| **4:15 PM** | Exploration of novel solvents for MA separation for future rational nuclear fuel cycle based on the MA interim storage concept | Masahiko Nakase, Tokyo Tech |
| **4:40 PM** | A direct conversion method for the separation and temporary storage of MA | Tomoo Yamamura, Kyoto University |
| **5:05 PM** | Chloride to Nitrate Conversion of Pyrochemical Residues | Rebecca Carter, SRNL |
| **5:30 PM** | Break (until 6:30 PM) | BREAK |

# First Principles Optimization of Plutonium Electrorefining

Chao Zhang[1], Alistair Parkes[2], Jeffrey Ramos[1], David Roberts[1], Scott Simpson[1], Brandon Smiddy[1], and Kiel Holliday[1]

[1]Lawrence Livermore National Laboratory, [2]AWE

Electrorefining is a process to produce high purity metal from impure metal or alloy. It is typically done in aqueous based solution with solid anode material and cathode product. Whereas, in Pu electrorefining the medium is molten salt at above 900 °C, and both the anode material and cathode product are in liquid phases. This simple process eliminates the complex aqueous based chemical purification processes. In addition, electrorefined metal is purer than that produced by metal produced via chemical conversion.[1,2]

Currently, there are two methods to operate Pu electrorefining, constant potential and constant current. Both methods are based on empirically determined parameters. These parameters need to be conservative to ensure product purity because the maximum operating current limit is not known. Moreover, the current limit changes during processing, and is equipment and setup dependent.

This work presents a means of controlling plutonium electrorefining at a maximum rate regardless of equipment setup through the derivation of power supply current and potential governing equations for normal and off-normal operations. The governing equations are demonstrated by electrorefining surrogate materials. A simple linear current sweeping method was used to determine the maximum electrorefining current for the surrogate system. This method can be used to develop autonomous process optimization, real-time online processing monitoring, and real-time process endpoint detection. Ultimately, this research provides the foundation to optimize the liquid metal electrorefining rate to decrease the time needed to the physical limit for the process.[3]

1) Mullins, L.J., Leary, J.A., Morgan, A.N. and Maraman, W.J., **1963**. Plutonium electrorefining. *Industrial & Engineering Chemistry Process Design and Development*, 2(1), pp.20-24.
2) Bronson, M. C., and R. L. Thomas. Electrorefining cell evaluation. No. RFP-4207. Rockwell International Corp., Golden, CO (USA). Rocky Flats Plant, 1989
3) Zhang, C., Parkes, A.M. and Holliday, K.S., 2023. First principles optimization of plutonium electrorefining. *Journal of Nuclear Materials*, 577, p.154327.

# Alternating Current Superimposed on Direct Current Bismuth Electrorefining

Greg Chipman, Bryant Johnson, Devin Rappleye

Department of Chemical Engineering, Brigham Young University, Provo, UT 84602 USA

Electrorefining is the most time-intensive pyrochemical operation in the plutonium metal processing flowsheet. One simple way of potentially improving the efficiency and reducing the duration of electrorefining is to use an AC superimposed DC waveform. While this waveform has been used previously for electrodeposition with conflicting results, it has never been used in a molten metal, molten salt application. AC superimposed DC waveforms have been seen to consistently improve the compactness of the deposited layer while also decreasing the observed polarization of the electrodes. This work investigates the effects of using an AC superimposed DC waveform on bismuth electrorefining. Bismuth has been identified as a potential surrogate for plutonium electrorefining due to its ability to mimic the same physical configuration. Six electrorefining runs were conducted. Four with AC superimposed DC waveforms and two DC runs to establish a baseline for comparison.

While there were some differences seen in the measured electrorefining current between the different runs, the major differences appeared to be due to the order of the experiments rather than the applied waveform. All six runs showed a high level of yield and coulombic efficiency. All six cathode rings were confirmed to be high-purity bismuth using scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDS). While the results were inconclusive about the ability of AC superimposed DC waveforms to increase the efficiency of bismuth electrorefining, applying an AC superimposed DC waveform did not appear to decrease the efficiency or yield of the process. The change in waveform also did not result in impurities being present in the product cathode ring. The implementation of AC superimposed DC waveforms to electrorefining is low cost, simple, and compatible with typical pyrochemical processing systems. Conducting more runs to confirm the reproducibility of the obtained results is recommended, as the results were inconclusive.

# Separation of Uranium from FLiTh salt

Jinsuo Zhang, Brenton Davis

Virginia Polytechnic Institute and State University

With the plethora of different next generation reactor designs it is important to understand how fuels can be fabricated. This presentation will focus on how uranium can be electrochemically separated from LiF-$ThF_4$ salt commonly referred to as FLiTh. This is to simulate the process of removing protactinium and uranium from the blanket salt once thorium has been bred into these materials. This process can be done with a solid tungsten electrode but has also been shown to work with a molten bismuth electrode. The reduction potentials of uranium and thorium are close together on an inert electrode. However, the activity of uranium and thorium in molten bismuth causes the reduction potentials to shift positively and the reduction potential of uranium shifts more than thorium's so there is a larger gap between the two potentials. Also, using a molten bismuth electrode allows for a more continuous process where using a solid electrode requires stopping the process to change out the electrode once too much material has been built up. The diffusion rate of uranium in bismuth slows down the process and if too large of a current is applied thorium will co-deposit with the uranium. A continuous current along with a pattern of applying a current and stopping the current were tried to figure out how to get only uranium to deposit in the bismuth without thorium depositing.

# Production and Characterization of Accelerated Aged Alloy

S. A. Simpson[1], K. S. Holliday[1], D. J. Roberts[1], A. J. Swift[1], C. Zhang[1], A. M. Parkes[2], D. S. Rappleye[3]

[1]Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA
[2]AWE-Aldermaston, Reading, Berkshire, RG7 4PR
[3]Brigham Young University, Provo, UT

The Pu facility at Lawrence Livermore National Laboratory has demonstrated the full pyrochemical flowsheet at the 200g scale to meet the needs of various plutonium science programs. Interest in the aging behavior of plutonium has led to the need for producing accelerated aged alloys. Doping weapons grade Pu with various quantities of Pu-238 accelerates the long-term aging process of Pu allowing for studies at an accelerated rate. The processes needed to produce such an alloy include modified Direct Oxide Reduction (DOR), a Molten Salt Extraction (MSE), electrorefining (ER), alloying, casting, rolling and annealing. The first batch of this project processed metallic weapons-grade Pu through an MSE and ER, resulting in a 99.8% pure product. This initial batch will be used as the baseline for the aging comparisons. The second project batch started with a modified DOR comprised of 200g of weapons-grade Pu metal and 15g of Pu-238 oxide. During this process, the oxide was reduced to metal and consolidated into the metallic weapons grade Pu. From here the material is rolled and annealed to meet design specifications. The purified product is characterized using Differential Scanning Calorimetry (DSC), Metallography, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Interstitial Analysis. Finally, the material is packaged using a 3013 laser welding system with heat sink material and stored for a designated timeline to fulfil programmatic needs. In this presentation we discuss the challenges of scaling down these operations and the equipment modifications that were necessary for success.

Figure 1. Plutonium metal button product from modified DOR process.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

# Study on Nuclear Fuel Cycle Policy using Dynamic Simulator NMB4.0

Kenji Takeshita, Tomohiko Okamura* and Masahiko Nakase

Laboratory for Zero-Carbon Energy, Institute of Innovative Research,
Tokyo Institute of Technology, Japan

We developed a new dynamic nuclear fuel cycle simulator, NMB4.0. Assuming scenarios for the sustainable nuclear power generation until the middle of the 22nd century in which technical options related to nuclear power generation, reprocessing, partitioning-transmutation and geological disposal were included, the scenario analysis using NMB4.0 was carried out. Based on the analytical results of fuel cycle scenarios such as once-through cycle, LWR cycle, LWR multicycle and FR cycle, the effect of the introduction of these technical options on the geological disposal was evaluated. From these results, we obtained following conclusions.

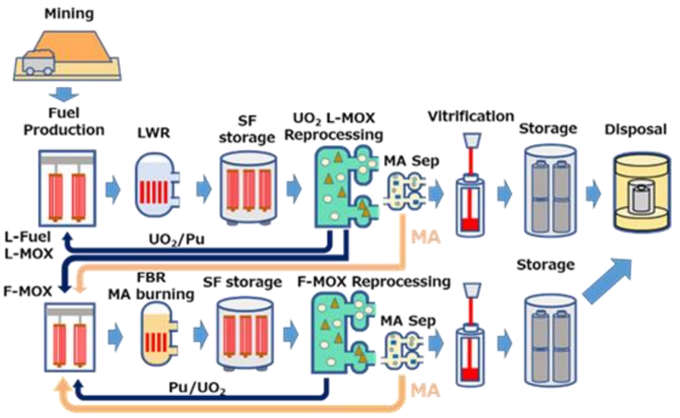


Fig.1 FR cycle introducing P&T Technology with MA separation

(1) The implementation of FR and FR cycle in the second part of this century is effective to reduce the disposal site area.

(2) By the further implementation of P&T technology with MA separation (Fig.1) and the additional technologies such as the long-term vitrified object storage, the separation of heat generation nuclides (Cs and Sr) and the high density package of vitrified objects (Multi-load PEM), as shown in Fig.2, the disposal site area was reduced remarkably and became less than that of the basic case (1.75km$^2$) which means the disposal site area of vitrified objects produced by the operation of a 800 t-HM/y reprocessing plant for 40y. Nuclear waste problem can be solved by the appropriate introduction of these technologies.

(3) Scenario study on nuclear fuel cycle using a dynamic fuel cycle simulator, NMB4.0, is very useful to make future nuclear policy for sustainable nuclear energy use. These results are also expected to be utilized as basic data for the discussions on future R&D policies.

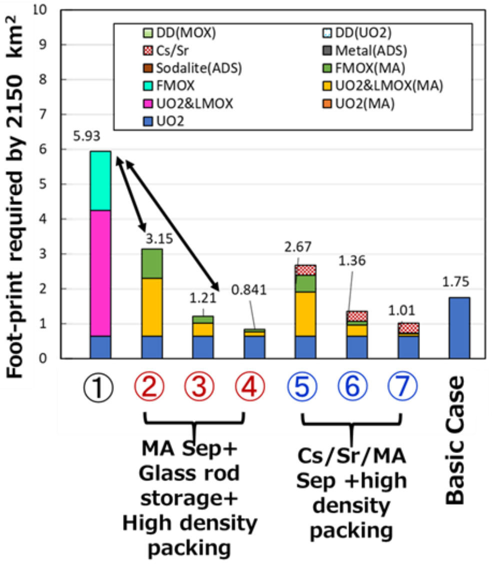


Fig.2 Effect of introduction of FR cycle with P&T technology on disposal site area

---

*Present affiliation : Hitachi-GE Nuclear Energy, Ltd

# Further optimization of the GANEX flowsheet

Michael Carrott, Dan Whittaker, Billy Keywood, Victoria Hayter, Mark Sarsfield, Chris Maher, Robin Taylor

National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, CA20 1PG, United Kingdom.

The processing of advanced fuels presents a number of technical challenges, including higher plutonium content than conventional thermal uranium oxide fuels, increasing fuel burn-ups, a requirement to avoid a separated Pu product (enhancing proliferation resistance), the flexibility to accommodate a range of fuel types and reduction of waste volumes. A key feature of many advanced fuel cycles is the requirement to recover the minor actinides (Np, Am and Cm), which in turn has a significant impact upon the radioactive waste burden of the deep geological repository. A range of aqueous reprocessing options are under development at varying stages of technical maturity[1]. These options can be broadly categorized depending upon whether the minor actinides are recovered as a separate product (heterogeneous recycling) or co-recovered with Pu (homogeneous recycling).

One option proposed for the homogeneous recycling of the minor actinides is the GANEX (Grouped ActiNide EXtraction) process. This process is based upon two solvent extraction cycles. In the first cycle a monoamide, di-2-ethylhexyl isobutyramide (1 M) in a kerosene diluent, is used to recover bulk uranium from the dissolved spent fuel. The second cycle employs a mixture of 0.2 M N,N,N',N'-tetraoctyldiglycolamide with 0.5 M N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide for the co-recovery of the transuranic actinides. The second cycle also requires the use of an aqueous soluble ligand to selectively strip and separate the trivalent actinides from the co-extracted lanthanides. Although both first and second cycle GANEX flowsheets have been successfully hot tested[2], further optimisation is required to increase the technology readiness levels, minimise waste volumes and improve the routing of some key species. Fundamental studies were undertaken to support development of the flowsheets and provide data that will underpin the development of process models. These studies addressed a number of key areas, including:

- Uranium distribution data under process conditions to assess maximum solvent loading and third phase formation in the GANEX-1 flowsheet.
- Technetium and neptunium extraction, behaviour and routing in the GANEX-1 flowsheet.
- Optimization of selective stripping in GANEX-2 flowsheet using a CHON reagent.

Results from these fundamental studies will be reported in conjunction with selected data from the flowsheet trials.

1) Baron, P., Cornet, S.M., Collins, E.D., DeAngelis, G., Del Cul, G., Fedorov, Y., Glatz, J.P., Ignatiev, V., Inoue, T., Khaperskaya, A., Kim, I.T., Kormilitsyn, M., Koyama, T., Law, J.D., Lee, H.S., Minato, K., Morita, Y., Uhlir, J., Warin, D., Taylor, R.J.; A review of separation processes proposed for advanced fuel cycles based on technology readiness level assessments; Prog. Nucl. Energy, **2019**, 117
2) Malmbeck, R., Magnusson, D., Bourg, S., Carrott, M., Geist, A., Heres, X., Miguirditchian, M., Modolo, G., Mullich, U., Sorel, C., Taylor, R., Wilden, A.; Homogeneous recycling of transuranium elements from irradiated fast reactor fuel by the EURO-GANEX solvent extraction process; Radiochim. Acta; **2019**, 917

# Exploration of novel solvents for MA separation for future rational nuclear fuel cycle based on the MA interim storage concept

Masahiko Nakase[1], Kenji Takeshita[1], Shinta Watanabe[1], Takashi Kajitani[1], Tohru Kobayashi[2], Chihiro Tabata[2], Tomoo Yamamura[3], Kota Matsui[4], Kenji Shirasaki[5], Ryo Takahashi[6], Taishi Tsukamoto[6], Hitomi Ishida[6] and Takashi Shimada[6]

[1]Tokyo Institute of Technology, [2]Japan Atomic Energy Agency, [3]Kyoto University, [4]Nagoya University, [5]Tohoku University, [6]Mitsubishi Heavy Industries

Separating Minor Actinide (MA) from High-Level-Liquid-Waste (HLLW) can minimize the burden of vitrified waste disposal. However, the development of the practical MA separation process still requires time, especially due to the finding of good extractants, and the time of introduction of fast breeder reactors (FBRs) is not necessarily visible. Our recent scenario study revealed that even the simplified MA separation, which allows for an accompany of a certain amount of Lanthanide (Ln), can lower the disposal burden. Therefore, we aim to develop such a simplified MA separation process with the concept of "interim storage of MA" to wait until the implementation of FBRs. To realize the simplified MA separation process, we are finding novel solvents with higher extraction performance and intrinsic safety. To find the solvents with higher performance and high engineering applicability, the chemoinformatics approach is also implemented, as well as experiments and chemical calculations.

## Experiments

Solvent extraction of Ln and MA was done with a series of solvents, including *n*-dodecane (DD) and hydrofluorocarbon (HFC) with a typical extractant such as *N*, *N*, *N′*, *N′*-tetra(2-ethylhexyl)-diglycolamide (T2EHDGA). Solubility tests with 100 mM extractant were first done, and the solvent extraction with Ln and MA with 3 M $HNO_3$ was implemented. Multiple regression was executed by some of the codes (such as RDkit on Python, KNIME, and HSPiP software) to determine the correlation between the experimental results and some features of solvents. Also, multistage extraction experiments with DD and HFC were implemented to see the applicability to the separation process.

## Result and Discussion

Solubility tests with a series of solvents revealed that the fluorinated solvents with smaller molecular sizes were suitable for T2EHDGA, which has large side alkyl chains. Also, when fluorinated solvent is used, extractants may not need long side chains to increase the solubility. The HFC showed high extractability of lanthanide (Ce, Nd, Eu) and MAs (Am, Cm, and Np). DFT and MD simulations were also implemented to understand the solvent effects on MA extractability, and some correlation between extractability and energy parameters was seen. Multistage extraction experiments were successfully implemented, and the Technical Readiness Level (TRL) of the HFC solvent was increased. For practical use, the design of the extractor suitable for the HFC solvents should also be studied.

## Acknowledgments

This study is supported by the MEXT Innovative Nuclear Research and Development Program Grant Number JPMXD0221459189. Actinide extraction experiments were done at the International Research Center for Nuclear Material Science, Institute of Material Research, Tohoku University (Proposal number; 202211-IRKAC-0037, 202212-IRKAC-0413, 202112-IRKAC-0026, 202012-IRKAC-0019, and 20F0023)

# A direct conversion method for the separation and temporary storage of MA

Tomoo Yamamura[1], Masahiko Nakase[2], Kenji Takeshita[2], Takashi Shimada[3], Taisuke Tsukamoto[3],
Hitomi Ishida[3], Ryo Takahashi[3]

[1]Kyoto University, [2]Tokyo Institute of Technology, [2] Mitsubishi Heavy Industries, Ltd.

In order to cope with global warming and the world situation concerning energy, in addition to LWRs and plutonium thermal reactors, next-generation LWRs, fast reactors, high-temperature gas reactors for hydrogen production, and even the introduction of small-scale reactors (SMRs) are envisioned. However, in the case of plutonium thermal utilization, for example, the reduction in the composition of Pu fissile nuclides and the increase in minor actinides (MAs) will be a major problem. Based on our analysis of the fuel cycle, we propose "actinide management" consisting of quality control of fissile Pu composition, MA disposal load, and transmutation technology, and are developing the fuel cycle and necessary technologies.

The currently envisioned MOX fuel fabrication process has the following problems: (1) the separation factor of Cm from Am needs to be high to reduce heat generation during fuel fabrication, (2) a large amount of secondary waste is generated due to the use of aqueous solution, and (3) the HLLW acceptance system from LWR is complicated and immature. In this paper, we report on the direct production method of (U, MA)$O_2$ solid solution (SS) to solve these problems by direct production of (U,MA)$O_2$ solid solution (SS) from HLLW, which uses HFC (hydrofluorocarbon) as a diluent.

## Results and discussions

The extracted organic phase (DGA-HFC) is solidified and converted to SS by two methods: A distillation method and B hydrothermal method. We are also conducting a CALPHAD study to predict the stability of SS over a wide composition range of MA and Ln. We are confirming, modifying, and improving the phase diagram with oxygen potentials using CALPHAD data (U-O, U-Ln-O, and U-MA-O) collected from the literature.

## Summary and future perspectives

We have proposed temporary storage of separated MA, whose process is expected to immediately convert the extracted MA into a stable fluorite $UO_2$ matrix by HFC dilution and produce stable SS containing MA and Ln after stabilization.

In the future, CALPHAD can be used to predict the stability of SS under various conditions and to identify constraints on the incorporation of MA into SS. Thermophysical property data such as specific heat and thermal conductivity of temporarily stored materials will be obtained.

1) C. Tabata, M. Nakase, M. Harigai, K. Shirasaki, A. Sunaga, T. Yamamura, Hydrofluorocarbon Diluent for CMPO Without Third Phase Formation: Extraction of Uranium(VI) and Lanthanide(III) Ions. *Separation Science and Technology* **2022**, *57*, 1097.
2) K. Shirasaki, C. Tabata, A. Sunaga, H. Sakai, D.X. Li, M. Konaka, T. Yamamura, Homogeneity of (U, M)$O_2$ (M=Th, Np) prepared by supercritical hydrothermal synthesis. *J. Nucl. Mater.* **2022**, *563*, 153608.
3) C. Tabata, K. Shirasaki, H. Sakai, A. Sunaga, D.X. Li, M. Konaka, T. Yamamura, Influence of additives on low-temperature hydrothermal synthesis of $UO_{2+x}$ and $ThO_2$. *CrystEngComm* **2022**, *24*, 3637.
4) C. Tabata, K. Shirasaki, A. Sunaga, H. Sakai, D.X. Li, M. Konaka, T. Yamamura, Supercritical hydrothermal synthesis of $UO_{2+x}$: Stoichiometry, crystal shape and size, and homogeneity observed using $^{23}$Na-NMR spectroscopy of (U,Na)$O_{2+x}$. *CrystEngComm* **2021**, *23*, 8660.

# Chloride to Nitrate Conversion of Pyrochemical Residues

Rebecca A. Carter, Morgan Cram, Grant Pollard

Savannah River National Laboratory

Recovery of plutonium from pyrochemical materials for the Savannah River Plutonium Processing Facility (SRPPF) will occur in aqueous nitrate operations, designated the Aqueous Recovery System (ARS). Pyrochemical residues from metal preparation such as the anode heel from electrorefining (ER) and salt scrub (SS) ingot will be processed in the ARS. The chlorides ($Cl^-$) entrained in the SS ingot—from being processed in molten calcium chloride—can cause detrimental corrosion when mixed with nitrates. Without a dedicated aqueous chloride line, SRPPF will need to take into consideration all potential effects caused by the presence of chloride residues in the nitrate-based ARS to mitigate corrosion of both process equipment and the downstream ventilation. The Savannah River National Laboratory (SRNL) has evaluated the ARS flowsheet with varying amounts of $Cl^-$ from simulated pyrochemical residues. Corrosion studies were also carried out to measure the potential effects on the materials of construction for the ARS.

The baseline flowsheet includes the use of both nitric acid and potassium fluoride to dissolve the anode heel and SS ingot. An alternative flowsheet is presented which relies on a higher concentration of nitric acid to directly dissolve salt residues from molten salt extraction (MSE) and ER directly in the ARS, skipping the SS step. Experiments to further optimize both the baseline flowsheet and alternative flowsheet show complete $Cl^-$ removal at initial nitric acid concentrations of 12-14 M. Parallel corrosion testing of 304L stainless steel, representing the piping material after the dissolver and before the scrubber, exhibited significant localized corrosion, even at the baseline flowsheet with low initial chloride concentrations of 0.2 M. Additional corrosion testing of Inconel 690 coupons, representative of the dissolver material, showed more corrosion to exposure of the off-gas in the headspace of the dissolver than to coupons submerged in the solution. Inconel 690 performed better than the 304 L stainless steel.

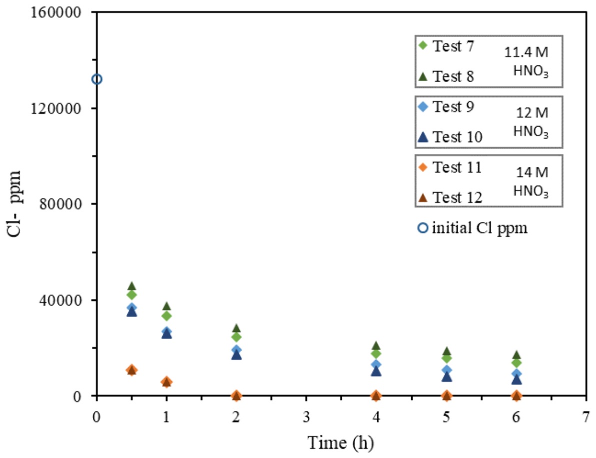


Figure 2. Chloride removal from solution at 11-14 M $HNO_3$.

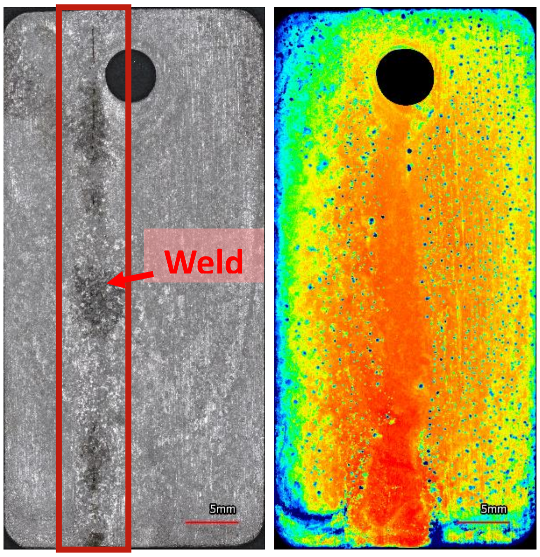


Figure 2. Images and 3D maps of Inconel 690 coupons after exposure to dissolution conditions in dissolver headspace.

May 16, 2023

Poster Session
EIL A-112

### Poster Session

### Tuesday Evening, May 16, 2023

Poster Session Chair: Travis Grimes, INL

| | | |
|---|---|---|
| **P01** | Los Alamos National Laboratory Nuclear Material Packaging and SAVY-4000 Update | Alexander Bishop, LANL |
| **P02** | Functionalizing Spiropyrans for Photochemically Controlled Metal Ion Binding and Release | Barbara Garcia, Florida International University |
| **P03** | Kinetics of Molybdenum Extraction from Nitric Acid Using HDEHP | Brandon Williams, UNLV |
| **P04** | Evaluation of the Functionalized Particles for Solid-Liquid Separations | Colt Heathman, INL |
| **P05** | Analysis of the Effects of Moisture on the Electrochemistry of Molten Calcium Chloride | Devin Rappleye, BYU |
| **P06** | Direct Analysis of Plutonium(IV) Process Solutions Using Chemometric Methods | Dider Maloubier, CEA |
| **P07** | Solubility-Based Separation of Lanthanides from Actinides via Pyrochemical Processing | Dmitry Maltsev, ORNL |
| **P08** | Text Summarization of Scientific Documents Using a Machine Learning Algorithm | Eric Hoar, SRNL |
| **P09** | Experimental System for Development of Metal Fuel Zone Refining Model | Ethan Rose<br>Jonathon Dromey, University of Utah |
| **P10** | Lanthanide Complexation by Tripodal Tris-(pyrazolyl) Ligands: An Investigation of Pyrazole Substituent Effects on Complexation | Gabriel Flores, Florida International University |
| **P11** | Group Hexavalent Actinide Separation via Co-Crystallization: The Behavior of Used Nuclear Fuel Bad Actors Mo, Tc, and Ru | Jennifer Pyles, Univ. of Alabama at Birmingham |
| **P12** | TBP Radiolysis Products' Effect on Ce and Np Valence and Speciation | Joshua Dunbar, Colorado School of Mines |
| **P13** | Nonproliferation Stewardship Program: Athena Plutonium Processing Initiative | Kevin Lyon, INL |
| **P14** | Extraction of Tetravalent Thorium and Plutonium by HEH[EHP] and T2EHDGA from Nitric Acid | Logan Smith, UNLV |

May 16, 2023

Poster Session
EIL A-112

## Poster Session (cont.)
## Tuesday Evening, May 16, 2023

Poster Session Chair: Travis Grimes, INL

| | | |
|---|---|---|
| **P15** | Photoelectrochemical Control of Actinide Oxidation State | Mariel Morales Duque, Florida International Univ. |
| **P16** | Los Alamos National Laboratory Material Recycle and Recovery | Nickolas Anderson, LANL |
| **P17** | Evaluation of Dry Scrubber Media for Chlorine Gas Neutralization in Pu Pyro Processing | Nikki Wolford, LANL |
| **P18** | Treatment of $UF_6$ in ionic liquid and pathways of recovery of $UF_4$ | Renee Olney, UNLV |
| **P19** | Effect of the Number of Extraction Stages on Uranium Recovery for a UREX Process | Tracy Rudisill, SRNL |
| **P20** | Preliminary Studies on the Electrochemical Preparation of Unusual Oxidation States of *f*-Elements in Concentrated Carbonate Solutions | Xiangyang Hou, Florida International University |
| **P21** | Development of Nuclear Salt Waste Options | Morgan Kropp, INL |
| **P22** | Modelling the gas generation of actinide bearing materials in storage containers | Sebastien Faure, CEA |

# Los Alamos National Laboratory Nuclear Material Packaging and SAVY-4000 Update

Alexander S. Bishop, Paul H Smith, Jonah J. Newton, John T. Davis, Tristan Karns, Jonathan G. Gigax

Los Alamos National Laboratory

## Los Alamos National Laboratory Nuclear Material Packaging

Nuclear material packaging at Los Alamos National Laboratory (LANL) encompasses a wide range of material forms and compositions. Additional variables are material and storage dependent, including age, wattage, external temperature, and relative humidity. Evaluation of these conditions has influenced the legacy container repackaging prioritization as well as the SAVY-4000 lifetime evaluation.

## The SAVY-4000 Nuclear Material Storage Container Update

The SAVY-4000 nuclear material storage container series was approved by the Department of Energy (DOE) for use at LANL on April 16th, 2014. The very first implementation of the SAVY-4000 as a nuclear material storage container was in 2011. This has provided 13 years of nuclear material storage to evaluate the container's response to storage conditions.

An original lifetime of the SAVY-4000 was taken to be 5 years. This was extended to 15 years through accelerated aging studies and surveillance activities of loaded containers. An additional lifetime extension beyond 15 years is being evaluated through similar means.

The projected path toward lifetime evaluation and extension consists of 3 unique activities: 1) Surveillance of nuclear material storage containers including the SAVY-4000 and its predecessor containers with longer service lives, 2) Systematic corrosion experiments on coupons to understand controlling mechanisms of corrosion at storage conditions, and 3) accelerated aging experiments to establish corrosion thresholds as related to container performance.

All experiments will be evaluated against the DOE and LANL accepted Safety Analysis Report, LANL facility requirements, and DOE Manual M441.1-1. The main testing metrics of focus include evaluation of the containment boundary under physical stress (drop test). These evaluations have been conducted primarily through helium leak testing pre- and post-drop. High speed photography, measurement of airborne release fraction and respirable release fraction have been included in the LANL drop tower as well.

# Functionalizing Spiropyrans for Photochemically Controlled Metal Ion Binding and Release

Barbara Garcia[1], Alberto Ruiz Reyes[1], Jeffrey McLachlan[1], Christopher Dares[1]

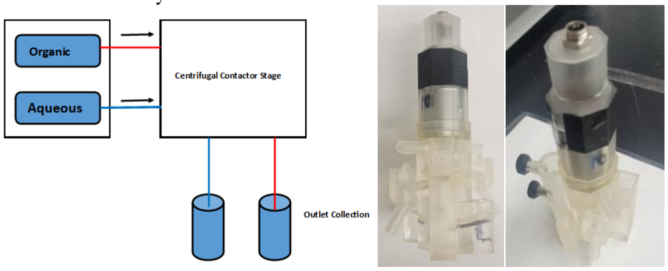
[1]Florida International University

The use of nuclear energy produces fission products and neutron capture products. Appropriate reprocessing of used nuclear material to separate these materials is of global interest. The most common strategy involves the development of ligands which optimize the separation of fission product Ln(III) from minor actinide neutron capture products by precisely balancing ligand binding strength and selectivity for a specific metal ion. Typically, the stronger the binding, the less selective a ligand is, though weaker binding typically results in inefficient separations. The most well-established nuclear separations process, PUREX (Plutonium Uranium Reduction Extraction) involves an initial solvent-extraction based separation that results in an aqueous phase that is comprised of 99.9% of the fission products and minor actinides (Np, Pu, Am, and Cm). There are alternative strategies which are less developed including the use of photoactive ligands for sensing and possible separations. One class of light responsive switch molecules is spiropyrans (SP). These molecules are responsive to light, redox variations, temperature, and pH. In the merocyanine form, they can be functionalized to bind metal ions. They can be further functionalized to tune the relative stability of each form (spiropyran and merocyanine) to make them more responsive or specific for complexing or releasing a metal ion of interest. The use of light or redox variations as a stimulus to bind or release the metal ions provides for a degree of separations control not possible with non-photoactive or redox-inactive ligands. This work will focus on the development and use of a functionalized SP for potential photochemical/electrochemical separations of actinides and lanthanides.

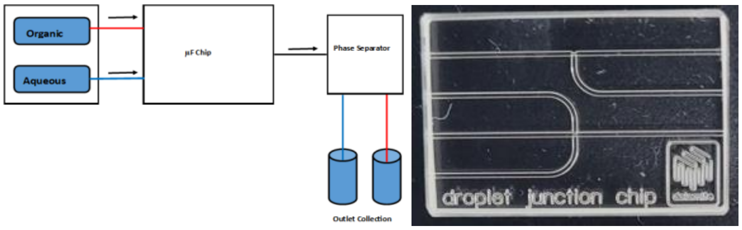
# Kinetics of Molybdenum Extraction from Nitric Acid Using HDEHP

Brandon Williams, Art Gelis
University of Nevada, Las Vegas
artem.gelis@unlv.edu

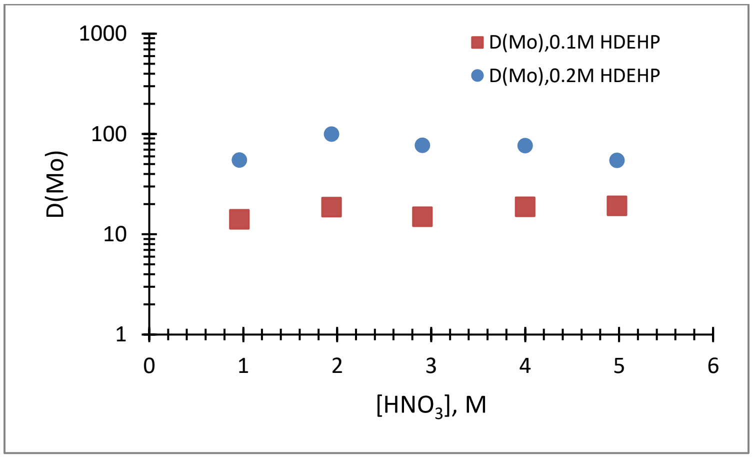
Molybdenum-99, a uranium fission product, is a critical isotope for the production of technetium-99m generators. Pressure to secure a stable quantity of molybdenum-99 has fueled interests in efficient and timely separation and purification methods. One such separation method involves extracting molybdenum-99 in solution using bis(2-ehtylhexyl) hydrogen phosphate (HDEHP). Microfluidics and centrifugal contactors are used to study the kinetics of this solvent extraction method on a lab scale.



Graphic 1: Schematic of the single-stage centrifugal contactor set-up alongside a picture of the contactor stage.



Graphic 2: Schematic of a droplet-forming microfluidic chip set-up next to the droplet junction chip used for experiments.



Graphic 3: Graph of distribution ratios of molybdenum, D(Mo), in the centrifugal contactor at 0.1M and 0.2M HDEHP in relation to nitric acid concentration.

# Evaluation of the Functionalized Particles for Solid-Liquid Separations

Colt R. Heathman, Corey D. Pilgrim, Gregory P. Horne

Idaho National Laboratory

The nuclear industry is currently undergoing a paradigm shift towards advanced reactor concepts with higher levels of enrichment to meet present and future societal energy demands. During this shift, there is also a strong need for advancing technologies that enable simpler approaches to waste management and the recovery of valuable resources from special nuclear materials (SNM). As a result of changing landscape new approaches to harvesting and managing fission and activation products from SNM presents opportunities for separations approaches, including liquid – liquid and solid-liquid separations approaches. In this work, we aim to develop a pathway to selectively functionalize support materials with metal chelators to enable selectivity controls suitable for solid-liquid separations in support of liquid-liquid nuclear fuel reprocessing effluent streams. This poster discusses the initial findings of this work and characterization techniques used for this analysis.

# Analysis of the Effects of Moisture on the Electrochemistry of Molten Calcium Chloride

Rankin Shum, Marah Fuller, Devin Rappleye

[1]Department of Chemical Engineering, Brigham Young University, Provo, UT 84602 USA

Calcium chloride is used in actinide metal processing for direct oxide reduction, molten salt extraction, and electrorefining. Additionally, recent efforts have been made to develop electrolytic oxide reduction in $CaCl_2$ for actinides.[1] Due to its deliquescent nature, $CaCl_2$ readily absorbs moisture. Moisture and its byproducts can reduce efficiency and increase corrosion within processes utilizing molten $CaCl_2$. Hence, careful drying of $CaCl_2$ is requisite to minimize undesirable byproducts. When drying $CaCl_2$ and its hydrates, multiple reactions occur depending upon the temperature and partial pressure of water. While the electrochemical behavior of oxide, hydroxide, and hydroxychloride ions generated from residual moisture in molten $CaCl_2$ has been extensively investigated,[2-4] the fate and behavior of hydrogen from residual moisture has received relatively less attention.

Our study seeks to investigate the electrochemical response of a postulated hydrogen gas evolution reaction in molten $CaCl_2$ and the effect, if any, of the drying treatment of $CaCl_2$ on the hypothesized hydrogen electrochemical response. The characterization of this response could enable rapid, *in situ* feedback on the quality of the $CaCl_2$ and the hydrogen content. Furthermore, the minimization of this response could decrease corrosion and increase the reduction efficiency in electrolytic oxide reduction, electrorefining, and other electrochemical processes in molten salts containing $CaCl_2$.

The electrochemical response and products in molten $CaCl_2$ were interrogated using voltammetric techniques and a residual gas analyzer. A peak at ~0.6 V vs. $Ca^{2+}/Ca$ was identified and confirmed to exchange $1.95\pm0.17$ and $1.87\pm0.17$ electrons using cyclic voltammetry (CV) and square wave voltammetry (SWV), respectively. Constant potential electrolysis was applied at the identified peak while analyzing the off gas from the cell with a residual gas analyzer. The 2 AMU signal intensity increased above the baseline while electrolysis was occurring and returned to baseline levels upon termination of electrolysis. The observations provide evidence that the peak is associated with the reduction of hydrogen ions to hydrogen gas (i.e., $2H^+ + 2e^- \leftrightarrow H_{2(g)}$).

Using the peak current with Randles-Ševčik equation and a diffusion coefficient for $^3H^+$ in FLiBe ($5.8\times10^{-5}$ cm$^2$ s$^{-1}$ at 1123K),[5] the concentrations of $H^+$ in molten $CaCl_2$ were estimated to be $3.85\text{-}6.46\times10^{-7}$ mol cm$^{-3}$ (0.192-0.323 ppmw). Hence, CV and SWV can be used to detect trace quantities of impurities from the reaction of moisture with $CaCl_2$. The concentration $H^+$ did not vary substantially despite some batches of salt being exposed to ambient air for up to 30 minutes at low humidity (<20%) and room temperature after vacuum drying.

1) Jackson, J. M.; Monreal, M. J.; Weisbrod, K. R.; Rodriguez, D. A. T.; Simpson, M. F. *Electrolytic Oxide Reduction of Plutonium Oxide Surrogates*; Los Alamos National Lab. (LANL), Los Alamos, NM (United States), 2018.
2) Zhang, C.; Rappleye, D.; Nelson, A.; Simpson, S.; Simpson, M. Electroanalytical Measurements of Oxide Ions in Molten CaCl2 on W Electrode. *J. Electrochem. Soc.* **2021**, *168* (9), 097502.
3) Mukherjee, A.; Kumaresan, R.; Ghosh, S. Redox Behaviour of CaCl2 Melts in Presence of Moisture as Impurity. Part I: Cyclic Voltammetry. *J. Electroanal. Chem.* **2021**, *902*, 115778.
4) Faulkner, E.; Monreal, M.; Jackson, M.; Simpson, M. F. Effect and Measurement of Residual Water in CaCl2 Intended for Use as Electrolyte in Molten Salt Electrochemical Processing. *J. Radioanal. Nucl. Chem.* **2020**, *326* (2), 1289–1298.
5) Lam, S. T.; Li, Q.-J.; Mailoa, J.; Forsberg, C.; Ballinger, R.; Li, J. The Impact of Hydrogen Valence on Its Bonding and Transport in Molten Fluoride Salts. *J. Mater. Chem. A* **2021**, *9* (3), 1784–1794.

# Direct Analysis of Plutonium(IV) Process Solutions Using Chemometric Methods

G. Bailly, D. Maloubier, G. Legay

CEA, DAM, Valduc, F-21120 Is-sur-Tille, France

The development of on-line analytical methods is an issue to control plutonium processing. However, on-line adaptation of some traditional techniques such as UV-Vis spectrophotometry is not straightforward. In nitric acid solutions, Pu(IV) forms various Pu – nitrate complexes which possess different electronic properties, leading to slightly different UV-Vis spectra. The formation of these complexes is controlled by nitric acid concentration. Therefore, it is impossible to quantify Pu(IV) concentration in solutions of unknown acidity with a single wavelength UV-Vis analysis if there is no sample preparation. This work presents preliminary tests on Pu(IV) quantification without sample preparation, using chemometric methods. Calibration and validation procedure will be presented, with a special emphasis on the strategy followed to construct a calibration set that can be representative of a real process where actual samples are difficult to obtain.

# Direct Analysis of Plutonium(IV) Process Solutions Using Chemometric Methods

G. Bailly, D. Maloubier, G. Legay

CEA, DAM, Valduc, F-21120 Is-sur-Tille, France

The development of on-line analytical methods is an issue to control plutonium processing. However, on-line adaptation of some traditional techniques such as UV-Vis spectrophotometry is not straightforward. In nitric acid solutions, Pu(IV) forms various Pu – nitrate complexes which possess different electronic properties, leading to slightly different UV-Vis spectra. The formation of these complexes is controlled by nitric acid concentration. Therefore, it is impossible to quantify Pu(IV) concentration in solutions of unknown acidity with a single wavelength UV-Vis analysis if there is no sample preparation. This work presents preliminary tests on Pu(IV) quantification without sample preparation, using chemometric methods. Calibration and validation procedure will be presented, with a special emphasis on the strategy followed to construct a calibration set that can be representative of a real process where actual samples are difficult to obtain.

# Text Summarization of Scientific Documents Using a Machine Learning Algorithm

Eric Hoar, Megan Hoover, Lindsay Roy

Savannah River National Laboratory

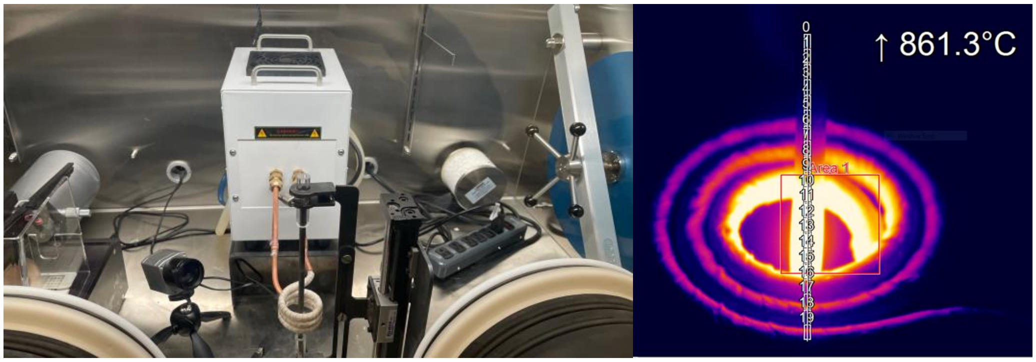
Knowledge preservation is vital to the scientific community. Unfortunately, troves of processing knowledge have left the nuclear community without transferring the years of information and hands-on experience to next generation workforce. To prevent this lapse in knowledge transfer, early- and mid-career scientists with future and recent retirees are establishing a mechanism for preservation and dissemination the information to the future nuclear workforce. This poster will report our efforts to capture decades of actinide separations peer-reviewed articles, reports, presentations, and other types of notes in various formats at Savannah River National Laboratory in conjunction with machine learning to summarize scientific documents. Utilizing this generalized methodology, the proposed model can produce a summary of a single peer-reviewed article, in hopes of demonstrating proof of concept for a more complex natural language processing model.

# Experimental System for Development of Metal Fuel Zone Refining Model

Ethan Rose[1], Jonathon Dromey[1], Tae-Sic Yoo[2], Mason Childs[2], David Horvath[2], and Michael F. Simpson[1]

[1]University of Utah, [2]Idaho National Laboratory

Idaho National Laboratory and the University of Utah are currently collaborating on an ARPA-E funded project to develop a zone refining (ZR) process to separate uranium and transuranic (U/TRU) actinides from fission products in metallic spent nuclear fuel (SNF). In support of building a predictive computational model for the process that can be used to optimize process conditions for testing with either surrogate or real SNF, an experimental system has been assembled at the University of Utah in the Nuclear PyroMetallurgy Laboratory and is now generating data for the model. This system (shown below, left) features a 15-kW/30-80 kHz induction heater operational inside of an argon-atmosphere glove box with less than 10 ppm of both $H_2O$ and $O_2$.



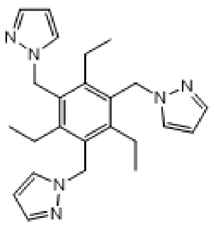
Custom heating coils with major diameter of 2.5 cm and up to three turns have been fabricated with coils in either a uni-axial helical or uni-axial concentric configuration (see above, right). Metal rods with about 6-mm diameter can be fixed at both ends while being translated in the vertical direction using an automated traversing slide. Temperature distribution along the heated rods can be measured using an infrared (IR) camera. SNF treatment requires heating of the rod to at least 1200°C to melt a 1-2 cm length of the rod to traverse the length of the rod. Based on published phase diagrams, U/TRU and fission products should form two or more immiscible liquid phases. Movement of the molten zone slowly through the rod's length should, thus, cause actinides and insoluble fission products to segregate to opposite ends of the metal fuel rod. The IR camera was tested for accuracy of temperature measurement by melting an aluminum rod. A 6°C difference between the maximum temperature measured (654°C) and the published melting point of aluminum (660°C) was observed. Stainless steel rods have similarly been melted with this system. Results of tests to control shape of the molten zone of surrogate metals, including aluminum and copper, will be presented. Also presented are plans for assembling uranium-rare earth alloy rods for surrogate SNF testing.

# Lanthanide Complexation by Tripodal Tris-(pyrazolyl) Ligands: An Investigation of Pyrazole Substituent Effects on Complexation

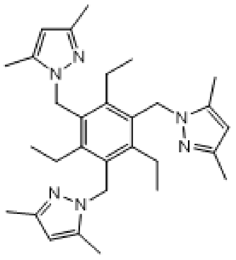
Gabriel A. Flores, Alexander N. Morozov, Zanders Peraza, Tosin M. Jonah, Alexander M. Mebel, Konstantinos Kavallieratos

Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199

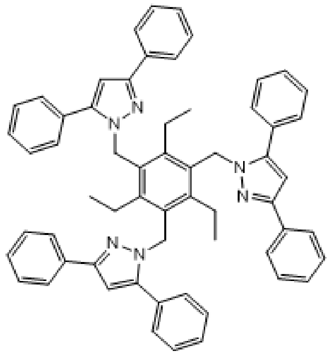
The complexation of a family of tripodal tris-(pyrazolyl) ligands with trivalent lanthanides was investigated in order to determine their potential application as extractants of An(III) from alkaline aqueous media. The substitution on the pyrazole ring affected the ligand ability to complex Ln(III), substantially. Fluorescence and NMR titration experiments provide evidence for the complexation of Ln(III) by ((2,4,6-triethylbenzene-1,3,5-triyl)tris(methylene))tris(1H-pyrazole) (**1**) and ((2,4,6-triethylbenzene-1,3,5-triyl)tris(methylene))tris(3,5-dimethyl-1H-pyrazole) (**2**). The phenyl substituted analog ((2,4,6-triethylbenzene-1,3,5-triyl)tris(methylene))tris(3,5-diphenyl-1H-pyrazole) (**3**) did not bind Ln(III), presumably due to steric hindrance that prevents ion pairing. **1** and **2** were found to be different types of fluorescence sensors: Upon addition of Ln(III), **1** shows fluorescence quenching and **2** generally shows fluorescence enhancement. Fluorescence titration experiments of **1** and **2** with Sm(III) and subsequent nonlinear regression analysis of the 1:1 binding isotherm gave $K_{11} = 1.5 \times 10^3$ $M^{-1}$ and $K_{11} = 3.6 \times 10^4$ $M^{-1}$ for **1** and **2**, respectively. Theoretical DFT calculations were in good agreement with experimental data and determined the likely structure of the complexes formed: Complexes the type $[\mathbf{L}\cdot Sm\cdot(NO_3)_2]NO_3$ , where **L** = **1** or **2**, with a 7-coordinated Sm(III) center, bound to the three N-binding sites of the tripyrazole ligand, and four O-sites from the two nitrates coordinated in the 1st sphere in a bidentate fashion were found to be thermodynamically favored. Spectroscopic and preliminary theoretical studies with additional newly-synthesized bis(pyrazolyl) analogs of **1**-**3**, that contain two instead of three pyrazolyl sites will also be discussed.



1



2



3

# Group Hexavalent Actinide Separation via Co-Crystallization: The Behavior of Used Nuclear Fuel Bad Actors Mo, Tc, and Ru

Jennifer M. Pyles[1], Jeffrey D. Einkauf[2], Luke R. Sadergaski[3], Lætitia H. Delmau[3], and Bruce A. Moyer[2], and Jonathan D. Burns[1]

[1]Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL
[2]Physical Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN
[3]Isotope Science and Engineering Directorate, Oak Ridge National Laboratory, Oak Ridge, TN

The burning of fossil fuels has been the primary source of energy for modern civilization. However, recently, the negative environmental impacts from these processes including, the emission of pollutants and greenhouse gases, which excellerate climate change, have garnered much attention. This has nesseitated the development of green, renewable energy, with one of the few energy sources that can be scaled to meet the growing demand being nuclear power. To enable the expansion of nuclear power several challenges need to be addressed. One of the main challenges is developing a separation/recycling scheme for used nuclear fuel (UNF) that enhances the recovery of the U, Pu, and other actinide (An) species. Sequentially, the ideal separation process should minimize the impact of waste bound for a geological repository, maintain the nonproliferation standards, and have the ability to scale the process for a diverse fleet of reactor fuels.

The aim of this research explores a single-step separation technology for the recovery of the actinides ranging from U-Am as a group, utilizing a co-crystallization with uranyl nitrate hexahydrate (UNH). Recent studies have shown the transuranic (TRU) species in their hexavalent state, Np(VI), Pu(VI), or Am(VI), which exist as the dioxo actinyl molecular ion, $AnO_2^{2+}$, have near proportional removal from solution to that of U(VI). The co-crystallization approach has extremely high selectivity for the An(VI) species, while completely discriminating against fission products. Aspects of the separation of the hexavalent actinides from fission products will be discussed, with special attention on the problematic fission product species like Mo, Tc, and Ru. These experiments will be analyzed by UV-Vis and ICP-MS to determine the separation of each element. Samples for analysis will be taken from pre-crystallization, post-crystallization supernatant, and from a solution of the dissolved crystalline product.

# TBP Radiolysis Products' Effect on Ce and Np Valence and Speciation

Joshua Dunbar[1], Mark Jensen[1,2]

[1]Chemistry Department and [2]Nuclear Science and Engineering Program, Colorado School of Mines

Advanced nuclear fuel cycles require selective separation of the minor actinides in order to achieve full product recovery and purity[1]. In this respect neptunium (Np) poses a challenge, as its variety of stable oxidation states allow it to distribute between both the aqueous and the organic phase over a wide range of conditions[2]. One complicating factor is the high radiation field found in reprocessing systems, which causes radiolysis of extractant molecules, creating radiolysis products that may have different chemistry with the minor actinides. In tributyl phosphate (TBP) based processes such as PUREX, UREX, COEX or CoDECON, the primary radiolysis product, dibutyl phosphoric acid (HDBP), is known to alter the speciation of extracted metals and complicate stripping in reprocessing systems[3].

Cerium (Ce) was chosen as a preliminary system to investigate, as it has an accessible (IV/III) redox couple and Ce(IV) is readily extracted into TBP. We pursued a combined spectrophotometric and electrochemical approach to probe the effect of HDBP on the behavior of Ce in TBP. The Ce(IV/III) couple is found at decently oxidizing potentials, +1.303 V vs Ag/AgCl in HDBP-free TBP equilibrated with 7 M $HNO_3$. It was found that HDBP strongly stabilizes the Ce(IV) state, shifting the couple to lower potentials. Additionally, the dependence of the $E_{1/2}$ of the couple on the HDBP concentration is indicative of a two-electron transfer and the presence of polynuclear Ce complexes. Spectrophotometric investigation of the behavior of Ce in TBP with varying amounts of HDBP showed different behavior for Ce(IV) as compared to Ce(III). Both strongly prefer to complex to HDBP in the nitric acid equilibrated organic phase as compared to TBP, but while Ce(III) binds to dimers of HDBP, Ce(IV) is complexed to $DBP^-$ monomers. The equilibrium constants for HDBP binding were also measured. Tetravalent cerium was found to suffer from precipitation issues with high HDBP concentrations. Again, HDBP was found to strongly stabilize Ce(IV) over Ce(III). With completion of the Ce study, the electrochemical behavior of Np in TBP was considered. Initial results on the Np system will also be presented.

1) Glatz, J. P., Souček, P. & Malmbeck, R. Key challenges in advanced reprocessing of spent nuclear fuels. In *Reprocessing and Recycling of Spent Nuclear Fuel* 49–62 (Elsevier Inc., 2015).
2) Mincher, B. J. *et al.* The redox chemistry of neptunium in γ-irradiated aqueous nitric acid. *Radiochim Acta* **101**, 259–265 (2013).
3) Mincher, B. J., Mezyk, S. P. & Martin, L. R. A pulse radiolysis investigation of the reactions of tributyl phosphate with the radical products of aqueous nitric acid irradiation. *Journal of Physical Chemistry A* **112**, 6275–6280 (2008).

# Nonproliferation Stewardship Program: Athena Plutonium Processing Initiative

Kevin Lyon[1], Brienne Seiner[2], Gregg Lumetta[2], Michael Miller[1], Harris Eldridge[3], Matthew Griffin[3], Candido Pereira[4]

[1]Idaho National Laboratory, [2]Pacific Northwest National Laboratory, [3]Savannah River National Laboratory, [4]Argonne National Laboratory

The United States' National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation has recently initiated a new program, the Nonproliferation Stewardship Program (NSP). NSP's objective is to ensure that the nation's competencies in nonproliferation are maintained by cultivating a robust and enduring workforce of experts to meet present and future needs.

NSP's Athena initiative is building and modernizing the necessary infrastructure and executing the relevant science and technology (S&T) to develop the next generation of nonproliferation experts in processing of irradiated fuel and targets for the recovery of plutonium and other fissile materials. Athena aqueous processing unit operations focus on head-end treatment, dissolution, and chemical separations using solvent extraction and ion exchange. Several new testing environments ranging from hot cells to gloveboxes and fume hoods are being established, including the Plutonium Recovery and Conversion System (PuRCS) at PNNL, the Actinide Science and Engineering Test-bed (ASET) at SRNL, and the Beartooth Test-bed at INL. A multidisciplinary S&T approach is being pursued emphasizing nuclear material processing, material monitoring & characterization, computational modeling & simulation, and data science. This presentation will provide an overview of Athena's approach to nonproliferation stewardship, recent advances in workforce development activities, and stakeholder engagement strategies to maximize NSP's benefit and scientific impact across the U.S. government.

# Extraction of Tetravalent Thorium and Plutonium by HEH[EHP] and T2EHDGA from Nitric Acid

Logan Smith, Artem Gelis

Radiochemistry Program, University of Nevada, Las Vegas

The extraction of tetravalent thorium and plutonium by the phosphonic acid extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and the diglycolamide extractant N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA) from nitric acid media was investigated. Both these extractants have long histories in the arena of actinide separations, but recent research has focused chiefly on their utility in partitioning the minor actinides. Structurally, the extractants both feature 2-ethylhexyl groups (Fig. 1). Dilutions of both extractants were done in n-dodecane.

In the case of thorium, batch tests were performed using a Th-234 tracer and liquid scintillation counting. The results of slope analysis (example, Fig. 2) of extraction by HEH[EHP] suggest that two major species are involved, one dominating at lower acidities (approx. 0.4N $HNO_3$) and one dominating at higher acidities (approx. 4.0N $HNO_3$), neither of which have previously been proposed. EXAFS spectra of Th-HEH[EHP] complexes will be presented. In the extraction by T2EHDGA, results suggest that the ligand ratio is 3:1.

In the case of plutonium, batch tests were performed using Pu-242 (Fig. 3) and liquid scintillation counting. Early results will be presented.

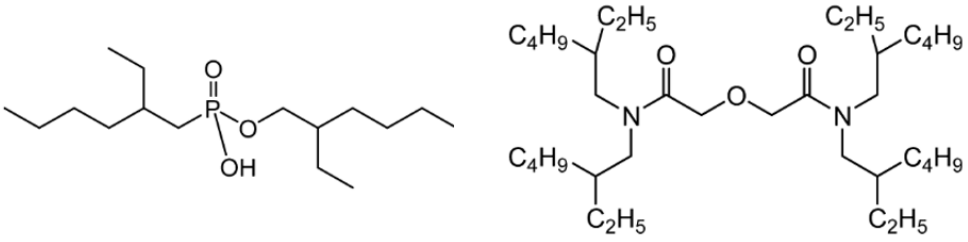


*Fig. 1: HEH[EHP] (left), T2EHDGA (right)*

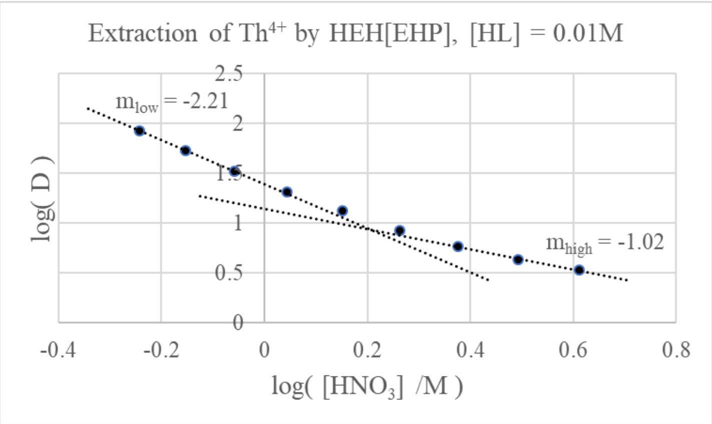


*Fig. 2: Example slope analysis*

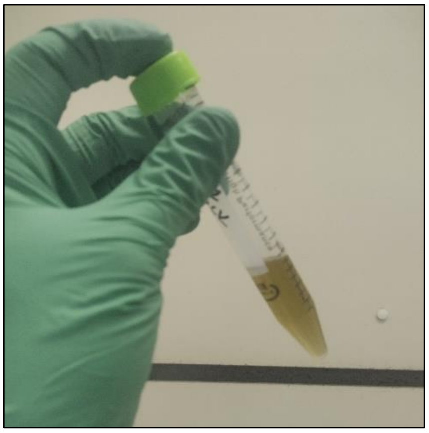


*Fig. 3: Pu-242 stock*

# Photoelectrochemical Control of Actinide Oxidation State

Mariel Morales Duque[1], Johan Gonzalez-Moya[1], Jeffrey McLachlan,[2] Christopher Dares[1]

[1]Florida International University, [2]Lawrence Berkeley National Laboratory

Reprocessing used nuclear fuel (UNF) requires control of oxidation states of various components. The hexavalent oxidation state for actinides is often considered the most convenient for separation of actinide from (UNF). The effort required to place actinides in the hexavalent state increases across the series, with no examples of hexavalent actinides in acidic solutions beyond Am. There is a need to develop methods to generate and maintain actinide such as (Np, Pu, Am) in the hexavalent state with as little energy input as possible. Previously, our group highlighted the photocatalytic oxidation of Am(III) to Am(VI) using $TiO_2$ under UV illumination[1] when applying potential of (1.55 V vs SCE). Work here includes using (MO) electrodes such as: $TiO_2$, $SnO_2$, and *n*ITO as a base layer combined with a different metal oxide like $Fe_2O_3$ added subsequently, to improve photocatalysis using visible light absorption. Initial studies have been conducted for water oxidation, comparing the catalytic properties of bare *n*ITO and functionalized *n*ITO with $Fe_2O_3$, by illuminating with UV and visible light. This preliminary work demonstrates that functionalized nITO|$Fe_2O_3$ can absorb visible light, lowering the onset potential required for water oxidation. Future studies will be conducted using lanthanides (Ce) and then actinides (U, Np, Pu, Am).

1) Sheridan, M.; Gonzalez, J. R.; McLachlan, J.; Grimes, T.; Dares, C. Photocatalytic Conversion of Am(III) to Am(VI) Using a $TiO_2$ Electrode. *ACS Appl. Energy Mater.* **2021**, 4, 11854-11857. https://doi.org/10.1021/acsaem.1c026352

# Los Alamos National Laboratory Material Recycle and Recovery

Nickolas H. Anderson

Los Alamos National Laboratory

Pit Technologies division at Los Alamos National Laboratory (LANL) is responsible for the production of plutonium pits for the United States. This is a relatively new purpose for LANL and there is a lot of work and unknowns that are associated with this new mission. While much of this effort is focused on pit production, it is the purpose of those in the material recycle and recovery (MR&R) program to act as good stewards of the plutonium in the United States stockpile. This includes the formation and purification of metal through pyrochemistry, the recovery of plutonium wastes in aqueous processing, and the storage and management of plutonium inside the facility.

The strategic investments portfolio in particular oversees investments in projects that are geared towards the retention and creation of plutonium metal inside the facility. These strategic investments that the MR&R program is making range from low technical readiness level (TRL) research and development projects to large scale process implementation. The impacts of these investments are already having operational benefits inside of the plant and the results, and people that are contributing to them, are worth highlighting.

# Evaluation of Dry Scrubber Media for Chlorine Gas Neutralization in Pu Pyro Processing

Nikki J. Wolford, Andrew C. Akin, Kristen A. Pace

Los Alamos National Laboratory

Chlorine gas is used extensively in some plutonium pyrochemical processes. A scrubber system is used to ensure any chlorine gas that escapes the process is captured and neutralized prior to exhausting into the facility ventilation system. Current processes at LANL utilize a wet caustic scrubber system. Due to potential criticality concerns associated with the introduction of water, this system is required to be contained within a separate glovebox, isolating it from processing areas but increasing the footprint of operations. This project is focused on the testing of commercially available dry scrubber alternatives to determine if they are viable replacements to the caustic scrubber at LANL, with the ultimate goal of 1) eliminating the accumulation of water in the gloveboxes and 2) utilizing space more efficiently by allowing for scrubber operation directly within the processing area rather than in a separate limited operations glovebox. Two media types were tested, and it was determined that the amount of water produced during the chlorine neutralization reaction in the media would preclude dry scrubber operation within the processing area. Additionally, in an off-normal condition where the scrubber is needed to mitigate an unintended chlorine leak, the quantity of media required to neutralize the anticipated volumes of chlorine would be substantial and impractical given the useable operating space. Considering these findings, along with the probability that the dry air flow and high temperatures of the process would overall negatively impact the media, it was decided that continued utilization of the wet caustic scrubber is currently LANL's most viable solution.

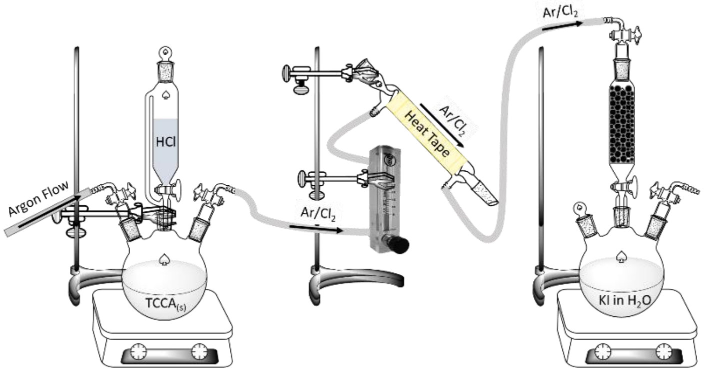


Figure 3. Schematic of small-scale dry scrubber, consisting of a chlorine generator, media column, and breakthrough/indicator solution.

# Treatment of $UF_6$ in ionic liquid and pathways of recovery of $UF_4$

Renee Olney, Cassara Higgins, Ken Czerwinski, Kavid Hatchett

University of Nevada, Las Vegas

Treatment of uranium hexafluoride ($UF_6$) can open applications for its use in advanced nuclear fuel cycles. Uranium in the form of $UF_6$ from enrichment processes is highly reactive with water, corrosive, and has a high vapor pressure. However, conversion of $UF_6$ into more stable forms, such as tetrafluoride ($UF_4$), would allow this product to be reintroduced into the nuclear fuel cycle. This route is explored using ionic liquids for the conversion of $UF_6$. Previous experiments using water extraction of $UF_4$ from $UF_6$/ionic liquid solutions resulted in the oxidation of 25% of uranium to the aqueous phase as uranyl fluoride. By removing the agitation step from this process, water extraction of $UF_4$ from ionic liquid has been observed to take place at the water/IL interface. Furthermore, a significant reduction of the production of uranyl fluoride has been observed in the absence of agitation with water. Additionally, propionitrile has been used as fluoride solubilizing agent to achieve $UF_4$ extraction. Various methods of treatment were employed to determine the highest percent yield of $UF_4$ using both techniques. Finally, the aqueous phase was determined to have a lower concentration of fluoride ions compared to uranium concentration, suggesting that most of the fluoride is partitioning to the ionic liquid phase due to the low solubility of the ionic liquid cation in the aqueous phase. This research demonstrated a more efficient method of conversion spent nuclear fuel components.

# Effect of the Number of Extraction Stages on Uranium Recovery for a UREX Process

Tracy Rudisill, Gene Daniel

Savannah River National Laboratory

The NNSA's Material Management and Minimization ($M^3$) Office is providing support to commercial businesses to establish a reliable domestic source of Mo-99 produced without the use of HEU. One mechanism used by the $M^3$ Office is to provide direct funding to the national laboratories to assist in the commercialization of the Mo-99 production processes. The SRNL is providing support to Eden Radioisotopes (Eden) which plans to produce Mo-99 using a low power reactor fueled using a core consisting entirely of LEU targets. Following irradiation and a one-day cooling time, the cladding is removed from the target and the LEU is dissolved using a nitric acid solution. The initial Mo-99 separation is performed using a small column filled with a titania absorbent. The raffinate from the column is retained for U recovery and purification by solvent extraction for recycle to the Mo-99 target production process.

A UREX process was previously designed and demonstrated for the recovery of U from the column raffinate. The UREX process was designed to recover nominally 90% of the material. The loss of the U was desired to maintain the U-235 enrichment as high as possible during subsequent Mo-99 production cycles using the recycled U by blending fresh HALEU prior to target fabrication to minimize the production of Pu. The Eden U recovery flowsheet demonstration was performed using two banks of miniature mixer-settlers containing 16 stages each. Since the mixer-settlers were not prototypical of the equipment which would be used by Eden for U recovery, a subsequent demonstration was performed to measure the U recovery efficiency as a function of the number of extraction stages using 12 stages of 2-cm diameter centrifugal contactors of similar size to equipment required to meet the Eden processing needs.

The U recovery efficiency was measured using a feed solution that only contained U. To design a UREX process in which only 90% of the U is recovered, flowsheets were modeled with 8 extraction/scrub stages and 4 strip stages using the Argonne Model for Universal Solvent Extraction (AMUSE). The flow ratios were optimized using a baseline flowsheet with 2 extraction and 6 scrub stages which was predicted to recover approximately 90% of the U. During flowsheet demonstrations, the equipment was configured with 1, 2, 3, and 6 extraction stages. Once steady-state conditions were achieved (based on a constant specific gravity of the U product), samples were taken from all exit streams. When the equipment was configured with 6 extraction stages, samples were also taken from individual stages in the extraction and scrub sections to allow comparison of U and nitric acid concentration profiles with predictions from the AMUSE model. Results from the flowsheet demonstrations will be presented including comparison of the measured and predicted U recovery efficiencies and stage concentration profiles.

# Preliminary Studies on the Electrochemical Preparation of Unusual Oxidation States of *f*-Elements in Concentrated Carbonate Solutions

Xiangyang Hou[1], Christopher Dares[1]

[1]Florida International University

Understanding the valence properties of *f*-elements is crucial for their separations. The common oxidation states of lanthanides (+3) and actinides (+4, +5 +6 for U, Np, Pu and +3 for Am) have been studied widely. However, investigations of lanthanides and actinides in unusual oxidation states (+4 for Tb, Pr) (+4 for Am, Cm, and Cf) are limited by their high oxidation potentials and instability in aqueous conditions. Exploring the approaches to access these valence species would assist in enriching our knowledge of *f*-elements and provide valuable information to assist in the development of separation processes. Herein, we discuss the possibility of using a phosphate ligand modified ITO electrode (nanoITO|$P_3$) to lower the oxidation potential of $Am^{3+}$, $Tb^{3+}$, and $Pr^{3+}$ in carbonate solutions by taking advantage of the strong complexing ability of phosphate groups to *f*-elements. To begin, cerium and uranium were chosen as minor actinide surrogates to optimize the oxidation conditions as its lower oxidation potential compared to Am, Tb, and Pr, and allows us to observe their redox events which are beneficial for the future experimental design. The interactions between the tripolyphosphate ligand and cerium or uranium were studied in acidic solutions. It demonstrated that phosphate ligands could stabilize the high valent *f*-elements and catalyze their electron transfers. The $Ce^{3+}$ oxidation at various electrodes in concentrated carbonate solutions indicates that nanoITO exhibits the best performance compared to FTO or GCE, which currently was attributed to its both mesoporous structure and surface groups. These findings suggest that the nanoITO|$P_3$ electrode is a potential candidate to prepare tetravalent Am, Tb, and Pr in carbonate solutions.

# Development of Nuclear Salt Waste Options

Morgan Kropp[1], Kevin Tolman[1], James King[1], Ken Marsden[1], Brian Riley[2], Bill Ebert[3]

[1]Idaho National Laboratory, [2]Pacific Northwest National Laboratory, [3]Argonne National Laboratory

Research into waste forms is a critical component of repository development and is needed to provide disposition pathways for used nuclear material. INL's on-going collaborative efforts with domestic and international partners have led to significant advances in waste form development, improving immobilization and durability characteristics. Technical challenges for future technologies include fabricating mechanically, thermally, and chemically durable waste forms suitable for storage in geological repositories. Material and chemical interactions among complex systems such as ceramics (crystalline and amorphous), molten salts, metals, and containment vessels require additional investigation. These waste form studies typically involve high temperatures in extreme radiological and chemically corrosive environments, which must be performed in inert containment facilities, requiring material characterization using advanced analytical methods. The major areas that were explored with this work included crystallization salt recovery (Figure 1), waste immobilization, and waste characterization.

Figure 1. Crystal of clean OR LiCl salt in HFEF

1) Ebert, W.L et al. Designing Advanced Ceramic Waste Forms for Electrochemical Processing Salt Waste. *Office of Scientific and Technical Information*, **2016**, *Technical Report*, https://doi.org/10.2172/1326909.
2) Lee, I. R. et al. Investigation of physical and chemical properties for upgraded SAP ($SiO2Al2O3P2O5$) waste form to immobilize radioactive waste salt. *Journal of Nuclear Materials*, **2019**, Vol 515, 382-291.

# Modelling the gas generation of actinide bearing materials in storage containers

C. Méhault, S. Faure, G. Bourgès

CEA, DAM, VALDUC, F-21120 Is sur Tille, France

Sebastien.Faure@cea.fr

Actinides processing generates by-products with low contents of radioactive elements. These products are placed in dedicated packaging arrangements with several containers for medium to long interim storage. However, during storage, the products evolve by generating gases as a result of radiochemical reactions. Indeed, molecules of the plastic parts of the packaging (containers, plastic envelopes), adsorbed water and matrix material of the product (salts) can be decomposed under ionizing radiation leading to the generation of primary radicals that react with others by homogeneous reactions to form stable gases[1-5].

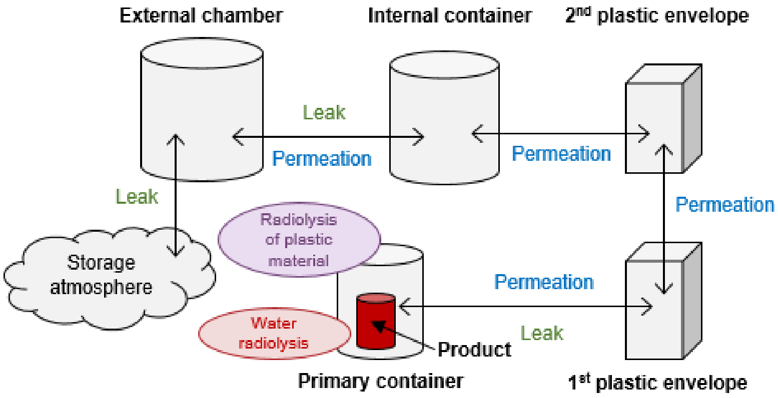


*Figure 1: Scheme of each phenomenon taken into account in the model*

To improve our knowledge of the evolution of these items containing alpha emitters, a model was developed using a macroscopic approach. This phenomenological model can be divided in two parts. First, plastic and water radiolysis models were used to evaluate gas generation closed to the nuclear materials. Secondly, the transportation of gases between the different containers were evaluated. The model takes into account two transfer phenomena: leakage as a result of a total pressure difference between two compartments and permeation as a result of a partial pressure gradient from each side of a plastic wall. The model was computed in Matlab using ODE solvers and was confronted to experimental measurements. Chosen key parameters were adjusted to fit the experimental data. The model allows us to highlight the parameters influencing the gas generation.

1) Berg, J.M., et al., Moisture and Gas Production in Storage Containers of Plutonium Oxide, in Plutonium Futures - The Sciences. 2010
2) Veirs, D.K., et al., Evidence of Corrosive Gas formed by Radiolysis of Chloride Salts in Plutonium-bearing Materials. Journal of Nuclear Materials Management, 2010. 38(3), p. 25-31.
3) Vladimirova, M.V. and I.A. Kulikov, Formation of $H_2$ and $O_2$ in Radiolysis of water sorbed on $PuO_2$. Radiochemistry, 2002. 44(1), p. 86-90.
4) Almond, P.M., et al., Gas Analysis from Headspace of Plutonium-Bearing Materials Containers. 2010, Savannah River National Laboratory: Aiken, SC 29808.
5) Tandon, L., Radiolysis of Salts and Long-Term Storage Issues for Both Pure and Impure $PuO_2$ Materials in Plutonium Storage Containers, in LA-13725-MS. 2000, Los Alamos National Laboratory: New Mexico

May 17, 2023 Wednesday Morning Technical Session 3
EIL A-102

## Technical Session 3: "Radioisotope Recovery/Purification"

### Wednesday Morning, May 17, 2023

Session 3 Chair: Daniel McAlister, Eichrom Technologies

| | **3: Radioisotope Recovery/Purification** | |
|---|---|---|
| **8:30 AM** | Separation and Purification of the Potential Medical Isotope U230 from Irradiated Th232 Target | Miting Du, ORNL |
| **8:55 AM** | A combined TEVA-DGA chromatography chemistry for purifying Pu, Am, and Np for U materials | John Engel, LANL |
| **9:20 AM** | Recovery of $^{252}$Cf from Californium Campaign Solutions | Lætitia Delmau, ORNL |
| **9:45 AM** | Morning Break | BREAK |
| **10:05 AM** | Actinide Aqueous Separations and Irradiation Capabilities at Argonne | Peter Tkac, ANL |
| **10:30 AM** | Improvements to Accelerator-Produced $^{225}$Ac Processing at Oak Ridge National Laboratory | Ashleigh Kimberlin, ORNL |
| **10:55 AM** | First Results from LLNL's Aqueous Recovery Laboratory | Helen Deaguero, LLNL |
| **11:20 AM** | Badging for Tour Attendees | |
| **12:00 PM** | Conference Tour | |

# Separation and Purification of the Potential Medical Isotope U230 from Irradiated Th232 Target

Miting Du

Oak Ridge National Laboratory

Uranium-230 ($t_{1/2}$ = 20.8 *d*) is of interest because of its decay daughter Thorium-226 ($t_{1/2}$ = 30.6 min), a promising medical isotope for targeted alpha therapy (TAT) of cancer. Since 2019 a collaborative project supported by the DOE-IP (Department of Energy -Isotope Program) is ongoing between the University of Washington (UW), Oak Ridge National Laboratory (ORNL), and Los Alamos National Laboratory (LANL).

As part of a 3-year R&D plan[1], UW will irradiate eight thorium-232 metal targets at an elevated irradiation intensity to produce protactinium-230 ($t_{1/2}$ = 17.4 day), which decays to $^{230}U$ (7.8%). After irradiation, the thorium-232 targets would be shipped one at a time to ORNL for target treatment. Prior to the arrival of the first target, ORNL should develop a processing scheme for rapid separation of $^{230}U/^{232}Th/^{230}Pa$/FPs and deliver purified $^{230}U$ to UW for the study of the $^{230}U/^{226}Th$ generator and the chelation of $^{226}Th$ with the selected targeting ligands.

ORNL began developing a rapid processing scheme for the separation of U/Pa/Th/impurities using on-hand isotopes such as $^{234}U$, $^{233}Pa$ and others. The developed separation scheme is easy, rapid, and effectively separates U-230 from the Th-230 target. The entire separation process takes only three days to complete with a recovery rate of >90% for $^{230}U$. Additionally, if something goes awry during the first harvest, the separated $^{230}Pa$ fraction can be used for the second harvest of ingrowth $^{230}U$.

The paper discusses the development of rapid separations, resin selections, connections between processing steps, and some challenges encountered during impurity removal. The results of the separation and purification of uranium-230 from the eight irradiated thorium-232 targets have been presented, as well as the chances of $^{230}U$ becoming a routine product after R&D has been completed.

1) Wilbur, Boll, Fassbender, Application to DE-FOA-0001896, "Medium Energy Cyclotron Production of $^{230}U$ from $^{232}Th$ Targets", June 11, 2018

# A combined TEVA-DGA chromatography chemistry for purifying Pu, Am, and Np for U materials

John Engel[1], Joanna Denton[1], Theresa Kayzar-Boggs[1]

[1]Los Alamos National Laboratory

Trace actinide impurities present within uranium (U) material are diagnostic signatures of U processing history, and may be used in nuclear forensic investigations to determine when, where, and how interdicted material was produced *i.e.,* source attribution. Providing reliable isotopic evidence to authorities in a timely manner is imperative to guiding the Nation's measured response to a nuclear crime. We have developed a combined TEVA-DGA chromatography chemistry to purify trace levels (pg-level) of Pu, Am, and Np from a single aliquot of bulk (mg-level) U materials as a means to expedite nuclear forensic investigations. Our method produces high-purity, single-element fractions of Pu (90% recovery), Am (98% recovery), and Np (62% recovery) from mg-levels of U, and does so in three days of column chemistry.

We employ a "stacked" column arrangement, where the eluent from the TEVA column drips directly into the DGA column. Plutonium and Np are first sorbed onto TEVA resin in 3M $HNO_3$ using a 4+ redox adjustment with a hydroxylamine hydrochloride and sodium nitrite treatment, with U+Am eluting directly onto DGA resin. The columns are then split apart; Am is purified from U on DGA using 0.1 M $HNO_3$ as a U eluent, and Pu+Np are stripped from TEVA using 0.1M HCl + 0.005M HF. A subsequent TEVA column is used to separate Pu from Np using hydrogen peroxide to oxidize Np into the >4+ oxidation state for elution through TEVA.

Our findings demonstrate that 3M $HNO_3$ as a load solution reduces Np valence state degeneracy during washes (*i.e.,* maintains the 4+ state) while minimizing U sorption to either column. Furthermore, we establish that additional TEVA and/or DGA columns may be added to this procedure for further U purification without detrimental loss of the trace actinide signatures. Our optimized procedure for mg-levels of U is the (TEVA/DGA)-TEVA-TEVA for Pu and Np purification (U separation factors > $1x10^6$), and (TEVA/DGA)-DGA for Am purification (U separation factor of ~150,000). In conclusion, our combined TEVA-DGA procedure can generate single-element fractions of Pu, Am, and Np from a single U aliquot within three days of chemistry, thereby significantly expediting pre-detonation nuclear forensic investigation timelines.

# Recovery of $^{252}$Cf from Californium Campaign Solutions

Lætitia H. Delmau[1*], Laura K. Harvey[1], Stacy L. Queern[1], Roger J. Weaver[2], Dennis E. Benker[1]

[1]Radioisotope Science and Technology Division,
[2]Isotope Production and Manufacturing Division
Oak Ridge National Laboratory,
1 Bethel Valley Rd., Oak Ridge, TN 37831, USA

[*]Corresponding author: delmaulh@ornl.gov; 865-576-2093

Californium-252 has been recovered from campaign solutions using diglycolamide resin and tailored elution sequences, providing a supplementary source of $^{252}$Cf for wire production. Californium campaigns are conducted at Oak Ridge National Laboratory every other year to produce nominally 50–100 mg of this valuable isotope. Produced from the irradiation of curium targets in the High Flux Isotope Reactor, californium requires several processing steps to be obtained in a purity adequate for wire fabrication. Because of the number of processes, rework solutions are unavoidably generated and are commonly set aside for the next campaign. For the 2021 $^{252}$Cf campaign, the decision was made to recover californium present in back-filtration solutions and to harvest the californium present in rework solutions. Surrogate tests were first carried out with lanthanides to determine a range of acceptable conditions, and these tests were followed by glove box tests involving either a very small amount of actual rework solution or surrogate feed spiked with actual rework solution. Results from the small-scale tests done inside the hot cells allowed researchers to refine the conditions for full-scale runs. This endeavor yielded the recovery of 6 mg of californium from back-filtration solution and 5.2 mg from rework solutions, which is approximately 15% of the original amount present in the irradiated targets.

# Actinide Aqueous Separations and Irradiation Capabilities at Argonne

Peter Tkac

Chemical and Fuel Cycle Technologies Division, Argonne National Laboratory

The National Nuclear Security Administration's Material Management and Minimization Office works with U.S. commercial entities and the U.S. national laboratories to accelerate the establishment of a reliable supply of the medical isotope $^{99}$Mo by supporting the development of a diverse set of technologies to produce $^{99}$Mo without the use of highly enriched uranium.

Argonne has worked with commercial partners to design, demonstrate, and scale up aqueous separation processes for treating a variety of irradiated targets. This presentation will briefly discuss approaches for handling radiolytically- and fission-produced gasses, like hydrogen, oxygen, iodine, krypton, and xenon; implementation of various solvent extraction processes like MOEX (TBP-based) or MOLLE (HDEHP-based) to recover Mo; approach for fumeless dissolution of up to 750g of U-metal targets using nitric acid; development of solvent extraction flowsheets to recycle U targets; and radiation effects on various components, equipment, chemicals, and corrosion rates.

Work supported by the U.S. Department of Energy, NNSA's Material Management and Minimization office, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

# Improvements to Accelerator-Produced $^{225}$Ac Processing at Oak Ridge National Laboratory

Ashleigh Kimberlin, Andrew Burgoyne, Mikayla Molnar, Linda Lewis, Allison Peacock, Dave Rotsch, and Roy Copping

Oak Ridge National Laboratory, Oak Ridge, Tennessee

Targeted alpha therapy (TAT) is poised to be one of the most prominent radiotherapies for cancer treatments. One problem delaying TAT is the difficulty to obtain necessary radioisotopes in the quantities needed to meet demand. Accelerator-based production of $^{225}$Ac has been developed in a collaboration between Oak Ridge National Laboratory, Los Alamos National Laboratory, and Brookhaven National Laboratory (TriLab effort). This effort currently produces $^{225}$Ac that is used in clinical trials. When providing an isotope product, the reliability and reproducibility of production is mandatory. In part 1 of this presentation, I will discuss mitigation strategies for the release of gaseous radioisotopes from processing. These strategies involve the development and testing of a gas capture system that is hot cell–compatible and capable of trapping several elements emitted from this process. In part 2, I will discuss R&D efforts into the scale-up of target size and how that scale-up will affect the chemical processing. In part 3, I will go over the R&D and modeling the research team performed to optimize the thorium debulking step. This presentation highlights the importance of modeling and optimization of separations development in radioisotope production.

This research is supported by the U.S. Department of Energy Isotope Program, managed by the Office of Science for Isotope R&D and Production.

# First Results from LLNL's Aqueous Recovery Laboratory

Helen Deaguero, Kiel Holliday

Lawrence Livermore National Laboratory

After nearly a decade of demolition, construction, and readiness assessments, the Recovery Glovebox Lines at LLNL were approved for startup in April of 2022. The glovebox lines boast a number of unique features such as entry hoods for material introduction, a central vacuum system for liquid transfers, and a vertical bag out port that mates with a 55-gallon drum for waste removal. These features streamline processes, enhance worker safety, and minimize the amount of waste generated. This laboratory can process varying feeds, typically dissolving oxides and metals in concentrated nitric acid. If the material contains salt, a RIAR washer is used to remove the salts prior to dissolution. The dissolved plutonium is adjusted to a +4-oxidation state, and the solution is adjusted to a concentration above 7M, creating a negatively charged plutonium nitrate. This solution is loaded onto an anion exchange column and a green band, indicative of the plutonium (IV), becomes visible. After loading, the column is washed with additional 7M nitric acid to remove contaminants. The resulting solution is collected as waste and will later be pH adjusted and solidified. A 0.5M low nitric acid solution is then introduced onto the column to convert the plutonium nitrate anion to a cation. This results in the elution of the plutonium from the column into solution. This solution is collected and the plutonium is reduced to a +3 oxidation state before it undergoes an oxalic acid precipitation. Filtration results in the collection of a purified plutonium oxalate solid, which is allowed to dry overnight. The solid is then placed into a crucible and calcined to produce a purified plutonium oxide. The filtrate in turn undergoes a caustic precipitation using sodium hydroxide. Any solid that is collected from this precipitation will be calcined separately, and the filtrate will be treated as waste. Here we present the results from the first two items that have been processed and lessons learned.

May 18, 2023 Thursday Morning Technical Sessions 4 and 5
EIL A-102

## Technical Session 4: "High Temperature Non-Electrochemical Separations"
## Technical Session 5: "Advancements in Molten Salt Measurements"

**Thursday Morning, May 18, 2023**

Session 4 Chair: Michael Simpson, University of Utah
Session 5 Chair: Kiel Holliday, LLNL

| | **4: High Temperature Non-Electrochemical Separations** | |
|---|---|---|
| **8:00 AM** | Zone Refining Capability Development at INL for Induction Heating of U/TRU Metal Based Fuel Rods | David Horvath, INL |
| **8:25 AM** | Computational Modeling of Induction Heating of Uranium Metal-Based Fuel Rods for Development of a Zone Refining Process | Hayden Hansen, Univ. of Utah |
| **8:50 AM** | Reaction of U Metal with $NH_4Cl$ in Molten LiCl-KCl | Nathan Rood and Collin Andersen, Univ. of Utah |
| **9:15 AM** | Novel Chloride Volatility Scheme for Reprocessing Advanced Reactor Used Nuclear Fuel | Jason Torrie, BYU |
| **9:40 AM** | In-Situ Generation of $Cl_2$ via Molten Salt Electrolysis for Chloride Volatility Separations | Tyler Williams, BYU |
| **10:05 AM** | Morning Break | BREAK |
| | **5: Advancements in Molten Salt Measurements** | |
| **10:20 AM** | Actinide-Molten Salt Density using Neutron Radiography | Marisa Monreal, LANL |
| **10:45 AM** | Changes in the Liquidus Temperature of the NaCl-$PuCl_3$ Binary Salt System Due to the Presence of Pu-metal | Toni Karlsson, INL |
| **11:10 AM** | Electrochemical Investigation of Uranium Redox Behavior in Molten Chloride Salts using Boron-Doped Diamond | Hannah Patenaude, UNLV |
| **11:35 AM** | New Capabilities to Access and Analyze Pure Inorganic Chlorides | Karla Erickson, LANL |
| **12:00 PM** | Lunch Break (until 1:20 pm) | |

# Zone Refining Capability Development at Idaho National Laboratory for Induction Heating of Uranium/Transuranics Metal-Based Fuel Rods

David Horvath[1], Tae-Sic Yoo[1], Mason Childs[1], Michael F. Simpson[2]

[1]Idaho National Laboratory, [2]University of Utah

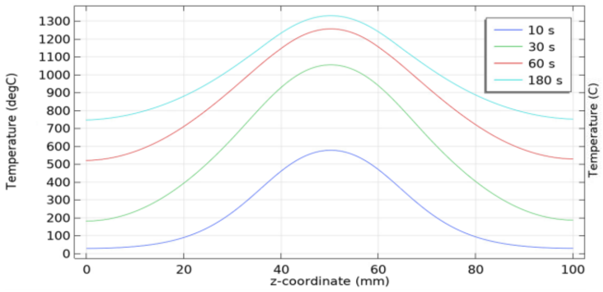
The presented research describes the development of a novel method to separate uranium/transuranics from fission products in metallic spent nuclear fuel. This work is funded by the Advanced Research Projects Agency-Energy (ARPA-E) and is a collaborative effort between the Idaho National Laboratory and the University of Utah. In the initial studies, metal charges of depleted uranium and rare earths were annealed in a resistance box furnace, and SEM techniques were used to analyze the metallic samples. Additionally, a mixture of depleted uranium, transuranics, and rare earths were melted together in a resistance furnace at the Fuel Manufacturing Facility (FMF) to examine transuranics behaviors. These experiments demonstrate promising results in separating uranium/transuranics from fission products based on immiscible liquid metal phases formation, density differences, and minimal solubilities. The next phase of the project involves the development of a crucible-less process concept, travelling molten zone refining process, which utilizes an induction heating operation and a linear actuator control to move immiscible metal phases through the heating zone. The scoping experimental results suggest a rapid formation of an actinide-rich phase segregating actinides from the insoluble fission products. The expected outcome of this project is a simplified pathway for an advanced metal fuel cycle through the partitioning of fission product species.

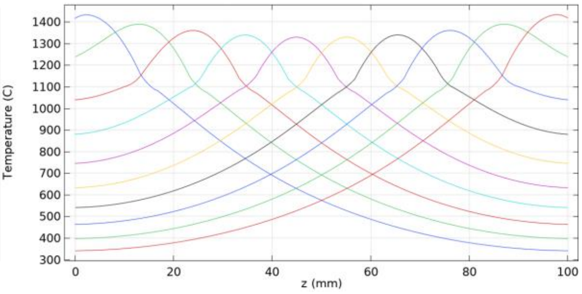
# Computational Modeling of Induction Heating of Uranium Metal-Based Fuel Rods for Development of a Zone Refining Process

Hayden Hansen[1], Tae-Sic Yoo[2], Mason Childs[2], David Horvath[2], and Michael F. Simpson[1]

[1]University of Utah, [2]Idaho National Laboratory

Idaho National Laboratory and the University of Utah are collaborating on an ARPA-E funded project to develop a zone refining (ZR) process to separate uranium and transuranic (U/TRU) actinides from fission products in metallic spent nuclear fuel (SNF). As part of a predictive computational model for the process that can be used to optimize process conditions for separation of actinides from fission products, a model of induction heating of a metal rod was built and tested on the COMSOL platform. The model calculated temperature distribution and forces generated from inductively heating either a steel or uranium metal rod of 6-mm diameter and 100-mm long. Key uranium properties (density, electrical conductivity, thermal conductivity, and heat capacity) were compiled from literature sources and used to construct temperature dependent functions. Initially modeling uniaxial helical coils, a range of heating parameters (current and frequency) and coil parameters (major diameter, minor diameter, and number of turns) were examined with respect to time to achieve 1200°C. The figure below on the left shows an example of temperature profiles along a uranium rod at different times since initiation of heating. Heat-up time was found to be improved by decreasing the coil diameter (major diameter), decreasing the copper pipe diameter (minor diameter), increasing the number of coil turns, increasing the current, and increasing the frequency. This parametric study was successful in informing experimentalists how to configure an exploratory ZR system in the university laboratory, which initially melted stainless steel rods using 3.2-cm diameter coils at maximum current of 600 A and maximum frequency of 80 kHz. Excellent agreement was observed between the COMSOL model and experimentally measured maximum temperatures for stainless steel rods from 3.2 to 7.6-cm diameter coils. An attempt to utilize the built-in COMSOL function for modeling translational motion resulted in temperature distributions that appeared to be erroneous, so an alternative approach based on experimentally validated steady-state temperature profiles has been formulated, which is illustrated in the figure on the right below. Another application of this modeling effort is to predict how the molten zone will be deformed by the Lorentzian forces generated by the magnetic field. Deformation has not been modeled yet due to limitations of the COMSOL platform. But forces and fluid flow velocities have been calculated assuming fixed sample geometry. These results indicate that Lorentzian forces may enable formation of the liquid zone without causing the rod to split into two pieces.





# Reaction of Uranium Metal with $NH_4Cl$ molten LiCl-KCl

Nathan Rood[1], Collin Andersen[1], Krista Carlson[2], and Michael F. Simpson[1]

[1]University of Utah, [2]University of Nevada at Reno

Ammonium chloride ($NH_4Cl$) is known to thermally decompose into $NH_3$ and HCl gases. Since uranium metal readily reacts with HCl gas to form $UCl_3$, ammonium chloride could be a convenient reactant for chlorinating uranium for systems such as electrorefiners and molten salt reactors. Previously this reaction has been reported to be performed successfully starting with reagents in powder form. If the goal is to infuse an electrorefiner or molten salt reactor with $UCl_3$, however, the reaction needs to occur in a molten salt phase. The specific molten salt mixtures that would be found in an electrorefiner or a molten salt reactor are typically kept molten at temperatures of 450°C or higher. This presents a challenge for how to decompose $NH_4Cl$ such that the formed HCl can efficiently react with solid U metal and form $UCl_3$ that subsequently dissolves in the molten salt. If the ammonium chloride decomposes too fast, it will have poor utilization due to incomplete reaction. In this project, we have investigated multiple methods to feed HCl formed from $NH_4Cl$ decomposition into molten LiCl-KCl for chlorination reactions. Two chlorination reactions have been successfully observed--conversion of $Li_2O$ to LiCl and conversion of U metal to $UCl_3$ and $UCl_4$. Using thermogravimetry, it was determined that $NH_4Cl$ decomposition initiates at 200°C under ambient atmospheric pressure. The process is apparently reversible, as the gases recombine and condense readily on cold surfaces. In an effort to create a stand-alone HCl feed generator that could be flowed over a distance in unheated tubing, a bed of H-exchanged ultra-stable Y zeolite was placed directly downstream of the decomposition zone. The intended function of the zeolite was to selectively absorb $NH_3$ and create a stable stream of HCl gas. This did not work, as the $NH_4Cl$ absorbed and condensed on the zeolite bed. The method for feeding the HCl into the molten salt that worked was to nest a quartz decomposition cell inside of a larger quartz vessel that contained the molten salt. The $NH_4Cl$ reaches a constant temperature of 325°C, while the molten salt below it is held at a constant 450°C. Argon was passed through the decomposition cell, and the resulting gases were bubbled into the molten salt. Experiments were performed in which eutectic LiCl-KCl was spiked with $Li_2O$ to 1 wt%. $NH_4Cl$ decomposition rates of 0.57 to 0.98 g/hr were measured in these tests. After as short of a time as 3 hours of bubbling $NH_3$/HCl vapor into the salt, all the $Li_2O$ was chlorinated. It was also observed that the salt retains a significant concentration of HCl after all the $Li_2O$ has reacted. One experiment has been run to date in which U metal was loaded into a stainless steel basket immersed in the molten salt. The $NH_3$+HCl vapor was directly bubbled into the basket. While this caused some corrosion of the basket, the U metal was completely consumed in less than 3 hours. Salt samples were taken for inductively coupled plasma mass spectrometry (ICP-MS) analysis to measure dissolved U concentration over time. Electrochemical analysis was performed using cyclic voltammetry and open circuit potentiometry to determine the ratio of $UCl_4/UCl_3$ in the product. Initial observations indicate that the reaction resulted in formation of $UCl_4$ because of the complete depletion of U metal. To form only $UCl_3$, it is necessary to prevent complete reaction of the U metal.

# Novel Chloride Volatility Scheme for Reprocessing Advanced Reactor Used Nuclear Fuel

Jason Torrie, Jeffery Adams, Bryant Johnson, Devin Rappleye

Department of Chemical Engineering, Brigham Young University, Provo UT 84602 USA

With the development of generation IV advanced nuclear reactors, it is advantageous to investigate feasible methods for reprocessing used nuclear fuel (UNF) from these reactors. Developing reprocessing strategies now before these reactors are constructed mitigates future accumulation of UNF and enables more efficient usage of fissile material. UNF types from advanced reactors include metals and metal chlorides. A chloride volatility scheme could reprocess both fuel types as the chlorination of metals has been well explored. This presentation will detail preliminary experiments exploring a two-step chloride volatility (TSCV) scheme for reprocessing advanced reactor UNF.

Experiments with surrogates show that the TSCV process has the potential to reprocess 1 kg U/hr which corresponds to 0.5 mol/m$^2$/hr of uranium chlorides. This process rate would make the TSCV process comparable to existing reprocessing strategies. $FeCl_2$ and $BiCl_3$ are natural surrogates for $UCl_4$ because all three have similar solid-phase vapor pressure profiles. Our experimental apparatus is based on that used in transpiration vapor pressure studies. The initial experiments achieved 1.27 mol $FeCl_2$/m$^2$/hr and 3.58 mol $BiCl_3$/m$^2$/hr. Each of these values exceeds the minimum needed to compete with existing reprocessing methods.

In addition, the presentation includes a discussion of a method for quantifying water content in NaCl and $MgCl_2$. The titration method quantified the amount of hydroxides present in the salt. At high temperatures, hydroxides form from the reaction of water with the salts. As a result, the water content in the salt can be inferred from the hydroxide content in post-melted salt. This method shows that the water content in both NaCl and $MgCl_2$ are both below 1 wt. %.

The presentation will conclude with a discussion on the complexity introduced by working with a mixture of metal chlorides. All preliminary work has been done with pure component surrogates. A mixture of metal chlorides will have a different vapor pressure profile than the sum of the profiles for each component. To date, there are few studies on the vapor pressure for liquid multi-component chloride salts, and a search found no studies on vapor pressure of solid multi-component chloride salts. Future study of the vapor pressures of species in solid multi-component chloride salts is critical to determining the feasibility of the TSCV process.

# In-situ Generation of $Cl_2$ via Molten Salt Electrolysis for Chloride Volatility Separations

Tyler Williams[1], Simon Calabuig[1], Mark Schvaneveldt[2], Devin Rappleye[1]

[1]Brigham Young University, [2]Argonne National Laboratory

Chloride volatility separation processes have shown great potential for separating rare earth elements (REEs) and actinides from other metallic chlorides in used nuclear fuel (UNF) processing.[1-3] However, shipping, storing, and plumbing $Cl_2$ into existing processes introduces significant hazards and costs. To make chloride volatility separations more accessible, a process which generates $Cl_2$ *in-situ* using non-toxic reactants has been developed. The steps of this process are: (1) electrosynthesis of $Cl_2$ from a molten chloride salt with a low vapor pressure (e.g., $CaCl_2$), (2) chlorination of UNF, (3) separation of chlorinated UNF based on volatility differences, (4) electroreduction of separated actinide or rare earth chlorides to pure or group (e.g., co-deposition of REEs) metals as the counter reaction for step 1. Both gram and kilogram-scale reactors have been built that electrolyze molten salts to produce $Cl_2$. The purity of the produced gas has been evaluated and REE samples have been successfully chlorinated. Anodic reactions have been investigated using electrochemical techniques and a residual gas analyzer.

1) Okabe, P.; Newton, M.; Rappleye, D.; Simpson, M. Gas-solid reaction pathway for chlorination of rare earth and actinide metals using hydrogen and chlorine gas. *Journal of Nuclear Materials*, **2020**, *534*, 152156.
2) Okabe, P.; Rappleye, D.; Newton, M.; Simpson, M. Development of metallic nuclear material purification process via simultaneous chlorination and volatilization. *Journal of Nuclear Materials,* **2021**, *543,* 152626.
3) Schvaneveldt, M.; In-Situ Chlorine Gas Generation for Chlorination and Purification of Rare Earth and Actinide Metals. *BYU Master's Thesis,* **2022**.

# Actinide-Molten Salt Density using Neutron Radiography

Marisa Monreal[1], S. Scott Parker[1], Alexander Long[1], Travis Carver[1], J. Matt Jackson[1]

[1]Los Alamos National Laboratory

Actinide-molten salts are complex systems integral to pyroprocessing for actinide metal purification and recovery, to the next-generation nuclear energy reactor concept that is the molten salt reactor, as well as to a growing number of additional energy applications. There remain gaps in the literature on the chemistry and thermophysical properties of these systems, especially in data collected with well-documented methodology and experimental detail, using salts with analytical data confirming purity, and reported with quantified uncertainty and error analysis. With the overarching goal to contribute to a better understanding of these systems that enables prediction of their behavior, we have been developing a suite of analytical techniques for the precise measurement of molten salt properties, with a focus on actinide-bearing systems. For the measurement of actinide-molten salt density, we have developed a method using neutron radiography, and successfully demonstrated it on uranium-bearing molten salts at the Los Alamos Neutron Science Center (LANSCE). We have recently further developed and improved our experimental methodology and apparatus for the measurement of plutonium-bearing molten salts. This capability and supporting characterization techniques will be described, including results from uranium- and plutonium-bearing salt experiments.

1) Parker, S.; Long, A.; Lhermitte, C.; Vogel, S.; Monreal, M.; Jackson, J. M. Thermophysical properties of liquid chlorides from 600 to 1600 K: Melt point, enthalpy of fusion, and volumetric expansion. *J. Mol. Liq.*, **2022**, *346*, 118147.
2) Long, A.; Parker, S.; Carver, T.; Jackson, J. M.; Monreal, M.; Newmark, D.; Vogel, S. Remote Density Measurements of Molten Salts via Neutron Radiography, *J. Imaging*, **2021**, *7*, 88.

# Changes in the Liquids Temperature of the NaCl-PuCl$_3$ Binary Salt System Due to the Presence of Pu-metal

Toni Karlsson, Cynthia Adkins, Ruchi Gakhar, Steven Monk, James Newman, Stephen Warmann

Idaho National Laboratory

Samples containing sodium-chloride (NaCl) and plutonium-trichloride (PuCl$_3$) were fabricated for thermophysical property investigations with the goal of informing molten salt reactor fuel development and verification of the NaCl-PuCl$_3$ phase diagram. A simultaneous thermal analyzer (STA) was employed to first investigate the purity of the PuCl$_3$ feedstock used for sample fabrication. Results from the STA were then used to develop a phase diagram for the NaCl-PuCl$_3$ salt using six different molar ratio salt samples. The phase diagram results were compared with the limited available literature values for this binary salt system. It was determined that the PuCl$_3$ starting material contained some Pu-metal. This work develops an approach for determining the concentration of unchlorinated Pu in PuCl$_3$ and summarizes the changes in liquidus temperatures in the binary NaCl-PuCl$_3$ salt system when using impure PuCl$_3$.

# Electrochemical Investigation of Uranium Redox Behavior in Molten Chloride Salts Using Boron-Doped Diamond

Hannah K. Patenaude[1,2], Charles R. Lhermitte[2], Nastasija Damjanovic[2], Jason Rakos[2], Kenneth R. Czerwinski[2], Cory A. Rusinek[2], Marisa J. Monreal[1]

[1]Los Alamos National Laboratory, [2]University of Nevada, Las Vegas

The liquid salt fuel system and fast reactor technology of Generation IV Molten Salt Reactors (MSRs) simultaneously address concerns over waste, safety, and nonproliferation. However, work is still needed to understand the impacts of the harsh fuel salt systems and their subsequent containment corrosion. Electroanalytical chemistry methods can probe several fundamental aspects of complex high-temperature actinide molten salt chemistry so long as the electrodes can withstand the molten salt environment for prolonged periods. Boron-doped diamond (BDD) is expected to be resilient against harsh environments, given its primarily $sp^3$-carbon structure. As such, BDD could be used to characterize dynamic molten salt fuel matrices and *in situ* corrosion control and monitoring within the core containment vessels. However, the corrosion and performance of BDD as an electrode material in molten salts are not yet fully understood. In this study, we investigated the corrosion resistance of BDD by soaking the material in chloride and molten fluoride salts (LiCl-KCl, NaCl-KCl, LiF-KF, and FLiNaK) between 500-700 ºC for over 250 hours in air. Scanning electron microscopy was used to identify topographical changes in diamond crystal structures. Little, if any, corrosion or change to the BDD was observed. As a result, we pursued the use of free-standing BDD for electrochemical measurements in harsh molten salt analytes. The Eu(II/III) and U(III/IV) redox couples were studied in LiCl-KCl and $MgCl_2$-NaCl solvent salts. Comparisons were also made between the two solvent systems to study the impact of cation size on oxidation state stabilization. Techniques like cyclic voltammetry provided valuable insight regarding the lanthanide and actinide species with improved resolution of redox peaks that metal electrodes often struggle to capture fully, given the complex f-block redox behavior occurring in MSR fuels. This work advances the understanding of both MSR fuel chemistry and fundamental actinide chemistry by probing f-block oxidation states within molten salts. Additionally, this work is proof-of-concept for the feasibility of BDD as electrode material for harsh environments and as a potential candidate for *in-situ* MSR fuel characterization. Future studies include soak-testing inside an inert environment, comparisons to other chloride and fluoride solvent salt systems, and analytical electrochemical investigations of other actinide redox couples like Pu(III/IV).

# New Capabilities to Access and Analyze Pure Inorganic Chlorides

Karla A. Erickson[1], Charles R. Lhermitte[2], Sarah M. Hickam,[3] Adam Altenhof,[4] Harris Mason,[1] Stephen S. Parker[3], Marisa J. Monreal[1]

[1]Los Alamos National Laboratory, Chemistry Division
[2]Los Alamos National Laboratory, Sigma Division
[3]Los Alamos National Laboratory, Materials Science and Technology Division
[4]Los Alamos National Laboratory, Materials Physics and Applications Division

Molten Salts play a pivotal role in nuclear molten salt reactors, concentrated solar power and metal electrorefining technologies. One challenge associated with their use is their highly hygroscopic nature. The reaction between water and metal chloride can result in the generation of more corrosive species, accelerating materials deterioration. Metal chlorides can be treated with pyrophoric or caustic chemicals such as calcium metal or ammonium chloride to dehydrate them. However, simpler methods to thermally dehydrate purchased salts is preferred. Our research program routinely obtains pure salts (i.e. group 1 and group 2 metal chlorides) through procedures that utilize a custom vacuum-furnace antechamber attached to an inert-atmosphere glovebox. Noting this is not standard, we sought to identify additional methods to dry salts that would be accessible to research laboratories. As a result, we have developed a vacuum apparatus that utilizes off-the-shelf components and minimal customization to dry as-received group 1 and group 2 chloride salts. The apparatus has additionally been used to remove ligands from cerium chloride and uranium trichloride. In the course of assessing the purity of these materials, several analytical techniques have been employed and new analytical approaches will be discussed.

May 18, 2023 Thursday Morning Technical Session 6
EIL A-110

## Technical Session 6: "Aqueous and Vapor Phase Actinide Separations"

*Special session supporting the Materials Recovery and Waste Form Development Campaign*

**Thursday Morning, May 18, 2023**

Session 6 Chair: Bill Del Cul, DOE

| | **6: Aqueous and Vapor Phase Actinide Separations** | |
|---|---|---|
| **8:00 AM** | Preparations for Simplified Single-Cycle Flowsheet Testing | Leigh Martin, ORNL |
| **8:25 AM** | Low Temperature Liquid-Based Chlorination of Metal Alloys | Richard Mayes, ORNL |
| **8:50 AM** | Interactions of Lanthanide Oxides in Tributyl Phosphate | Jarrod Gogolski, SRNL |
| **9:15 AM** | Dissolution of Used Nuclear Fuel Components Directly into Organic Solvent | Gabriel Hall, PNNL |
| **9:40 AM** | Morning Break | BREAK |
| **10:20 AM** | Recovery of Uranium and Distribution Ratios of Neptunium, Plutonium, and Technetium from Direct Dissolution-Loaded Solvents | Nathan Bessen, PNNL |
| **10:45 AM** | Suppression of Neptunium Extraction into *N,N* di-2-ethylhexyl-isobutyramide (DEHiBA) Solvent by Butyraldehydes: a Spectrophotometric Study in a Closed Two Phase System with Direct Redox Speciation Monitoring of both Phases | Sergey Sinkov, PNNL |
| **11:10 AM** | Maximizing Uranium Recovery: Strategies for Process Enhancement | Santa Jansone-Popova, ORNL |
| **11:35 AM** | Data-driven Uranium/Plutonium Separation | Ping Yang, LANL |
| **12:00 PM** | Lunch Break (until 1:20 pm) | |
| **1:20 PM** | Radical assays used as a screening tool for determining the radiolytic stability of monoamide complexants | Modi Wetzler, Clemson Univ. |
| **1:45 PM** | Impact of trivalent *f*-element complexation and chemical environment on the radiation-induced chemical reactivity of TODGA and HOPO ligands | Stephen Mezyk, CSULB |
| **2:10 PM** | Discussions | |

# Preparations for Simplified Single-Cycle Flowsheet Testing

Leigh Martin, Allison Greaney, Katie Johnson, Joanna McFarlane,
Trent Walker, Chase Cobble, Matt Vick

Oak Ridge National Laboratory

Advanced voloxidation of spent nuclear fuel (SNF) using $NO_2$ as an oxidizing agent is being considered as an alternative front end for separation of volatile fission products and recovery of actinides. Several studies have described the $NO_2$ voloxidation process and reviewed the advantages of advanced voloxidation compared with other processing methods. Some of these studies have tested $NO_2$ voloxidation in shielded facilities with SNF. However, questions remain as to the effectiveness of advanced voloxidation, especially regarding the evolution of volatile and semivolatile fission products during the process. Thus, Oak Ridge National Laboratory (ORNL) is researching the process to (1) determine the optimal voloxidation process conditions, (2) determine the parameters necessary for direct dissolution of $UO_3$ in organic solvents, and (3) determine the partitioning behavior of fission products during voloxidation. A special focus is given to tracking the behavior of volatile and semivolatile fission products that may partition into the gas phase during this reaction and will need to be scrubbed from the voloxidation off-gas.

A first set of tests determined the percentage of iodine that is volatilized during reaction with $NO_2/O_2$ under representative voloxidation temperatures with the off-gas venting directly to a caustic scrubber. Gaseous $I_2$ was generated from the reaction of CsI. The volatilized iodine captured in the caustic scrubber was quantified with novel ultraviolet – visible light spectroscopy (UV-VIS) spectroscopic techniques, and the resulting data was compared to traditional inductively coupled plasma mass spectrometry (ICP-MS) data. As there is interest in minimizing $NO_2$ usage during voloxidation by using a recirculating loop, a second set of tests determined whether a gas stream of iodine could be recirculated through a closed circuit. In some tests, a sorbent scrubber technology was employed to capture the iodine. Results from the recirculation experiments and behavior of the silver-impregnated sorbents will be presented in the talk.

Ultimately, a decision about the feasibility of $NO_2$-voloxidation will require further testing with SNF. As hot cell tests have long lead times and are expensive, tests with representative SIMFUEL are underway. Analytical methods are being developed for the online analysis of fission products, to isolate those that remain with the fuel, the cladding, or are trapped in the piping of the voloxidation reactor, in addition to quantifying those that are trapped in off-gas components. These detailed transport data are needed to reduce the uncertainty in locating fission products throughout the voloxidation process.

# Low Temperature Liquid-Based Chlorination of Metal Alloys

Richard Mayes[1], Breanna Vestal,[1] Emory Collins,[1] Joanna McFarlane,[1] Craig Barnes[2]

[1]Oak Ridge National Laboratory, [2]University of Tennessee, Knoxville

Chlorination of the metals associated with spent nuclear fuel has been identified as a significant means of metals recovery and purification, enabling a 25% (wt.) or greater reduction in waste requiring geologic disposition. Several chlorinating agents have been identified over the last few years, including gases and liquids. In particular, high-temperature gas phase chlorination reactions have been the primary means to chlorinate reactor alloys of zirconium. However, due to challenges associated with these reactions two new liquid-based oxidative chlorination reactions have been investigated for zirconium chlorination at low temperatures.

A protocol using two sulfur chloride reagents has been developed for zirconium alloys, whereby nearly 100% of the zirconium product stream may be recovered as purified zirconium chloride.[1] In sulfur monochloride, the zirconium can be quantitatively chlorinated to $ZrCl_4$ at temperatures less than 150°C. The reaction is completed in 2 – 4 hours via surface etching and exhibits 0th order kinetic behavior, which means that the rate does not change over the period of the experiment. Elemental sulfur is a byproduct, but it can be quantitatively chlorinated to produce recycle sulfur monochloride immediately following the zirconium alloy chlorination. Thus, the only consumed material is chlorine. In thionyl chloride, the reaction is completed in 7 – 40 hours with a variable induction period.

Recently, low-temperature chlorination reactions are being considered for reaction with other matrix alloys, such as the aluminum associated with Advanced Test Reactor (ATR) fuels. Similar to the Zr project, the goal is to provide proof-of-principle data that will aid in developing an advanced, low-temperature recycling protocol for the recovery of the Al metal in spent nuclear fuels. Aluminum can be quantitatively chlorinated to aluminum trichloride using thionyl chloride or sulfur monochloride. Based on preliminary experiments, the reactivity and exothermicity of the reaction between aluminum metal and the sulfur chloride reagents is highly dependent on the surface area to volume ratio of the metal. During aluminum chlorination via sulfur monochloride, it has been determined gravimetrically and via elemental analysis that elemental sulfur is produced as a byproduct. Preliminary experiments investigated the rechlorination of the sulfur byproduct to form sulfur monochloride, regenerating the solvent for the chlorination. Additional experiments are underway investigating the ability to recycle (reuse) the regenerated sulfur monochloride.

Experiments are planned to monitor the chlorination of Al in the presence of U metal and U alloys. In addition, scale up will require a transition to metal reactors from the glass reactors presently being used. Hence, testing of various metals and alloys under process conditions is planned. Surfaces of coupons will be examined by scanning electron microscopy and quantitative elemental analysis after contact with the sulfur-chloride reagents. Previous experiments suggest that typical chemical reactor alloys are resistant to chlorination, but this has not been a focus of the project to date.

1) Vestal, B.K, et al. A novel protocol to recycle zirconium from zirconium alloy cladding from used nuclear fuel rods. *Journal of Nuclear Materials*, **2023**, *578*, 154399, doi.org/10.1016/j.jnucmat.2023.154339.

# Interactions of Lanthanide Oxides in Tributyl Phosphate

Jarrod Gogolski, Tracy Rudisill, Robert Lascola, Patrick O'Rourke

Savannah River National Laboratory

A potentially more efficient method to reprocess used nuclear fuel (UNF), instead of acid dissolution and actinide recovery using a traditional PUREX process, is to combine the dissolution of UNF in the organic solvent (containing an extractant like tributyl phosphate-TBP) with two cycles of solvent extraction. Implementation of this scheme would require voloxidation of the UNF using either pure $O_2$ or a mixture of $O_2$ and $NO_2$ to oxidize the uranium in the fuel to the trioxide or uranyl nitrate form, respectively. The treated UNF would then be dissolved in the organic solution. While the dissolution of uranium nitrates and oxides into TBP have been demonstrated, it was uncertain how well the other elements in UNF will dissolve, particularly the lanthanide fission products. We studied the dissolution mechanism of several lanthanide oxides in TBP (pre-equilibrated with nitric acid) using UV-visible absorbance. Trivalent elements are poorly extracted by TBP; however, the trivalent lanthanides will readily complex the TBP in the absence of an aqueous phase. Specifically, the lanthanide nitrates bind to TBP within seconds to minutes. The lanthanide oxides first need to be converted to their nitrate form, which will occur with nitric acid present in the organic phase. Interestingly, the oxide to nitrate conversion is faster for the lighter than the heavier lanthanides. Co-dissolution studies were done to ascertain additional effects on the interactions of the lanthanide oxides with TBP, namely using $CeO_2$, as a surrogate for $PuO_2$, with $Nd_2O_3$ and $Er_2O_3$. Results from the dissolution studies including kinetic measurements of selected lanthanide oxides and a range of nitric acid concentrations which were pre-equilibrated with the TBP solvent will be presented.

| | $Nd(NO_3)_3$ | $Nd_2O_3$ | | | | | |
|---|---|---|---|---|---|---|---|
| Solution No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Nd Added (M) | 0.048 | 0.047 | 0.049 | 0.05 | 0.049 | 0.021 + 0.024 $CeO_2$ | 0.012 |
| Pre-equilibrated with # M $HNO_3$ | 0 | 10 | 4 | 1 | 0 | 10 | No Org/ 1 M $HNO_3$ |
| Undissolved Solids | No | No | No | Yes | Yes | Yes | No |

Figure 1: Neodymium in 30 vol % TBP-paraffin (Vials 1-6) and Nitric Acid (Vial 7)

## Dissolution of Used Nuclear Fuel Components Directly into Organic Solvent

Gabriel B. Hall[1], Daria Boglaienko[1], Nathan P. Bessen[1], Allison Greaney[2], Joanna Mcfarlane[2], Gregg J. Lumetta[1]

[1]Pacific Northwest National Laboratory, [2]Oak Ridge National Laboratory

The traditional head-end for reprocessing used nuclear fuel is to chop the fuel and dissolve it in hot mineral acid. This is then followed by solvent extraction to recapture desirable components. Voloxidation of the fuel offers the advantage of releasing volatile fission products prior to dissolution, which in turn can simplify the off-gas treatment system in a plant. Similarly, directly dissolving the fuel into process solvents has the potential to reduce plant footprint and simplify flowsheets by combining two operations (dissolution and extraction) into a single step.

The dissolution of three forms of voloxidized fuel simulants ($U_3O_8$, $UO_3$, and uranium nitrosonium nitrate) directly into 1.5 M bis-(2-ethylhexyl)-iso-butyramide (DEHiBA) in *n*-dodecane is examined. Prior to dissolution of $U_3O_8$ and $UO_3$, the process solvent is first loaded with nitric acid to allow oxidation and dehydration of the uranium, respectively. When uranium is in the chemical form of uranium nitrosonium nitrate it dissolves without the need for nitric acid. Sufficiently high loading of uranium in the organic phase is achieved for all three chemical forms of uranium, however consideration with respect to radiological degradation of the solvent during dissolution will have to be examined in the future. The dissolution of trivalent elements is found to be minimally suppressed by comparison to 30% tributyl phosphate (TBP) in *n*-dodecane.

# Recovery of Uranium and Distribution Ratios of Neptunium, Plutonium, and Technetium from Direct Dissolution-Loaded Solvents

Nathan Bessen[1], Gabriel Hall[1], Daria Boglaienko[1], Gregg Lumetta[1]

[1]Pacific Northwest National Laboratory

Direct dissolution of voloxidized used nuclear fuel presents an opportunity to simplify and reduce the plant footprint of reprocessing operations by combining dissolution and extraction steps into a single process.[1,2] Additional benefits may be gained by replacing tributyl phosphate (TBP) with bis-(2-ethylhexyl)-iso-butyramide (DEHiBA) as the extractant for such a direct dissolution process. DEHiBA provides significant selectivity for the hexavalent actinides[3] over TBP while also being fully incinerable and easier to dispose due to following the CHON principle. Furthermore, the use of a higher DEHiBA concentration of 1.5 M in place of the typically used 1.0 M provides an increase in the metal loading capacity while still retaining acceptable hydraulic properties. However, less is known about the steps that would follow dissolution. This includes the behavior of the solvent after being loaded under direct dissolution conditions or how the actinides may be recovered from the solvent.

Here, the distribution ratios for U, Np, Pu, and Tc from direct dissolution with DEHiBA are presented along with comparisons to those found by regular solvent extraction. Distribution ratios were found to be comparable to those from traditional solvent extraction once corrected for discrepancies in nitric acid concentration due to the direct dissolution solvent's nitric acid concentration not being in equilibrium with the aqueous phase. Oxidation states for the dissolved Np was determined by UV-vis-NIR spectroscopy and further confirmed for both Np and Pu by comparison of distribution ratios.

1) Rudisill, T. S.; Shehee, T. C.; Jones, D. H.; Del Cul, G. D. Dissolution of used nuclear fuel using a tributyl phosphate/*n*-paraffin solvent. *Separation Science and Technology*, **2019**, *54*, 1904 – 1911.
2) Arm, S. T. Direct Dissolution of Used Nuclear Fuel in PUREX Solvent: Review and Flowsheet Development. *Nuclear Technology*, **2022**, *208*, 1124 – 1136.
3) Condamines, N.; Musikas, C. The extraction by N.N-dialyklamides. II. Extraction of actinide cations. *Solvent Extraction and Ion Exchange*, **2019**, *10*, 69 – 100.

# Suppression of Neptunium Extraction into *N,N* di-2-ethylhexyl-isobutyramide (DEHiBA) Solvent by Butyraldehydes: a Spectrophotometric Study in a Closed Two Phase System with Direct Redox Speciation Monitoring of both Phases

Sergey I. Sinkov, Amy L. Speelman, Gabriel B. Hall, and Gregg J. Lumetta

Nuclear Chemistry and Engineering Group, Pacific Northwest National Laboratory

Among a number of *N,N*-dialkylamide extractants *N,N* di-2-ethylhexyl-isobutyramide (DEHiBA) received a lot of attention recently due to its low affinity to both tetravalent and pentavalent metal cations, including Np(IV) and Np(V) due to branching of the alkyl group attached to the acyl carbon.[1] This property of DEHiBA may be exploited to develop a single cycle flowsheet for uranium recycling, where co-extraction of Np with the U is suppressed so that the Np is routed to the high-level waste (HLW) raffinate. To achieve this goal, it is important to introduce a reductant into extraction process to reduce highly extractable hexavalent Np to a lower oxidation state. Several "salt free" reagents are being tested in our laboratory for this purpose, including in situ production of $HNO_2$ by photolysis, or $NO_2$ gas sparging to create nitrous acid without using $NaNO_2$, as well as hydroxyurea. According to technical literature, water soluble aldehydes with 3 carbon atoms in the alkyl chain (butyraldehydes) proved to be effective reductants for the valency adjustment of Np(VI) to Np(V) to suppress its partitioning to organic phase in the TBP-based flowsheets. Therefore, it has been decided to test their applicability for the Np redox control with the DEHiBA-based extraction.

A number of single aqueous phase experiments in 3M nitric acid were conducted first to verify reduction kinetics of Np(VI) with n-butyraldehyde and iso-butyraldehyde. This was followed by switching to a two phase system with 1.5 M DEHiBA in dodecane as organic solvent using a mixture of 9 mM Np(VI) and 1 mM Np(V) to achieve Np partitioning between the phases before introduction of the aldehyde via the organic phase. A series of short vortexing contacts was then applied and both phases were spectrophotometrically measured between the contacts to monitor Np redox speciation and partitioning in this system. The optical measurements were performed directly through a glass wall of the extraction container (a tube with a 11.6 mm inner diameter) by adjusting its depth of insertion into a standard spectrophotometric cell holder to probe the phase of interest without the light beam hitting the meniscus zone between the phases. In several cases the extraction tube contents were left to stand undisturbed for longer periods between the contacts to study how redox kinetics proceeded with no mixing. It was found that after 6 contacts of 15 seconds duration each all Np(VI), which was initially distributed between the phases with D = 3.3, was fully converted to Np(V) and the latter was rejected to the aqueous phase.

With longer standing time without re-equilibration, a gradual conversion of Np(V) to Np(IV) was detected in the aqueous phase. This gave us an opportunity to examine extraction behavior of these two oxidation states of Np by contacting both phases several more times to determine their relative extractability in the presence of each other.

1) Gogolski, J. Using N,N,-dialkylamides to Partition Actinides for Space Power Applications. PhD Dissertation, Colorado School of Mines, 2020.

# Maximizing Uranium Recovery: Strategies for Process Enhancement

Santa Jansone-Popova[1], Jopaul Matthew[1], Luke Gibson[1], Alexander Ivanov[1], Vyacheslav Bryantsev[1], Peter Zalupski[2], Travis Grimes[2], and Corey Pilgrim[2]

[1]Oak Ridge National Laboratory, [2]Idaho National Laboratory

The use of monoamide DEHiBA as an extractant for uranium has been found to be superior to tributyl phosphate (TBP). However, a major challenge during the solvent extraction process using monoamides is the co-extraction of technetium, Tc(VII), in the form of pertechnetate due to its increased lipophilicity over nitrate ion. This poses a challenge in terms of addressing the Tc(VII) problem. In addition, it is important to improve the loading capacity of uranium in the monoamide solvent while maintaining good solvent viscosity to ensure good phase disengagement in the solvent extraction equipment. The primary focus of this research is to design, synthesize, and test effective extractants for uranium and aqueous complexants for pertechnetate. The overarching goal of this research is to reduce reprocessing costs associated with nuclear waste.

Our recently developed monoamide extractants demonstrate a higher U(VI) loading capacity compared to DEHiBA. Despite the lower viscosity of monoamide solvent, the U(VI)-monoamide complexes exhibit reduced lipophilicity, leading to the significant co-extraction of water/acid adducts and the formation of a 3rd-phase in liquid-liquid extraction tests. Additionally, we have identified that aminoguanidinium-based aqueous complexants exhibit remarkable affinity for tetrahedral oxoanion pertechnetate ($TcO_4^-$) over trigonal planar oxoanion nitrate ($NO_3^-$). Use of complexing agents rather than aqueous reducing agents to manage Tc(VII) simplifies the U(VI) separation process. Our approach combines both theoretical and experimental investigations to identify the most efficient and robust extractants for selective extraction of uranium and aqueous complexant for the selective sequestration of pertechnetate.

# Data-driven Uranium/Plutonium Separation

Ping Yang[1], Sara L Adelman[2], Stosh A Kozimor[2], Yufei Wang[2], Logan Augustin[1], Danny Perez[1]

[1]Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, [2]Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM

The plutonium uranium redox extraction (PUREX) process has been the reference aqueous process to recycle uranium and plutonium from spent nuclear fuel using solvent extraction. Separating these elements from one another in high purity and in high yield is essential to the success of the DOE NE mission.

While developing a separation system for this process that eliminates the need for a Pu reductant, scientists have proposed amides as a potential replacement for the phosphorous-based extractant TBP, which tends to undergo radiolytic degradation. The current top candidates are N,N- di(2-ethylhexyl)butyramide (DEHBA) and its branched isomer N, N-di(2-ethylhexyl)isobutyramide (DEHiBA). Still, the best separation condition remains elusive, mostly because of the large number of factors that contribute to efficient separations, including the extractant identity and concentration, diluent identity, acid concentration, ionic strength, extraction kinetics, temperature, etc. The lack of predictive models for these separations has made innovation slow, incremental, and labor intensive, resulting in only fragmentary exploration of the vast chemical space. Our central goal is to accelerate *f*-element separation science using an integrated data-driven approach, in a way that provides fundamental molecular-level understanding of the separation process.

Specifically, machine learning algorithms will be applied to optimize the experimental conditions for DHEiBA/DHEBA extractants. High-throughput experimentation using a robotic instrument will be adopted to measure the distribution ratios for U and Th (surrogate of Pu) in DEHiBA/DEHBA mixed extractant systems. Parameters to be investigated include the DEHiBA and DEHBA concentrations, nitric acid concentration, U concentration, and temperature. In this talk, we will present our recent progress on toward achieving a comprehensive exploration of the chemical space of this challenging system.

# Radical assays used as a screening tool for determining the radiolytic stability of monoamide complexants

Modi Wetzler[1], Madison R. Vicente[1], Brandon G. Wackerle[1], Dean R. Peterman[2], and Julia L. Brumaghim[1]

[1]Clemson University, Clemson, SC 29634, [2]Idaho National Laboratory, Idaho Falls, ID 83415

The PUREX (Pu and U Reduction EXtraction) process commonly uses tributyl phosphate (TBP) as the extractant to separate out uranium and plutonium from nuclear waste. Using TBP results in third-phase formation and makes waste disposal more difficult because the presence of phosphorus in TBP complicates incineration. To avoid these drawbacks, *N*,*N*-dialkyl amides (monoamides) are increasingly being studied as CHON-only alternatives to TBP. The radiolytic stability of any potential complexants must be thoroughly understood to facilitate scale-up. γ-Radiolysis is the gold standard technique for predicting radiolytic degradation products and kinetics, but it is also a low-throughput, high-cost process, so studies of monoamide radiolytic stability are limited. To help narrow the pipeline for radiolytic screening of potential complexants for nuclear waste separations, we are developing non-radioactive radical assays as a potential screening tool for use in conjunction with radiolysis.

In toluene, azohydroperoxide releases hydroxyl and organic *tert*-butyl radicals that degrade monoamides, including process-relevant DEHBA and DEHiBA. Using GC-MS methods, we have identified correspondence of the same degradation products from this radical assay with γ-radiolysis of the monoamides in toluene, including amine, secondary amide, amide - $H_2$, and solvent-adduct products. We are working to extend the qualitative agreement of products to dose-dependence and semi-quantitative predictions of degradation product ratios as well as to nitric-acid contacted solutions. Based on these correlations, these radical assays show promise as a screening tool to quickly examine the potential radiolytic stability of monoamide complexants prior to γ-radiolysis studies.

# Impact of trivalent *f*-element complexation and chemical environment on the radiation-induced chemical reactivity of TODGA and HOPO ligands

Gregory P. Horne[1], Stephen P. Mezyk[2], Travis S. Grimes[1], Cristian Celis-Barros[3], Jacy. K. Conrad[1], Yufei Wang[4], Andrew R. Cook[5], and Rebecca J. Abergel[6]

[1]Idaho National Laboratory Center for Radiation Chemistry Research, [2]California State University Long Beach, [3]Colorado School of Mines, [4]Los Alamos National Laboratory, [5]Brookhaven National Laboratory, [6]Lawrence Berkeley National Laboratory,

Understanding the impact of ionizing radiation on ligands employed and proposed for the separation, recovery, and transport of actinide ions is of vital importance for the innovation of nuclear fuel cycle technologies. In the presence of ionizing radiation fields, complexing ligands are subject to radiolytic processes, that lead to their destruction and the formation of potentially detrimental degradation products. Consequently, mastery of the radiation-induced behavior of these ligands is essential for predicting and optimizing their effectiveness, longevity, and minimizing the negative impacts of radiolysis. Furthermore, this knowledge is critical for the design of more radiation resistant molecules to be incorporated into advanced separation technologies. That said, the radiation chemistry of most actinide complexants have only been studied in the absence of their targeted metal ion complexes, which can lead to inaccurate conclusions on their radiolytic robustness and impacts on performance.

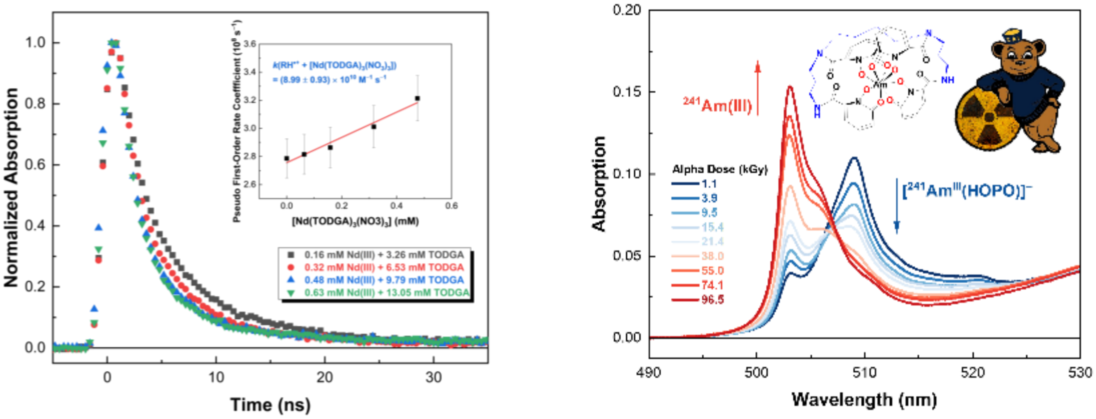


**Figure 4. (Left)** Normalized kinetic traces at 800 nm for electron pulse irradiated solutions of TODGA in the presence of Nd(III) in aerated 0.5 M DCM/dodecane: 0.16 (■), 0.32 (●), 0.48 (▲), and 0.63 (▼) mM Nd(III). *Inset:* Second-order determination of the rate coefficient for the reaction of $[Nd(TODGA)_3(NO_3)_3]$ with $RH^{\bullet+}$. The weighted linear fit corresponds to $k([Nd(TODGA)_3(NO_3)_3] + RH^{\bullet+}) = (8.99 \pm 0.93) \times 10^{10}\ M^{-1}\ s^{-1}$. **(Right)** Changes in the absorption spectrum of 0.5 mM $^{241}$Am(III) in aqueous 0.1 M HCl solution with the addition of 0.5 mM HOPO as a function of absorbed alpha dose. Color gradient (**blue** to **red**) indicates increasing absorbed alpha dose.

With this in mind, we present our findings on the impact of *f*-element complexation and chemical environment on the radiation-induced chemical reactivity of *N,N,N′,N′*-tetraoctyl diglycolamide (TODGA) and the model octadentate hydroxypyridinone ligand 3,4,3-LI(1,2-HOPO) (abbreviated as HOPO), **Figure 1**, both promising candidates for actinide separations.[1–2]

## References

1) Sasaki, Y.; Sugo, Y.; Suzuki, S.; Tachimori, S. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in $HNO_3$-*n*-dodecane system. *Solvent Extr. Ion Exch.* **2001**, *19*, 91–103.
2) Wang, Y.; Zhang, Z.; Abergel, R.J. Hydroxypyridinone-based stabilization of Np(IV) enabling efficient U/Np/Pu separations in the Adapted PUREX process. *Sep. Purif. Technol.* **2021**, *259*, 118178.

May 18, 2023 Thursday Afternoon Technical Sessions 7 and 8
EIL A-102

## Technical Session 7: "Actinide Chemistry Fundamentals"
## Technical Session 8: "Data Science, High-Throughput and Automation in Actinide Separations"

### Thursday Afternoon, May 18, 2023

Session 7 Chair: Laetitia Delmau, ORNL
Session 8 Chair: TBD

| | **7: Actinide Chemistry Fundamentals** | |
|---|---|---|
| **1:20 PM** | Trapping Unexpected/Unprecedented Hexanuclear Ce(III) Hydrolysis Products with Neutral 4-Amino-1,2,4-triazole: Mechanistic Information on Pu Colloid Formation? | Robin Rogers, Univ. of Alabama |
| **1:45 PM** | A Study on Plutonium(IV) Peroxide Degradation at Ambient Temperature: Combination of Reflectance Spectroscopy and Pu Redox Speciation after Acidic Dissolution | Sergey Sinkov, PNNL |
| **2:10 PM** | Selectively Precipitating Plutonium from Americium Using Cesium | Brian Arko, LANL |
| **2:35 PM** | Uranium Redox Chemistry at Bare and Functionalized Metal Oxide Electrodes | Christopher Dares, FIU |
| **3:00 PM** | Impact of the electronic properties of chalcogenide ligands in complexation free energies with uranyl nitrate complexes | Cristian Celis-Barros, CSM |
| **3:25 PM** | Afternoon Break | BREAK |
| | **8: Data Science, High-Throughput and Automation in Actinide Separations** | |
| **3:40 PM** | Applying Machine Learning and Quantum Chemical Simulations to Actinide Process Modeling | Hiroshi Saito, LLNL |
| **4:05 PM** | Automation for high-throughput separations to purify critical materials | Yufei Wang, LANL |
| **4:30 PM** | Development of a Multi-Sensor Data Science System for Monitoring a Solvent Extraction Process | Mitchell Greenhalgh, INL |
| **4:55 PM** | Design of an Analytical Chemistry/Material Characterization Laboratory to Support Plutonium Pit Production | Maria Kriz, SRNL |
| **5:20 PM** | Break (until 6:30 PM) | BREAK |
| **6:30 PM** | Conference Banquet | |

# Trapping Unexpected/Unprecedented Hexanuclear Ce(III) Hydrolysis Products with Neutral 4-Amino-1,2,4-triazole: Mechanistic Information on Pu Colloid Formation?

Robin D. Rogers[1-4]

[1]Department of Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, AL 35401,
[2]Department of Chemistry, The University of Wyoming, Laramie, WY 82071, [3]Wyonics LLC, 1604
Grand Avenue, Laramie, WY 82070, [4]525 Solutions, Inc., P.O. Box 2206, Tuscaloosa, AL 35403

Using Ce(III) and Nd(III) as both representative lanthanides and actinide analogs, we have explored the ability of mixtures of acidic and basic azoles to allow direct access to homoleptic N-donor f-element complexes in one pot reactions from hydrated salts as starting materials by reacting mixtures of 4-amino-1,2,4-triazole (4-$NH_2$-1,2,4-Triaz), 5-amino-tetrazole (5-$NH_2$-HTetaz), and 1,2,3-triazole (1,2,3-HTriaz) in 1:1 and 1:3 ratios with $CeCl_3 \bullet 7H_2O$, $[C_2mim]_3[CeCl_6]$ ($[C_2mim]^+$ = 2-ethyl-1-methylimidazolium), and $Ln(NO_3)_3 \bullet 6H_2O$ (Ln = Ce, Nd). Although unsuccessful in our goal, single crystal X-ray diffraction revealed that neutral 4-$NH_2$-1,2,4-Triaz is structure directing via $\eta^2\mu_2\kappa^2$ bridging, with the formation of the dinuclear complexes $[Ce_2Cl_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_4(H_2O)_8]Cl_4 \bullet 4H_2O$, $[Ce_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_4(4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_2(Cl)_6]$, and $[4\text{-}NH_2\text{-}1,2,4\text{-HTriaz}][Ln_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_2(\mu_2\text{-}NO_3)(NO_3)_6(H_2O)_2]$ (Ln = Ce, Nd). When the synthetic conditions favored hydrolysis, the hexanuclear Ln(III) complexes $[Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_2(\mu_3\text{-}Cl)_2(Cl)_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_{12}] \bullet 7H_2O$ and $[Nd_6(\mu_3\text{-}OH)_8(Cl)_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_{12}][Cl_4] \bullet 2H_2O$ were isolated (**Figure 1**). These hydrolysis products represent the first examples of a high nuclearity lanthanide complex where all Ln atoms are pairwise connected through 12 N-donor ligands or 12 neutral bridging ligands of any type, a rare example of incorporation of non-oxo coordinating anions in the $M_6X_8$ core, and the first reported Ce(III) hexanuclear complex. We will now spend significant effort to understand the serendipitous discovery that certain azoles seem capable of trapping *f*-element hydrolysis products in reproducible solid-state $M_6O_8$ motifs and transfer this chemistry to Pu(III).

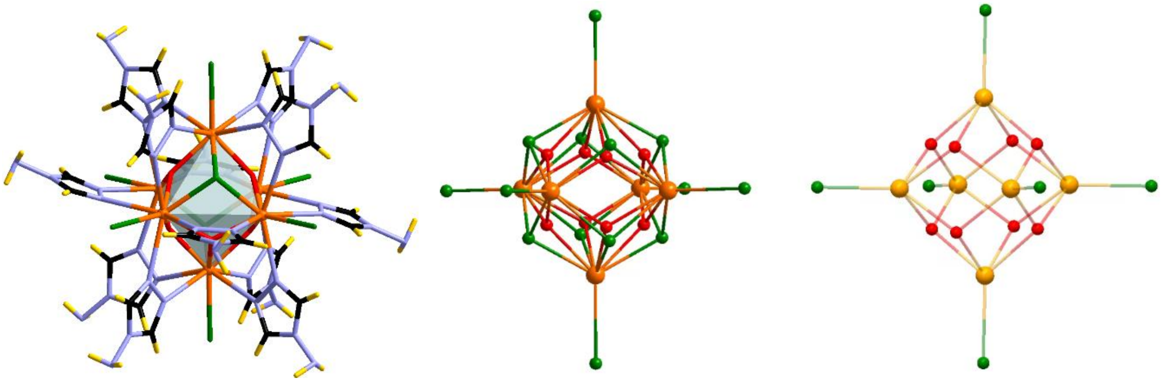


**Figure 1.** An ordered model of the primary coordination sphere (**left**) and the locations of the statistical mixture of 50% $O^{2-}$, 25% $OH^-$, and 25% $Cl^-$ $\mu_3$-bridges (**middle**) in $[Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_2(\mu_3\text{-}Cl)_2(Cl)_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_{12}] \bullet 7H_2O$, and the ordered core in $[Nd_6(\mu_3\text{-}OH)_8(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-Triaz})_{12}(Cl)_6][Cl_4] \bullet 2H_2O$ (**right**).

# A Study on Plutonium(IV) Peroxide Degradation at Ambient Temperature: Combination of Reflectance Spectroscopy and Pu Redox Speciation after Acidic Dissolution

Sergey I. Sinkov, Cody A. Nizinski, Scott H. Swenson, Richard A. Clark, and David E. Meier

Nuclear Chemistry and Engineering Group, Pacific Northwest National Laboratory

Among a number of plutonium compounds used in large scale production of PuO2 by thermal decomposition, peroxide of Pu(IV) used to play a significant role since its precipitation from nitric acid solution provided superior purification factors from many fission and corrosion products. Several research groups contributed to characterization of this compound by employing a variety of chemical analysis techniques, as well as XRD and vibrational spectroscopy. In particular, it was established that this compound can be prepared in two crystalline modifications: a cubic form, favored at lower acidity and a hexagonal one, forming at higher acidity. Compositionally, these two phases show very minor differences with hexagonal form exhibiting a slightly higher peroxy oxygen-to-plutonium ratio as well as a higher fraction of charge compensating anions in the formula. Much less is known about chemical and radiolytic stability of this compound.

In our laboratory a recent effort has been undertaken to prepare Pu(IV) peroxide as an intermediate compound for production of PuO2 in order to compare physical-chemical characteristics of the latter with those of PuO2 derived by thermal decomposition of Pu(III) and Pu(IV) oxalates. A small subsample of washed and air-dried Pu(IV) peroxide was not subjected to calcination but was reserved for acquisition of its reflectance spectrum and for evolution of this signature in time to observe potential degradation effects in this material. To better understand these aging processes the peroxide sample was further split into several tiny portions which were used for dissolution in concentrated hydrochloric acid with subsequent acidity reduction to 2M HCl and acquisition of optical absorbance spectra of the Pu ions. This approach revealed redox speciation changes in initially pure tetravalent Pu and provided insight into interaction of remaining O22- constituent of the material with Pu ions in acidic solution. Spectroscopic and chemical equilibrium data on Pu(IV) interaction with hydrogen peroxide as a fully protonated form of the O22- anion in 0.5 M HCl published 74 years ago [1] were employed in determination of peroxy oxygen-to-plutonium ratio in these partially degraded samples.

1) Connick, R.E., and McVey, W.H., The Peroxy Complexes of Plutonium(IV). *J. Am. Chem. Soc.*, **1949**, *71*, 1534-1542.

# Selectively Precipitating Plutonium from Americium Using Cesium

Brian Arko,[1] Sara Adelman,[1] David Kimball,[1] Stosh Kozimor[1]

[1]Los Alamos National Laboratory

Americium-241 naturally accumulates in Plutonium. These actinides have been separated in aqueous processing using solvent extraction and ion exchange chromatography for decades.[1–3] However, with the evolving Los Alamos National Labs (LANL) mission and the need to beat the 30 pit per year goal, there is interest in diversifying aqueous plutonium and americium processing.[4,5] One exciting option that researchers at LANL's Actinide Material Processing and Power (AMPP-4) group have been investigating is a selective precipitation of Pu from Am in the form of $Cs_2PuCl_{6(s)}$. This Pu/Am separation technique shows potential to be quick and require minimal hands-on work. This processing technique has been tried before at LANL and Rocky Flats, but with limited success.[6–8] This research is centered on advancing understanding into the basic principles that limit the $Cs_2PuCl_{6(s)}$ selective precipitation. Early results shown in Figure 1 suggest matrix effects may be the culprit for $Cs_2PuCl_{6(s)}$ precipitation's limited success as well as these risks may be mitigated by selecting feeds compatible with this processing technique. Future work associated with $Cs_2PuCl_{6(s)}$ precipitation is focused on testing scale-up and viability for other aqueous feed material.

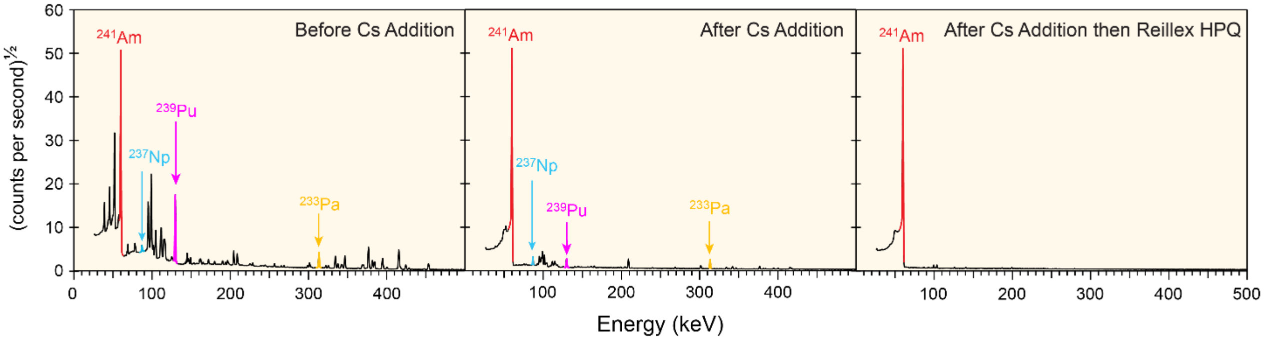


**Figure 1.** Gamma spectrographs of **(left)** starting Pu (magenta) with ingrowing $^{241}$Am (red), $^{237}$Np (blue), and $^{233}$Pa (yellow) **(middle)** after precipitating using 3 M CsCl dissolved in concentrated $HCl_{(aq)}$ (Pu:Cs 1:3, by mass) with >97% yield Pu with no observed co-precipitation of $^{241}$Am **(right)** after passing the supernatant over Reillex HPQ™ to produce an isotopically pure $^{241}$Am solution.

1) T. Feder, *Phys. Today*, 2015, 68, 22–24.
2) P. Paviet-Hartmann, C. Riddle, K. Campbell and E. Mausolf, *Overview of Reductants Utilized in Nuclear Fuel Reprocessing/Recycling Global 2013 Overview Of Reductants Utilized In Nuclear Fuel Reprocessing/Recycling*, 2013.
3) A. C. Muscatello and M. E. Killion, in *American Nuclear Society Winter Meeting*, Los Angeles, 1987, vol. 55.
4) R. M. Gates, *Nuclear Posture Review Report*, DIANE Publishing, 2010.
5) B. Roberts, *Wash. Q.*, 2021, **44**, 123–142.
6) A. C. Muscatello, J. R. Stevens, M. E. Killion, J. D. Valdez and R. L. Ames, *PILOT-SCALE PRODUCTION OF DICESIUM HEXACHLOROPLUTONATE (CS2PuCl6) AND FILTRATE RECOVERY*, Golden, CO, 1990.
7) M. A. H. Reimus, B. T. Martinez, J. R. Stevens and T. E. Boyd, *PILOT-SCALE ASH DISSOLUTION AND DICESIUM HEXACHLOROPLUTIONATE (DCHP) PRECIPITATION*, Golden, CO, 1994.
8) A. C. Muscatello and M. E. Killion, *CHLORIDE ANION EXCHANGE COPROCESSING FOR RECOVERY OF PLUTONIUM FROM PYROCHEMICAL RESIDUES AND CS2PUCL6 FILTRATE*, Department of Energy, Golden, CO, 1990.

# Uranium Redox Chemistry at Bare and Functionalized Metal Oxide Electrodes

Christopher Dares[1], Jeffrey McLachlan,[2] Xiangyang Hou,[1] Rodrigo Lacau,[1] Gregory Horne[3], Travis Grimes[3]

[1]Florida International University, [2]Lawrence Berkeley National Laboratory, [3]Idaho National Laboratory

In high-activity, low-enriched uranium (HALEU) fuels, it's important to maintain uranium enrichment. Tetravalent uranium can be used as a reducing agent for transuranic reductions, but it's use can decrease this enrichment. Control of the uranium oxidation state and structure is critical to used fuel reprocessing. We herein present electrochemical studies involving uranium at bare, and ligand modified indium tin-doped oxide (ITO) electrodes both in the absence and presence of trivalent lanthanides. In aqueous pH 4.8 solutions, $UO_2^{2+}$ is reductively deposited onto the surface as $UO_2$ at -0.5 V vs. SCE. This oxide layer can be oxidatively stripped from the electrode in fresh solutions. The composition of the uranium at the surface was confirmed using x-ray photoelectron spectroscopy. The electrode can be repeatedly used to electrochemically separate uranium with no loss in function, and a Faradaic efficiency of 70 %. The electrode has a uranium loading capacity of approximately 2.2 μmol/cm$^2$. At pH $\leq 1$ $UO_2^{2+}$ is reduced to $U^{4+}$ though some $UO_2$ is still deposited. When lanthanides are present, or at lower temperatures, $UO_2^+$ generated from the reduction of $UO_2^{2+}$ is stabilized. The stabilization of $UO_2^+$ in the presence of lanthanides is presumed to be through cation-cation interactions. In carbonate solutions, a chemical reversible and electrochemically quasi-reversible U(VI/V) couple is observed with $UO_2^{2+}$ when using a bare ITO electrode. This differs from the behavior observed with glassy carbon or planar ITO or FTO electrodes which are irreversible. When surface modification of the ITO electrode changes to composition of the tetravalent uranium generated from $UO_2^{2+}$, where even at pH 4.8 the predominant species generated is ligand-coordinated $U^{4+}$, not $UO_2$, indicating the ligand facilitates the proton-coupled electron-transfer (PCET) required to destroy the uranyl structure. These results can be used to establish design criteria for electrodes to electrochemically generate tetravalent actinides rather than using chemical reductants like $U^{4+}$.

# Impact of the electronic properties of chalcogenide ligands in complexation free energies with uranyl nitrate complexes

Cristian Celis-Barros[1], Christopher A. Zarzana[2]

[1]Department of Chemistry and Nuclear Science and Engineering Center, Colorado School of Mines, Golden, Colorado; [2] Idaho National Laboratory, Center for Radiation Chemistry Research, Idaho Falls, ID, P.O. Box 1625, 83415, USA

The idea of covalency being directly correlated with selectivity in f-element separations has gained attention over the years. However, "covalency" as a concept is still under debate as it is not an experimental nor quantum mechanical observable. Regardless, covalency along with ionicity are still the main concepts used to explain the nature of the chemical bond of coordination complexes. Another concept that has gained the attention in the separations community is the hard-soft acid-base (HSAB) theory, which favors soft-donor ligands having the potential to increase selectivity for actinides (An) over the lanthanides (Ln) due to their ability to engage more effectively f-electrons in covalent interactions. However, it has been shown that while using softer donor ligands in fact increased orbital mixing and covalency with the actinides, it compromises the strength of the interaction owing to a decrease in the metal-ligand electrostatic interactions.[1]

Herein, we study the electronic structure of different types of chalcogenide ligands (LE, E = O, S, Se), their interaction with the uranyl ion, and their complexation free energies. Surprisingly, contrary to the expected order of covalency, i.e. An–LSe > An–LS > An–LO, our results suggest that the degree of covalency and associated complexation free energies depend on the nature of the coordinating moiety rather than solely on the directly coordinated atom.

1) Sadhu, Biswajit, and Michael Dolg. Enhancing actinide (III) over lanthanide (III) selectivity through hard-by-soft donor substitution: exploitation and implication of near-degeneracy-driven covalency. *Inorganic Chemistry*, **2019**, *58*, 9738 – 9748.

# Applying Machine Learning and Quantum Chemical Simulations to Actinide Process Modeling

Hiroshi Saito[1], Jeremy Scher[1], Eddy Banks[1]

[1]Lawrence Livermore National Laboratory

With the kind cooperation of other US Department of Energy (DOE) Laboratories, Lawrence Livermore National Laboratory (LLNL) has been tasked to create chemical process models that simulate plutonium processing from recovery to desired products. To overcome the limitations of typical equilibrium-based chemical process simulations, our project considers new species using quantum chemical simulation programs such as Gaussian 16 to estimate thermochemical properties and increases models' accuracy by leveraging machine learning tools to develop missing mixtures properties. This presentation will discuss our technical approach, the data requirements, and our early efforts in our model development.

# Automation for high-throughput separations to purify critical materials

Yufei Wang[1], Sara L. Adelman[1], Stosh A. Kozimor[1], Mark Jensen[2]

[1]Los Alamos National Laboratory, [2]Colorado School of Mines

Separation and purification of strategic materials, particularly critical rare earth elements (REEs) and actinides, are unequivocally of national interest [1]. One of the most commonly used separation techniques for REEs purification is liquid-liquid extraction (LLE). However, improving separation efficiency for these systems is difficult, due to large number of variables in LLE (in-going metal concentration, acid concentration, solvent identity, phase modifier identity and concentration, etc.). High-throughput experimentation (HTE) represents one of the most obvious avenues to run parallel reactions and quickly acquire large datasets to screen separation conditions. To expedite the optimization of physiochemical conditions and achieve more efficient separation of critical rare earth materials, we have implemented a robotic platform capable of automating LLE, the LANL Super Separator (Fig 1). A study of the extraction of Nd, Eu, Dy, and Ho by a diglycolamide has shown that the robot can perform 588 reactions (7 acidities × 7 metal loadings × 4 elements × in triplicate) in ~30 h and the equilibrium curves used for the McCabe-Thiele diagrams can be easily obtained, paving the way for the rapid optimization of separating rare earth critical materials. These large datasets, collected via the Super Separator, can be used to train a machine learning (ML) model to eventually predict new separation conditions. Combining the ML platform with the Super Separator can be transformative in separation process research and make (radio)chemical separations more efficient.

Fig 1. LANL Super Separator – an automation system for high-throughput separation.

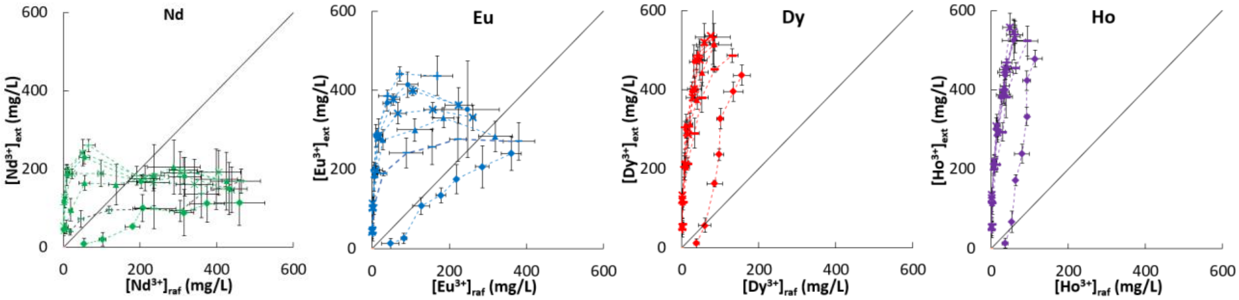


Fig 2. Equilibrium curve data for the McCabe-Thiele diagrams collected by the LANL Super Separator.

1) Critical Minerals and Materials: U.S. Department of Energy's Strategy to Support Domestic Critical Mineral and Material Supply Chains (FY 2021-FY 2031).

# Development of a Multi-Sensor Data Science System for Monitoring a Solvent Extraction Process

Mitchell R. Greenhalgh, Edna S. Cárdenas, Louis A. Ocampo Giraldo, Jay D. Hix, Camas M. Walker,
James T. Johnson, Katherine N. Wilsdon

Idaho National Laboratory

Idaho National Laboratory is designing and constructing a solvent extraction test bed, Beartooth, as part of a nuclear fuel cycle stewardship initiative. The test bed will provide facilities and equipment for testing novel extraction processes and give early career scientists opportunities to gain skills in performing separations chemistry. The test bed is being uniquely designed to enable machine learning capabilities for the characterization of chemical process operations. One of the intentions of incorporating machine learning methods is to provide process operators with enhanced situational awareness for the optimization of separations techniques and possible detection of a diversion event. As a result, the objective of this Laboratory Directed Research and Development project is to develop a multi-sensor data collections system and implement machine learning techniques on signals from an existing centrifugal contactor cascade to identify equipment usage and process events. This presentation will provide an overview of sensors used and experiments conducted to date.

# Design of an Analytical Chemistry/Material Characterization Laboratory to Support Plutonium Pit Production

Maria R. Kriz, Brian McElwain, Nathan Wyeth

Savannah River National Laboratory

## Savannah River Plutonium Processing Facility

The Savannah River Plutonium Processing Facility (SRPPF) is the pit production facility under development at the Savannah River Site and it will contain Analytical Chemistry and Material Characterization laboratories to support plutonium operations. The design and development of the analytical laboratories are occurring alongside the main production facility development. Most researchers and scientists do not have the opportunity to design laboratory facilities from the ground up and instead work in pre-established laboratories. The process of designing a laboratory involves interactions with multiple organizations not normally encountered on a routine basis by researchers, such as life and safety, ventilation and airflow, seismic and structural, fire protection, nuclear operations and safety basis. This presentation will discuss the design considerations evaluated for the Analytical Chemistry and Material Characterization laboratories and how these influenced the overall layout of the laboratories and the equipment selections.

## Laboratory Design Considerations and Equipment Selection

The role and function of the Analytical Chemistry and Material Characterization laboratories inside SRPPF are to support a production facility, not research and development. Operational difference between a research environment and a production scale environment are reflected in the layout of the laboratories to facilitate sample movement, throughput, and turn-around times. Types and quantities of equipment required for analysis can be approached differently whether one has an analytical mindset (e.g., multiple techniques for an analyte) or a production mindset (e.g., a single measurement per analyte).

Equipment selection and laboratory design considerations will be discussed for the following types of required analyses in the Analytical Chemistry laboratories:

- plutonium assay measurements
- plutonium isotopic measurements
- impurity analysis by Inductively Coupled Plasma Mass Spectrometry and Optical Emission Spectroscopy
- plutonium metal dissolutions

## REGISTRANT CONTACT LIST

| | | |
|---|---|---|
| Paige | Abel | emily.abel@inl.gov |
| Towfiq | Ahmed | towfiq.ahmed@pnnl.gov |
| COLLIN | ANDERSEN | Collin.andersen@utah.edu |
| Kash | Anderson | kash.anderson@inl.gov |
| Nickolas | Anderson | nhanderson@lanl.gov |
| Brian | Arko | barko@lanl.gov |
| Sang-Eun | Bae | sebae@kaeri.re.kr |
| Beau | Ballard | beau.ballard@inl.gov |
| Addyson | Barnes | addyson.barnes@inl.gov |
| Nathan | Bessen | nathan.bessen@pnnl.gov |
| Alexander | Bishop | Alexander_s@lanl.gov |
| Jacob | Brookhart | jacob.brookhart@inl.gov |
| Edna | Cardenas | edna.cardenas@inl.gov |
| Michael | Carrott | michael.j.carrott@uknnl.com |
| Rebecca | Carter | rebecca.carter@srnl.doe.gov |
| Cristian | Celis Barros | ccelisbarros@mines.edu |
| Gregory | Chipman | chipm@byu.edu |
| Richard | Clark | richard.clark@pnnl.gov |
| Timothy | Coons | tpcoons@lanl.gov |
| Justin | Cooper | justin.cooper@inl.gov |
| Harry | Cornell | harry.cornell@awe.co.uk |
| Samuel | Cross | sam.cross@awe.co.uk |
| Christopher | Dares | cdares@fiu.edu |
| Helen | Deaguero | deaguero1@llnl.gov |
| Guillermo | Del Cul | bill.delcul@nuclear.energy.gov |
| Lætitia | Delmau | delmaulh@ornl.gov |
| Jonathan | Dromey | jonathan.dromey@utah.edu |
| Miting | Du | dumiting@yahoo.com |
| Joshua | Dunbar | joshuadunbar@mines.edu |
| Peter | Eckert | peckert@visionaryfiber.com |
| Courtney | Eckley | u0891161@utah.edu |
| Madeleine | Eddy | meddy@eichrom.com |
| John | Engel | jengel@lanl.gov |
| Nick | Erfurth | nick.erfurth@inl.gov |
| Karla | Erickson | kaericks@lanl.gov |
| Richard | Farrar | richard.farrar@inl.gov |
| Sebastien | Faure | sebastien.faure@cea.fr |
| Forest | Felling III | u1033176@umail.utah.edu |
| Casey | Finstad | finstad@lanl.gov |
| Gabriel | Flores | gflor039@fiu.edu |
| Mac | Foster | info@marshalltonlabs.com |
| Margaret | Foster | info@marshalltonlabs.com |

| | | |
|---|---|---|
| Meghan | Fujimoto | Meghan.Fujimoto@inl.gov |
| Ranon | Fuller | ranongf@byu.edu |
| Barbara | Garcia | bgarc223@fiu.edu |
| Jarrod | Gogolski | jarrod.gogolski@srnl.doe.gov |
| Mitchell | Greenhalgh | mitchell.greenhalgh@inl.gov |
| Travis | Grimes | Travis.Grimes@inl.gov |
| Jonathan | Haling | jhaling@lanl.gov |
| Gabriel | Hall | Gabriel.Hall@pnnl.gov |
| Hayden | Hansen | haydenhansen08@gmail.com |
| Victoria | Hayter | Victoria.Hayter@uknnl.com |
| Colt | Heathman | colt.neathman@inl.gov |
| Eric | Hoar | eric.hoar@srnl.doe.gov |
| Brett | Holley | bholley@mfgsci.com |
| Kiel | Holliday | holliday7@llnl.gov |
| Megan | Hoover | megan.hoover@srnl.doe.gov |
| Gregory | Horne | Gregory.Horne@inl.gov |
| David | Horvath | david.horvath@inl.gov |
| Xiangyang | Hou | xhou004@fiu.edu |
| Santa | Jansone-Popova | jansonepopos@ornl.gov |
| Paige | Jones | paige.jones@pxy12.doe.gov |
| Toni | Karlsson | toni.karlsson@inl.gov |
| Ashleigh | Kimberlin | kimberlinae@ornl.gov |
| James | King | james.king@inl.gov |
| Maria | Kriz | maria.kriz@srnl.doe.gov |
| Morgan | Kropp | morgan.kropp@inl.gov |
| K Stephen | Kung | stephen.kung@nuclear.energy.gov |
| Eddie | Kyser III | edward.kyser@srnl.gov |
| Alexander | Langton | alex.langton@awe.co.uk |
| Lindsey | Lecrivain | Lindsey.Lecrivain@inl.gov |
| Gregg | Lumetta | gregg.lumetta@pnnl.gov |
| Kevin | Lyon | Kevin.Lyon@inl.gov |
| Didier | Maloubier | didier.maloubier@gmail.com |
| Dmitry | Maltsev | maltsevd@ornl.gov |
| Ken | Marsden | ken.marsden@inl.gov |
| Leigh | Martin | martinlr@ornl.gov |
| Tatsuro | Matsumura | matsumura.tatsuro@jaea.go.jp |
| Richard | Mayes | mayesrt@ornl.gov |
| Daniel | McAlister | dmcalister@eichrom.com |
| Jess | Meiers | jessica.meiers@inl.gov |
| Edward | Mercado | devin_rappleye@byu.edu |
| Stephen | Mezyk | Stephen.Mezyk@csulb.edu |
| James | Miller | jpmiller@lanl.gov |
| Marisa | Monreal | mmonreal@lanl.gov |

| | | |
|---|---|---|
| Mariel | Morales Duque | mmora379@fiu.edu |
| Masahiko | Nakase | nakase.m.aa@m.titech.ac.jp |
| Aaron | Nicholas | aaron.nicholas@pnnl.gov |
| Michael | Norato | michael.norato@inl.gov |
| Donna | O'Kelly | donna.okellly@inl.gov |
| Renee | Olney | olneyr1@unlv.nevada.edu |
| Kristen | Pace | kpace@lanl.gov |
| Hannah | Patenaude | hpatenaude@lanl.gov |
| Dean | Peterman | dean.peterman@inl.gov |
| Marek | Piechowicz | marekpiechowicz@shinefusion.com |
| Corey | Pilgrim | corey.pilgrim@inl.gov |
| Simon | Pimblott | simon.pimblott@inl.gov |
| Jennifer | Pyles | pyles@uab.edu |
| Ross | Radel | rossradel@shinefusion.com |
| Devin | Rappleye | devin_rappleye@byu.edu |
| Monica | Regalbuto | Monica.Regalbuto@inl.gov |
| David | Roberts | roberts59@llnl.gov |
| Rachael | Roenfeldt | rachael.roenfeldt@inl.gov |
| Robin | Rogers | rdrogers@ua.edu |
| Ethan | Rose | u0954530@utah.edu |
| Tracy | Rudisill | tracy.rudisill@srnl.doe.gov |
| Stephen | Schreiber | sschreiber@lanl.gov |
| Anna | Servis | aservis@anl.gov |
| Scott | Simpson | simpson52@llnl.gov |
| Michael | Simpson | michael.simpson@utah.edu |
| Bradley | Skidmore | skidmorebe@ornl.gov |
| Logan | Smith | smithl59@unlv.nevada.edu |
| Mathew | Snow | mathew.snow@inl.gov |
| Amy | Speelman | amy.speelman@pnnl.gov |
| Brian | Storms | Brian.Storms@inl.gov |
| Kenji | Takeshita | takeshita.k.ab@m.titech.ac.jp |
| Sukhpreet | Talewar | sukhpreet.talewar@awe.co.uk |
| Emma | Tardiff | tardiff3@llnl.gov |
| Evgeny | Taskaev | evgeny.taskaev@gmail.com |
| Peter | Tkac | tkac@anl.gov |
| Terry | Todd | Terry.Todd@inl.gov |
| Jason | Torrie | jason.m.torrie@gmail.com |
| Cameron | Vann | camvann13@gmail.com |
| Yufei | Wang | yufeiw@lanl.gov |
| Melissa | Warner | melissa.warner@inl.gov |
| Taylor | Weilert | taylor.weilert@ezag.com |
| Modi | Wetzler | mwetzle@clemson.edu |
| Steven | Wilcock | steven.wilcock@awe.co.uk |

| | | |
|---|---|---|
| Tyler | Williams | wtylerb@byu.edu |
| Brandon | Williams | willib39@unlv.nevada.edu |
| Nikki | Wolford | nwolford@lanl.gov |
| Donald | Wood | don.wood@inl.gov |
| Tsuyoshi | Yaita | yaita@spring8.or.jp |
| Tomoo | Yamamura | yamamura.tomoo.2e@kyoto-u.ac.jp |
| Ping | Yang | pyang@lanl.gov |
| Jacob | Yankey | Jacob.Yankey@utah.edu |
| Peter | Zalupski | Peter.Zalupski@inl.gov |
| Jinsuo | zhang | zjinsuo5@vt.edu |
| Chao | Zhang | zhang57@llnl.gov |
| Haiyan | Zhao | zhaohaiyan10@gmail.com |

**NOTES**

## NOTES

## NOTES

## NOTES