

**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

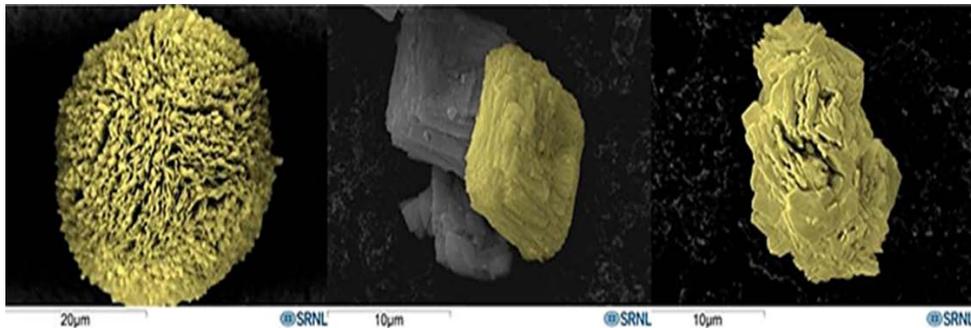
- 1 ) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2 ) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

## Synchrotron Based Microstructural Characterization Method Development for Pu Oxides

Identification of new plutonium oxide signatures is a high priority focus area of the technical nuclear forensics and nonproliferation communities. Comprehensive materials science studies of plutonium oxide are needed to advance the understanding of the microcrystalline properties and their relationship to macro-scale morphologies and signatures. Plutonium oxide particle growth is dependent on the microcrystalline structures, grain size, and orientation. Microcrystalline structures have been found to vary for plutonium oxide based on the oxidation state of plutonium, concentration of reactants, and the physiochemical conditions of precipitation. Empirical observation confirms the relationship between processing conditions and particle morphology. High sensitivity, non destructive analysis of individual microcrystalline grains requires the use of bright sources of X-rays produced by synchrotron radiation, such as those at the Advanced Photon Source. The light source can reveal higher resolution crystallographic mapping, more sensitive chemical analysis, and higher fidelity morphological information than any current methods at SRNL.

Progress in FY18 focused on shipping of plutonium to both Clemson University and Argonne National Laboratory, beamline X-ray experiments at the Advance Photon Source, and embedding and polishing of plutonium particles at Clemson with SEM/EDS techniques for analysis



## Awards and Recognition

## Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

## SRNL Legal Signature

---

**Signature**

---

**Date**

## Synchrotron Based Microstructural Characterization Method Development for Pu Oxides

Project Team: J. Venzie (Primary),  
M.A. DeVore II, T.S. Shehee

Collaborators: J. Fortner (ANL), B.  
Powell, L. Schuller-Nickels (Clemson)

Thrust Area: Non-proliferation and  
Nuclear Deterrent

Project Type: Standard

Project Start Date: October 1, 2016  
Project End Date: September 30, 2018

*Advanced microstructural analysis techniques were used to probe the internal structure of plutonium oxide particles as part of the development of new forensic signatures. Samples of Pu(III)O<sub>2</sub> and Pu(IV)O<sub>2</sub> with and without metal contaminants were prepared and shipped to Clemson University for SEM/EDS analysis, and to the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) for X-ray fluorescence, X-ray diffraction, and X-ray Absorption Near Edge Spectroscopy (XANES) measurements. These techniques can probe samples at sub-micron spectral resolution to provide information on local crystallographic orientation, gradients, and strains.*

*SRNL was able to create unique sample ladders for containment of PuO<sub>2</sub> particles that met the APS safety standards for radioactive materials. X-ray fluorescence maps were created to find particles of interest and revealed that AFS 2 material also contains iron dispersed throughout the sample. Full XANES analysis has not been scrutinized; however, there seems to be a mixture of oxidation states of Pu(III) and Pu(IV) in the samples. Further analysis of all beamline data will take place in FY19.*

### FY2018 Objectives

Efforts within FY18 concentrated on the shipping and sample preparation aspects, before performing experiments towards the end of FY18 at the Advanced Photon Source

The focus areas of the effort included:

- Contracts placed with Clemson and ANL
- Shipment of samples to Clemson and ANL
- ANL sample preparation and holder approval
- Successful APS general user proposal (GUP)
- Beam line experiments

### Introduction

The pre-detonation technical nuclear forensic (TNF) community is investing in the research, development, and exploitation of new non-isotopic forensic signatures of plutonium oxide. The community is interested in it as an intermediate form in the fuel and weapons cycle, and as the most common storage form for plutonium. Isotopic signatures, while useful, only provide limited information about the provenance of plutonium oxide. The TNF community is interested in exploring chemical and morphological characteristics to better understand the type of flowsheet used, scale of facilities, expertise of operators, etc. Detailed material science studies of plutonium oxide are needed to advance the understanding of the crystalline properties and their relationships to macro-scale signatures.

The process to which particles grow is dependent on their crystal structures, grain size, and orientation of grains within a particle. Variations in density and microstructure of  $\text{PuO}_2$  powder have led to differing particle sizes and morphologies (Figure 1). The microstructure is controlled by calcination temperature and the physiochemical conditions of precipitation, including shape of mixing tank, valance of plutonium, mixing sequence of plutonium and oxalic acid, precipitation temperature, and molar concentrations of oxalic acid, plutonium, and nitrate. Calcination has little effect on overall size of particle, but a great effect on surface roughness and particle morphology.

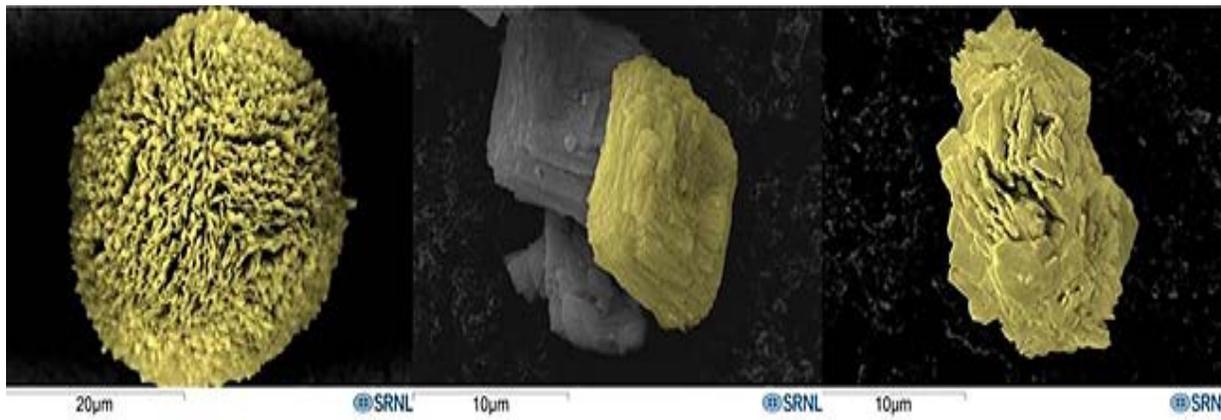


Figure 1 Three microcrystalline morphologies of  $\text{PuO}_2$  observed in a single production batch.

Nondestructive analysis of individual  $\text{PuO}_2$  particles requires the use of bright sources of X-rays produced by synchrotron sources such as those produce at the Advance Photon Source at Argonne National Laboratory. The light source can reveal higher resolution crystallographic mapping, more sensitive chemical analysis, and higher fidelity morphological information than any methods currently available to SRNL. APS will allow the ability to simultaneously map XRD and XRF grains on a particle. These allow the measure of grain sizes, shapes, and orientations for investigation. Further analysis of the data includes interrogation of oxidation states via XANES, X-ray diffraction pattern matching, and analyzing particle morphology to XANES spectra.

## Approach

Due to the complexity of working with plutonium samples, the administrative and procedural aspects of sending samples to APS are directly addressed and explicitly outline in the project. The largest risk is the development of procedures, processes, and agreements necessary to prepare, package, and ship radiological plutonium samples and are addressed in the first year of the project.

Specific activities included:

- Shipment of  $\text{PuO}_2$  solids to Clemson and prepared samples on ladders to ANL in Type A containers
- Prepare samples with double containment for final ladder preparation at ANL
- GUP approval for beam line experiments
- Execution of beam line experiments

The third year will cover analysis of the ANL data for future publications.

- Verification of oxidation state of Pu in various samples
- Changes in diffraction or XANES due to contamination by other metals

## Results/Discussion

Figure 2 shows the elaborate process for creating samples of  $\text{PuO}_2$  particles for analysis at the APS beamline. Approximately 1 inch by 1 inch squares of Kapton tape were cut out and placed on an SEM stub as a base. Three fiducial wires (Cu, Ni, Ti) were cut and placed in a triangle pattern.  $\text{PuO}_2$  was sprinkled on the Kapton tape by a lint-free cotton-swab. A layer of epoxy was deposited and then a layer of Kapton film was placed on top and waited for the epoxy to harden. After hardening, another layer of Kapton tape was placed on the bottom in a clean hood to avoid contamination. The small coupons were shipped in separate petri dishes to ANL for final assembly. The samples were placed in the ladders connected to kinematic mounts and another layer of Kapton film as a bag was wrapped around each ladder (Figure 3). A ladder mounted in front of the beam is shown in Figure 4. The fluorescence detector is indicated by the white tip and the diffraction detector is not seen in the photo.

Figure 2: Transmission mode sample holders and encapsulation

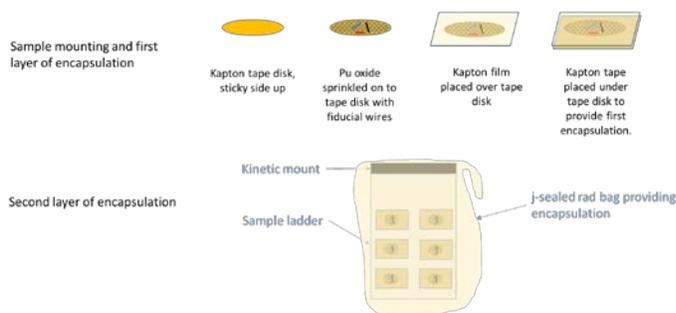
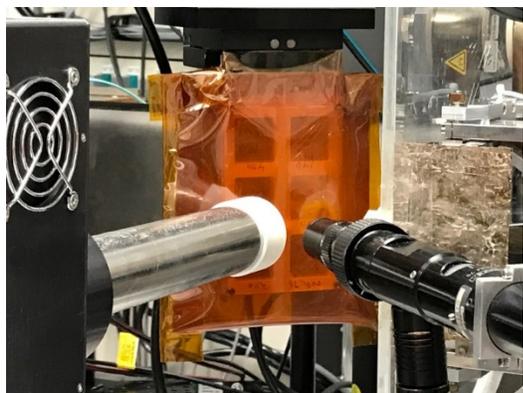
Figure 2  $\text{PuO}_2$  sample preparation out for APS samples.Figure 3 Finally assembly of  $\text{PuO}_2$  samples on ladder, and final encapsulation

Figure 4 : Sample ladder attached to kinematic mount. The black tube is from the beam line, and the silver is the fluorescence detector.

The kinematic mounts move on a X and Y translational stage allowing for complete control and location of mapping. Four maps are presented below in Figure 5 that shows the XRF map for lab synthesized  $\text{PuO}_2$ , AFS 2 production material, lab synthesized  $\text{PuO}_2$  with uranium contaminant, and lab synthesized  $\text{PuO}_2$  with Fe contaminant. The map was used to locate the fiducial wires and the regions of particles that were subject to further analysis by X-ray diffraction and X-ray Absorption Near Edge Spectroscopy (XANES). The Pu containing particles show as blue, while the Fe containing particles show as green. Typical XRF spectrum of each sample is shown in Figure 6 and the elements are determined by the major X-ray lines (Pu La1, U La1, Fe Ka1 and Ka2). Only two of the samples show significant quantities of Fe (AFS2 and Pu/Fe). The XRF of AFS 2 material is mostly plutonium without Fe, but the Fe indicated portions also contain Pu. The Fe contaminant in AFS 2 could be caused by several reasons, the simplest is the stainless-steel B-vial the material is stored and transported. The most complex is from the production processes used in the plant that produced the material.

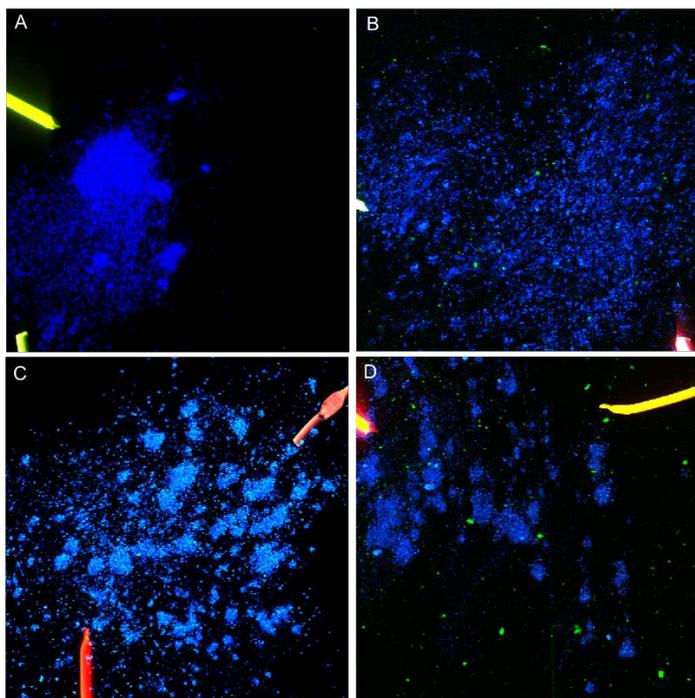


Figure 5 XRF maps of individual samples A) Lab synthesized clean  $\text{PuO}_2$  B) AFS 2 production  $\text{PuO}_2$ , C) Lab synthesized  $\text{PuO}_2$  with U Contaminant D) Lab synthesized  $\text{PuO}_2$  with Fe contaminant. Blue – plutonium particles, green – Fe containing particles,

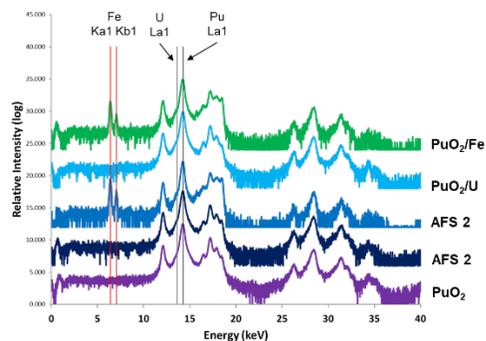


Figure 6 X-ray fluorescence of various samples from the beam line. Lines indicate elements present.

The typical XANES spectrum for each sample is shown in Figure 7. The XANES has not been fully scrutinized but the first two peaks are typical for an actinide oxide as would be expected for  $\text{PuO}_2$ . There appear to be slight differences in the location of the troughs between the first two peaks which could lead to other information about the particles and their makeup. Further analysis may show that there are different oxidation states for the samples as Pu(IV) and Pu(V) are very close in energy.

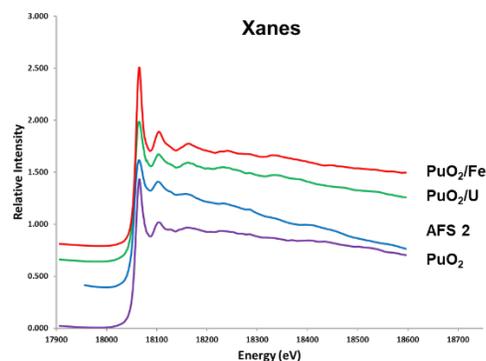


Figure 7 XANES spectra of samples from APS beam line. Further analysis is needed to fully dissect the spectra.

Clemson University was able to prepare dilute plutonium oxide particulates on SEM stubs and successfully polish them revealing their internal microstructures (Figure 8). Unfortunately, it appears that the grain size is too small to detect Kikuchi bands associated with EBSD. Clemson was also able to take samples to the Tender Energy X-ray Absorption Spectroscopy (TES) beamline at Brookhaven National Laboratory and perform XANES on the  $M_5$  edge of Pu. Unfortunately, all samples exhibited similar absorption peaks at the 3755 eV edge. Comparison with a Pu(VI) standard indicates that the SRNL samples have a different oxidation state (Figure 9) as would be expected when precipitating from Pu(III) and Pu(IV). Further analysis is needed to determine the exact oxidation state of SRNL samples.

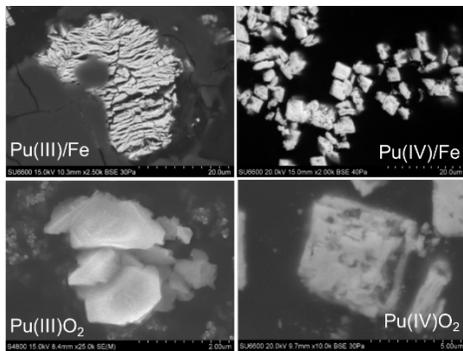


Figure 8 SEM images of  $\text{PuO}_2$  particles after polishing revealing their internal structures

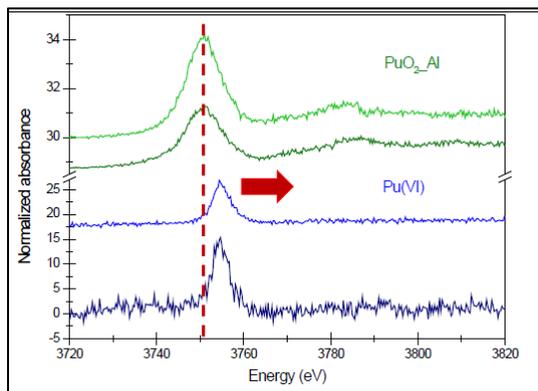


Figure 9 XANES  $M_5$  edge of  $\text{PuO}_2$  with standard  $\text{Pu(VI)}$  material to show differences in oxidation state

## FY2018 Accomplishments

- Successful shipments of plutonium particles to both Argonne and Clemson
- Successful beam line proposal originally scheduled for April 18.
- Successful beam line experiments in August 2018
- Sample preparation and analysis by electron microscopy

## Future Directions

The future direction of his project is solely focused on analysis of the gigabytes of data accumulated at the Advanced Photon Source. Data analysis will include interpretation and matching of X-ray diffraction patterns, oxidation state analysis of XANES spectrum, and interactions of other elements such as Fe on XANES spectra. Efforts will also be made to match XANES, XRD, and XRF to morphology of  $\text{PuO}_2$  particulates.

A technical document of steps that need to be completed to achieve success and provide a road map for other scientists to perform experiments at the Advanced Photon Source with less pushback of safety concerns.

## FY 2018 Publications/Presentations

## References:

### Acronyms

ANL – Argonne National Laboratory

APS – Advanced Photon Source

GUP – General User Proposal

XANES – X-ray Absorption Near Edge Spectroscopy

XRD – X-ray Diffraction

XRF – X-ray Fluorescence

### Intellectual Property

No invention disclosures, copyright disclosures, patent applications, or patents were sought as part of this effort. This is primarily due to the basic chemical and material science of the effort.

### Total Number of Post-Doctoral Researchers

0