ACTINIDE RESEARCH QUARTERLY

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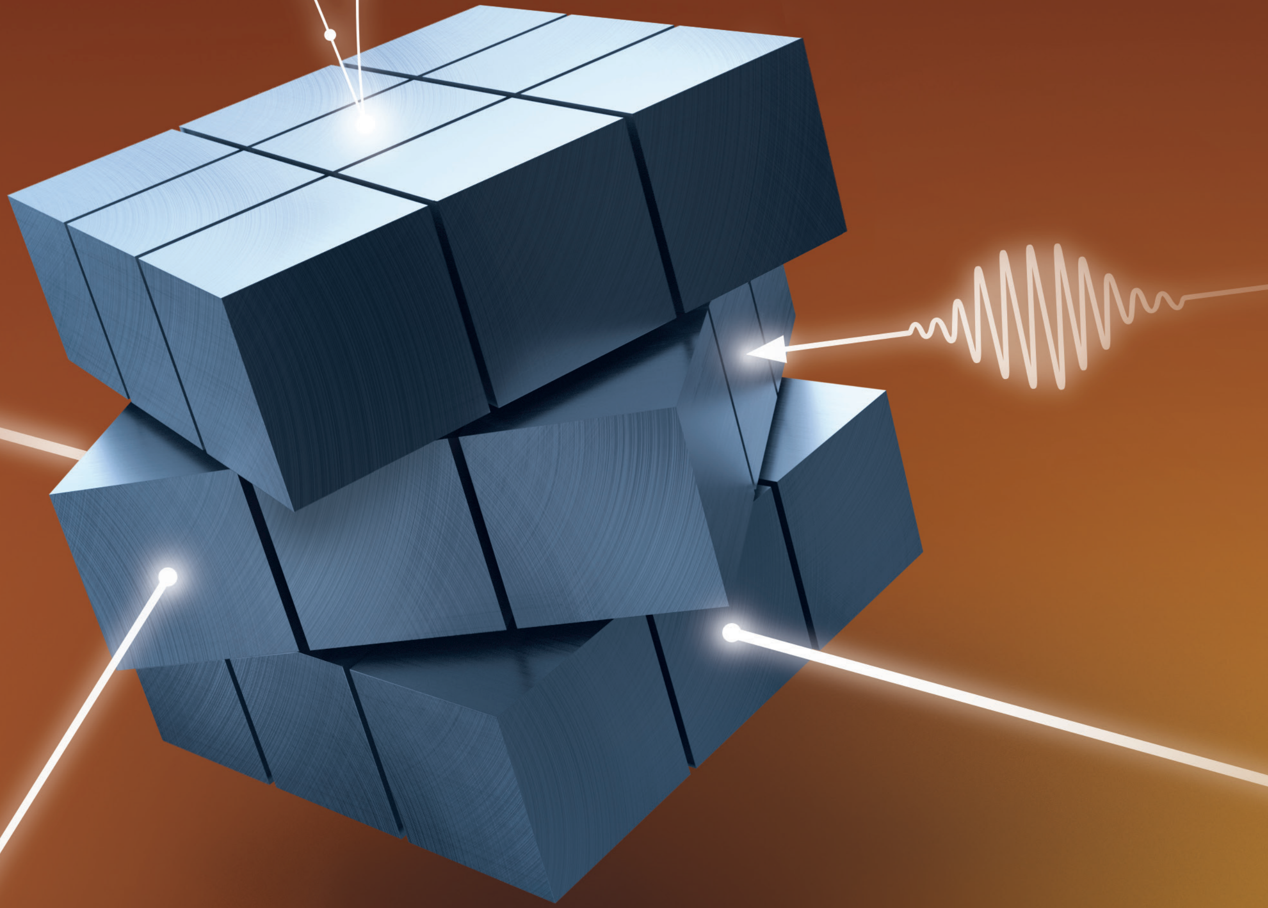
Second Quarter 2021

In-Situ Process Monitoring



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Foreword

The articles included in this issue are derived from presentations given at the recent workshop "In-situ Sensing and Process Monitoring for NNSA Relevant Materials and Processes" held as a two-day virtual workshop at Los Alamos National Laboratory (LANL) in late August 2020. The workshop was co-sponsored by the State of Technology Awareness Initiative (STAI) and the Seaborg Institute at LANL, and organized by Bjørn Clausen and Donald Brown (LANL/MST-8), John Carpenter (LANL/SIGMA-2), and Brian Crone (LANL/INP-PUE). The Technical Director for STAI is Richard Sheffield (LANL/ASO: Accelerator Strategy Office) whose focus is advancing the science, technology, and engineering to enable the Dynamic Mesoscale Materials Science Capability (DMMS) at LANL.

The workshop had over 100 registered participants, which included 6 keynote talks and 10 invited talks, as well as 4 discussion sessions. Presenters were from LANL, Lawrence Livermore National Laboratory (LLNL), National Institute of Standards and Technology (NIST), Air Force Research Laboratory (AFRL), Colorado School of Mines (CSM), and Westinghouse Electric Company. In addition, the workshop also included participants from Pacific Northwest National Laboratory (PNNL), Kansas City National Security Campus (KCNSC), Y-12 National Security Complex (Y-12), and the Pantex Plant.

Our goals were to discuss and identify the most promising in-situ sensing and process monitoring techniques that provide a path towards rapid qualification of the material or certification of the component. We also aimed to identify techniques that best respond to current programmatic gaps or technology pulls. The workshop was focused on National Nuclear Security Administration (NNSA) programmatic needs and included both actinide and non-actinide materials. Processes discussed were very diverse, ranging from aqueous actinide processing, casting and heat treatment of actinides, to additive manufacturing of steels and nickel alloys. Many of these ideas followed Design for Manufacture (DfM) approaches, meaning that parts, components, or products are designed specifically for ease of manufacturing.

The discussion began with a wide range of sensor categories (including chemical, acoustic, thermal, force, and metrological) that can be employed in-situ on both existing and future production operations (e.g., casting, welding, additive manufacturing, hot pressing, heat-treatment, forming, and machining) to ensure processing conditions are within the specified envelope. By simulating these processes on advanced beamlines equipped with analogous sensors we can obtain in-situ microstructural characterization using diffraction, imaging, and small angle scattering. This feedback can be linked to sensor response during manufacture, or specifically during off-normal transients.

As a stretch goal, we aimed to identify methods that allow real-time sensor response to be correlated to specific microstructural features which control properties, thus enabling on-the-fly informed decisions during fabrication. Inherent in these discussions is the topic of advanced data reduction methods (e.g., machine learning and advanced physics-based materials and process modeling).

The talks and discussions all included pragmatic considerations of what can actually be measured and/or controlled on the factory floor and covered several traditional probes (e.g., thermocouples, pyrometry, off-gas analysis) and novel probes (e.g., LIBS: Laser Induced Breakdown Spectroscopy, RUS: Resonant Ultrasound Spectroscopy), in addition to imaging and scattering.

A promising method that was identified as having strong potential to be implemented on the factory floor is the use of LIBS for in-situ monitoring, which addresses both qualification and compliance needs. Moreover, it was shown that in-situ scattering probes coupled with additional instrumentation (e.g., thermocouples, RUS) can reveal the microstructural underpinnings of macroscopic events, providing the linkage between the process control "knobs" (the actual physical control input parameters that can be altered for the process) and properties of the product.

Among the challenges identified were issues such as how to relate control knobs to performance. In other words: What can we control or measure in the factory? What controls microstructure? And how does that influence properties? Another important challenge is to reduce the amount of the time from discovery to implementation, both for materials and processes. We can tackle this in part by increasing the dialogue between core mission (mission pull) and the science base (technological push). This may be effected by bringing together people from production and science, theorists/modelers, and experimentalists to enhance the cross-fertilization of ideas and knowledge between the disciplines. A practical example of this would be establishing mini-sabbaticals internally (e.g., between LANL science/technology and production divisions) or externally (e.g., between LANL and KCNSC). Another direct suggestion was to develop NNSA-sponsored beamlines at existing DOE/BES user facilities, enabling research on materials/processes that do not fit the typical BES mandates of cutting edge science leading to high visibility publications. Instead, this would enable experiments on mission-relevant materials and processes, including the ability to safely and securely handle sensitive, hazardous, and/or radioactive materials.

The following articles represent a good cross-section of the techniques discussed during the workshop: A new efficient and fast method for identifying actinides in aqueous waste streams based on rapid actinide identification via luminescence (RAIL) that also presents opportunities for in-situ sensing and improved process control (*p3*); A novel use of LIBS for in-situ determination of the chemical composition of nuclear materials that can be used in production lines as well as to determine processing needs for legacy materials (*p9*); A neutron diffraction based study of long term aging in Pu-Ga alloys from self-irradiation and cryogenic temperature exposure, which identified development of lattice strains that will impact the kinetics of defect evolution in the material (*p17*).

— Bjørn Clausen, MST-8, Los Alamos National Laboratory

Dung Vu and John Auxier II testing a portable LIBS system in a radiologically hot glovebox (*p11*). Photo by Carlos Trujillo.

Contents

Material Characterization for Aqueous Processing

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Production efforts at Plutonium Facility 4 (PF-4) at Los Alamos National Laboratory (LANL) generate large amounts of byproducts and waste. Storage space for these byproducts and waste is limited and very expensive. Continued production relies on having enough space for these materials. Reducing the volume of material sent to these storage locations by consolidating the byproducts and minimizing waste is therefore essential.

For over 40 years, special nuclear material (SNM) has been processed using aqueous methods at PF-4 in part to help reduce the volume of material in the vault and material sent for waste disposition. Aqueous processing supports a variety of efforts including recovery of plutonium (Pu) and americium (Am) from pit production byproducts, stabilization of oxides for long-term storage, and production of americium dioxide (AmO_2) for sales via the DOE Office of Science Isotope Sales Program. Aqueous processing takes production byproducts as feed and separates the special nuclear material in a form that will occupy less space in the vault. The aqueous teams then safely consolidate and dispose of the remaining material as waste in cement drums for disposition at the Waste Isolation Pilot Plant (WIPP) and liquid sent to the Radioactive Liquid Waste Treatment Facility (RLWTF). Aqueous processing can be divided into two categories based on different acid media: nitric or hydrochloric acid. Aqueous chloride processing alone is capable of removing 800 drums worth of material from the pit production waste stream per year (mainly by removing americium from the feed).

Separating the flowsheet into nitrate and chloride halves allows for the optimal handling of the greatest variety of feedstocks (Figs. 1a,b). Trace actinides, such as americium, naturally grow into aging feedstock. The material in these processes requires monitoring at various stages to ensure each segment is performing as expected, to track inventory and to identify trace elements. Material is analyzed between each identified operation.

Processing stages and monitoring

It is vital that solutions and residues are monitored throughout the processing stages to track the quantities of radioactive material that are removed. Solutions are analyzed after dissolution and after each treatment (anion exchange, evaporation, etc.) and are sampled multiple times during anion exchange (Fig. 2). They need to be analyzed before they are added to the anion exchange columns, after the columns are loaded with Pu and impurities are washed away, and once the Pu is eluted. Monitoring at these stages is important to track the amount of Pu adsorbed onto and eluted from the resin, as well as the impurities that are removed.

Current tools used for this monitoring include thermal neutron counters (TNCs), solution in-line alpha counters (SILACs), and gamma spectrometry-based solution assay instruments (SAIs) as screening methods. Our SAI provides in-line, plutonium mass assays and is capable of rapid plutonium mass measurements using attenuation-corrected methods that enable the assay of samples independent of

John Ahern

John Ahern is a scientist and process engineer in AMMP-4 working on the aqueous nitrate processing team. Development of the RAIL sensor builds off his experience from developing a lanthanide sensor at the National Energy Technology Laboratory (NETL) as a postdoc. He received his PhD in Chemistry from the University of Maine in 2015. The picture is of John on top of Pico de Orizaba which overlooks the LANL co-sponsored High Altitude Water Cherenkov (HAWC) Observatory in Mexico.

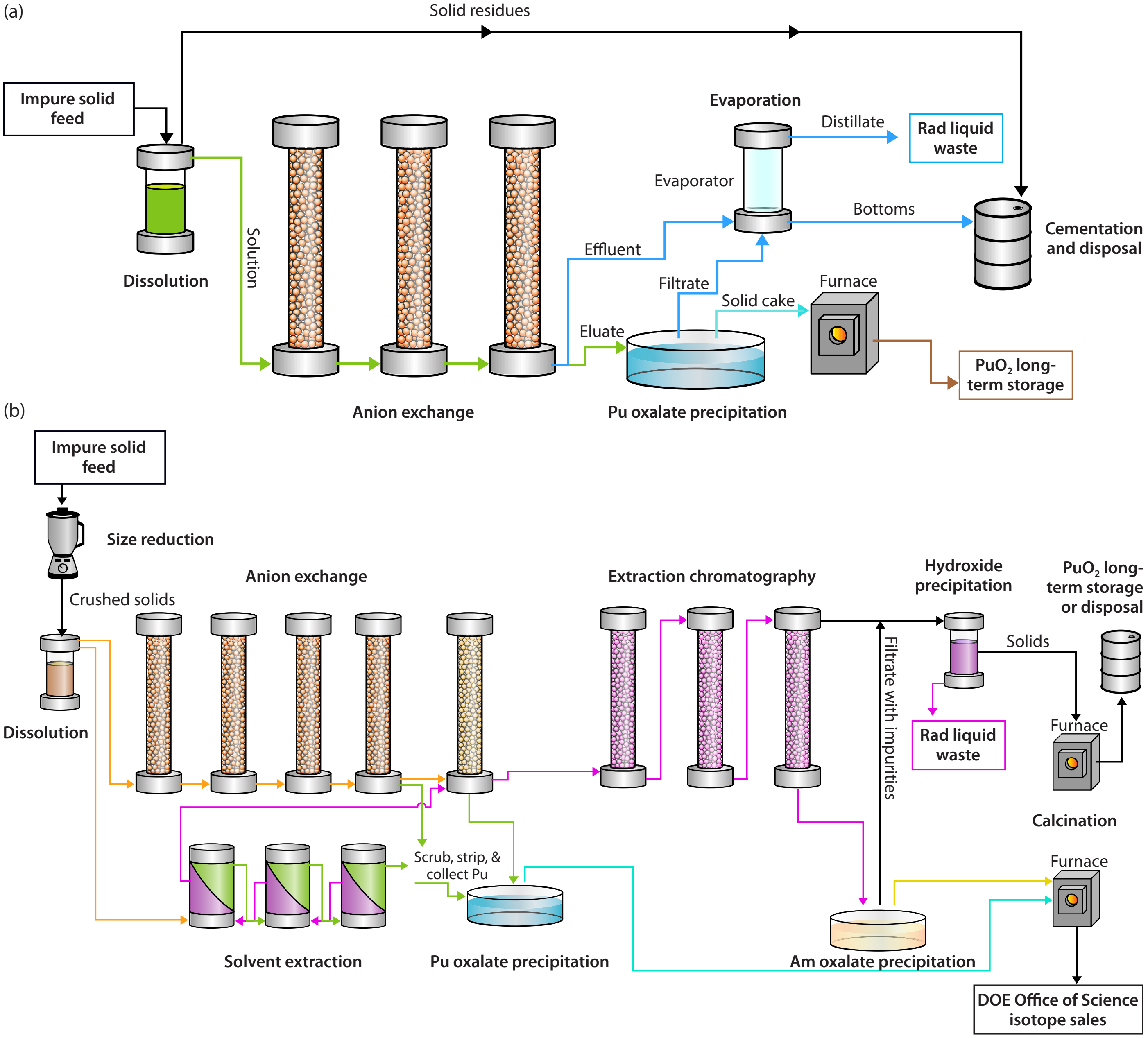

Figure 1. Flowsheets for: (a) Aqueous nitrate processing; (b) Aqueous chloride processing of plutonium and americium.

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chemical composition. It is currently commissioned exclusively for plutonium assays, however, development of the direct measurement of the Am-241 is in progress.

These monitoring methods have their limitations. TNCs have a detection limit of a few grams of Pu and they are only suitable for dry residues such as those from dissolution. They are not suitable for aqueous solutions or hydrogenous solids since the water present could attenuate the signal. The SILAC method has limits of detection in tens of mg/L but it cannot discriminate between different actinides and it is not suitable for quantitative concentration determination. Instruments currently used with lower limits of detection include inductively coupled plasma mass spectrometry

Figure 2. Anion exchange resin columns used in aqueous nitrate processing.

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(ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and calorimetry. However, the ICP-MS/AES and calorimetry methods are more expensive and time-consuming because samples have to be removed from the glovebox and sent to another room/facility for measurements which introduces the possibility for error due to extensive sample handling. Additional or improved screening methods would be helpful, particularly if they reduce the number of samples removed from the glovebox line and sent for calorimetry, ICP-MS/AES, or other analyses. So far, proposed methods to fill this niche have been inadequate, such as in-line handheld X-ray fluorescence (XRF) which is not well suited for measuring transuranics in liquid samples.

Rapid actinide identification via luminescence (RAIL)

We have recently proposed an alternative to said methods using a rapid actinide identification via luminescence (RAIL) sensor. Certain actinides can be detected optically via their luminescence much like the green glow in particular uranium-containing glasses (Fig. 3). The RAIL device uses sensitized luminescence to rapidly identify actinides in-situ at lower concentrations than conventional screening methods, including SAI or TNC. This device may also reduce the number of samples sent for costly time-intensive operations such as sample-outs and mass spectrometry analyses in production environments. If approved as a material accountability measurement method, this enhanced process characterization capability will allow for less downtime waiting for measurements and therefore increase annual throughput of byproduct feed.

Figure 3. Uranium luminescence observed as a green glow when exposing the uranium-impregnated glass to UV light. Photo courtesy of Kirstie and John Ahern.

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I have recently developed a sensor for detecting trace lanthanides using luminescence spectroscopy. Extending the use of this detector to trace actinides, particularly transuranics, has however been limited due to the inherent safety measures associated with handling highly radioactive actinides and their lower quantum yields. The latest work develops the technology by focusing on selected actinides. The RAIL sensors are functioning in a simulated environment pending approval for incorporation into a glovebox line.

The Actinide Research Facility (ARF) at LANL serves as the laboratory for preparation of samples. Work began with lanthanide surrogates and depleted uranium, with and without the selected sensitizer ligands (f-element concentrations in these solutions range between µg/L and g/L in 0.1–7 M nitric acid). Each sample consists of 0.5–5 milliliters of solution in a sealed quartz cell. Work is progressing to include Am-243 and other minor actinides now that the sample preparation and analysis is well-practiced.

Ligands for luminescence

Using ligands that are selective for actinides of interest will reduce the amount of unwanted ligand coordination with transition metal and other ions (including Pu). Ligands being evaluated include phenanthroline-based ligands such as 1,10-phenanthroline-2,9-dicarboxylic acid (H_2PhenDA) and 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen). These ligands are designed to offer improved selectivity and simplicity of use in acidic solutions relative to selective actinide extraction (SANEX) or group actinide extraction (GANEX) processes which require multiple steps and extractants. They are also stable in acidic conditions experienced in the processing lines of PF-4. Furthermore, they have higher reported stability constants for the actinides versus lanthanides including preferential separation of Am^{3+} over Eu^{3+} by a factor of 934. BTPhen ligands were even shown to preferentially bind and extract Am^{3+} over the similar Cm^{3+} in nitric acid solution by nearly a factor of five.

Based on similar studies performed by myself and others, including a patent filing for a similar device on lanthanides, energy transfer from the sensitizer ligand to the donor will increase the luminescent signal of the selected actinides and thereby lower their limits of detection (LOD) below 50 parts-per-million (mg/L).

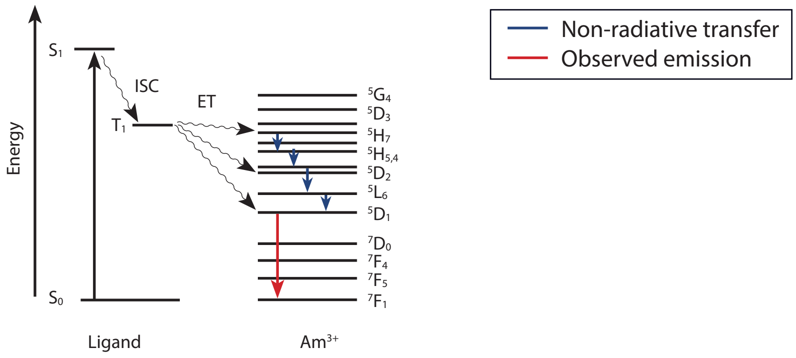

Figure 4. Energy from the excited singlet (S_1) state of the ligand can be transferred to a triplet (T_1) state via intersystem crossing (ISC) and then to the donor Am^{3+} via energy transfer (ET). Adapted from Sturzbecher-Hoehne et al. 2016.

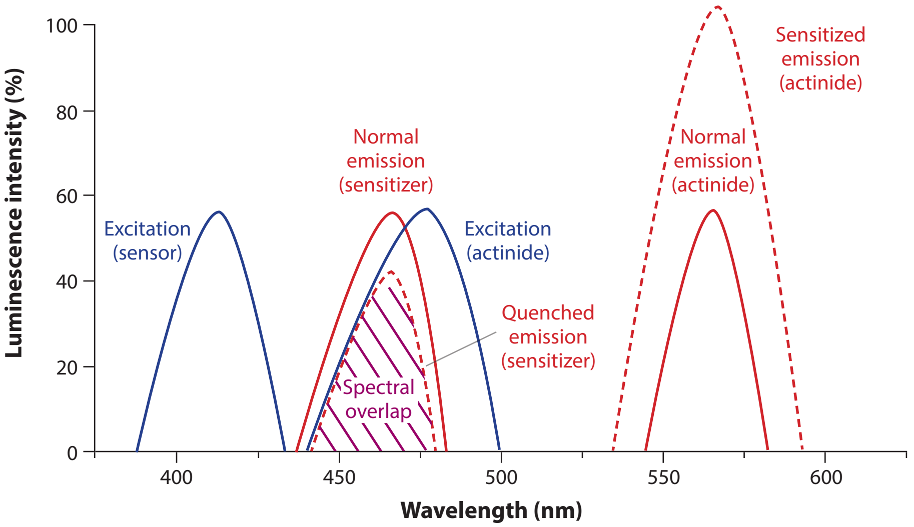

Figure 5. The spectral overlap between the emission energy of the sensitizer (donor) and the excitation energy of the actinide (acceptor) allows for energy transfer from the sensitizer to the actinide. This quenches the emission of the sensitizer and sensitizes (boosts) the emission intensity of the actinide.

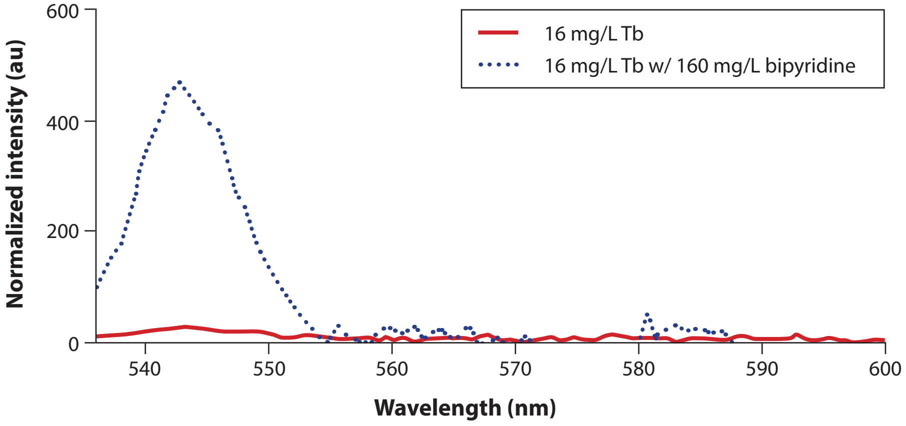

Figure 6. Luminescence signal for terbium with and without 2,2 byppridine ligand. This shows signal enhancement of terbium in the presence of a sensitizer ligand. © 2017 IEEE.

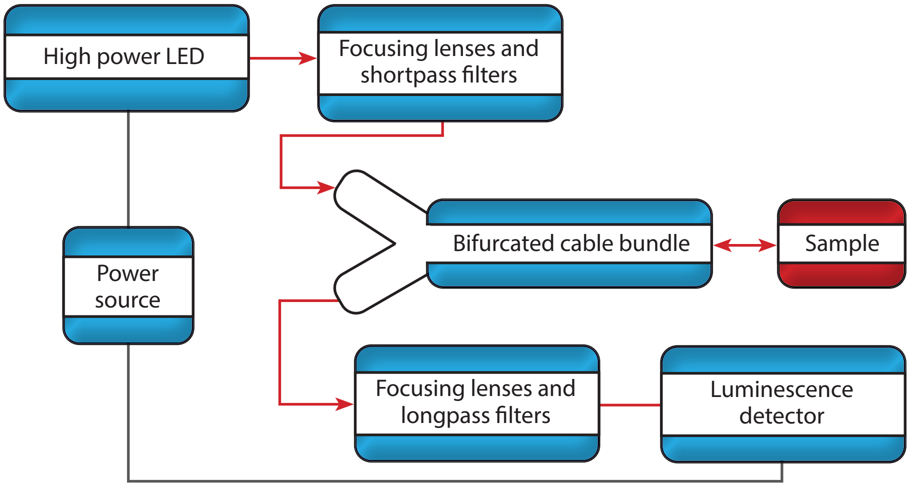

Figure 7. The RAIL sensor system with direction of light denoted by red arrows. This device will be placed in a (<1 ft^3) light-tight box.

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Energy transfer is possible when there is spectral overlap between the emission energy level of the sensitizer and the excitation energy of the actinide (Figs. 4,5). This can create an overall enhancement of spectroscopic signal in the presence of a sensitizer ligand (Fig. 6). The luminescent signal from actinides can be easily discriminated from each other and background species (transition metals, organics) because most f-elements including heavier actinides to the right of Pu on the periodic table tend to have multiple sharp, characteristic peaks that do not significantly shift with changes in background species expected in processing streams. This is a major advantage of the chosen sensitizers and the method.

The luminescence of these solutions has been evaluated using a RAIL system composed of a series of high-powered LEDs, a solarization-resistant 19-fiber bifurcated cable bundle, optical components, and an Ocean Insight QE Pro spectrometer (Fig. 7). Solutions can be probed in-situ by using a replaceable immersion probe attached to the bifurcated cable (Fig. 8a). This method can simultaneously identify many possible signatures including actinides without destroying the analyte or using large amounts of solvent. Coating the fibers with a sol-gel impregnated with the sensitizers is an alternative to adding sensitizers to each sample solution (Fig. 8b). These coated probes could be prepared in advance and dropped into the glovebox line, which would reduce the time and effort in sample preparation using cumbersome glovebox gloves.

A major challenge of this research is selectively coordinating the ligands to actinides of interest and increasing the actinide luminescent signal above the other species in solution. This risk can be mitigated however as actinides of interest can be identified in solution without these sensitizer ligands, albeit with higher LODs (at least five times higher). This higher LOD may be avoided by adding excess sensitizer.

Another challenge for this project will be devising a method to compensate for the effect of impurities which quench luminescence signals. The effects of aqueous signal quenching from the O–H stretch band of water will be mitigated by using

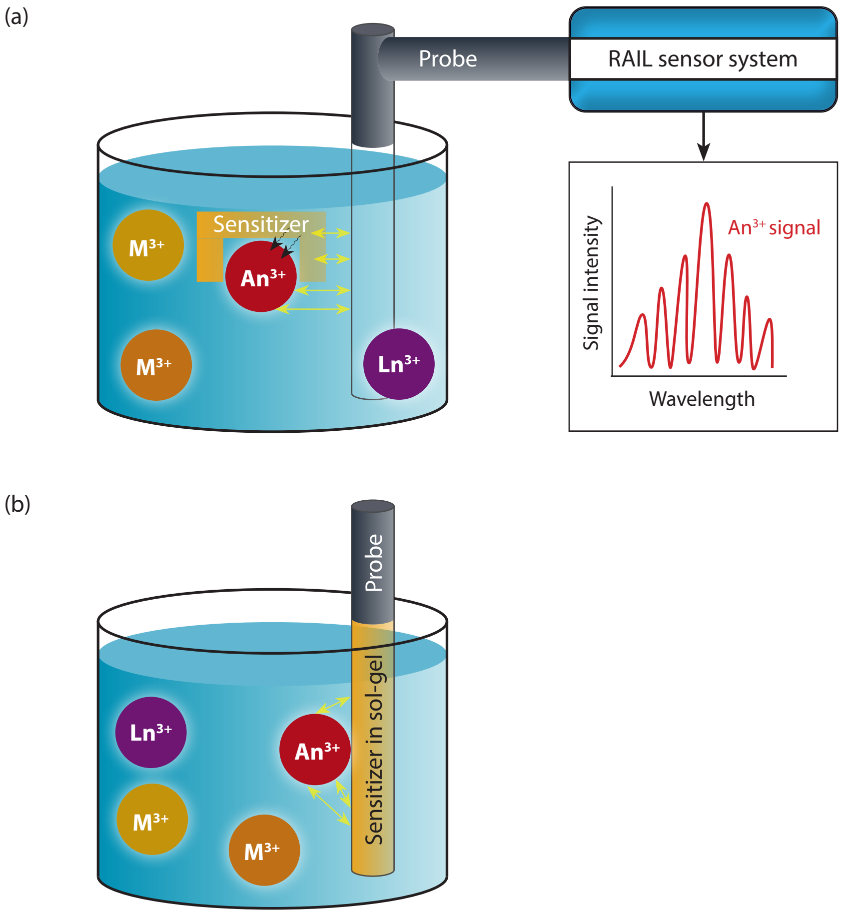

Figure 8. (a) Experimental design showing actinides of interest (An) coordinating with the sensitizer ligand and light being transmitting from the nine-fiber arm of the bifurcated probe bundle probe to the sensitizer, transferring that energy to the actinide and collecting the resulting emission from the actinide via the ten-fiber arm within the probe bundle. (b) An alternative probe tip design with the sensitizer impregnated in a sol-gel coated on the probe tip.

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surfactants like Triton-X 100. Additional sources of signal quenching will be reduced by using flocculation agents and filters to remove particulate matter that could quench the actinide signal.

With the proper sensitizer ligands, uranium and minor actinide (Np, Am, Cm, Bk, Cf, and Es) in-situ monitoring will be possible below 50 mg/L to hundreds of µg/L and can be accomplished faster than conventional measurement methods, reducing operational downtime. Combining this method with others suited for trace transition metal detection would provide a more comprehensive understanding of the process in real-time, in-situ. These efforts build understanding of plutonium science and aging by making advances in diagnostics and in-situ sensor materials for improved process control. The RAIL sensor technology is purpose-built for a plutonium processing facility such as PF-4. Once sufficiently low detection limits are achieved in media representative of processing streams, approval for the method will be sought for accountability measurements. This will reduce downtime waiting for measurements and therefore increase batch processing rate of material.

Summary

Processing of production byproducts and proper disposition of waste is an essential part of maintaining operations in PF-4. Monitoring these process streams is a necessary step in their handling and disposal. The RAIL sensor will identify and quantify selected actinides in process solutions at lower limits than conventional screening methods and faster (minutes versus days) than removing samples from the glovebox to send for analysis. A more sensitive and rapid screening method such as the RAIL sensor would provide better characterization of these process streams and potentially allow for more batches per year. Aqueous nitrate and chloride process streams are among the most appropriate and ready to implement applications for this device. However, the use of this technology could extend beyond aqueous processing. This type of device could be adapted for detecting uranium in process streams from uranium electrodecontamination activities. Sensitizers may not even be needed for sufficiently low detection limits for uranium. The device could also be adapted to field use for non-proliferation purposes given its compact size and limited power requirements.

Further reading:

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Portable LIBS for In-Situ Identification of Nuclear Materials

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Chemical analysis of nuclear materials is challenging, costly, and time-consuming. This is especially true at the Los Alamos National Laboratory (LANL) Plutonium Facility. Some of the limitations working in this facility include limited space for analytical instrumentations inside and outside our radiologically "hot" gloveboxes, material handling restrictions, difficulties in packaging and transporting samples to a separate analytical facility, and timely measurements and analysis. An in-situ analytical technique that could provide rapid analysis of the chemical composition of nuclear materials could save LANL considerable time and costs. Laser induced breakdown spectroscopy (LIBS) could potentially help with these efforts.

LIBS is a fast analytical technique that can quickly characterize the elemental composition of a target sample. It operates by producing a focused laser pulse that transforms sample surface (less than a microgram) into a plasma. Within that plasma, atoms and ions are excited to higher energy states. The excited species emit photons with characteristic wavelengths that are indicative of the chemical elements present in the sample—LIBS probes this "atomic fingerprint" of the target material. In order to extend its applications to the nuclear industry, we (and others) have been developing LIBS by targeting the detection of actinide materials and nuclear processes. In particular, we are employing recent advances in portable handheld LIBS instrumentation to explore the viability of this technique for in-situ nuclear material identification and manufacturing needs at the LANL Plutonium Facility. LIBS has the potential to decrease analysis times from many weeks to just a few minutes. In short, the characteristics that makes this technique desirable are:

1) In-situ and near real-time measurements
2) Rapid measurement time (seconds to minutes)
3) Minimal sample destruction (ng–μg)
4) Little to no sample preparation
5) Ease of instrumentation set up

Challenges

One of the challenges we hope to address with portable LIBS is the identification of legacy nuclear material, a need that is often encountered at the LANL Plutonium Facility. In many cases, legacy nuclear materials are poorly characterized and knowledge of the chemical composition is limited to the material's known processing history. The use of portable handheld LIBS could provide a rapid assessment of these nuclear materials to determine if additional analytical actions are needed and to map a recovery or disposal path for them. The speed and efficiency with which these determinations can be made will allow for significant time and cost savings by reducing the need for a full chemical analysis by more sensitive and costly techniques.

Dung Vu

Dung Vu's research interests involve the integration of chemistry, biology, and physics scientific fields. She has more than 25 years of experience in applying spectroscopic techniques to understanding the dynamics and function of biomolecules, synthesizing bionanomaterials, discovering disease-related biomarkers, developing biosensors, and characterizing actinide materials. Her current projects include applying and developing LIBS techniques to analyze nuclear materials for in-situ nuclear manufacturing processing and actinide material identification and elemental quantification.

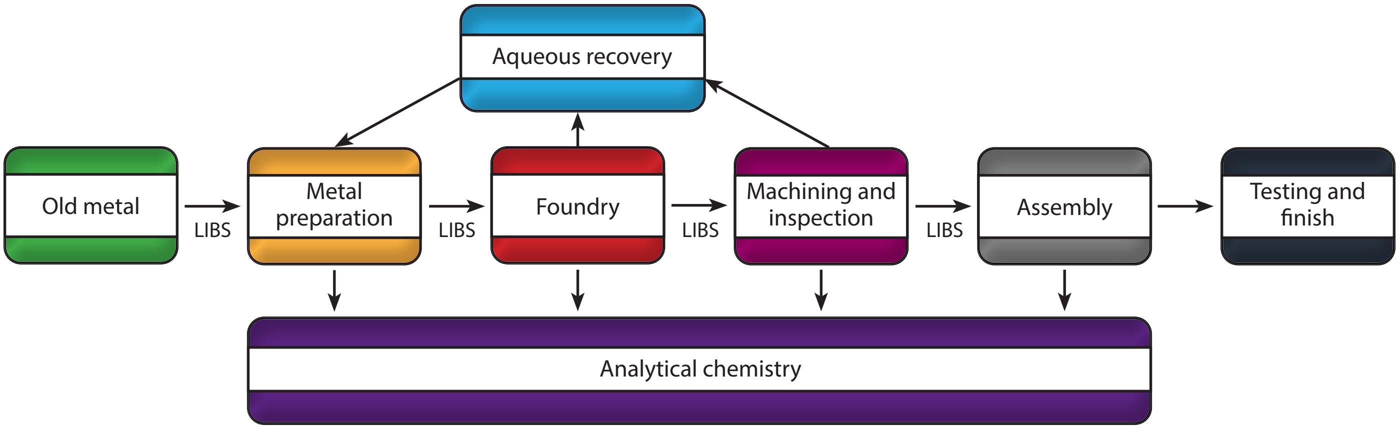

Figure 1. Schematic flow diagram of the nuclear manufacturing process. The deployment of LIBS at some of these steps could potentially shorten the analytical characterization times by providing a quick go/no-go answer for the presence of certain elemental impurities or alloying constituents.

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Another major challenge we aim to address is in the application of LIBS to in-situ nuclear manufacturing. Our goal is to be able to develop a rapid in-situ LIBS analytical tool for the in-line application of nuclear manufacturing of plutonium metal and its associated alloys (Fig. 1). In several of these steps, we usually deploy a suite of off-line analytical techniques (e.g., inductively coupled plasma optical emission spectroscopy and X-ray fluorescence) to quantify the various elemental impurities or alloying constituents (e.g., gallium) to allow us to proceed to the next steps with confidence and to eventually certify the end product.

Since the portable LIBS instrument has a low spectral resolution, we want to integrate LIBS with modeling and machine learning techniques to improve the accuracy of our data analyses. We will start by empirically "learning" the elemental plutonium spectrum from the measurements and then identify impurities in the LIBS spectrum. Our goal is to develop an automated tool to give a binary go/no-go answer for the presence of impurities and to ultimately derive the impurity concentration with a known level of confidence. The machine learning tools we are currently developing, based on convolutional neural networks, show promising results for identifying the presence of gallium impurities. The deployment of LIBS at some of these steps (Fig. 1) can potentially shorten the analytical characterization times. The development of portable LIBS with an integrated processing technique can potentially provide additional capabilities to our current suite of analytical tools.

Deployment of portable LIBS inside radiologically hot gloveboxes

In this research, we demonstrate the application of the portable LIBS at the LANL Plutonium Facility to help identify and characterize legacy nuclear materials and to show the feasibility of using this technology for current manufacturing needs.

We used the commercial, off-the-shelf SciAps Z300 LIBS instrument inside a radiologically hot glovebox—because of its compact size and portability, this instrument can be easily set up in different glovebox locations. In the configuration presented here (Fig. 2), the instrument can either be transported to the sample, or vice-versa. The LIBS instrument is equipped with three spectrophotometers to provide a total continuous spectral range of 185–950 nm (180–365, 365–620, and 620–950 nm, individually). This

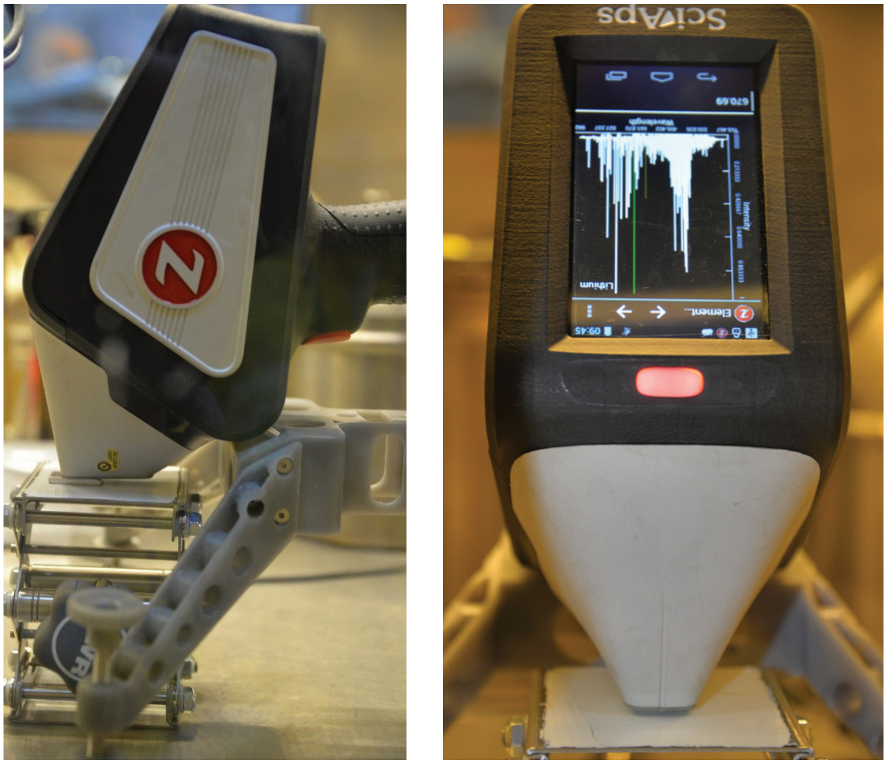

Figure 2. Z300 LIBS Analyzer deployed inside our glovebox. The spectra shown on the screen is a Pu standard (CRM 126). The spectral resolution is 0.1 nm full width half-maximum below 400 nm and 0.3 above 400 nm. A 5 mJ diode-pumped solid state laser (1064 nm, 2 ns FWHM pulse duration) is used with a 10 Hz firing rate and a focused beam size on the order of 50 µm.

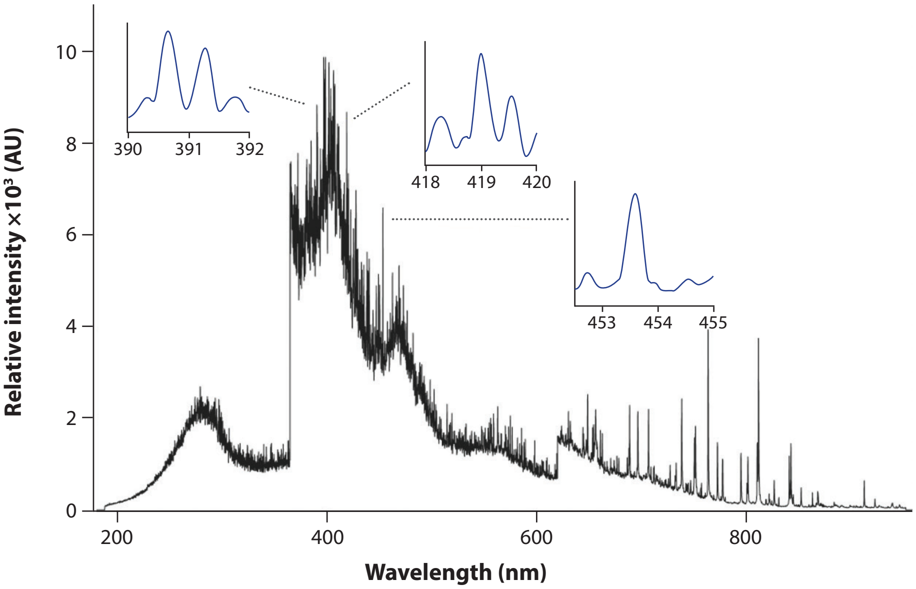

Figure 3. Plutonium LIBS spectrum. Data was collected with 250 ns gate delay time with a 1 ms integration time. For each measurement, 16 sequential spots were analyzed at four different locations (20 µm distance interval) to provide an average of 64 shots per spectrum. The average of 384 spectra is presented here. No cleaning shots were employed before the collection of data scans. The total collection time for generating these measurements was minutes.

instrument can detect all the naturally-occurring elements in the periodic table from hydrogen to uranium. In our current work, we have also been able to extend this to plutonium and americium.

The observed complexities in the plutonium atomic emission spectra arise from numerous transitions between the quantum states of the atoms and ions (Fig. 3). The complex atomic structure of plutonium results in a very rich emission spectrum involving thousands of transitions involving the ground level and many of the excited levels. Even though the emission line spectrum is intricate and the instrument has low spectral resolution, peak fitting or other analysis can be used to deconvolve some of these emission lines. We are in the process of assigning these peaks.

LIBS for nuclear material identification

Elemental and chemical identification of legacy nuclear materials is one of the important applications we are exploring with portable LIBS. As we continue with the cleanup of nuclear materials stored at LANL, we want to be able to rapidly identify and confirm the chemical constituents of many legacy nuclear materials.

As a test, we used the portable LIBS instrument to identify an unknown legacy inventory item (Fig. 4), believed to be the product of a salt-stripping process on a molten salt extraction residue. Based on the creation date, name, and visual appearance of the item, it was assumed that it was a product of a 30-year-old experimental research and developmental campaign to recover plutonium from chloride-based americium extraction salts. These mixtures typically contain sodium, potassium, and magnesium chloride salts, 3 wt.% of ^{241}Am (as $AmCl_3$), and 5–20 wt.% plutonium (as $PuCl_3$). The actinide isotopes are co-oxidized.

The amount of entrained plutonium required that the salts were treated using a time-consuming aqueous recovery operation. An experimental effort was undertaken to develop an alternative pyrochemical-based process to separate the Pu and Am in the extraction salts, using the same furnaces that generated them. The experimental effort examined several possible routes for the selective removal of these actinides from the extraction salts:

1) Co-reduction of the $PuCl_3$ and $AmCl_3$, followed by selective extraction of Am into an excess amount of Ca metal.
2) Selective reduction of $PuCl_3$ by a sub-stoichiometric amount of Ca metal.
3) Selective reduction of $PuCl_3$ using La metal.

Since the acceptance criteria for the discard of pyrochemical residues must meet stringent requirements for the absence of potentially pyrophoric materials (such as calcium or its substitute aluminum), it was important to determine the elemental composition of the original, legacy inventory item.

By interrogating freshly fractured surfaces of the legacy inventory item (Fig. 6) using LIBS we were able to rule out reaction route 3 for this product. Additionally, we also observed that the item was chemically heterogeneous (Fig. 4). While the overall chemical composition of the sample highlights its chemical constituents, the elemental distribution within the sample differs significantly. The Pu present is mainly located in the interior of the sample (Fig. 4 insert). It also contains a significant amount of Am. Therefore, through the use of our portable LIBS instrument, we were able to rule out one of the possible reaction routes and provide qualitative and localized elemental composition of this material.

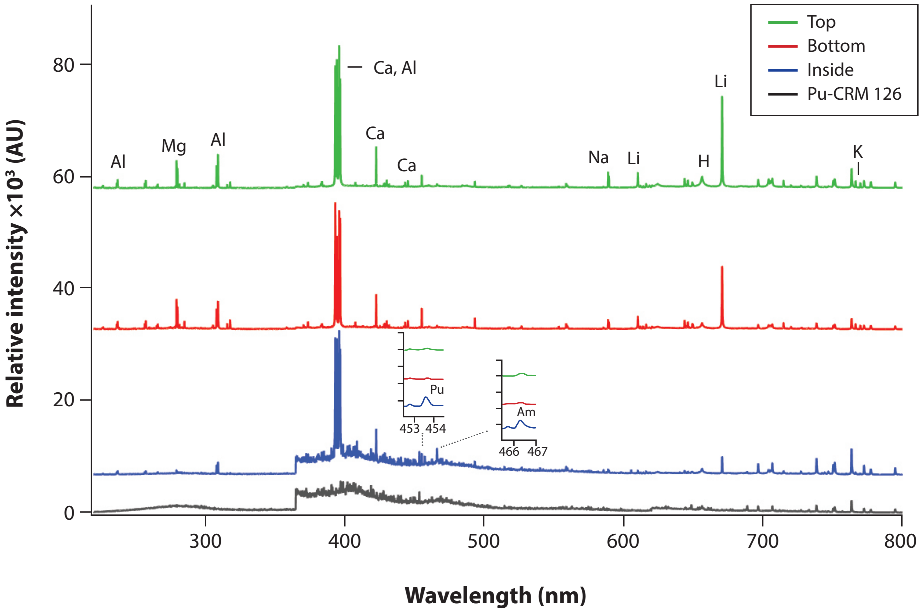

Figure 4. LIBS spectra and analysis of the legacy nuclear material item. The plot shows the chemical composition comparison of the various regions (colored traces) of the legacy item in Fig. 6. The major elements identified in the traces are derived from the metal and chloride salts from the salt-stripping reaction. The Pu LIBS spectrum (gray trace) is also depicted in this plot for comparison. The plutonium and americium that are present in this item are mainly localized in the inside region (blue trace).

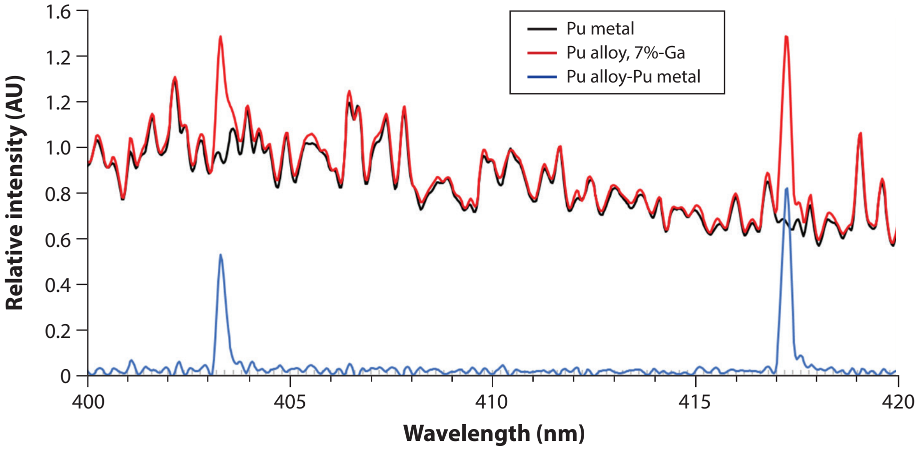

Figure 5. Comparison of Pu metal (CRM 126) and 7 wt. % Ga-Pu alloy. Prominent Ga LIBS peaks are at 403.3 and 417.2 nm. As we can clearly see, these peaks are very distinct from the Pu lines and are easily identifiable.

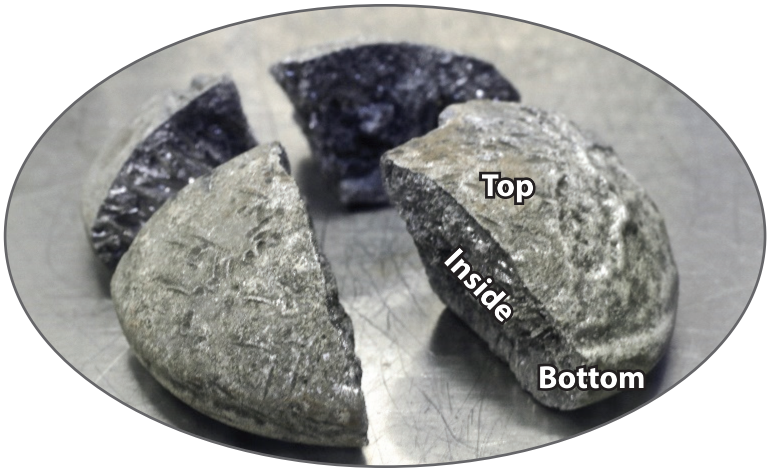

Figure 6. Example of a legacy nuclear material item removed from storage. Shown is the material fractured into four pieces.

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LIBS for nuclear manufacturing monitoring

Another goal is to develop a rapid in-situ LIBS analytical tool for monitoring nuclear manufacturing of plutonium metal and its associated alloys. One of the major challenges to achieving this goal is to be able to quantify key impurities and constituents (e.g., Ga) in bulk Pu metal. We are beginning to tackle this problem (Fig. 5). Ongoing LIBS measurements and analyses on other Pu-Ga alloy systems are being pursued to help determine the limit of detection for Ga and to build a suitable calibration data set to quantify its concentration.

Summary

We have demonstrated that a commercial off-the-shelf portable LIBS system has wide-ranging capabilities for elemental analysis of nuclear materials. Qualitative and potentially quantitative analyses of many impurities and constituents in plutonium metals, oxides, and other matrices are possible and should prove valuable to a number of ongoing LANL projects and programs.

Acknowledgments

Funding for this work is provided by the Materials Recovery and Recycle, Plutonium Sustainment, Advanced Simulation and Computing Programs. We thank Jeremy Mitchell and Clarissa Yablinsky for providing us with the 7 wt.% Ga-Pu alloy sample to perform LIBS measurements and analysis. We thank Brad DiGiovine for working with us to design a lightweight, compact, and stable LIBS instrument holder for use inside our radiologically hot gloveboxes. We thank Laura Worl, James Rubin, and Stephen Willson for initially recognizing the utility of LIBS for applications inside the LANL Plutonium Facility.

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Self-Irradiation Effects in Delta-Phase ^{239}Pu-Ga Alloys

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Plutonium is an important and highly complex element in which spontaneous self-irradiation drives lattice defects that damage the bulk solid over time. This damage includes lattice interstitials, vacancies, and defect accumulation, e.g., helium bubbles and other daughter product impurities. X-ray diffraction and dilatometry studies have revealed that the room temperature self-irradiation of δ-phase Pu-Ga alloys results in swelling of the lattice that saturates after 0.1–0.2 displacements per atom (dpa) of accumulated lattice damage. For a more complete picture of the less-understood aging processes of defect accumulation and damage evolution in δ-phase Pu-Ga alloys, we must consider additional factors such as dose, dose rate, thermal history, and alloy composition.

This article describes a time-of-flight (TOF) neutron diffraction investigation of the self-irradiation effects in δ-phase ^{239}Pu-Ga alloys, with various histories of annealing, ambient temperature storage times, and cryogenic temperature exposure. The observed self-irradiation at ambient conditions is explained in terms of damage to long-range order and associated lattice strain.

Overview of plutonium

In May 1941, Joseph W. Kennedy, Glenn T. Seaborg, Emilio Segre, and Arthur C. Wahl reported the fission of element-94^{239} with slow neutrons in an article submitted to Physical Review, and published several years later in 1946. The new element, subsequently named plutonium, discovered at Berkeley's Radiation Laboratory in 1940 showed an alpha-activity of about 60,000 alpha emissions per minute which corresponded to a half-life of about 30,000 years.

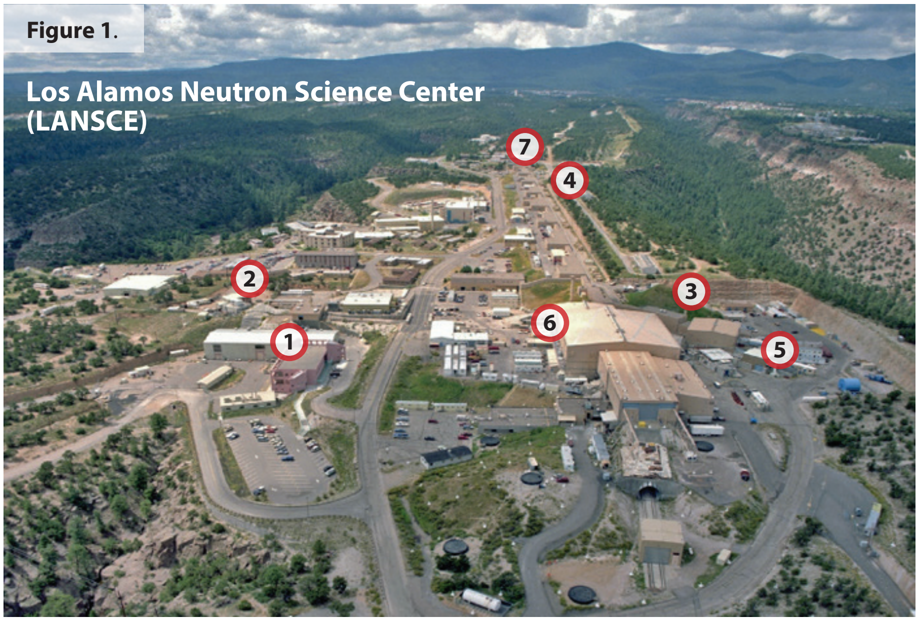
Plutonium proved to be the most unusual element of the periodic table, highly unstable with no less than six allotropes from room temperature to its melting point of 640°C. Many phases of elemental plutonium metal are sensitive to temperature, pressure, and time, which strongly affects the thermodynamic and mechanical properties and crystallographic structure in ways that are not yet completely described or even understood.

Of particular interest for technological applications is the face-centered cubic (fcc) δ-phase which exhibits unusual properties such as negative thermal expansion, large low-temperature electronic specific heat, high electrical resistivity, and other unusual behaviors. This high-temperature δ-phase, stable from 320–450°C, can be achieved at room temperature and below by the addition of a small proportion of certain trivalent elements (i.e., Ga, Al, Ce, Am, or Sc). The alloying process affects the lattice parameters and other physical properties correlated to the part of the electronic structure which is determined by the 5f electron state. It is further convoluted by the dual nature of 5f electron localization and bonding. The resulting alloys are metastable and more easily machined than the other phases, which is a very useful and important property for these materials.

Alice Smith

Alice Smith joined Los Alamos National Laboratory as a postdoctoral research associate at the Lujan Neutron Scattering Center, and is currently a Staff Scientist in the Materials Science and Technology Division, Nuclear Materials Science (MST-16) group. Her research interests are focused on actinide science, with emphasis on plutonium science: self-irradiation damage and aging, thermodynamic properties and kinetics of phase transformations, and microstructure and defect formation of plutonium and its alloys.

Figure 1.



1 **Lujan Neutron Scattering Center**: Neutrons used in engineering, chemistry, nanotechnology, and the materials, biological, medical, and geological sciences.
2 **Weapons Neutron Research** (WNR): Nuclear data crucial to the Stockpile Stewardship Program in addition to other basic, applied, and defense-related research.
3 **Proton Radiography**: 800-MeV protons for imaging dyamic experiments in support of national and international weapons science and thr Stockpile Stewardship Program.
4 **Isotope Production Facility**: Radioactive isotopes for medicine and research (strontium-82 is produced to aid 20,000 heart patients each month).
5 **Ultracold Neutrons**: Intense, ultracold needed for experiments on the fundamental laws of physics and aid in the quest for new particles.
6 **Materials Test Station** (MTS): Materials and fuels testing for use in advanced fast reactors.
7 **Linear Accelerator**: Facilities support.

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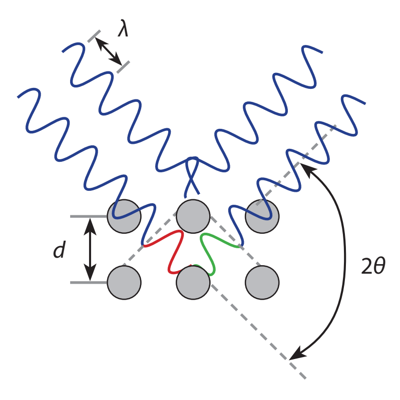
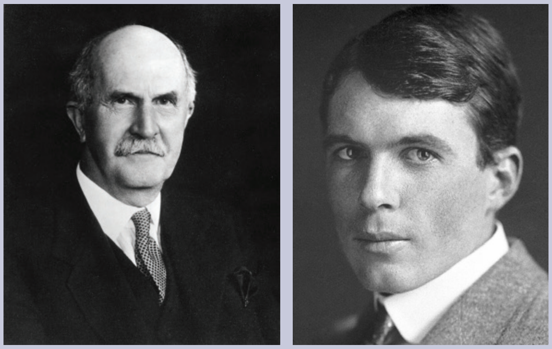
Most fcc alloys exposed to neutron irradiation and fission gases undergo changes in the microstructure (e.g., lattice distortions, steady-state void swelling rates of 0.8–1.5% dpa/yr, or changes to physical and mechanical properties). The fcc δ-phase Pu-Ga alloys experience self-irradiation with a defect production rate of 0.1 dpa/yr and helium accumulation. Consequently, they exhibit helium bubble formation and lattice/long-range order swelling to a saturated value of 0.1% at 0.2 dpa, but with minimal changes to the microstructure.

The large quantities of lattice damage in δ-phase Pu alloys induced by self-irradiation over thousands of hours at cryogenic temperatures are usually annealed when returned to ambient conditions. However, results from various ambient temperature investigations emphasize the influence of structural changes induced by self-irradiation, along with the stress and strain field changes in δ-phase Pu alloys.

These structural changes induced by radiation damage, detectable by means of X-ray or neutron diffraction, provide valuable information about the impact of aging or self-irradiation effects on the long-range order of the material (such as lattice strain and crystallinity). They also act as a measure of disorder and second phase inclusions. Compared to X-rays, neutrons have the added advantage of being highly





Bragg diffraction was first proposed by Lawrence Bragg (right) and his father William Henry Bragg (left) in 1913.

Diffraction

A form of elastic scattering, diffraction is a powerful nondestructive technique used to study crystalline materials to determine the static structure (from lattice parameters, phase composition, grain size, stress and strain, preferred orientation, crystallinity/amorphicity to thermal expansion, and phase transitions). X-rays and neutrons are diffracted by crystalline materials according to Bragg's law, the result being a pattern that shows absolute intensity as a function of the diffraction angles (2θ) or the d-spacing. From its peaks (shape, intensity, position), the diffraction pattern provides valuable information about the crystal structure, the unit cell, d spacing, the crystallite size, stress, texture, and defects. It is specific to the material being measured.

penetrating and non-destructive, which makes them a more suitable probe for bulk measurements, and ideal for investigations that require massive experimental setups, such as those used in temperature and pressure studies.

Neutron scattering

Neutron scattering is a condensed matter technique that provides information on the structure, dynamics, and magnetic properties of materials. It encompasses a large array of methods, such as diffraction, pair distribution function analysis, small-angle scattering, reflectometry, and inelastic scattering.

X-ray diffraction was an important part of the first efforts of characterizing plutonium's structures, establishing the space group and lattice parameters of its allotropes, and understanding its behavior under non-ambient conditions such as variable temperatures and pressures. In the early 1940s, X-ray diffraction was the only analytical tool available for these type of investigations. The pioneering work of W. H. Zachariasen, considered the father of plutonium crystal chemistry, is well known and broadly used today, providing identification for most of the plutonium phases, and the first one to identify the six allotropes of Pu (see ARQ First Quarter 2020, "Reflections of Plutonium— In Search of Solutions to a Difficult Problem in Crystallography", pp 56–60).

Neutron diffraction, performed at neutron reactors (with constant wavelength) and at spallation neutron sources (with TOF method), came into play later. The first neutron diffraction experiments were carried out in 1936 (versus 1912 for X-ray diffraction) using low intensity neutron sources. During the Manhattan Project, the construction of nuclear reactors enabled neutron beams of higher intensities which were more suitable for neutron scattering experiments. The use of neutrons as a diffraction probe was established at the University of Chicago Metallurgical Laboratory, using the Chicago Pile 3 heavy water reactor, and at Oak Ridge National Laboratory (ORNL), using the X 10 graphite reactor. Later, neutron scattering research increased significantly with the development of spallation neutron sources. The Manuel Lujan Jr. Neutron Scattering Center (Lujan Center), part of the Los Alamos Neutron Science Center (LANSCE) at Los Alamos National Laboratory (LANL) is the only neutron facility in the US that accepts highly radioactive samples, such as plutonium, and can accommodate both unclassified and classified research. As a probe, neutrons have several advantages over X-rays:

- **Highly penetrating**. This makes them a bulk probe and suitable for massive experimental setup (e.g., high pressure and non-ambient temperature experiments).
- **Easier interaction**. Neutrons use the nuclear interaction (vs. electromagnetic interaction for X-rays, electrostatic interaction for electron beams, or polarizability for optical probes). Scattering by atomic nuclei results in detection of nearly all atoms.
- **Good scattering for low Z elements**. This is ideal for hydrogen- or deuterium-containing samples. Neutrons also have the ability of distinguishing between neighboring elements (e.g., Mn, Fe, Cr) and among different isotopes of an element.
- **Isotopic substitution**. The most common example is the substitution of hydrogen with deuterium in hydrogenous systems. Dependence of neutron scattering amplitude on isotopes of the same element allows the partial structure factors to be separated from the neutron diffraction data. This can then highlight the contribution of the substituted nuclei, revealing both structural and dynamical details of a sample without changing the chemical composition.

For many years, ^{239}Pu samples were considered unsuitable for neutron scattering experiments because of their large absorption cross section (σ_{abs} = 1017 versus 18.5 barns for ^{239}Pu and ^{242}Pu respectively). Therefore, ^{242}Pu samples were preferred. However, ^{242}Pu is less relevant for long term response to stimuli and aging studies (many old samples are ^{239}Pu), and more importantly, of lower availability than ^{239}Pu. Since 2011, redesigned sample containers and a more appropriate sample geometry allowed us to pursue neutron scattering measurements at the Lujan Center using both diffraction (neutron) and a more challenging pair distribution function analysis using ^{239}Pu samples, overcoming ^{242}Pu availability issues.

Pu-Ga Alloys investigated by TOF neutron diffraction

Neutron diffraction measurements using two high-purity polycrystalline samples of δ-phase ^{239}Pu stabilized with 2- and 7-at.%-Ga were conducted on the high pressure-preferred orientation (HIPPO) TOF diffractometer at the Lujan Center pulsed-neutron spallation source during the FY16, 17, and 19 run cycles (Figs. 1–4). In all three sets of experiments discussed here, samples underwent cooling from room temperature to cryogenic temperatures followed by a heating back to ambient.

The FY19 experimental series contains the most detailed data sets. For each cooling-heating sequence the material showed thermal expansion with a contraction of the lattice parameter upon cooling and expansion upon heating back to room temperature, consistent with previous results (Fig. 5). The final value of the lattice parameter measured upon return to room temperature was larger than the original starting value for each sequence, indicating that during each cooling-heating sequence the lattice expands beyond the initial state. This effect is most dramatic

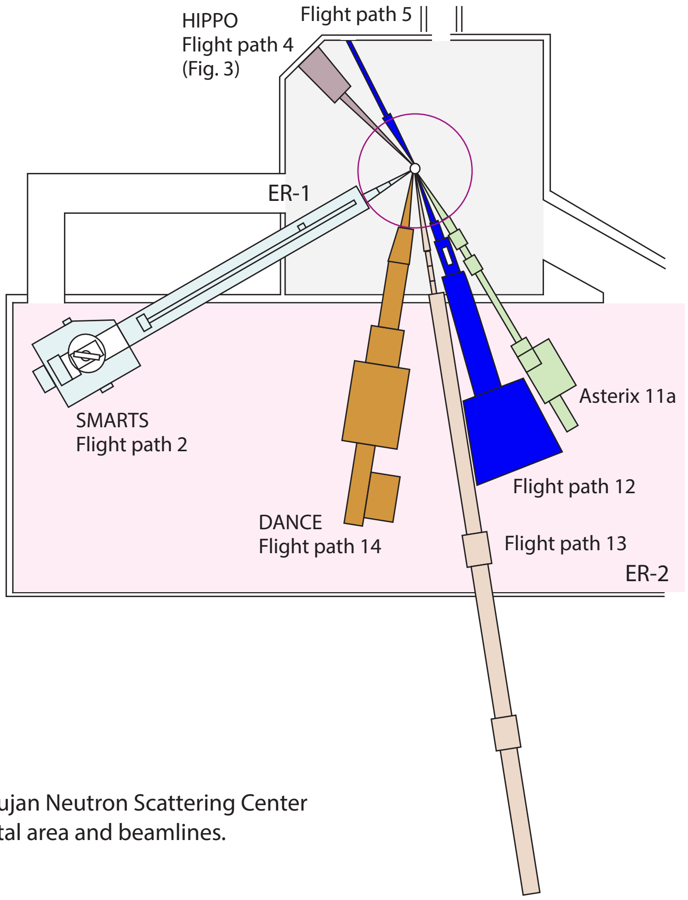


Figure 2. Lujan Neutron Scattering Center experimental area and beamlines.

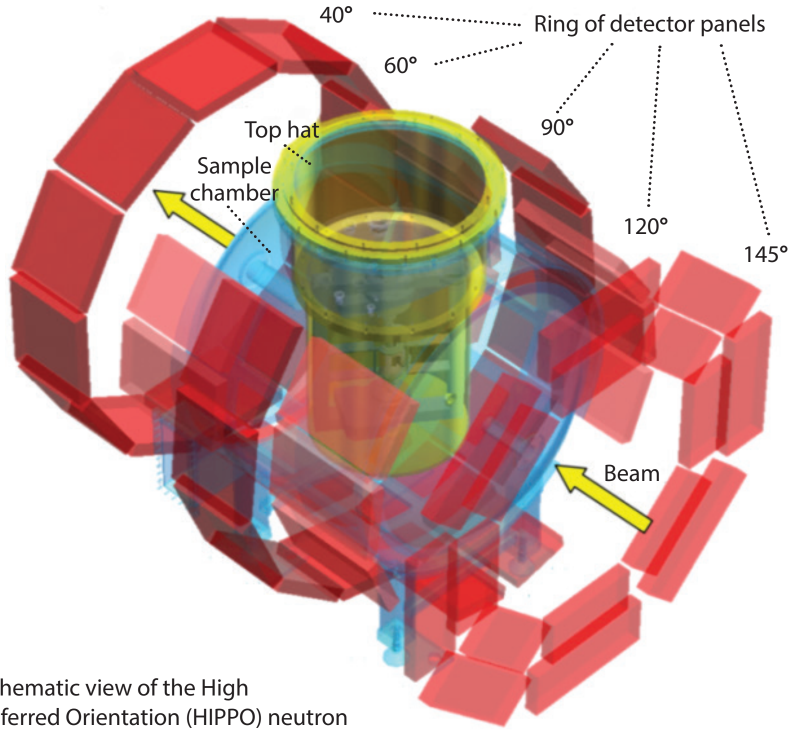


Figure 3. Schematic view of the High Pressure Preferred Orientation (HIPPO) neutron diffractometer with five banks of detector panels arranged on rings at Lujan Center.

Figure 4. Images of the δ-phase ^{239}PuGa alloy samples.

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with the first sequence—it decreases progressively with each subsequent cooling-heating sequence and is almost negligible for the final one, suggesting that the effect is reaching a saturation level. There is also a gradual decrease in the difference between the lattice parameters measured at the same temperature during cooling and heating segments.

Similar behavior was observed in the FY17 experiment using the δ-phase ^{239}Pu-2-at.%-Ga sample (Fig. 6a). However, the FY16 experiment using the same sample showed the opposite behavior, i.e., an overall contraction after being heated back to room temperature (Fig. 6b; as a reference, Fig. 6c shows the lattice parameter behavior as a function of temperature of the δ-phase ^{239}Pu- 2at.%-Ga sample during the first cooling measurement of the FY19 run cycle experiment).

Idling time of samples

For a better comparison of the thermally-induced lattice swelling behavior (FY17/19 experiments) versus the contraction (FY16), we considered the thermal history of the sample and the (room temperature) storage time. The so-called "idling time" was defined as the period between sample annealing (i.e., reaching RT) and the beginning of a measurement.

For the FY17/19 experiments using the δ-phase ^{239}Pu-2at.%-Ga sample, the annealing of the sample ended within a few hours of the start of the measurements, thus the sample can be considered fully annealed or "fresh", and free of self-irradiation induced defects. For the FY16 experiment using the same sample, the measurement occurred a few months after the sample annealing was completed. This was due to unfortunate events related to sample shipping.

When annealing was performed within hours of the measurement, the final lattice parameter value was significantly larger than the initial value. The FY16 data set, for which annealing was completed a few months prior to the start of the experiment, reveals the opposite effect, namely an overall contraction of the lattice. For newly annealed samples, the exhibited lattice swelling is similar to that observed by Ravat et al. with isothermal holds of up to three years, reported in the Journal of Nuclear Materials in 2007. A saturation of this effect was observed by these researchers after two years of isothermal hold, whereas values reported here (FY19) achieve saturation by the fourth sequence. If the material is kept for a long idling time and later cooled to cryogenic temperatures then it shows minimal lattice swelling and an overall contraction upon return to RT. In summary, the kinetic processes of

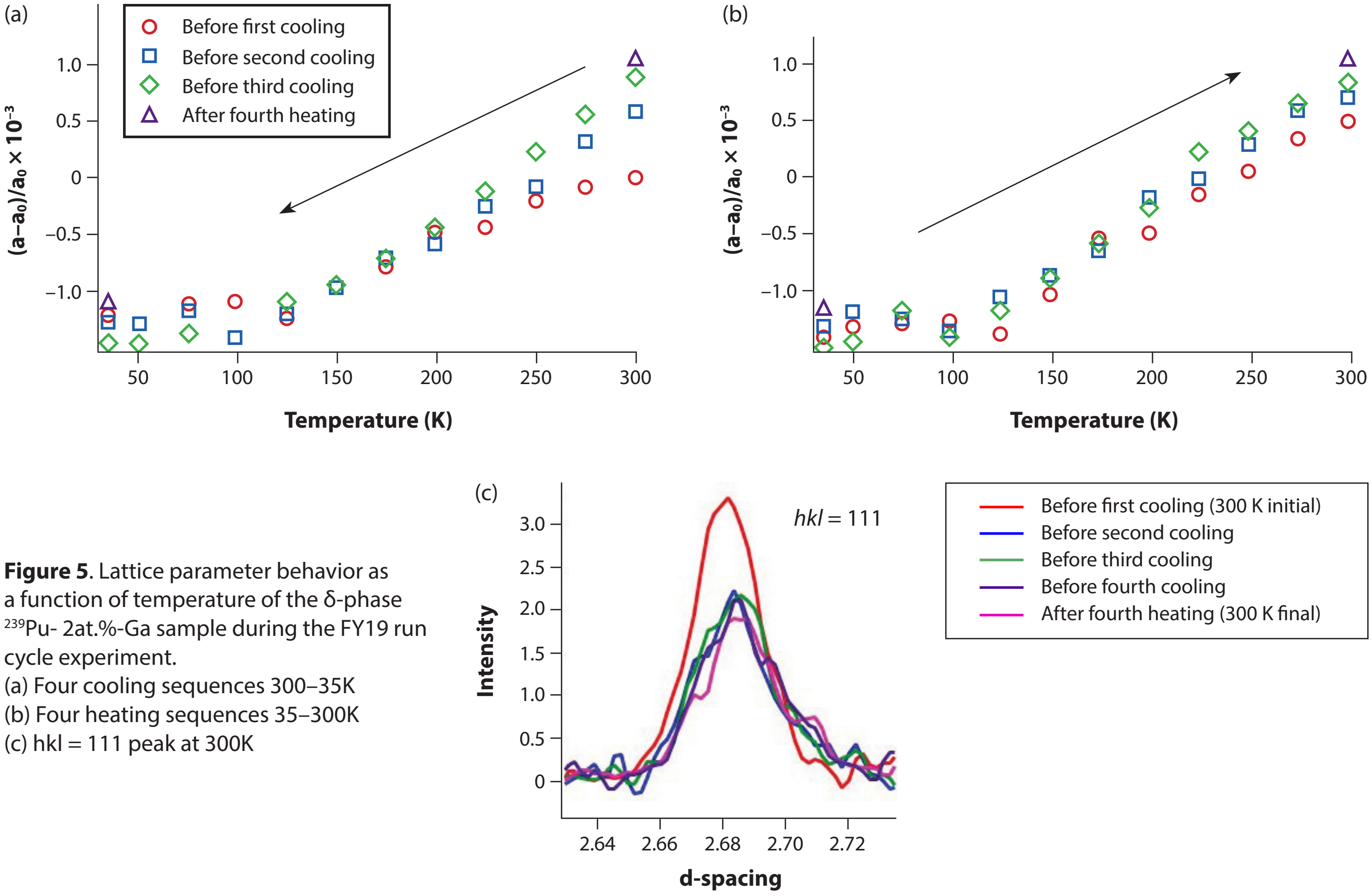

Figure 5. Lattice parameter behavior as a function of temperature of the δ-phase ^{239}Pu- 2at.%-Ga sample during the FY19 run cycle experiment.
(a) Four cooling sequences 300–35K
(b) Four heating sequences 35–300K
(c) hkl = 111 peak at 300K

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induced lattice contraction and lattice swelling behaviors proved to be dependent on the history of the sample.

Similar experiments performed during FY16/17 on the δ-phase ^{239}Pu-7at.%-Ga sample show comparable results in terms of overall contraction of the lattice when the idling times were significant, days to months (Figs. 6d,e). Therefore, the idling time effect appears to be the result of an incomplete recovery of the lattice parameters, and it has been observed for both δ-phase ^{239}Pu-2 and -7at.%-Ga and samples.

In terms of peak shape, the effect translates into significant changes when a freshly annealed sample is cooled from ambient to cryogenic temperatures (FY17, 12K; FY19, 35K; Figs. 6a,d inserts). Upon heating and returning to ambient temperatures, the height of the peaks is not recovered, and it exhibited little change when the cooling/heating sequence was repeated (FY19). The peak positions shifted to lower d-spacings as the sample was cooled, but recovered upon heating back to room temperature. The loss of peak height and integrated intensity may indicate a loss of crystallinity and the potential of deformation mechanism under radiation induced hydrostatic stress increase.

We can conclude that the changes in peak shape between room temperature and cryogenic point are significant for a fresh sample, as observed for both FY17 and 19. Additionally, for the FY19 measurements, no significant variation of peak parameters was observed over the subsequent cooling/heating sequences (second → fourth). The response of the material to peak shifting and FWHM/integral intensity is due to

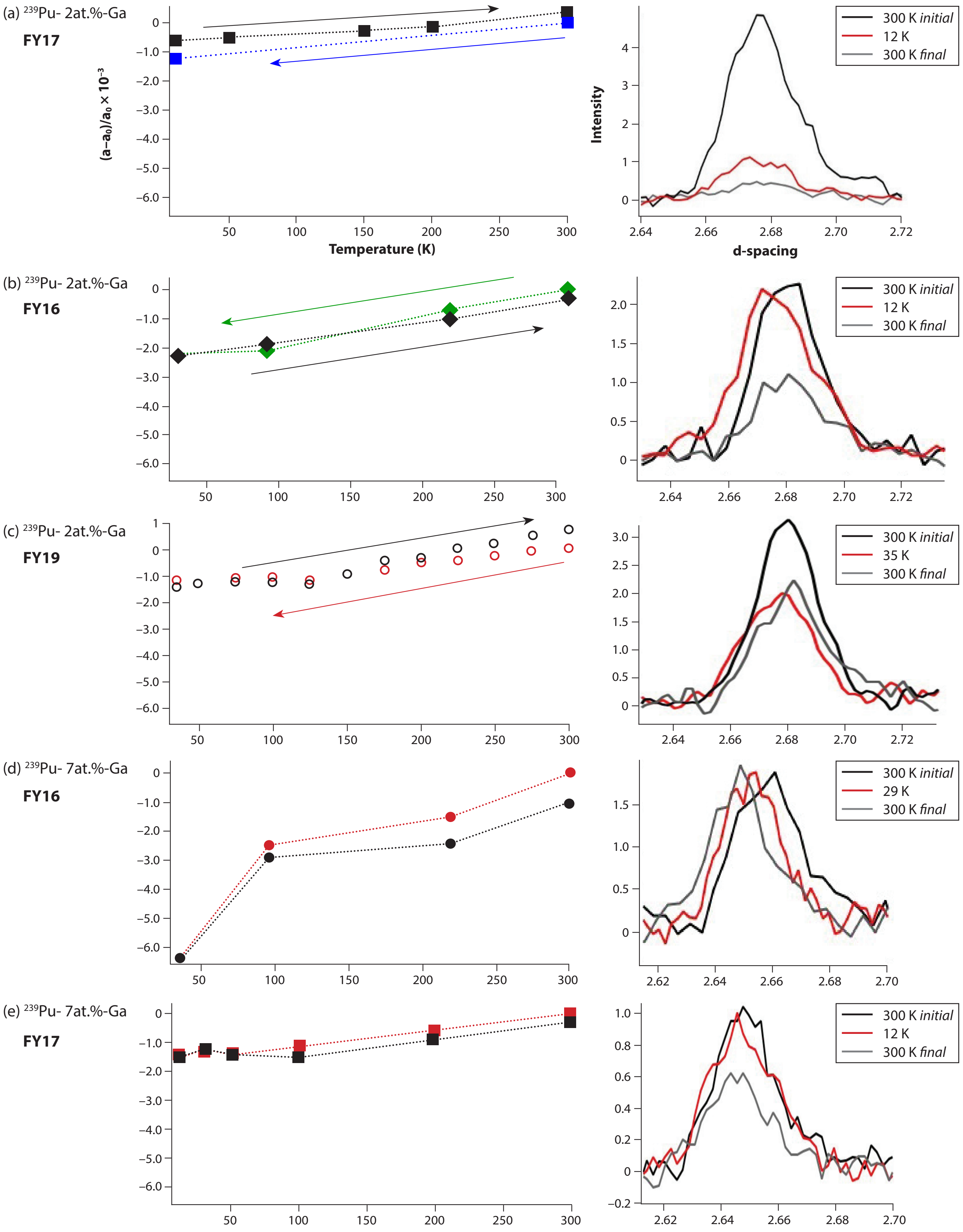
(a) ^{239}Pu- 2at.%-Ga
FY17
(a−a₀)/a₀ × 10⁻³
0
−1.0
−2.0
−3.0
−4.0
−5.0
−6.0
50
100
150
200
250
300
Temperature (K)
Intensity
4
3
2
1
0
2.64
2.66
2.68
2.70
2.72
d-spacing
300 K initial
12 K
300 K final
(b) ^{239}Pu- 2at.%-Ga
FY16
2.0
1.5
1.0
0.5
0
2.74
300 K initial
12 K
300 K final
(c) ^{239}Pu- 2at.%-Ga
FY19
1
3.0
2.5
300 K initial
35 K
300 K final
(d) ^{239}Pu- 7at.%-Ga
FY16
2.62
300 K initial
29 K
300 K final
(e) ^{239}Pu- 7at.%-Ga
FY17
1.0
0.8
0.6
0.4
0.2
−0.2
300 K initial
12 K
300 K final

Figure 6, opposite page. Lattice parameter behavior as a function of temperature of the δ-phase ^{239}Pu-Ga samples. *Right*, inserts are the hkl = 111 peak at different temperatures.

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either the thermal expansion under temperature change or to homogeneous strain, such as lattice response to hydrostatic stress due to irradiation changes. The response observed by Maiorov et al., reported in the Journal of Applied Physics in 2017, showed two stress components (kinetic adiabatic hydrostatic/adiabatic bulk elastic modulus and shear/shear elastic modulus) due to changes induced by self-irradiation. Ultimately, it is this idling time, during which the δ-^{239}Pu lattice accumulates point defects and kinetic factors control a very complex point defect diffusion, along with an evolution process that cause extended defects or damage and voids.

Long-range order

The most significant characteristic of this series of experiments is the impact on the long-range crystallographic order of these Pu-Ga alloy samples and on the kinetics associated with their varied thermal histories. In materials which are stable, the strain of thermal expansion stress which occurs with thermal cycling is observed and is repeatable. However, in these measurements of δ-phase ^{239}Pu-Ga alloys, which are metastable and undergoing self-irradiation, we have to consider additional stresses from defects and defect evolution, exhibited in Pu as additional stress and correlated strain.

Diffraction peak shifting was observed due to homogeneous strain such as thermal expansion under temperature change or as a lattice response to hydrostatic pressure changes. A combination of these effects was observed that were correlated with both the thermal history of the sample and the potential for defects which could induce internal stress (defect-induced hydrostatic or shear pressure). Furthermore, we observed some evidence of loss in diffraction peak integrated intensity which is indicative of long-range order lattice deformation leading to loss of crystallinity.

The results are clearly affected by the ambient isothermal storage time during which self-irradiation induced defects and other changes arise in the δ-phase Pu-Ga lattice. These effects have proven to be complex and challenging to elucidate. As shown by a number of other studies employing X-ray diffraction and dilatometry, the self-irradiation effects converge into a time-dependent lattice swelling or strain in δ-phase ^{239}Pu-Ga alloys. As a secondary observation, the bulk strain appears to impact the low temperature martensitic phase transformation $\delta \rightarrow \alpha'$, preventing it from taking place. Earlier neutron diffraction measurements of δ-phase ^{242}Pu-Ga alloys showed a hydrostatic and a shear component to the lattice strain that increases at cryogenic temperatures.

Summary

This study combines results from several experiments for a better understanding of the correlations among the complex thermal history, self-irradiation defects, and the kinetic processes associated with the evolution of long-range order damage in δ-phase Pu-Ga alloys. In-situ TOF neutron diffraction measurements were performed between room and cryogenic temperatures to explore the impact of ambient aging on the lattice effects. Specifically, those effects that were detectable during alternating temperature measurements on the lattice of a δ-phase ^{239}Pu-2at.%-Ga alloy. Our results showed that the self-irradiation damage at room temperature and the associated lattice strain introduce a hydrostatic stress state in δ-phase ^{239}Pu-Ga alloys. This impacts the kinetic evolution of defects which are generated from self-irradiation at low or cryogenic temperatures, as they evolve during heating to ambient temperatures.

Furthermore, in annealed δ-phase ^{239}Pu-Ga alloys which were exposed to repeated cooling and heating (i.e., cryogenic self-irradiation followed by annealing to ambient temperatures) we observed a lattice swelling similar to the room temperature self-irradiation damage accumulated over longer periods of time. This point of extensive accumulation of self-irradiation defects at cryogenic temperatures and the kinetic evolution of those defects with increasing temperature is a driver to similar lattice strain states as the same material would achieve at ambient temperature.

Acknowledgments

The author would like to thank her collaborators who contributed to this work: Franz J. Freibert (MST-16/NSEC), Jianzhong Zhang and Sven Vogel (HIPPO, Lujan Center/MST-8), Joan E. Siewenie (P-27), Scott Richmond, Mike Ramos and James Gallegos (sample preparation, MST-16).

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Nuclear Enterprise
SCIENCE & TECHNOLOGY

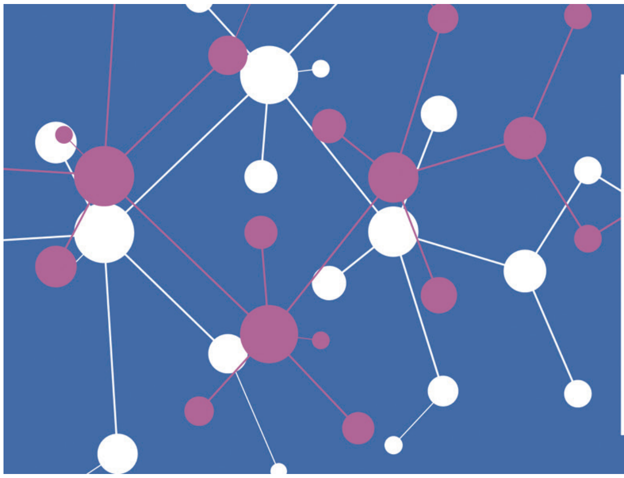
New academic program launched

A new education program for the Los Alamos National Laboratory (LANL) Technician/Technologist workforce has been launched this year that will provide essential science, operations, and business education on all aspects of working in a nuclear facility. The Nuclear Enterprise Science & Technology (NEST) certificate program, completed in a minimum of one year (two semesters), is now offered through the University of New Mexico-Los Alamos (UNM-LA) in conjunction with LANL. This is a result of a successful collaboration between Operational Readiness Implementation (ORI-1), the Glenn T. Seaborg Institute, and the National Security Education Center (NSEC).

Built upon the foundation of New Employee Training (NET) Academy, the NEST Certificate is designed to provide students with additional education and experience for work in nuclear material handling facilities. NEST will address all aspects of working with plutonium (and other related special nuclear materials) for the next generation of technicians, operators, scientists and engineers to establish an effective and safe operating culture. The content will address specialized operational and technological aspects relevant to the actinide science mission that includes:

- Physical design and operating requirements for working with special nuclear materials (SNM) in nuclear facilities.
- Specialized process equipment and unit operations used to produce plutonium-based products.
- Fundamentals of plutonium science, technology, and engineering that support national defense, energy and global security missions.
- Science underpinning and technical basis for safe handling, packaging, storage, material measurement, control and accountability, and disposal of radioactive materials.
- Biological effects from exposure to nuclear materials, and monitoring programs for plutonium handlers.
- Legal and administrative requirements that are captured in the Safety Basis for the facilities and process unit operations.

For more information contact: *nest-degree@lanl.gov*.



PLUTONIUM FUTURES
THE SCIENCE 2020

26–29 September 2022
AVIGNON (France)

Plutonium Futures – The Science is a topical conference that provides an international forum for the presentation and discussion of current research on physical and chemical properties of plutonium and other actinide elements.

Plutonium Futures 2022 is the 11th edition in the series of acclaimed international conferences initiated by Los Alamos and Lawrence Livermore National Laboratories. The 2022 conference will be held in the Popes' Palace conference center of Avignon (France).

KEY DATES

ABSTRACT SUBMISSION
from November 2021 to March 2022
Acceptance of abstracts: May 2022

REGISTRATION
from February to August 2022
Early booking: until June 2022

TOPICS

Condensed Matter Physics
Surface Science & Corrosion
Metallurgy & Materials Science Compounds
Complexes & Coordination Chemistry
Detection & Analysis • Nuclear Fuel Cycle
Environmental Behaviour & Chemistry
Solution & Gas-phase Chemistry

Organized by:

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Please subscribe to the mailing list if you would like to receive updated information on the event

Actinide Research Quarterly is published by Los Alamos National Laboratory and is a publication of the Glenn T. Seaborg Institute for Transactinium Science, a part of the National Security Education Center. ARQ (est. 1994) highlights research in actinide science in such areas as process chemistry, metallurgy, surface and separation sciences, atomic and molecular sciences, actinide ceramics and nuclear fuels, characterization, spectroscopy, analysis, and manufacturing technologies.

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