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Status of SRNL Radiological Field Lysimeter Experiment (RadFLEx) - Year 7

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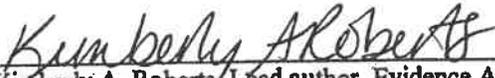
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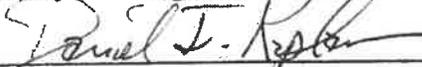


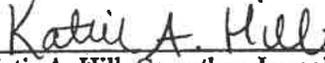
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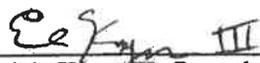
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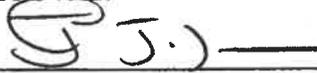

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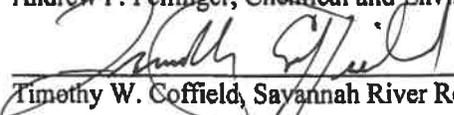
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EXECUTIVE SUMMARY

The Radiological Field Lysimeter Experiment (RadFLEx) began in 2012 and is a collaboration between the Savannah River National Laboratory (SRNL) and Clemson University. The purpose of this facility is to study the long-term (2 to 20 years) fate and transport of radionuclides in the Savannah River Site (SRS) vadose zone under natural field and meteorological conditions. The unique facility houses 48 5-L cores filled with sediments amended with various radionuclide sources. The results from these studies have been applied to the development of geochemical models used to assess the risk posed by subsurface nuclear waste disposal, environmental remediation, and waste form development. This report describes the refurbishment of the exterior of the RadFLEx facility and the synthesis and deployment of six plutonium (Pu) sources, four neptunium (Np) sources and one radium (Ra) source. It is anticipated that these newly installed lysimeter cores will be studied for up to 10 years.

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LIST OF ABBREVIATIONS

DOE	Department of Energy
EDS	Energy Dispersive Spectroscopy
ICDD	International Center for Diffraction Data
Np	Neptunium
PDF	Powder Diffraction File
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
Pu	Plutonium
Ra	Radium
RadFLEx	Radiological Field Lysimeter Experiment
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
STEM	Scanning Transmission Electron Microscopy
UV-VIS	Ultraviolet-Visible Absorption Spectroscopy
XRD	X-ray Diffraction

1.0 Introduction

The Radiological Field Lysimeter Experiment Facility (RadFLEx) was established in 2012 and is a collaboration between the Savannah River National Laboratory (SRNL) and Clemson University. The objective of this facility is to better understand the behavior of radionuclides in the subsurface environment. This is accomplished by placing radioactive sources in the middle of lysimeters (10-cm diameter x 60-long PVC) packed with 60cm of soil representative of the SRS subsurface. The details for baseline construction and implementation are documented in Roberts et al. (2012). Status after the first year of operation is described in Kaplan et al. (2013). A more recent review of output from the lysimeter program was described by Kaplan et al., (2018). It included listings of: RadFLEx results used in SRS risk calculations, 16 journal publications, 7 theses and dissertations, 9 reports, and 17 M.S., Ph.D., and post-doc programs. Detailed annual reports have been published describing leachate chemistry as a function of time (Peruski et al., 2018b; Peruski et al., 2017b; Powell and Witmer, 2013; Witmer and Powell, 2013; Witmer and Powell, 2014), radionuclide soil-depth profiles and adsorption/desorption radionuclide geochemical studies (Miller et al., 2012; Peruski et al., 2017a; Peruski et al., 2018a), and hydrology measurements (Dixon, 2017).

The objective of this report is to provide a detailed description of refurbishment and deployment of new radionuclide sources at the RadFLEx facility during 2019. During this year, RadFLEx was taken offline in order to refurbish the lysimeter roll-off pans. During this operational hiatus, new radiological sources were also prepared and installed.

2.0 Refurbishment

During the 7 years since RadFLEx has been operational, wear and tear on the roll-off pans had become increasingly evident. As concern grew for the integrity of the containers, an assessment was requested to determine what could be done for rust abatement. SRNS's Site Support Services was contracted to perform rust abatement and repainting of RadFLEx and funded by SRR.

On July 16-17, 2019, research personnel conducted lysimeter sample (leachate) collection, disconnected sample bottles, and capped all of the lysimeters, taking the experiment offline. The lysimeters were then disconnected, the bottle sheds were removed from the concrete pad, and the lysimeter penetrations from the side of the roll-off pan were covered with plastic bags and sealed with tape. Construction personnel started refurbishment the following week (7/22/19). They scraped, sanded and pressure washed the exterior of the facility. Macropoxy 910 (Sherwin-Williams Co., Cleveland OH) was applied to treat and inhibit rusted areas. Finally, the entire experimental facility was primed and painted white with top coat. After the rust abatement and painting, secondary-containment tubing and leachate-sample sheds were replaced. Finally, a new SRNL sign was also provided. Figures 1-3 show images before and after the rust abatement and repair.



Before



After

Figure 1. Photos of the east side before and after rust abatement and repainting



Before



After

Figure 2. Photos of the northeast corner before and after rust abatement and repainting



Before



After

Figure 3. Photos of the south side before and after rust abatement and repainting

3.0 Newly Installed Sources

3.1 Np Sources

A detailed description of Np(IV)O₂ source preparation conducted at Clemson University, can be found in “Appendix A: NpO₂ source preparation for RadFLEX.” In short, Np(IV) stock solution was made by chemically reducing Np with potassium iodide. Np(IV) formation was confirmed by UV-vis (see Figures A-1 and A-2). Np(IV)-oxalate was precipitated and underwent calcination to convert Np(IV)-oxalate to desired NpO₂ source material. Morphological and element characterization of the precipitated NpO₂ were conducted with a Hitachi S4800 high resolution field emission scanning electron microscope (SEM) (Figure A-5) and an Oxford Instruments energy dispersive spectroscopy (EDS) detector (Figure A-6). Additional characterization was conducted with a Scanning Transmission Electron Microscopy (STEM) which confirmed the SEM results that NpO₂ crystals were 30 to 80 nm (Figure 4). Selected Area Electron Diffraction (SAED) measurements were used to determine d-spacings and lattice constants of NpO₂ (Figure A-8 and Table A-1), which provided useful information regarding the crystallinity of NpO₂ (important for assessing mineral solubility and tendency to be released into the mobile aqueous phase). Two samples were prepared by placing <2 mg quantities (Table 1) into Whatman glass fiber filter “pita pockets.” These pita pockets are two filters sewn together with dental floss. The pita pockets were used for ease of transporting from the lab and deploying the radionuclides in the RadFLEX facility.

Np amended goethite samples were prepared in duplicate by suspending 200 mg of goethite in 9 mL of distilled deionized water to which 0.36 mL of 1 N NaOH was added. Then 0.36 mL of a 5.5 mg/mL ²³⁷Np solution in 1.0 N HNO₃ was added. The suspension was mixed and small amounts of 0.1 M HNO₃ and

NaOH were added to adjust the pH to 7.5. The samples were placed on an end over end tumbler at 8 rpm for approximately 16 hours (overnight). The samples were then centrifuged at 8000 rpm for 20 minutes in a Allegra C1015 rotor (calculated to remove particles greater than 100 nm from solution using Stoke’s Law). The supernatant was decanted and the wet goethite paste was transferred to the center of a filter paper “pita pocket” using a plastic spatula. As it was not possible to transfer all of the goethite from the tube, the total activity of ^{237}Np was determined using direct low energy HPGe analysis of the two “pita pocket” filters.

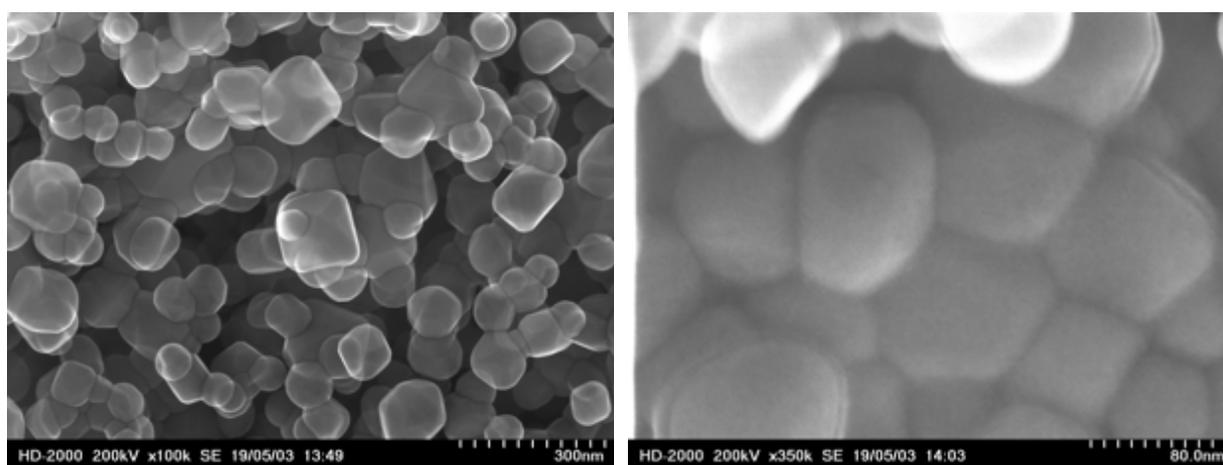


Figure 4. Scanning mode images of NpO_2 from STEM

Table 1. Np source information

Lysimeter	Isotope	Source	Preparation	mg
8-2	^{237}Np	$\text{NpO}_2(\text{s})$ on filter paper	A	1.944
29-2	^{237}Np	$\text{NpO}_2(\text{s})$ on filter paper	B	0.914
31-2	^{237}Np	Np-Goethite on filter paper	A	0.738
33-2	^{237}Np	Np-Goethite non filter paper	B	0.625

3.2 Ra Source

For the ^{226}Ra source, 0.5 mL of 2 $\mu\text{Ci/mL}$ solution was pipetted onto a 13 mm diameter Whatman glass fiber filter, which was then placed in the pita pocket. The ^{226}Ra stock solution was in 1 M HNO_3 and purchased from Isotope Products (Burbank, CA).

3.3 Pu (VI) Compounds

Pu(VI) compounds were prepared at SRNL following the same methodology used previously (Roberts et al. 2012) and described in greater detail in “Appendix B: Pu(VI) Source Preparation for RadFLEx.” Six Pu(VI) carbonate sources containing approximately 27 μCi of Pu were made for deployment in RadFLEx. An additional sample was prepared as a verification sample for XRD analysis (Figure 5). The compound was identified as $\text{NH}_4\text{PuO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$. Weapons grade plutonium was used to prepare the compound. The

solution used had an internal designation of Cr361 Hearts and this solution was most recently purified by anion exchange in March 2016. Based on the measured values in Table 2 using an isotopic ratio of 94% ^{239}Pu and a 70% assay, the estimated weights on the filters range from 0.03 to 0.27mg. A photograph of the material drying on filters is presented in Figure 6.

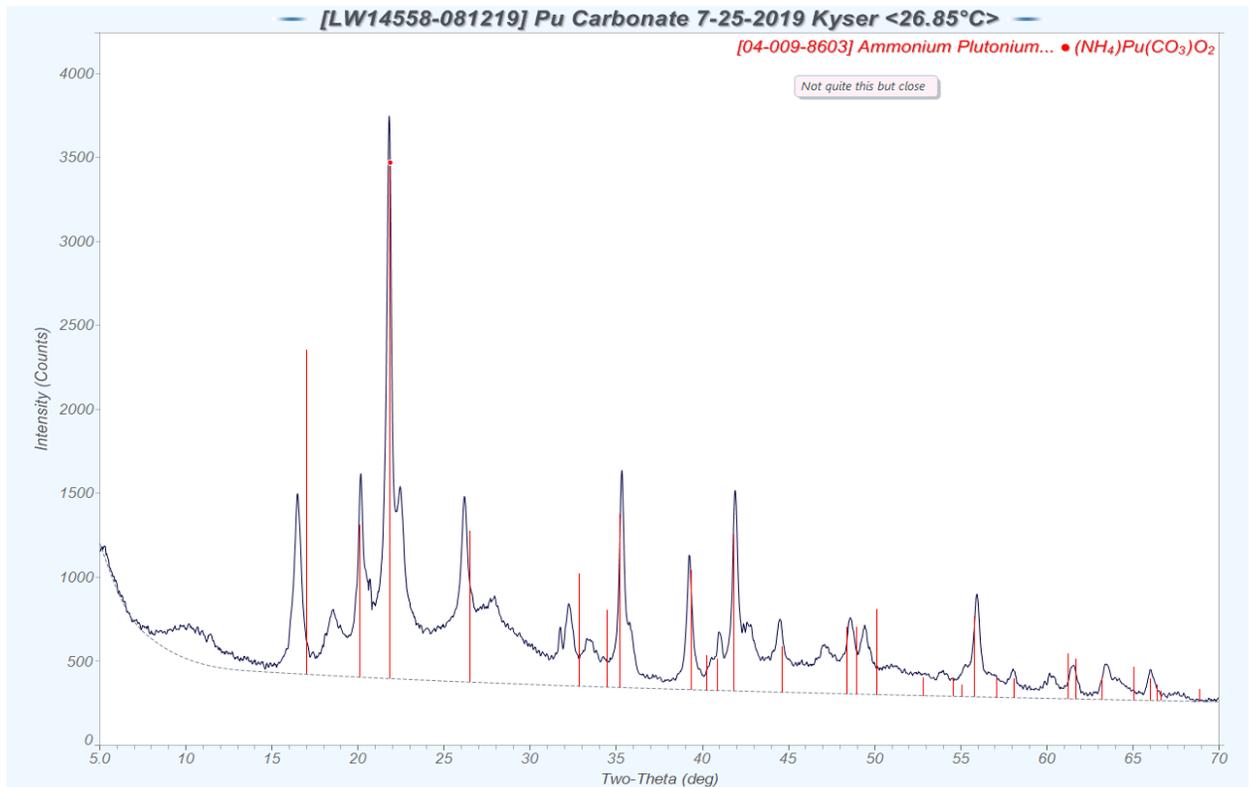


Figure 5. XRD results of Pu carbonate with reference $(\text{NH}_4)\text{Pu}(\text{CO}_3)$

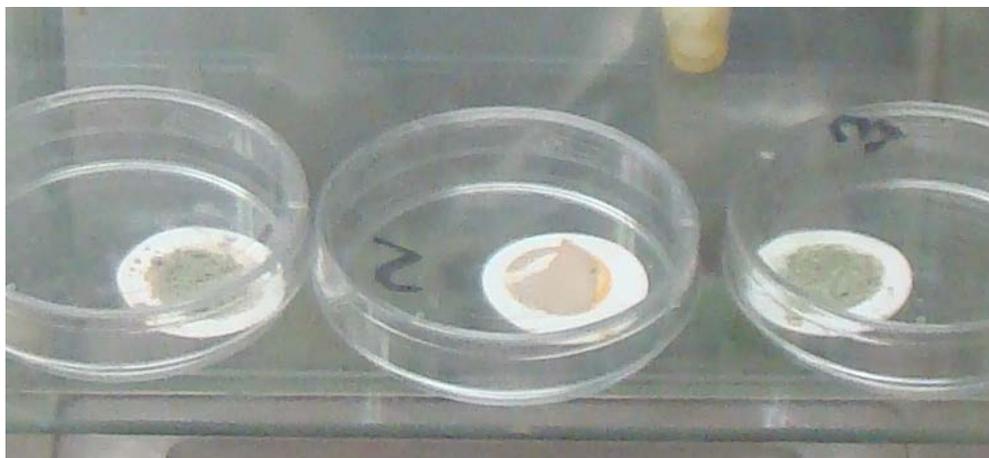


Figure 6. Pu carbonate drying on filters

This process was conducted in a radiological glovebox at SRNL. The transfer of material could not be quantified, so each filter was sent to Analytical Development Section at SRNL for radiochemistry analysis (Table 2). It is expected that all items removed from a glovebox used for Pu and Am have external contamination. Care was taken to minimize introduction of alpha particles other than the intended Pu compound to the experimental system. To achieve this, the samples that were removed from the glovebox were transferred to a radiological fume hood and repackaged in a source delivery system described in Roberts et al. (2012) and in more detail in section 3.4.

Table 2. Pu source activities measured by Analytical Development, SRNL

Lysimeter that received Pu	Sample ID	²³⁷ U (dpm/sample)	1 sigma % uncertainty	²³⁹ Pu (dpm/sample)	1 sigma % uncertainty	²⁴¹ Am (dpm/sample)	1 sigma % uncertainty	²⁴¹ Pu (dpm/sample)	1 sigma % uncertainty
38-3	15189	1.78E+02	6.85	1.36E+07	5.00	7.77E+03	5.00	1.17E+07	11.80
41-3	15190	1.90E+02	6.16	1.49E+07	5.00	7.81E+03	5.00	1.49E+07	8.98
44-3	15191	3.42E+02	5.00	2.38E+07	5.00	1.26E+04	5.00	1.88E+07	10.20
14-2	15192	3.07E+02	5.11	2.49E+07	5.00	1.33E+04	5.00	2.48E+07	7.23
20-2	15193	3.16E+02	5.00	1.83E+07	5.00	9.00E+03	5.00	1.14E+07	13.30
21-3	15194	2.83E+02	5.00	1.21E+07	5.00	6.66E+03	5.00	7.48E+06	15.30
Archive	15195	4.76E+01	23.40	2.92E+06	5.00	1.45E+03	5.00	<6.77E+06	MDA
Archive	15196	1.63E+02	5.28	8.10E+06	5.00	3.61E+03	5.00	7.80E+06	13.10

3.4 New Source Installation

As noted earlier, the new sources were loaded in “pita pockets” that are comprised of two 47-mm glass fiber filters (Whatman Grade GF/F) stitched together with PFTE (Teflon) dental floss (Oral-B Glide) with an opening to introduce the source. The pita pockets were packed in the center of 7.6 cm polycarbonate core tubes surrounded by the same test soil source as found in the lysimeter to which it was deployed resulting in a mini-core delivery system (Figure 7). The mini-core was transported to RadFLEX. Each lysimeter was pre-packed with 30 cm of test soil. The bottom cap of the mini-core delivery system was

removed, the mini-core was placed on the pre-packed dirt, the top cap was removed and the mini-core was extruded into the lysimeter. The lysimeter was then filled and packed with another 30 cm of the test soil above the mini-core.



Figure 7. Filter pita pocket in half-filled mini core delivery system. Before deployment, another 3.8 cm of sediment was placed on top of the filter pita pocket and then the sediment and filter pita pocket were extruded out of the polycarbonate tube into the field lysimeter core.

4.0 Summary

In July 16-17, 2019, RadFLEx was taken offline for rust abatement, repainting and replacement of the sample bottle housings. While offline, 11 new radiological sources were prepared at SRNL and Clemson University. On October 24, 2019 the new sources were placed in their respective lysimeter position, the caps removed and the experiment resumed. Figure 8 shows the current status of RadFLEx since the changes in 2019. Since restart, monitoring has continued. Leachate sampling will be conducted monthly for the Np sources and quarterly for all other sources. All leachate samples will continue to be shipped to Clemson University for analyses and funded by SRR and results will be reported annually (SRR, 2019). Installation of an additional Ra and two I samples are presently scheduled for FY20 and will fill 3 of the 5 empty lysimeters.

Lysimeter Map of Treatments				
Updated: 1/15/20				
North ----->	Description	Lysimeter No.	Description	Lysimeter No.
	Empty	1-3	Pu(IV)-oxalate, grass	13/9
	Empty	2-3	Pu(V)NH4 (CO3)/OM	14-2
	Cement Control	3	Saltstone Control	15
	Cement gamma Suite	4	Saltstone gamma suite	16
	Cement gamma Suite	5	Saltstone gamma suite	17
	Cement gamma Suite	6	Saltstone gamma suite	18
	Cement Tc & I (capped)	7	Saltstone Tc & I (capped)	19
	Np(IV)O2	8-2	Pu(V)NH4 (CO3)/OM	20-2
	Ra-228	9-2	Pu(V)NH4 (CO3)/OM	21-3
	Pu(IV)-oxalate, grass	10	Pu(V)NH4(CO3)/OM	22
	Pu(IV)-oxalate, grass	11	Pu(V)NH4(CO3)/OM	23
	Grass control	12	Instrumented control	24
	Sediment Control	25	Instrumented Control	37
	Gamma Suite	26	Pu(V)NH4 (CO3)/Sand	38-3
	Gamma Suite	27	Pu(IV)oxalate	39
	Gamma Suite	28	Pu(IV)oxalate	40
	Np(IV)O2	29-2	Pu(V)NH4 (CO3)/Sand	41-3
	Np(V)nitrate	30	Pu(V)NH4(CO3)	42
	Np(V)-nitrate	31-2	Pu(V)NH4(CO3)	43
	Np(IV)O2	32	Pu(V)NH4 (CO3)/Sand	44-3
	Np(V)-nitrate	33-2	Pu colloids	45
	Pu(III)oxalate	34	Pu colloids	46
	Pu(III)oxalate	35	Empty	47-2
	Empty	36	Empty	48-2
New Sources - 2019				
Empty lysimeter locations				

Figure 8. RadFLEEx map with sample IDs and locations. New sources and empty locations are color coded at the bottom. “- #” corresponds to the number of lysimeters deployed in that position, e.g. - 2 means this is the second lysimeter in that position.

5.0 References

- Cullity, B. D., and Stock, S. R. (2001). "Elements of X-ray Diffraction," Prentice Hall New Jersey.
- Dixon, K. L. (2017). "Hydraulic and Physical Properties of Central Shops Borrow Pit Sediments," Rep. No. SRNL-L3200-2017-00119. Savannah River National Laboratory, Aiken, SC.
- Miller, T. J., Kaplan, D. I., and Powell, B. A. (2012). "Laboratory and Lysimeter Experimentation and Transport Modeling of Neptunium and Strontium in Savannah River Site Sediments," Rep. No. SRNL-STI-2012-00052. Savannah River National Laboratory, Aiken, SC.
- Peruski, K., Maloubier, M., and Powell, B. A. (2017a). "Analysis of plutonium soil concentrations in field lysimeter experiments," Rep. No. SRRA021685SR. Clemson University, Anderson, SC.
- Peruski, K., Maloubier, M., and Powell, B. A. (2018a). "Analysis of plutonium soil concentrations in field lysimeter experiments: Soil Pu concentration profile from a $\text{NH}_4\text{Pu}(\text{V})\text{O}_2\text{CO}_3(\text{s})$ source." Clemson University, Anderson, SC.
- Peruski, K., Parker, C. J., Maloubier, M., Patel, M., and Powell, B. A. (2018b). "Determination of constituent concentrations in field lysimeter effluents." Clemson University, Anderson, SC.
- Peruski, K., Pope, R., Maloubier, M., and Powell, B. A. (2017b). "Determination of constituent concentrations in field lysimeter effluents." Clemson University, Clemson, SC.
- Powell, B. A., and Witmer, M. (2013). "Determination of radionuclide concentrations in field lysimeter effluents," Rep. No. SRR Project G-SOW-Z-00007. Clemson University, Clemson, SC.
- SRR. (2019). "Statement of Work for Technical Support Provided by Clemson University," G-SOW-H-00259. Savannah River Remediations, Aiken, SC.
- Witmer, M., and Powell, B. A. (2013). "Determination of constituent concentrations in field lysimeter effluents - FY13 final report." Clemson University, Anderson, SC.
- Witmer, M., and Powell, B. A. (2014). "Determination of constituent concentrations in field lysimeter effluents," Rep. No. SRRA021685SR. Clemson University, Anderson, SC.

Appendix A: NpO_2 Source Preparation for RadFLEx Lysimeters

Kathryn Peruski, June 2019

Np(IV) Stock Preparation

Neptunium (IV) stock was prepared via chemical reduction using potassium iodide (KI) solid. Initial solution of Np in 5M HCl was a mix of Np(V) and Np(IV), as measured by UV-Vis (Figure A-1). Reference peak locations for Np(IV) and Np(V) are taken from Yoshida et al., (2010).

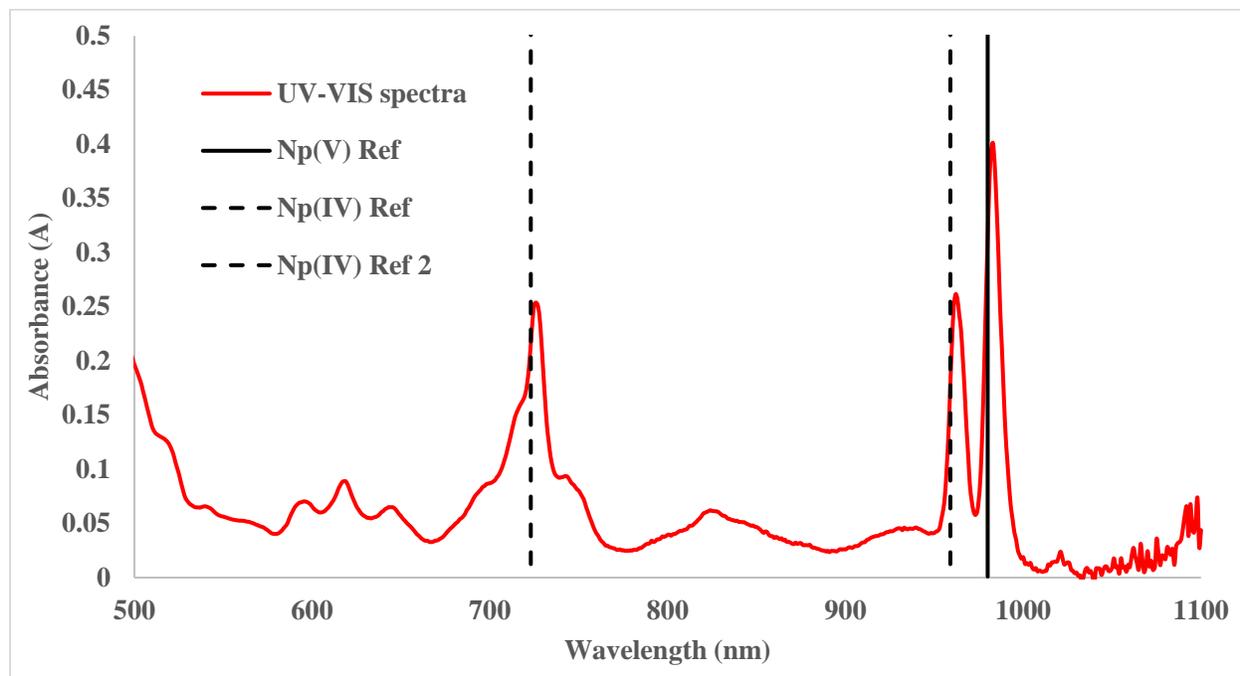


Figure A-1. UV-Vis spectrum of initial neptunium solution in 5M HCl

Excess solid KI is added to Np solution, resulting in final concentration of 10 mM Np and 90 mM KI. Solution color immediately changed from bright yellow to dark orange, and the reaction was allowed to proceed for 30 minutes before a secondary UV-VIS measurement. The secondary UV-VIS measurement shows that Np(V) peak has disappeared, leaving only Np(IV) peaks (Figure A-2).

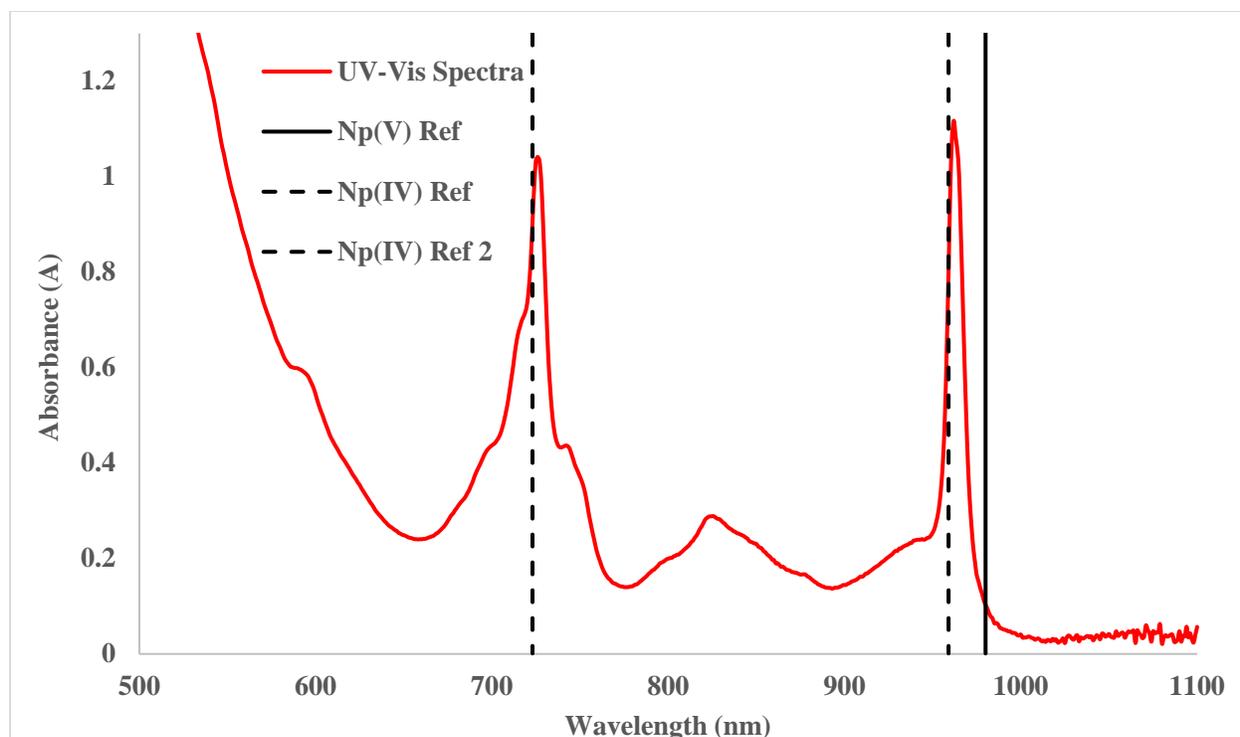


Figure A-2. UV-VIS spectrum of neptunium solution in 5M HCl/90mM potassium iodide

Np(IV) Oxalate Precipitation

Neptunium oxalate is a commonly used precursor for NpO_2 (Porter, 1964; Duffey, 2003a; Duffey 2003b). While it is typically prepared in HNO_3 , plutonium oxalate has been successfully prepared in HCl (Runde, 2009) and preliminary tests with thorium indicated that the precipitation would be successful in HCl. Neptunium oxalate was precipitated from Np(IV) stock (10mM Np, 90mM KI in 5M HCl) within one hour of stock preparation to prevent re-oxidation to Np(V) in solution. Precipitation was performed in a hood, loading 10mL of feed stock into a 30 mL Teflon vial and placing vial on magnetic stir plate with a stir bar, set to 500 rpm. Over a 45-minute period, 6.6 mL of 0.25M oxalic acid solution was added to Np(IV) feed stock to reach final oxalic acid concentration of 0.1M. Oxalic acid was added in 146 microliter increments per minute to avoid supersaturation and promote formation of a uniform product. Precipitation of solid was evident after approximately 20 minutes. After complete addition of oxalic acid, solution was stirred for an additional 30 minutes, then solid slurry was removed from Teflon vial into a 50 mL centrifuge tube and centrifuged for 30 minutes at 9500 rpm to isolate and separate the product. A green powder was visible at the tip of centrifuge tube (Figure A-3, left). Supernatant was decanted and saved for Np recovery, while transferring oxalate solid into doubly-contained porcelain crucibles (Figure A-3, right). Solid was air dried for at least 1 hour to remove residual liquid before calcination, at which points lids were placed on crucibles and transferred into the oven.



Figure A-3. Neptunium oxalate precipitate in potassium iodide solution (left) and after separation (right). Sheen on right image is small amount of solution still present on oxalate solid.

NpO₂ Calcination

Neptunium oxalate solid was calcined in a programmable furnace in multiple steps to fully dry the solid and then convert the oxalate to an oxide. The porcelain crucibles used in this experiment cannot withstand temperature gradients greater than 100 degrees Celsius per hour, so ramp speeds were determined accordingly. Temperature was ramped to 150 degrees Celsius over 1.5 hours, held at 150 degrees Celsius for 1 hour, ramped to 700 degrees Celsius over 5.5 hours, then held at 700 degrees Celsius for 36 hours before cooling to 25 degrees Celsius over 7 hours. After calcination, solid was a dark gray-brown (Figure A-4).

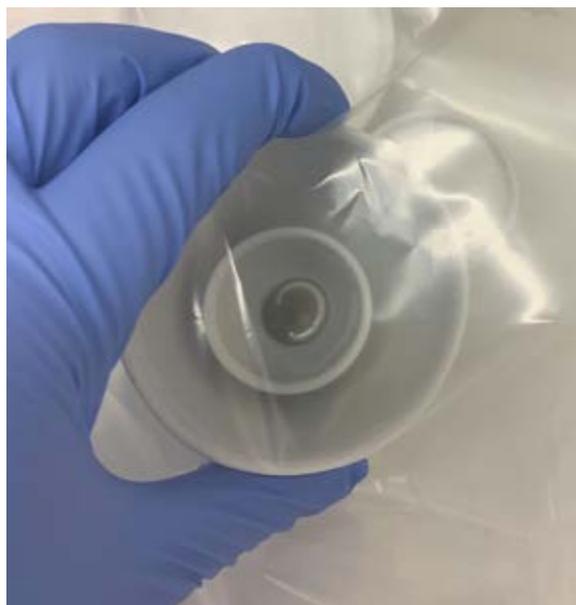


Figure A-4. Solid after calcination

NpO₂ Characterization

Scanning Electron Microscopy (SEM)

A small amount of the final product was suspended in ethanol and deposited onto carbon tape on aluminum SEM stub using a transfer pipette. Samples were not sputter-coated prior to analysis. A Hitachi S4800 high resolution field emission scanning electron microscope at Clemson University was used for analysis. Imaging was performed at 15 keV. The calcined solid consisted of approximately 5 micron cubic aggregates (Figure A-5, left). Grains within the aggregates were approximately 50 nanometers, with clearly defined grain boundaries and significant porosity in the solid (Figure A-5, right).

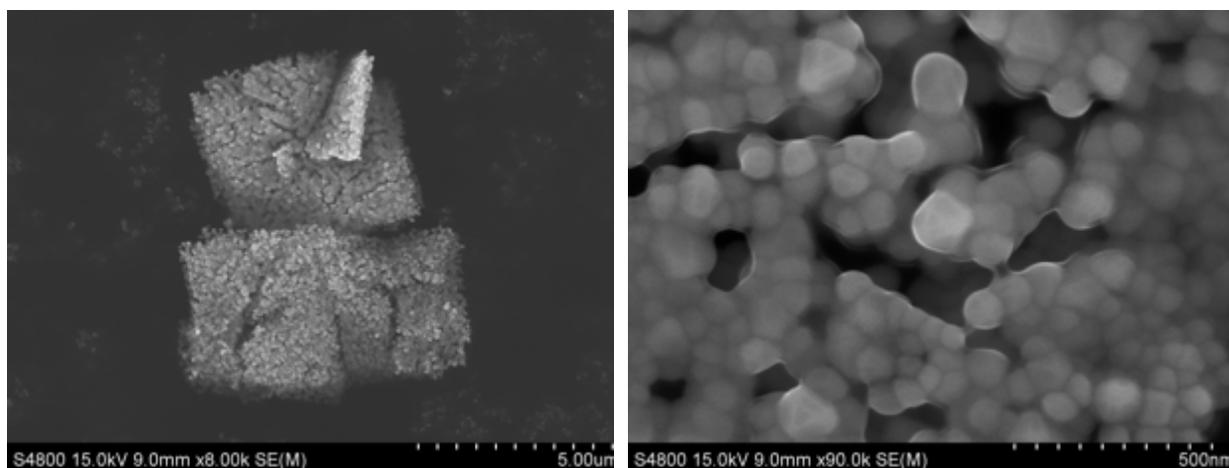


Figure A-5. SEM images of calcined NpO₂

An Oxford Instruments energy dispersive spectroscopy (EDS) detector attached to the SEM was used to confirm presence of Np (Figure A-6). EDS analysis was performed at 20keV.

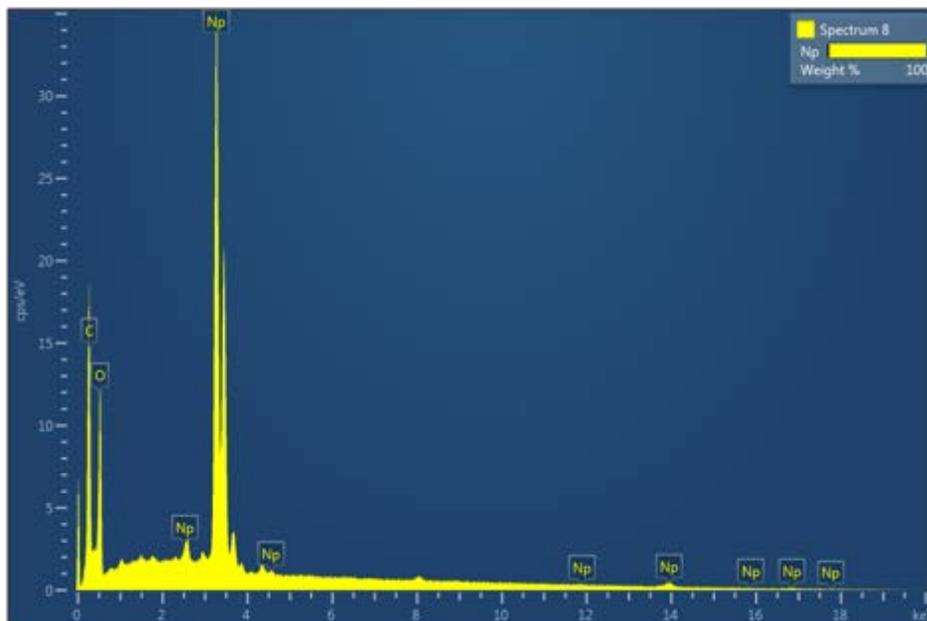


Figure A-6. Energy dispersive spectra of calcined NpO₂
Scanning Transmission Electron Microscopy (STEM)

The calcined product was slurried in ethanol and a few microliters were deposited onto a lacey carbon TEM grid. Excess liquid is blotted with a KimWipe. A Hitachi HD2000 scanning transmission electron microscope at Clemson University was utilized to probe the surface features in higher resolution than permitted by SEM. Grain sizes were confirmed to be between 30 and 80 nanometers (Figure A-7), which is in good agreement with SEM images.

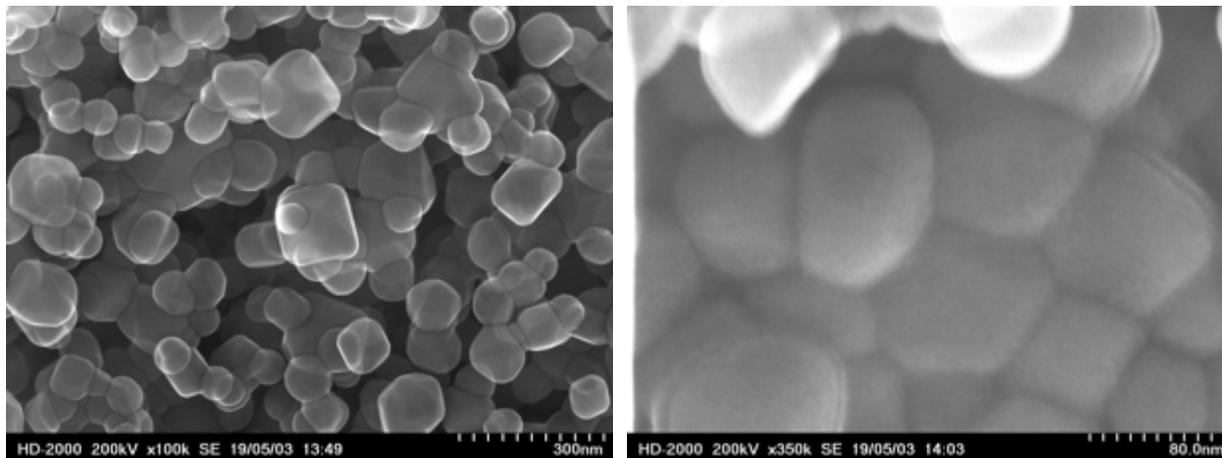


Figure A-7. Scanning mode images of NpO₂ from STEM

Transmission mode was also employed on the STEM in the attempt to confirm that the crystals are NpO₂ using lattice spacing, but resolution limitations on the instrument prevented measurement. TEM images are shown at maximum resolution in Figure A-8.

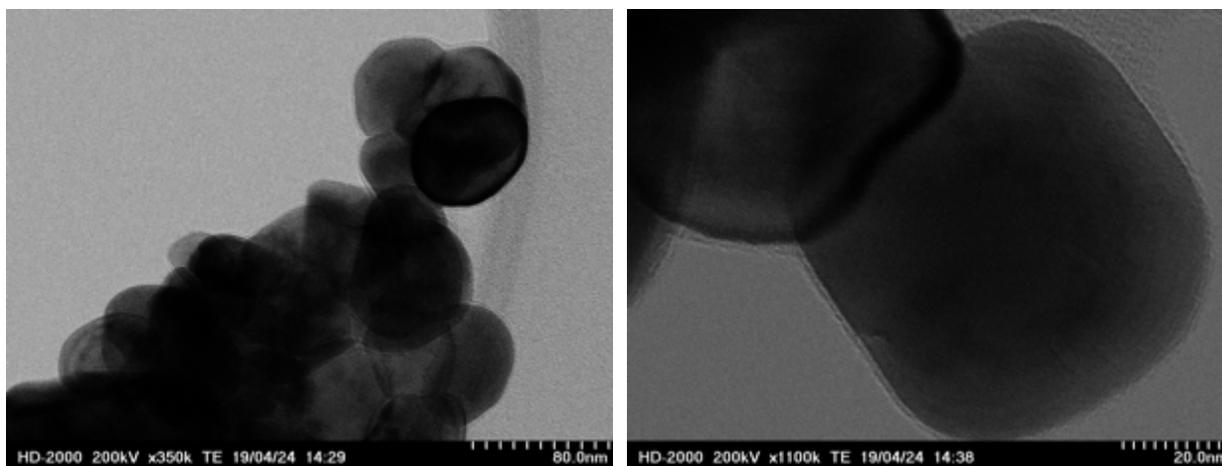


Figure A-8 Transmission mode images of NpO₂ from STEM

Selected Area Electron Diffraction (SAED)

To confirm the solid prepared is NpO₂(cr), selected area diffraction attachment is utilized on the Hitachi HD2000 STEM with an AMT CCD camera. The d-spacing of a crystal structure via electron diffraction is given by (Cullity and Stock, 2001):

$$d = \frac{L\lambda}{R} \quad (\text{Equation 1})$$

Where L is the camera length, λ is the electron wavelength, and R is the radius of the diffraction ring. The camera length must be calibrated for the instrument for each set of electronic and magnetic conditions. Using a constant energy of 200kV, the electron wavelength is a constant of 0.0251 Å. To calibrate the camera length, an evaporated aluminum diffraction standard (Ted Pella, Inc.) was exposed to the identical electronic and magnetic conditions as the unknown sample and diffraction patterns were recorded. Camera length was calculated using a rearrangement of Equation 1:

$$L = \frac{d \times R}{\lambda} \quad (\text{Equation 2})$$

Camera length is calculated using measured radii of diffraction rings in standard, known lattice spacing of standard, and constant wavelength. A total of 4 diffraction rings were measured in aluminum standards and camera length was averaged across the 4 d-spacings. The calculated camera length was then applied to unknown samples to calculate d-spacing.

A total of 10 diffraction patterns were collected from the calcined solid under constant electronic and magnetic parameters using z-contrast mode. A representative example of recorded pattern from calcined solid is shown in Figure A-9.

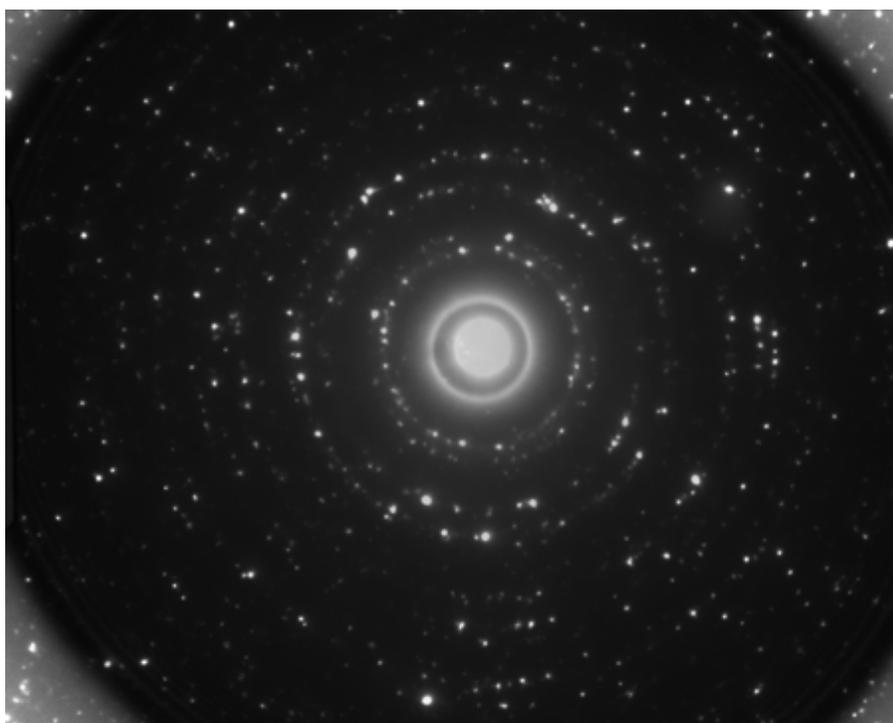


Figure A-9. Example of selected area diffraction pattern of NpO₂ solid

From a defined center point (transmission spot), the distance to a diffraction spot was measured. For each diffraction ring, 5 separate diffraction spots around the ring were used to prevent bias from stigmatism. The distances (R) for the 5 diffraction spots were averaged, then applied to Equation 1 along with constant wavelength and calculated camera length to calculate the d-spacings. Not all known rings for NpO₂ were observed in the calcined material (Table 1), due to the relatively low intensities. The lattice constant (a) for each Miller Index (hkl) was calculated for NpO₂ (a cubic system) using d-spacing (Cullity, et al., 2001):

$$a = d_{hkl} \times \sqrt{h^2 + k^2 + l^2} \quad (\text{Equation 3})$$

Where d_{hkl} is the d-spacing for a given Miller index (hkl). Lattice constants are averaged across all measured hkl's. The average measured d-spacing values and averaged lattice constant agree well with reference values for NpO₂ (Table A-1), indicating that the calcined solid is in fact NpO₂. Reference d-spacing and lattice constants were taken from International Center for Diffraction Data (ICDD) Powder Diffraction File (PDF) Card number 00-023-1269 for NpO₂ (2019).

Table A-1. Reference and measured d-spacings for NpO₂, as well as lattice constants

hkl	Intensity	Reference d-spacing (Å)	Average measured d-spacing (Å)	Standard Deviation of Measured d-spacing (Å)	Reference Lattice Constant	Measured Lattice Constant
111	100	3.140	3.137	0.039	5.439	5.433
200	30	2.717				
220	50	1.921	1.930	0.033	5.433	5.460
311	50	1.638	1.632	0.015	5.433	5.412
222	10	1.568				
400	10	1.358				
331	20	1.247	1.244	0.000	5.436	5.423
420	15	1.215	1.215	0.004	5.434	5.435
422	20					
				Average	5.435	5.432

NpO₂ Source Preparation

Calcined product produced above was suspended in ethanol for source preparation. Pre-prepared filter paper “pita-pockets” from Savannah River National Laboratory were loaded with small amounts of NpO₂ suspension and allowed to dry inside a petri dish. Two pita-pockets were prepared: NpO₂-A and NpO₂-B. To determine the mass of NpO₂ in each source, filters were counted on a high-purity germanium detector (HPGe) at Clemson University for approximately 60-minute count time. Np-237 concentration was analyzed using the 86-keV gamma peak (emission fraction 12.4%). The detector efficiency for Np-237 (4.62%) was determined using a NIST-calibrated Np-237 aqueous stock, pipetted onto a filter paper in the same geometry as the sources. The activity (A) of Np-237 (in Bq) in each sediment sample was then calculated from Knoll⁷:

$$A = \frac{(n_G - n_B)}{t * F * E} \quad \text{(Equation 4)}$$

Where E is the detector efficiency, F is the emission fraction, t is the count time, and nG and nB are gross and background counts in the region of interest, respectively. Activity of Np-237 was converted to mass of NpO₂ using a specific activity of 6.9E-4 Ci/g. Final source masses are shown in Table A-2 below:

Table A-2. Final mass of NpO₂ in each lysimeter source.

Source	mg NpO ₂
NpO ₂ -A	1.944
NpO ₂ -B	0.914

Appendix A References:

- Porter, J., Production of Neptunium Dioxide. *Industrial & Engineering Chemistry Process Design and Development* 1964, 3 (4), 289-292.
- Cullity, B. D.; Stock, S. R., *Elements of X-ray Diffraction*. Prentice hall New Jersey: 2001; Vol. 3.
- Knoll, G. F., *Radiation detection and measurement*. John Wiley & Sons: 2010.
- Duffey, J. Characterization of Neptunium Oxide Generated Using the HB-Line Phase II Flowsheet; SRS: 2003.
- Duffey, J. Lab Scale Production of NpO₂; SRS (US). Funding organization: US Department of Energy (United States): 2003.
- Porter, J., Production of Neptunium Dioxide. *Industrial & Engineering Chemistry Process Design and Development* 1964, 3 (4), 289-292.
- Runde, W.; Brodnax, L. F.; Goff, G.; Bean, A. C.; Scott, B. L., Directed synthesis of crystalline plutonium (III) and (IV) oxalates: accessing redox-controlled separations in acidic solutions. *Inorganic chemistry* 2009, 48 (13), 5967-5972.
- Yoshida, Z.; Johnson, S. G.; Kimura, T.; Krsul, J. R., Neptunium. In: *The Chemistry of the Actinide and Transactinide Elements*, Fourth ed.; Morss, L. R.; Edelstein, N. M.; Fuger, J., Eds. Springer: The Netherlands, 2010; Vol. 2, pp 699-812.

Appendix B. Pu(VI) Carbonate Synthesis

Eddie Kyser, July 2019

Pu(VI) Carbonate PuO₂CO₃

53.5 g/L Pu stock solution (Cr361 Hearts, purified by anion exchange March 2016)

AgNO ₃	3 mg
Na ₂ S ₂ O ₈	91 mg
(NH ₄) ₂ CO ₃	65 mg

Heat Water Bath to 70 °C.

Add 1 mL of Pu Stock solution (53.5 g/L) to 4 dram vial containing Ag(NO₃) and Na₂S₂O₈.

Heat Pu/Ag/S₂O₈ in water bath to 60-80 °C for 20 minutes (by setting the closed vial in a 50 mL beaker with 5 mL H₂O on a hot plate).

Remove vial and cool to near room temperature.

(check UV-Vis to confirm all Pu(VI).

Add 65 mg of solid (NH₄)₂CO₃ to precipitate (NH₄)₄PuO₂(CO₃)₃.

Filter solution with filtering apparatus.

Wash 3X with 15 wt% NH₄CO₃ solution.

Pump on solids for 1 hr.

Let air dry for 3 days to decompose to PuO₂CO₃:

(NH₄)₄PuO₂(CO₃)₃ → PuO₂CO₃ +NH₃ +2CO₂ +2H₂O

Submit < 50 mg of final material for characterization by XRD.

Place the remaining material in a new petri dish until needed.

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