Dissolution and Electrochemical Recovery of UO_2, UO_3, and U_3O_8 in Ionic Liquids

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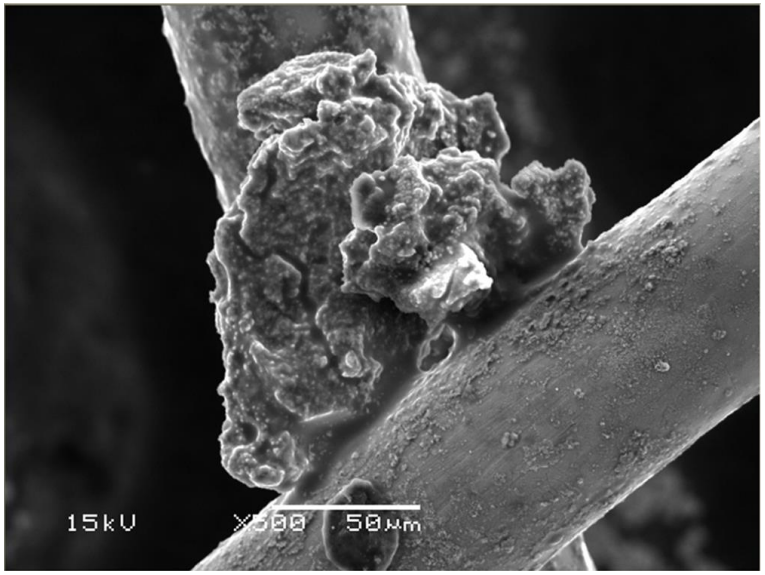
Introduction



Department and University: UNLV Radiochemistry Program
Academic Advisor: Dr. Frederic Poineau
NSSC Research Focus Areas: Radiochemistry and Nuclear Forensics
Planned Graduation Date: May 2022

Lab Mentor and Partner Laboratory: Dr. Robert Rundberg at Los Alamos National Laboratory (LANL)

Mission Relevance of Research:

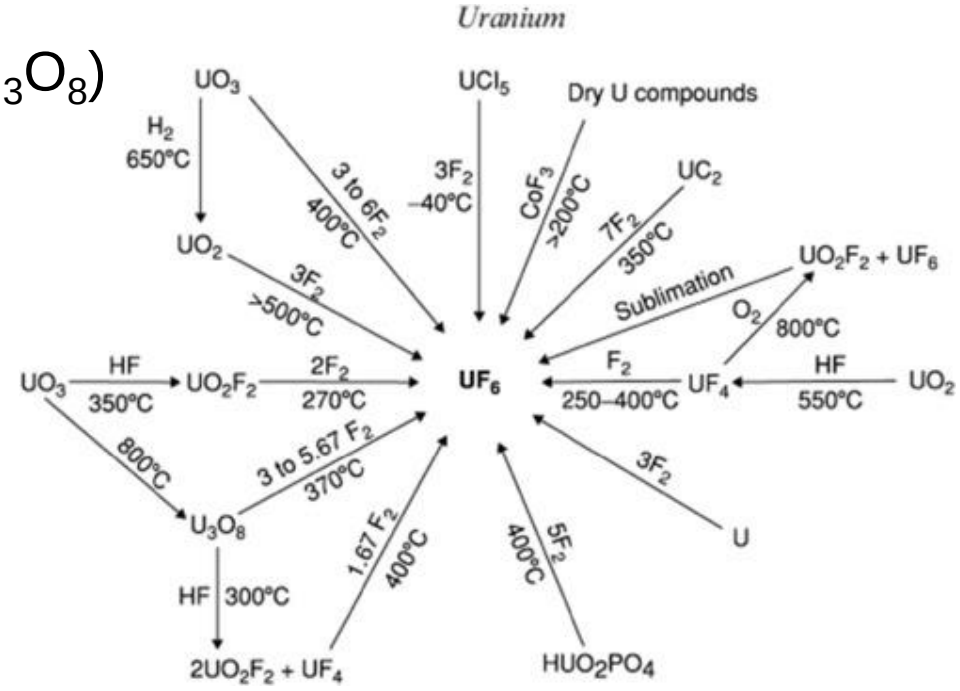
This work contributes to advances in characterization and detection of nuclear materials, by providing data on the dissolution, speciation, and recovery of uranium oxide materials. This data can contribute to nuclear forensics investigations and adds to the pursuit of knowledge regarding processing and recycling of nuclear materials.

Outline

- Synthesis of three uranium oxide compounds
- Dissolution of uranium oxides in ionic liquids with ozone
- Electrochemical deposition
- Liquid Scintillation Counting and UV-Vis spectroscopy of dissolved solutions
- Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy
- Conclusions and my NSSC experience

Synthesis of Uranium Oxides

- Purpose: To measure dissolution kinetics/speed through LSC counting
- Required materials
  - Soluble uranyl nitrate, water, dissolved U-233 spike, ammonium hydroxide, centrifuge, furnace
- After synthesizing each of the three oxides needed for dissolution (UO_2, UO_3, U_3O_8) experiments are run under standard conditions, and aliquots removed at specific time points
- The activity of the IL aliquot will show dissolution over time



Synthesis Parameters

- Solid uranyl nitrate hexahydrate is dissolved in 8-10 mL water
- U-233 spike (U-233 dissolved in nitric acid and diluted in water) added
- 1 mL ammonium hydroxide (excess) added
  - Bright yellow precipitate forms immediately
- Centrifuged for 5-10 minutes
- Drop of ammonium hydroxide added to test
- Supernatant decanted off
- Solid transferred to crucible for heating

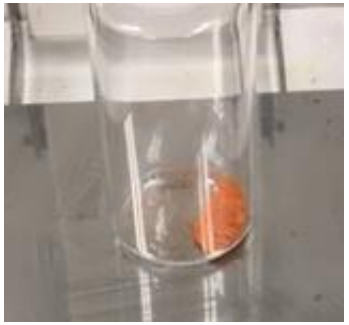
Synthesis Parameters

UO_2

- Requires inert atmosphere – H5 gas flowing through MTI
- Slow temperature increase to 600 C
- Hold for 90 minutes
- Slow temperature decrease to room temperature

UO_3

- Fastest synthesis
- Heat to 500 C for one hour in air
- Holding at temperature for one week showed little difference in structure on XRD

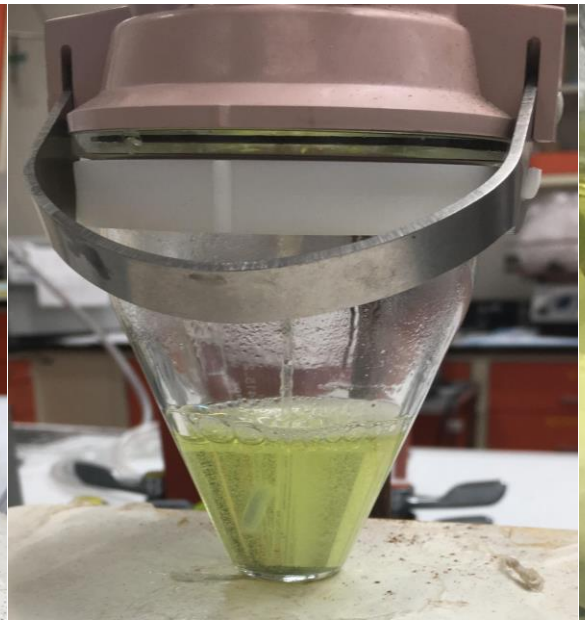


U_3O_8

- Any U oxide if heated above ~750 C in air will revert to U_3O_8
- Rapid temperature increase to 800 C
- Hold for six hours
- Rapid temperature decrease to room temperature

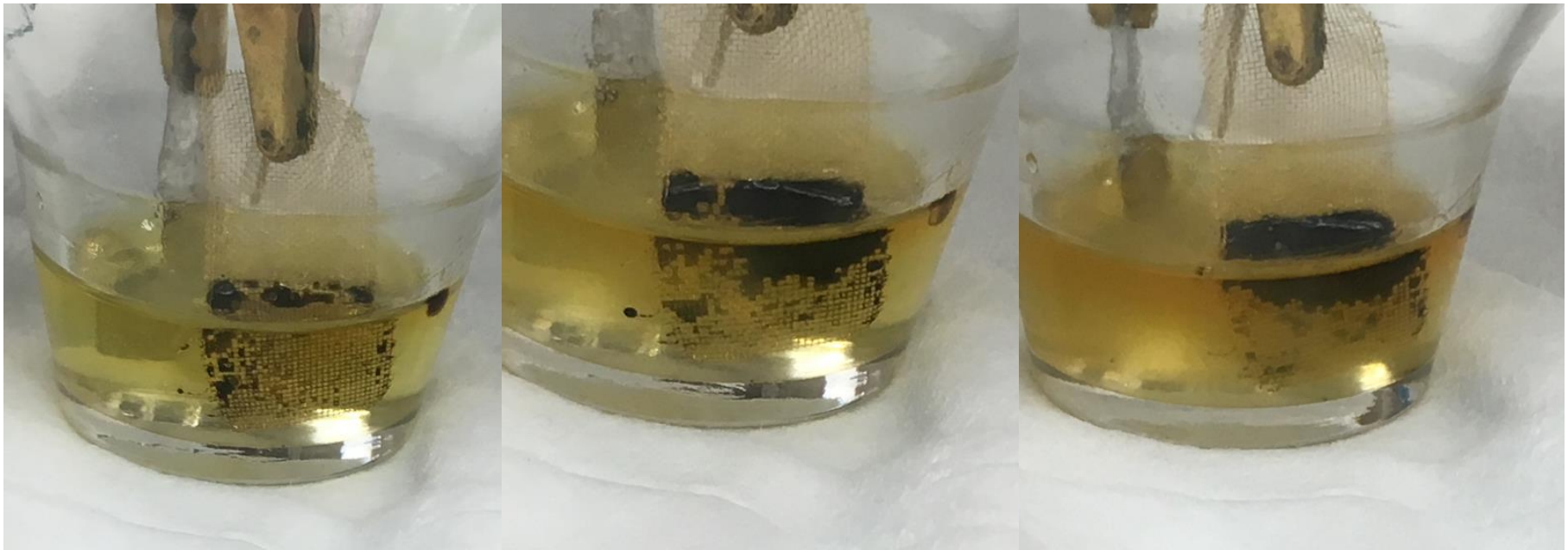
Dissolution with Ozone

- Uranium oxide material is placed in ionic liquid solution
- ILs are bulky organic cation/anion pairs that are liquid at room temperatures
- Dissolution with compressed air and an ozone generator takes 1-2 days
- Electrochemical bulk amperometry deposits are fragile, do not cling to electrode

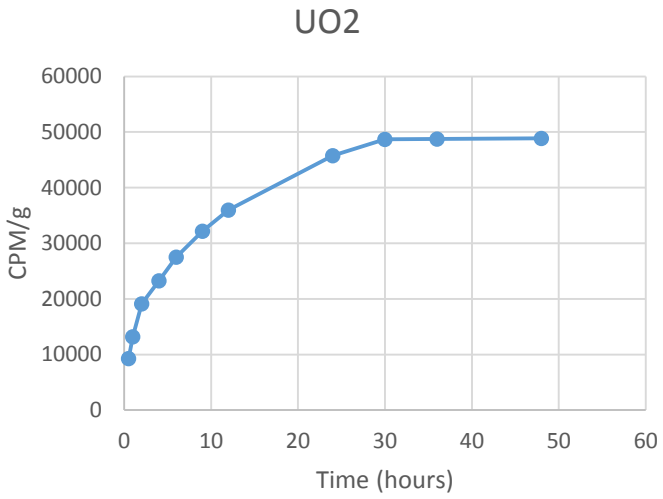



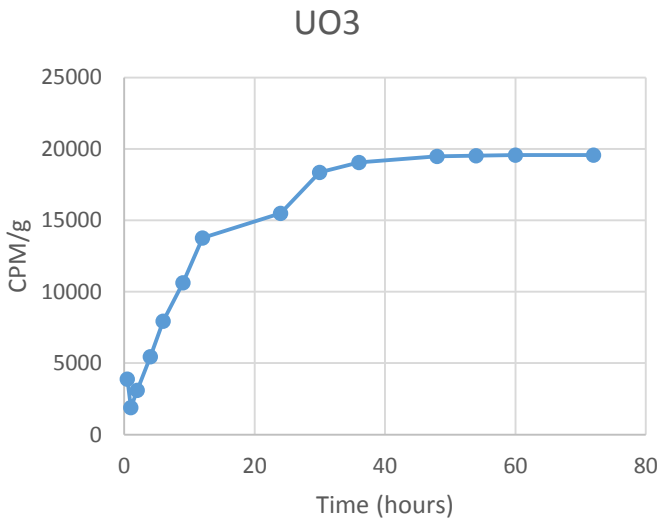

Electrochemical Deposition on Gold Mesh

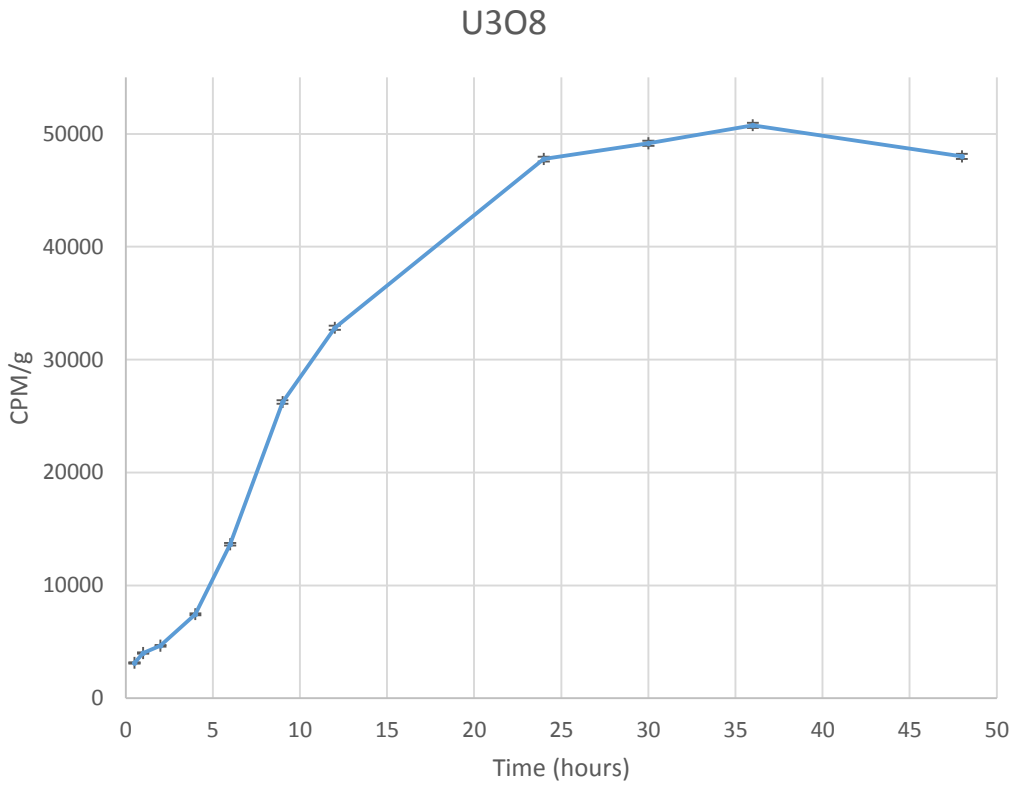
- Pulse deposition: alternating between “on” negative potential and “off” zero or positive potential
- Slower than bulk deposition: pictures at 48, 72, and 96 hours of pulse deposition



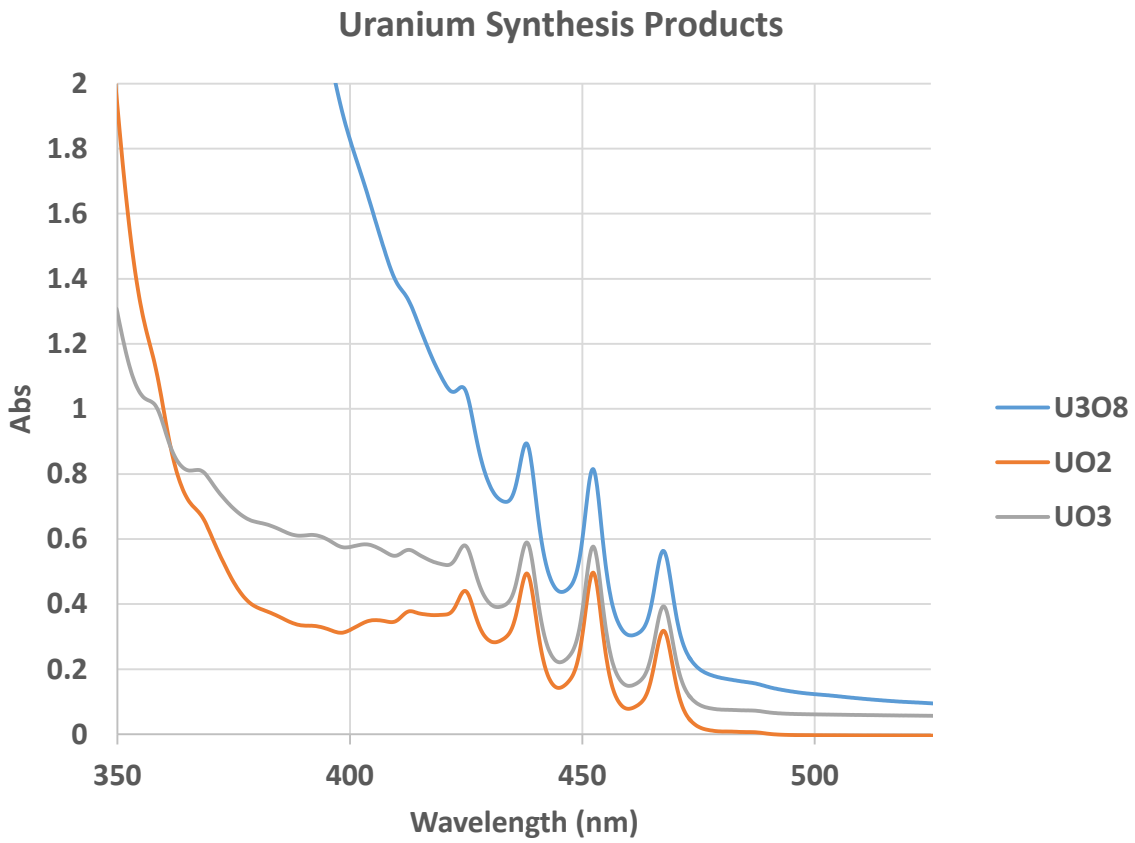
LSC Results


UO2
CPM/g
60000
50000
40000
30000
20000
10000
0
0
10
20
30
40
50
60
Time (hours)


UO3
CPM/g
25000
20000
15000
10000
5000
0
0
20
40
60
80
Time (hours)


U3O8
CPM/g
50000
40000
30000
20000
10000
0
0
5
10
15
20
25
30
35
40
45
50
Time (hours)

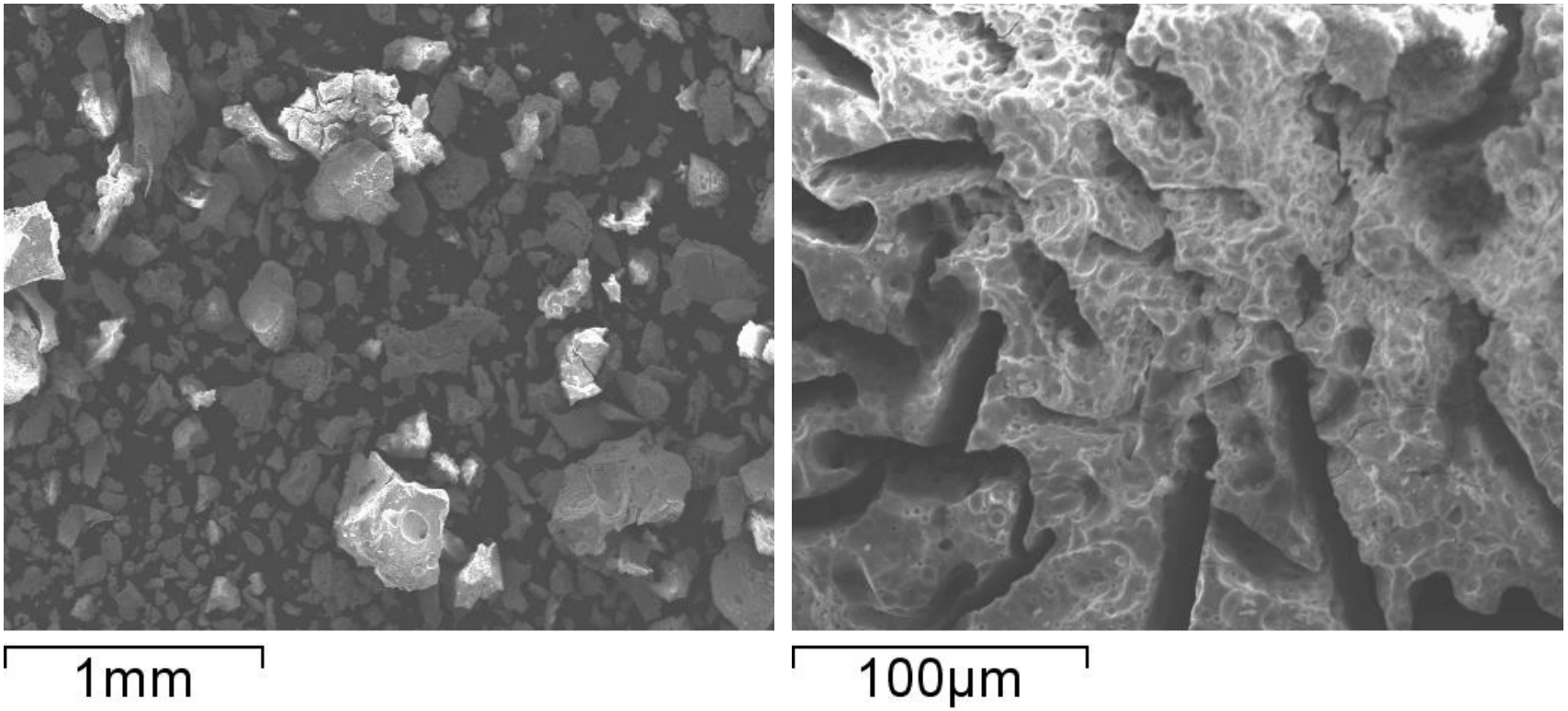
UV-Vis Results



- $U_3O_8 + 3\ O_3 + 4\ O_3^- + 10\ H^+ + 2\ O_2 \rightarrow 3\ UO_2^{2+} + 5\ H_2O + 11\ O_2$
- $UO_2 + 3\ O_3 + 2\ H^+ \rightarrow UO_2^{2+} + 4\ O_2 + H_2O$
- $UO_3 + 2\ H^+ \rightarrow UO_2^{2+} + H_2O$

Scanning Electron Microscopy Comparison

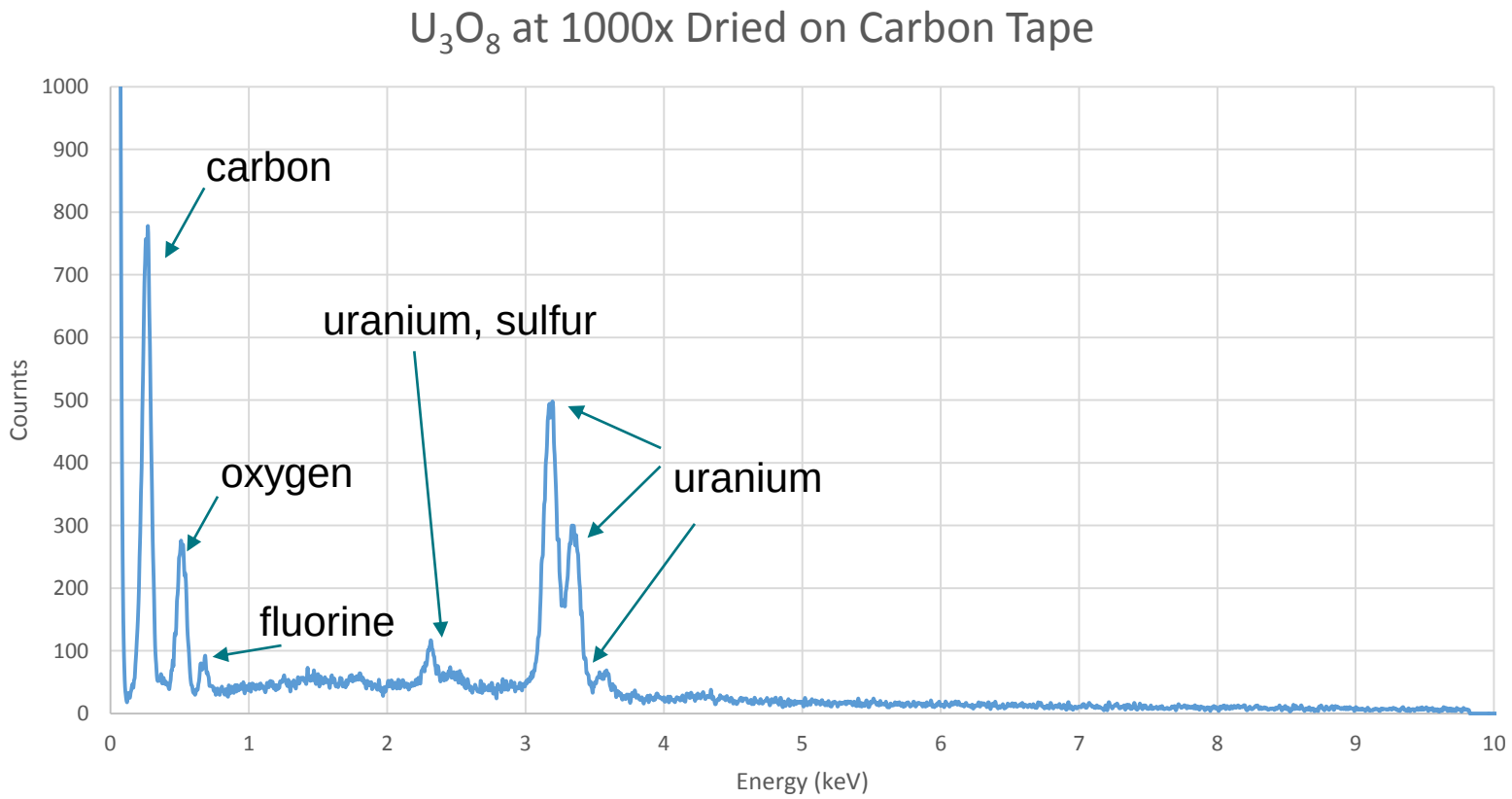
(U_3O_8 35x – left, U_3O_8 1000x – right)



Scanning Electron Microscopy - EDX

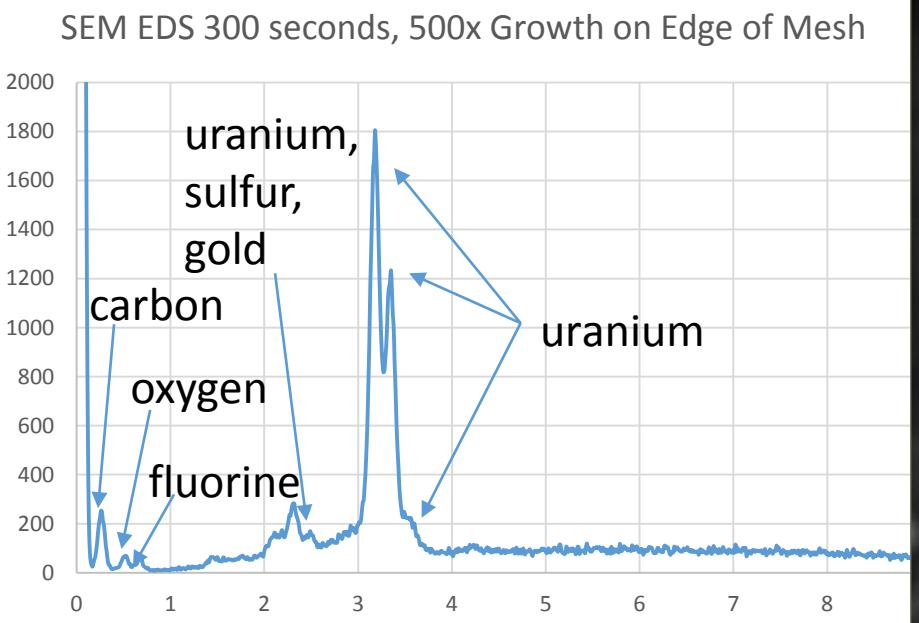
Peak(s) from 2.1 to 2.6 keV are uranium and sulfur. Peaks from 3.0 to 4.0 are uranium.

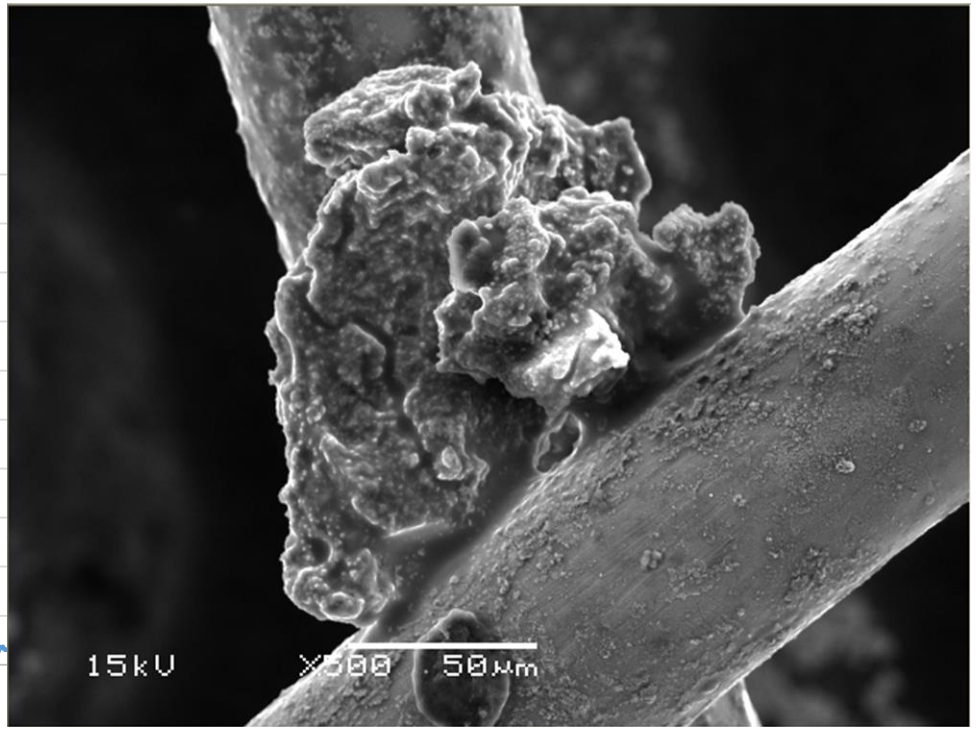
U_3O_8 sample was collected for 300 seconds, background for 30 seconds (counts are proportional to collection time)



Scanning Electron Microscopy of UO_2

Initial pulse deposition, followed by bulk deposition





Results

- All three synthesized oxides were confirmed by XRD
- All oxides were successfully dissolved under atmospheric benchtop conditions
  - Visual dissolution occurs at different times for each oxide
  - UO_2 ~24 hours, U_3O_8 ~36 hours, UO_3 ~60 hours
- LSC shows most of the dissolution is happening in the first 12 hours, with full dissolution at 24-30 hours depending on the oxide
- UV-Vis shows each final product is uranyl (UO_2^{2+})
- SEM/EDS indicate amorphous uranium oxide deposits

The NSSC Experience

- Keepin Non-proliferations Summer School at LANL, summer 2017 (featuring the “School of Nukes” training program used by the IAEA
- Introduction to my laboratory mentor, which led to receiving a Seaborg Fellowship at LANL, summer 2019
- Multiple UPR and NSSC consortium presentations, including a poster at the 2018 UPR meeting which won a best poster award
- New job as a Staff Scientist 2 position at LANL starting June!

Acknowledgements

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