Contract No:

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Disclaimer:

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 depenedent on the microcrystalline strucutures, 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 of FY19 was the analysis of the synchrotron data. Areas of focus included XANES oxidation state and EXAFS to measure bond distances with modeling. Most measurements for XANES indicated that the plutonium was in the +4 oxidation state, however, some indicated that there could also be a +5 oxidation state. The EXAFS measurements showed typical Pu – O bonding distance of 2.33 and Pu – Pu bonding distances of 3.81 Å; however, some samples also showed that there could be shorter Pu – O distances of approximately 1.81 Å, indicative of plutonium in the +5 oxidation state.

Awards and Recognition

None

Intellectual Property Review

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

SRNL Legal Signature

Signature **Date**

Synchrotron Based Microstructural Characterization Method Development for Pu Oxides

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Subcontractor:

Thrust Area: National Security

Project Start Date: October 1, 2017
Project End Date: September 30, 2019

Analysis was performed on the data collected from the APS experiments. Analysis included XRF, XANES to determine oxidation state, and EXAFS to determine bonding distances and coordination numbers. The oxidation state for most samples was the +4 as expected for PuO_2. Other measurements indicated that there could be +5 oxidation state. The bonding distances for typical PuO_2 are Pu – O of 2.33 and Pu – Pu of 3.81 Å. In evaluation of some measurements of EXAFS, there appears to be a shorter Pu – O distance of approximately 1.81 Å. This would be typical of plutonium in the +5 or +6 oxidation state with a -yl oxygen. Further analysis needs to be performed to ascertain exact distances.

FY2019 Objectives

- Data analysis of x-Ray Absorption Spectroscopy (XAS) data from APS beamline.
- Return of samples and waste handling

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 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.

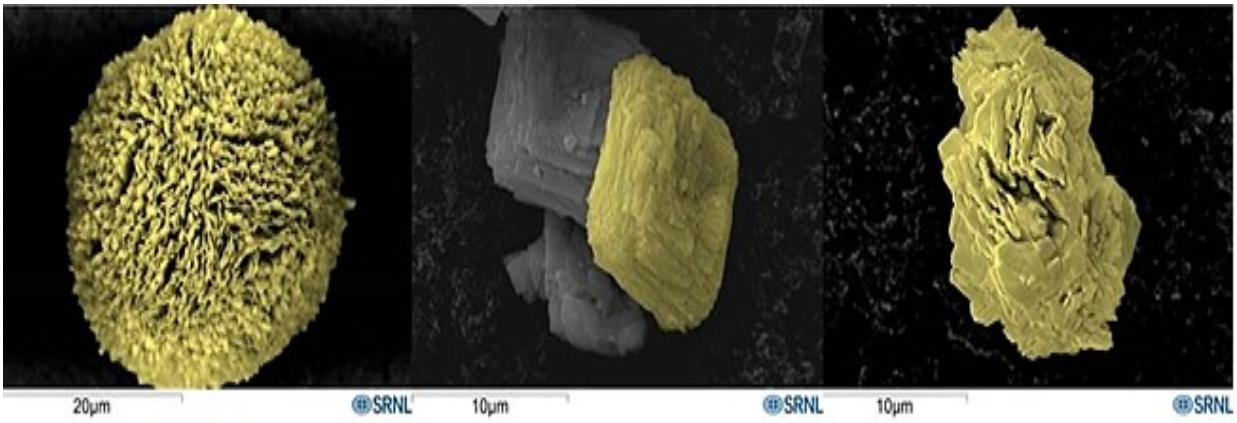

Figure 1 Three microcrystalline morphologies of PuO_2 observed in a single production batch.

Nondestructive analysis of individual 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 XAS spectra.

Approach

The final year of this project was used to perform analysis of the XAS data collected at the Advanced Photon Source at Argonne National Laboratory. The analysis consists of XANES and EXAFS with modelling to determine oxidation state, and modelled bond distances such as Pu – O and Pu – Pu distances that reveals information about coordination number and crystallographic unit cell.

Results/Discussion

Synchrotron radiation analysis of the data taken in late FY18 was evaluated in FY19. Two types of x-Ray absorption spectroscopy data were taken, X-Ray Absorption Near Edge Spectroscopy (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS). XANES is best used to determine the oxidation state of the plutonium in the samples, while EXAFS is used for bond distances and coordination numbers. Fluorescence mapping was also undertaken to locate particles and determine if any contaminants make it through the precipitation process.

Since the samples were first prepared in a glovebox, we were unsure of where particles would be located. This was revealed by the X-ray fluorescence mapping shown in Figure 4. The blue areas are plutonium, and the green is iron. Typical fluorescence spectrum of four samples is shown in figure . Each sample has the characteristic plutonium fluorescence line. Interestingly, AFS 2 material has both plutonium only regions, and plutonium/iron regions. The plutonium with iron addition sample is very similar to AFS 2 materials in the fluorescence. For Pu/U, there appears to be a small uranium fluorescence peak at the La1 line but is unconfirmed.

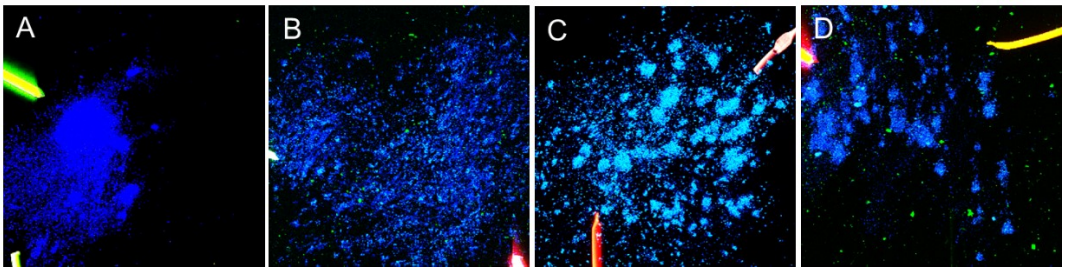

FIGURE 2 XRF maps of individual samples A) Lab synthesized clean PuO_2 B) AFS 2 production PuO_2, C) Lab synthesized PuO_2 with U contaminant D) Lab synthesized PuO_2 with Fe contaminant. Blue – plutonium particles, green – Fe containing particles, bars – fiducial wires

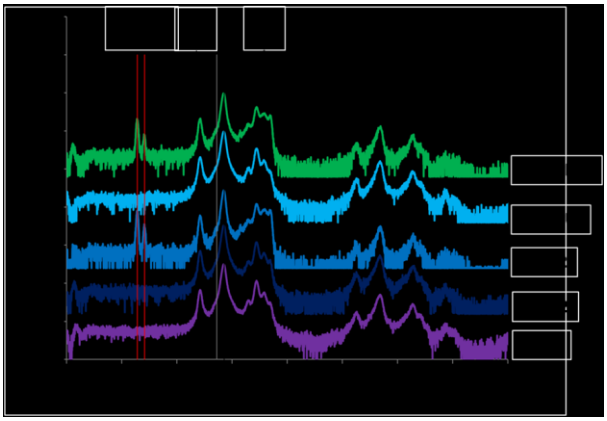

FIGURE 3 Typical X-ray fluorescence spectra of 4 samples. AFS-2 can have both iron and plutonium. The fluorescence lines listed are the major lines, others may be used.

Figure shows the typical full spectrum of XAS. The near edge region between the pre-edge and first peak determines the oxidation state. There appears to be little difference in the near edge region, but there are some small differences in the EXAFS that can only be revealed with fitting of the spectra.

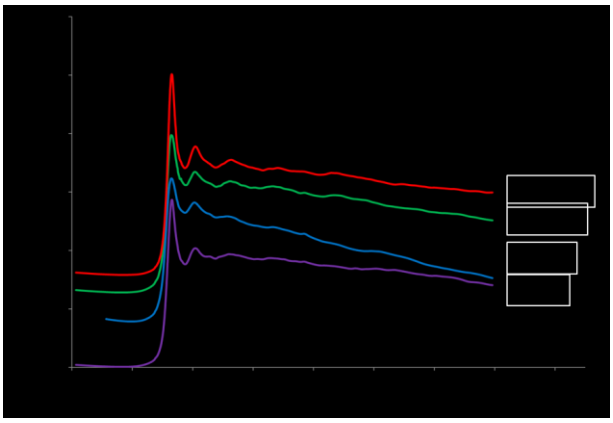

FIGURE 4 XAS spectrum of samples characterized at APS

Extended X-ray Absorption Fine Structure was analyzed by fitting computed X-ray scattering paths based on the crystal structure of PuO_2, and absorber to nearest neighbor distances for Fe/O, U(IV, VI)/O,

Pu(III,IV, V, VI)/O. All fitting calculations were performed in Artemis EXAFS software to determine the bands described in Figure 6. Pu-Pu distances of 3.80 Å are observed in each spectrum, with small shifts away from it, likely due to sample quality and preparation. Pu-O distances of 2.33 Å are very consistent across all the samples. AFS 2 PuO_2 is listed twice, the blue shows just plutonium in the XRF, while the green shows iron in the XRF with Pu. It is unclear at this time if the bands located below the 2.33 Å bands are related to a different oxidation state Pu, or a contribution from iron oxide. The small shoulder in the red spectrum is likely related to the same idea, but with uranium instead of plutonium.

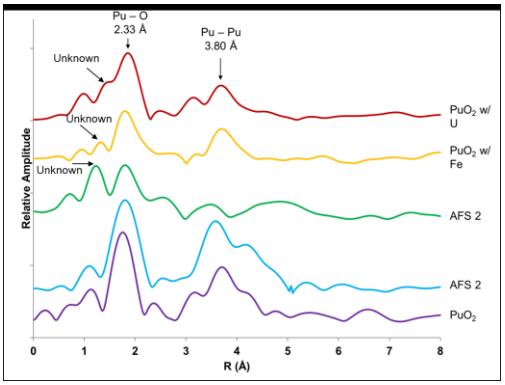

FIGURE 5 EXAFS of lab synthesized PuO_2, AFS 2, AFS 2 with Fe in XRF, PuO_2 with Fe contamination, and PuO_2 with U contamination. Bands are shifted, and determined by fitting the first and second shell nearest neighbors

FY2019 Accomplishments

Brief descriptions of accomplishments to date in bullet form. Whenever possible, accomplishments should be stated quantitatively, as in the examples below, and indicate the contribution to meeting the objectives as well as the magnitude of the improvement over past work.

- Attended an XAS workshop that allowed for better understanding of the synchrotron data. Data modelling techniques from the workshop show that there could be short Pu-O bonds indicative of other oxidation states of plutonium present in some characterized samples.
- Return of samples in a timely order
- Waste treatment of returned samples

Future Directions

The future direction should be a refinement of the techniques, and data processing of actinide samples. There were quite a few things learned, such as; having oxidation state standards when determining XANES, taking XAS class before trying to process data, or having a better particle encapsulation technique to locate individual particles. There is still a concern over safety at APS and any new encapsulation techniques will need to convince them it is safe to meet their standards.

FY 2019 Publications/Presentations

1. List all reports written from this work during the year and all presentations about this work that were made during FY 2018 and reports and presentations anticipated within the next six (6) months. Do not include internal presentations (i.e. mid-year review) or this annual summary report.

1. American Chemical Society Sci-Mix invited poster presentation, ACS Fall National Meeting San Diego, August 26.
2. American Chemical Society, Inorganic Chemistry Division, Actinides and Lanthanides subsection, ACS Fall National Meeting, San Diego August 27
3. In preparation – Publication for Minerals special issue, Nuclear Forensic Applications in Geoscience and Radiochemistry, Deadline for submission December 31, 2019

References

1. List any references used in the report.

Acronyms

APS – Advanced Photon Source
XAS – x-Ray absorption spectroscopy
EXAFS – Extended X-Ray Absorption Fine Structure
XANES – x-Ray Absorption Near Edge Spectroscopy

Intellectual Property

N/A

Total Number of Post-Doctoral Researchers

1. Joseph Mannion

Total Number of Student Researchers

0