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Characterization of the Environmentally Induced Chemical Transformations of Uranium Tetrafluoride

A key challenge with nuclear safeguards environmental sampling is identification of the materials post release due to subsequent chemical reactions with ambient water and oxygen. Uranium Tetrafluoride (UF_4) is of interest as an intermediate in both the upstream and downstream portions of uranium feedstock and metal production processes used in nuclear fuel production; however minimal published research exists relating to UF_4 hydrolysis. FY16 efforts were dedicated to in-situ Raman spectroscopy and X-ray diffraction characterization of UF_4 during exposure to various relative humidity conditions. This effort mapped several hydrolysis reaction pathways and identified both intermediate, and terminal progeny species.

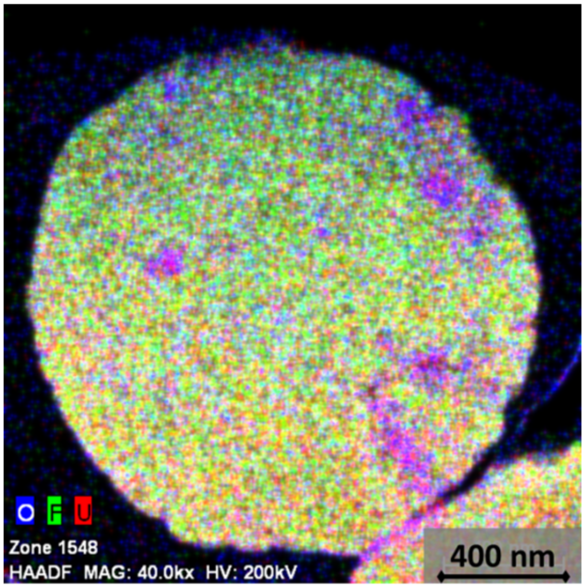

Figure 1: TEM/EDS tricolor composite elemental map of a partially hydrated UF_4 lamella specimen for U, O, and F.

Efforts in FY16 demonstrated that advanced analytical techniques were needed to better probe the chemical and structural transformations. As such FY17 efforts utilized techniques such as Electron Energy Loss Spectroscopy (EELS) coupled to Transmission Electron Microscopy (TEM) to characterize the elemental and chemical speciation of partially hydrolyzed UF_4 at the nanoscale. Solid state ^{19}F NMR was initiated to characterize the macroscale hydrolysis induced chemical changes. A series of UF_4 hydrate polymorphs ($UF_4 \cdot 2.5H_2O$, $UF_4 \cdot (H_2O)_{0.33}$, and $U_3F_{12}(H_2O)$) with known crystal structures were characterized by Raman, Infrared, and fluorescence spectroscopy to elucidate chemical, structural, and spectral feature correlations. Surrogate specimens were also analyzed by secondary ion mass spectrometry to establish viability of those methods for environmental characterization challenges associated with uranium oxyfluoride and oxide materials. Overall the FY17 effort involved several collaborations with other DOE laboratories, university partners, and commercial entities, and has successfully demonstrated characterization of environmentally induced chemical transformations in uranium via advanced microanalytical methods.

Awards and Recognition

Supporting efforts conducted during within this project were selected for presentation at the Microscopy and Microanalysis 2017 conference in St. Louis MO on August 9, 2017.

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**

LDRD-2016-00031
LDRD Report

Characterization of Environmentally Induced Chemical Transformations of Uranium Tetrafluoride

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Thrust Area: Non-proliferation and Nuclear Deterrent

Project Type: Standard
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Project End Date: September 30, 2017

Advanced characterization techniques were used to probe the complex chemical and microstructural aspects of hydrolyzed uranium tetrafluoride (UF_4). The effort utilized methods such as electron energy loss spectroscopy (EELS) coupled to Transmission electron microscopy (TEM) to probe the elemental and chemical speciation of partially hydrolyzed UF_4 at the nanoscale. Micro Raman, Infrared, and fluorescence spectroscopy were utilized to characterize a series of to elucidate crystalline structure and spectral relationships. Solid state ^{19}F nuclear magnetic spectroscopy (NMR) was initiated to characterize the macroscale hydrolysis induced chemical changes and attempt characterization of bulk scale kinetics. The effort has resulted in an enhanced understanding of the U-F systems, their hydrolysis products, and various advanced analytical capabilities which has culminated into one accepted and two in-preparation peer-review publications.

FY2017 Objectives

Effort for objectives in FY17 focused on method demonstration and development both at SRNL and with various collaborators.

- Demonstrate the preparation of lamella from hydrolyzed uranium fluoride specimens by focused ion beam preparation (FIB) and subsequently characterize them via TEM and EELS characterization.
- Characterize UF_4 hydrolysis kinetics via solid state ^{19}F NMR spectroscopy.
- Characterize a series of UF_4 hydrate polymorphs via Raman, Infrared, and fluorescence spectroscopy to probe chemical and structural phenomena.
- Determine suitability of secondary ion mass spectrometry methods for characterization of U-O-F solids related hydrolysis products.

Introduction

The chemistry of uranium fluorides is of continued interest due the relevance within chemical processing for the nuclear fuel cycle and related environmental concerns.[1-3] The two common uranium fluorides (UF_6 and UF_4) are ubiquitous within the nuclear fuel cycle as various chemical feedstocks and intermediates. However characterization of actinide fluorides has typically favored the fully oxidized +6 complex (UF_6) due to the relevance as the uranium enrichment feedstock within various nuclear enterprises.[3-5] As such UF_6 has been extensively studied both within the context of chemistry and chemical engineering; with recent focus on the hydrolysis product, uranyl fluoride, and the synthesis and characterization of various forms of uranyl fluoride hydrates.[6-12] The hydrolysis of the UF_6 is challenging physical chemistry problem and prior research has typically focused on the reaction products (e.g. uranyl fluorides) and their respective relevance to nuclear safeguards or advanced uranium chemical processing. The corresponding tetrafluoride (U^{+4}) complex has received less study, beyond physical properties and early characterization of hydrolysis products. Uranium tetrafluoride, unlike the hexafluoride, is solid at ambient conditions and relatively chemically inert to oxygen, but does undergo reaction with atmospheric or liquid water.

A family of U^{4+} fluoride hydrates has been identified and characterized with a stoichiometric formula of $UF_4{\cdot}xH_2O$; where x includes $^1/_3$, $^4/_3$, 2, and $2^1/_2$. Early efforts were reported in 1942 separately by Khlopin and Gerling, and Khlopin and Yeashenk who claimed to have isolated three U^{4+} hydrates, $UF_4{\cdot}xH_2O$ (x = $^1/_2$, 1, and 2), by electrolytic reduction of uranyl fluoride in aqueous hydrofluoric acid; however it was later shown all three were actually $UF_4{\cdot}2H_2O$.[5] Prior to 1969, only three crystal UF_4 hydrates were known and included the monoclinic $UF_4{\cdot}^4/_3H_2O$, cubic $UF_4{\cdot}2H_2O$, and orthorhombic $UF_4{\cdot}2.5H_2O$.[13] Structural data for the monoclinic $UF_4{\cdot}^4/_3H_2O$ is not available, but the structure was determined based on powder XRD, optical methods, thermography, and NMR.[14] Structural data for the orthorhombic $UF_4{\cdot}2.5H_2O$ was obtained by single crystal X-ray diffraction but did not appear in the open literature until 1971.[15] The $UF_4{\cdot}^1/_3H_2O$ was recently synthesized via mild hydrothermal reaction and the crystal structure was determined by single crystal X-ray diffraction.[3] Many of the UF_4 hydrates were synthesized via the reduction of U^{+6}, or suspensions of UF_4 with aqueous hydrofluoric acid.[5,16] Other methods to produce UF_4 hydrates have involved application of thermal energy to liberate structurally bound water from the 2.5 hydrate; however these methods can be complicated by the unintended production of uranyl fluorides ($UO_2F_2{\cdot}xH_2O$) and/or uranium oxides (UO_2; $U_3O_{8)}$.[5,17]

The primary characterization method of prior work has been single crystal and powder X-ray diffraction, although other characterization methods have been utilized, including Infrared (IR) spectroscopy and NMR, those efforts had not unambiguously identified the material crystal structure. The single prior example of IR spectroscopy published for UF_4 hydrates were derived from the thermalization of the 2.5.[17] Proton and ^{19}F NMR measurements were reported on three hydrates in 1969 ($UF_4{\cdot}xH_2O$; where x includes $^4/_3$, 2, and $2^1/_2$), but none has been published since and is likely due to the challenges associated with paramagnetic U^{4+} coupling to the proton and fluorine nuclei.[13] A prior effort did attempt to characterize hydrolyzed solid UF_4 via various X-ray spectroscopic methods but due to the surface complexity uranyl fluoride was the only product identified.[18] Within our efforts the UF_4 hydrolysis chemical changes are observed as nano- and micron scale changes in chemical structure of the solids; therefore there new analytical approaches are needed to characterize the system.

Approach

Our effort focused on both the microanalytical imaging methods and various spectroscopic techniques to characterize the complex structural phenomena with multiple chemical species simultaneously present in UF_4 hydrate systems. Raman, IR, and fluorescence spectroscopy methods were utilized as a means to characterize the bonding and chemical environment within the crystal structure of the three structurally well characterized single species uranium tetrafluoride hydrates. The advanced microanalytical technique TEM/EELS was applied to partially reacted UF_4 specimens to probe chemical-spatial qualities of the material surface and bulk ^{19}F NMR spectroscopy measurements are currently underway to qualify hydrolysis kinetics. Surrogate uranium samples were analyzed by secondary ion mass spectrometry (SIMS) techniques to assess method viability for future characterize of the U-O-F systems. Together the combination of these analytical methods have both advanced understanding of the UF_4 hydrolysis reaction and demonstrated previously untested capabilities for the characterization of uranium-based materials.

Results/Discussion

Prior FY16 efforts had shown multiple uranyl species were generated during the hydrolysis of UF_4; often with some dependence on relative humidity conditions. The primary characterization method used was Raman spectroscopy which identified the species as various uranyl fluorides and hydroxides, and/or uranium oxides; all often collocated within the same region of interest. Recognizing that high resolution methods capable of characterizing these specimen on the nanoscale was required, the FY17 effort prepared partially hydrolyzed UF_4 under a variety of varying humidity conditions and sent to a collaborator for TEM/EELS and TEM/EDS analyses. Test materials were mounted and then milled and polished with a FIB tool to generate thin lamella (<100 nm width) suitable for electron transmission measurements. An example lamella is shown Figure 2 along with the corresponding EELS measurement locations and spectra. The TEM image shows the partially hydrolyzed UF_4 material as a band approximately 500 nm in width at the surface interface with obvious changes in the internal material texture and image contrast consistent with a reaction region. The denoted EELS measurement locations transition from the exterior of the initial particle (#1) to the interior region (#5) and based on EDS mapping (not shown) regions #1-4 contain elevated oxygen content consistent with expected hydrolysis products. The EELS spectra in the low energy loss regime demonstrate both uranium O and P edges which are from electron beam induced electronic transitions from inelastic scattering.[19,20] Relative P_1 and $P_{2\text{-}3}$ edged intensity variations are observed between the regions #1-4 and #5 which may be indicative of differing chemical environments for the U atoms. Data analysis is ongoing and a total of six different samples were characterized by TEM/EELS for various U, O, and F edges in the low and intermediate energy loss regimes.

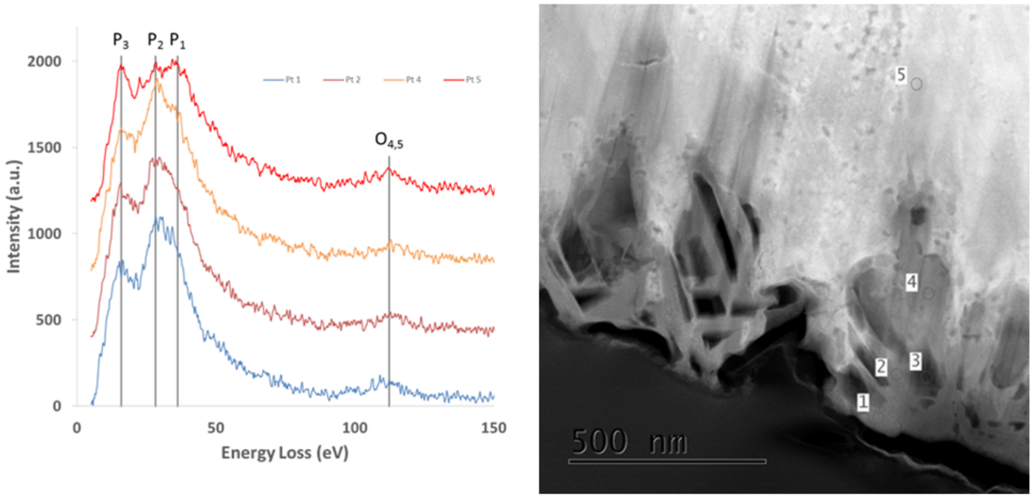

Figure 2: EELS spectra in the low energy loss region with various U transition edges denoted (left); TEM image of the lamella analyzed with numerical indicators for the corresponding EELS spectra, location #4 resulted in poor spectra and was omitted (right).

Raman, IR, and fluorescence spectra were collected for three different UF_4 hydrates polymorphs ($UF_4{\cdot}2.5H_2O$, $U_3F_{12}{\cdot}H_2O$, and $UF_4{\cdot}0.33H_2O$) which share some similarities in crystalline structure and interatomic bonding and anhydrous UF_4. The blue-green crystalline $UF_4{\cdot}2.5H_2O$ was prepared at SRNL via simple hydrolysis of UF_4 with neat water. Two additional hydrates, $U_3F_{12}{\cdot}H_2O$ and $UF_4{\cdot}0.33H_2O$, were provide by collaborators at the University of South Carolina and although share similar stoichiometry possess different crystalline structure.[3] Spectral assignment of various vibration and fluorescence bands relied on literature and simple group theory assessments. The team attempted to model the Raman and IR spectra with conventional computational tools but these efforts were not successful; likely due to the currently unresolved theoretical challenges associated outer the shell electrons of U^{4+}.[21,22] Regardless, some insights into the vibrionic and fluorescent structure for the family of compounds were determined. For example, Figure 3 shows an overall depiction of the 2.5 hydrate showing the interconnectivity of U-F polyhedra, interstitial water bound to the uranium as U-O/F polyhedra, and the presence of free water molecules within channels. Within the IR spectra two peaks are present in the H-O-H bending region (approximately 1600 cm^{-1}) and multiple peaks are present in the O-H stretching regions (> 3000 cm^{-1}); these are consistent with the two forms of water in the crystal structure. Similar analysis of the other hydrates and comparisons between the different crystal systems has resulted in identification of specific spectral features and their corresponding structural components.

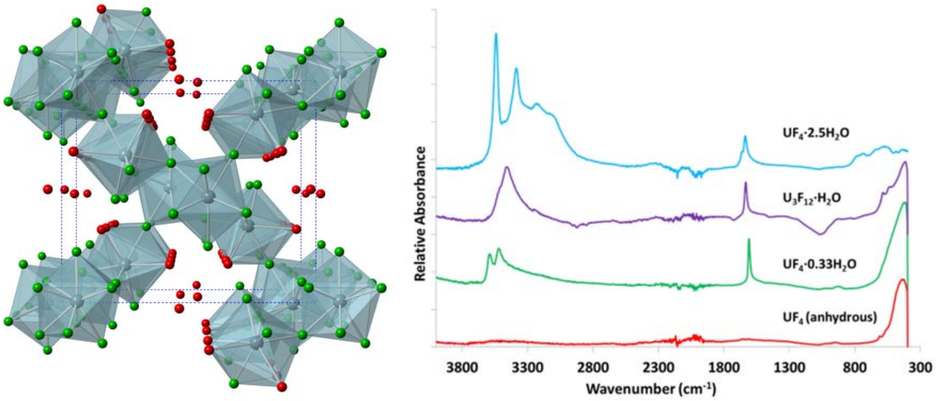

Figure 2: An overall depiction of the 2.5 hydrate showing the interconnectivity of the chains where uranium are blue, fluorine green, and oxygen red (left). FT-IR spectra of anhydrous UF_4 and the three hydrate polymorphs (right).

Two additional characterization methods for probing the macro scale elemental content were explored within FY17 and included SIMS and NMR spectroscopy. SRNL prepared uranyl particle test materials and shipped them to a collaborator at Los Alamos National Laboratory for a proof of concept measurement with a SIMS. Although these specimens did not contain fluorine the exercise established sample preparation technique, shipping requirements, and analysis parameters. Additionally the exercise determined that SRNL sample generation capabilities may be suitable for the generation of uranium particulate reference materials. Experiments to characterize the hydrolysis kinetics via ^{19}F NMR were designed and initiated with a collaborator at the Naval Research Laboratory. The NMR experiments were based on the Raman spectroscopy measurements of UF_4 hydrolysis conducted in FY16. The team designed and built a reaction vessel where water vapor pressure was controlled and delivered to unreacted UF_4 within the spectrometer; the equipment and UF_4 powder were delivered and setup in late FY17. Crystalline forms of $UF_4 \cdot 2.5H_2O$, $U_3F_{12} \cdot H_2O$, and $UF_4 \cdot 0.33H_2O$ were also shipped for ^{19}F magic angle spinning (MAS) NMR characterization. Both the kinetics NMR and MAS-NMR measurements are in progress.

FY2017 Accomplishments

Coupled with the prior FY16 work, this effort has successfully developed an initial chemical and structural basis for understanding UF_4 hydrolysis in the environment.

- Successful demonstration of the advanced characterization technique TEM/EELS to probe the elemental and chemical speciation of partially hydrolyzed UF_4 at the nanoscale.
- Solid state ^{19}F NMR was initiated to characterize the macroscale hydrolysis induced chemical changes.

- Complete Raman, IR, and fluorescence spectroscopy characterization of a series of UF_4 hydrate polymorphs and interpretation of structural, chemical, and spectral phenomena.
- Successful demonstration of SIMS methods for uranium-bearing particle analysis and a resulting peer review publication.

Future Directions

Uranium tetrafluoride hydrolysis characterization has demonstrated a complex series of potential reaction pathways and numerous chemically distinct progeny species. Future work includes finalizing data analysis of photon, electron, and NMR spectroscopy measurements for a variety samples, and a new project start focused on uranium particulate reference materials.

- Measurements of UF_4 hydrolysis by ^{19}F NMR and MAS-NMR have begun; data analysis is ongoing.
- TEM/EELS have been successfully utilized to characterize UF_4 hydrolysis and oxidation; data analysis is ongoing.
- Two publications are currently in progress for the photon based spectroscopy of the UF_4 hydrates, and the TEM/EELS of UF_4 partially hydrated solids.
- The effort to assess the applicability of SIMS methods has resulted in new FY18 project at SRNL funded by the Department of Energy, Nuclear National Security Administration.

FY 2017 Publications/Presentations

1. **Presentation** - “Characterization of Hydrolyzed Uranium Tetrafluoride Solids by Raman Spectroscopy” M. DeVore II, M. Wellons, M. Summer, R. Smith, T. Daroudi, *October Tech Talk*, October 11, 2016,
2. **Presentation** - Wellons, M.S.; DeVore II, M. A.; Rogers, R. A.; Hewitt, J. T, Williamson, T. L.; Tenner, T. J.; Darroudi, T. “Practical Utilization of Uranium-Containing Particulate Test Samples for SEM/EDS and SIMS Automated Particle Analysis Method Validation”, Microscopy and Microanalysis 2017 Conference, St Louis MO, August 2017
3. **Publication** - Wellons, M.S.; DeVore II, M. A.; Rogers, R. A.; Hewitt, J. T, Williamson, T. L.; Tenner, T. J.; Darroudi, T. “Practical Utilization of Uranium-Containing Particulate Test Samples for SEM/EDS and SIMS Automated Particle Analysis Method Validation”, Microsc. Microanal. 23 (Suppl 1), Microscopy Society of America 2017
4. **Publication** – Wellons, M. S.; DeVore II, M. A.; Villa-Aleman, E.; zur Loye, H.; Felder, J. “The Raman and IR Spectroscopy of Uranium Tetrafluoride Hydrates”, *in preparation.*
5. **Publication** – Wellons, M. S.; DeVore II, M. A.; Giannuzzi, G. A. “Transmission Electron Microscopy and Electron Energy Loss Spectroscopy of Partially Hydrated Uranium Tetrafluorides”, *in preparation.*

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Acronyms

EDS – Electron Dispersive Spectroscopy
EELS – Electron Energy Loss Spectroscopy
FIB – Focused Ion Beam
MAS-NMR – Magic Angle Spinning Nuclear Magnetic Resonance
NMR – Nuclear Magnetic Resonance
XRD –X-Ray Diffraction
RH – Relative Humidity
SEM – Scanning Electron Microscopy
SIMS – Secondary Ion Mass Spectrometry
TEM – Transmission Electron Microscopy

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 nature of the effort.

Total Number of Post-Doctoral Researchers

Two postdoctoral researchers worked on the project included Dr. Michael Devore II and Dr. Robert Rogers.