Probing Forensic Signatures of Nuclear Materials


11 July 2014
What is the problem that a Molecular and Chemical Forensic approach is addressing?

• Increasingly varied and asymmetric threats are expanding the scope of nuclear forensics

• Signatures are varied and can evolve, while any given sample may include multiple signatures

• The scale of a signature may be tiny or LARGE

• Accurate, effective technical analysis depends on
  - identifying new signatures
  - understanding measurement limitations
  - evaluating complementary nature between traditional and new measurements
  - assessing the value of the information

• Production, conversion and aging of actinide materials are chemical in nature
What do we mean by chemical speciation?

Physical (or Phase) Speciation
• Refers indirectly to the phase association: dissolved, or associated with various mineral or colloidal phases

Chemical Speciation
• Refers to the chemical form and generally includes a knowledge of phase
• Depending on the type of information, various levels exist
  • Identity of the element
  • Physical state
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  • Identity of the element
  • Physical state
  • Oxidation state
  • Empirical formula
  • Molecular formula
  • Molecular structure
Actinide processing is rich in chemical information

- > 10 phases between UO$_2$ and UO$_3$, in addition to hydrated forms of UO$_3$

- Deceptively simple formula and cubic structure of UO$_2$ masks incredibly complex speciation

- Weathering under environmental conditions may effect changes in morphology, chemical speciation

- Can chemical speciation of major and minor constituents be measured?
- Do signatures of chemical speciation change over time?
- How can we ground these measurements with standards?
What tools provide access to chemical speciation?

**Morphology**
- Scanning Electron Microscopy

**Elemental**
- SEM-Energy Dispersive Spectroscopy
- Inductively Coupled Plasma – Mass Spectrometry

**Structural (lattice)**
- X-ray diffraction analysis
- X-ray Absorption Spectroscopy
- γ-UO₃
Measurement Capabilities

Morphology

- FEI Quanta 200F Field Emission Scanning Electron Microscope
- Bruker D8 ADVANCE powder X-ray diffractometer

Elemental/isotopic Analysis

- Stanford Synchrotron Radiation Lightsource, Menlo Park, CA
- Thermo Finnigan Element XR ICP-MS

Chemical Speciation

- Stanford Synchrotron Radiation Lightsource, Menlo Park, CA
How is local structure through XAFS determined?

**XAFS** - X-ray Absorption Fine Structure
high energy X-rays allow for excitation of core electrons to bound states

**XANES** - X-ray Absorption Near Edge Structure
arises from differences in oxidation state, local structure

**EXAFS** - Extended X-ray Absorption Fine Structure
distribution of interatomic distances around atoms
Systematic experiments on UO$_2$ using EXAFS to measure sensitivity to oxidation.

**With H$_2$O, intermediate temperature**

![Graph showing EXAFS results for UO$_{2+x}$ with H$_2$O.

**Weak CO:CO$_2$ oxidizer, high temperature**

![Graph showing EXAFS results for UO$_{2+x}$ with weak CO:CO$_2$ oxidizer.

Increased oxidation yields monotonic changes.

Reference information is derived from high-purity uranium oxide bulk materials

\[ U^0 \rightarrow UO_2^{2+} \]

\[ UO_2^{2+} + H_2O_2 \xrightarrow{pH 3 \text{ air}} UO_2(O_2)\cdot xH_2O \]

\[ UO_2(O_2)\cdot 2H_2O \xrightarrow{400^\circ C \text{ air}} A-UO_3 \]

\[ A-UO_3 \xrightarrow{900^\circ C \text{ air}} U_3O_8 \]

\[ A-UO_3 \xrightarrow{500^\circ C \text{ H}_2} UO_2 \]

NIST SRM U960
NBL A112A

UO_2(O_2)\cdot xH_2O precipitation

Reaction vessel

Tube furnace
Can trace chemical species be measured from legacy samples of $\text{U}_3\text{O}_8$

<table>
<thead>
<tr>
<th>Precipitate Source</th>
<th>Precipitate</th>
<th>Sample Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNH</td>
<td>UO$_4$</td>
<td>$\text{U}_3\text{O}_8$</td>
</tr>
<tr>
<td>pH 1 20ºC</td>
<td>800ºC</td>
<td></td>
</tr>
<tr>
<td>UNH</td>
<td>UO$_4$</td>
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</tr>
<tr>
<td>pH 1 20ºC</td>
<td>975ºC</td>
<td></td>
</tr>
<tr>
<td>UO$_2$F$_2$</td>
<td>ADU</td>
<td>$\text{U}_3\text{O}_8$</td>
</tr>
<tr>
<td>pH 8.4 20ºC</td>
<td>800ºC</td>
<td></td>
</tr>
</tbody>
</table>

Age of samples: ~2-3 years
Common source of starting material
Preparation scale: 10 g
Comparison of SEM images of $\text{U}_3\text{O}_8$ materials at time 0

**S1**

- $900^\circ\text{C}$
- $\text{A-UO}_3 \rightarrow \text{U}_3\text{O}_8$
- Air

**L1**

- $20^\circ\text{C}$
- $800^\circ\text{C}$
- $\text{UNH} \rightarrow \text{UO}_4 \rightarrow \text{U}_3\text{O}_8$
- pH 1

**L2**

- $20^\circ\text{C}$
- $975^\circ\text{C}$
- $\text{UNH} \rightarrow \text{UO}_4 \rightarrow \text{U}_3\text{O}_8$
- pH 1

**L3**

- $20^\circ\text{C}$
- $800^\circ\text{C}$
- $\text{UO}_2\text{F}_2 \rightarrow \text{ADU} \rightarrow \text{U}_3\text{O}_8$
- pH 8.4
Comparison of reference lines with pXRD patterns of U$_3$O$_8$ materials identifies speciation

A-UO$_3$ $\rightarrow$ U$_3$O$_8$
900ºC

UNH $\rightarrow$ UO$_4$ $\rightarrow$ U$_3$O$_8$
900ºC

UNH $\rightarrow$ UO$_4$ $\rightarrow$ U$_3$O$_8$
800ºC

UO$_2$F$_2$ $\rightarrow$ ADU $\rightarrow$ U$_3$O$_8$
20ºC

20ºC 975ºC
UNH $\rightarrow$ UO$_4$ $\rightarrow$ U$_3$O$_8$
pH 1

20ºC 800ºC
UO$_2$F$_2$ $\rightarrow$ ADU $\rightarrow$ U$_3$O$_8$
pH 8.4

800ºC

20ºC 800ºC
A-UO$_3$ $\rightarrow$ U$_3$O$_8$
900ºC

air
EXAFS of $\text{U}_3\text{O}_8$ materials reveals disorder

**Graph:**

- **S1 t=0**
- **L1 t=0**
- **L2 t=0**
- **L3 t=0**

**Legend:**

- $\text{UO}_3 \rightarrow \text{U}_3\text{O}_8$
- $\text{UNH} \rightarrow \text{UO}_4 \rightarrow \text{U}_3\text{O}_8$
- $\text{pH} 1$
- $(\text{UO}_2(\text{O}_2) \cdot x\text{H}_2\text{O})$
- $\text{UNH} \rightarrow \text{UO}_4 \rightarrow \text{U}_3\text{O}_8$
- $\text{pH} 1$
- $(\text{U}_3\text{O}_8 + \text{UO}_3 \cdot x\text{H}_2\text{O})$
- $\text{UO}_2\text{F}_2 \rightarrow \text{ADU} \rightarrow \text{U}_3\text{O}_8$
- $\text{pH} 8.4$
- $(\text{U}_3\text{O}_8 + \text{UO}_2\text{F}_2 \cdot x\text{H}_2\text{O})$
Aging Vessels and Circulating Bath

Anovitz, L. M.; Ricuputi, L. R.; Cole, D. R.; Gruszkiewicz, M. S.; Elam, J. M.
Do these chemical signatures change over time?

Constant relative humidity (± 2%) is produced by an excess of a water soluble salt in contact with its saturated solution.

• ASTM International, Designation: E104-02, Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions

• CRC Manual, Constant Humidity Solutions

\[ RH = A \times \exp\left(\frac{B}{T}\right) \]

Lithium Iodide: 
25% RH at 278.15 K  
15% RH at 310.15 K

Potassium Nitrate: 
97% RH at 278.15 K  
89% RH at 310.15 K

Relative Humidity = Actual Vapor Density
Saturation Vapor Density

Conditions | Water vapor density
---|---
LTLH | 1.7e-06 g/cm³
HTLH | 6.6e-06 g/cm³
LTHH | 6.7e-06 g/cm³
HTHH | 39e-06 g/cm³
Liquid water | ~1 g/cm³

Note: LA-UR 14-24839
Morphology of S1 at all conditions after 0 and 2 years

- A-UO₃ → U₃O₈
  - 900ºC
  - Air

- LANL U₃O₈ T=0 yrs.
- T=2 yrs. LTHH-5ºC @ 97% RH
- T=2 yrs. LTHH-5ºC @ 25% RH
- T=2 yrs. HTHH-37ºC @ 15% RH
- T=2 yrs. HTHH-37ºC @ 89% RH
pXRD patterns of S1 at all conditions after 3 years reveals speciation

A-\(\text{UO}_3\) \(\rightarrow\) \(\text{U}_3\text{O}_8\)

900\(^\circ\)C
air

\(\text{S1, } t=0\)
\(\text{S1, HTHH(3 yr)}\)
\(\text{S1, LTHH(3 yr)}\)
\(\text{S1, HTLH(3 yr)}\)
\(\text{S1, TLTHH(3 yr)}\)

01-073-6293 > \(\text{U}_3\text{O}_8\) - Uranium Oxide

00-050-1601 > Schoepite - \((\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}\)
EXAFS of S1 at all conditions after 0 and 3 years

\[ \text{A-UO}_3 \rightarrow \text{U}_3\text{O}_8 \quad 900^\circ \text{C} \quad \text{air} \]

**Graph:**
- S1 LTHH (3 yr)
- S1 HTHH (3 yr)
- S1 LTLH (3 yr)
- S1 HTLH (3 yr)
- S1 t=0

**Graph axes:**
- X-axis: R - \( \phi \) (Å)
- Y-axis: Magnitude of FT \( k^2 \chi(k) \)

**Images:**
- LANL UO3 T=0 yrs
- HTTH-57C @ 15% RH
- HTTH-37C @ 35% RH

**Legend:**
- U-O
- U-U
Morphology of L2 U₃O₈ at all conditions after 0 and 2 years

20°C, 975°C
UNH → UO₄ → U₃O₈
pH 1
(U₃O₈ + UO₃·xH₂O)

T=2 yrs.
LTLH-5°C @ 25% RH

T=2 yrs.
HTHH-37°C @ 97% RH

T=2 yrs.
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T=2 yrs.
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pXRD patterns of L2 U₃O₈ at all conditions after 2 years reveals speciation

20°C  975°C
UNH → UO₄ → U₃O₈  (U₃O₈ + UO₃·xH₂O)
pH 1

UNH → UO₄ → U₃O₈

20ºC  975ºC

UNCLASSIFIED
EXAFS of L2 U$_3$O$_8$ at all conditions after 0 and 2 years

20ºC
UNH → UO$_4$ → U$_3$O$_8$

975ºC
pH 1
(U$_3$O$_8$ + UO$_3$·xH$_2$O)

20ºC

U-O

U-U

Magnitude of FT $k^3 \chi(k)$

R + $\Delta$ (Å)

L2 HTHH (2 yr)
L2 LTLH (2 yr)
L2 HTLH (2 yr)
L2 t=0
Morphology of L3 U₃O₈ at all conditions after 0 and 2 years

20°C, 800°C
UO₂F₂ → ADU → U₃O₈
pH 8.4

(U₃O₈ + UO₂F₂·xH₂O)

20ºC, 800ºC
UO₂F₂ → ADU → U₃O₈
pH 8.4

(U₃O₈ + UO₂F₂·xH₂O)
pXRD patterns of L3 U$_3$O$_8$ at all conditions after 2 years reveal oxidation.
EXAFS of L3 U₃O₈ at all conditions after 0 and 2 years

20°C  800°C
UO₂F₂ → ADU → U₃O₈  (U₃O₈ + UO₂F₂·xH₂O)
pH 8.4
20ºC  800ºC
(U₃O₈ + UO₂F₂·xH₂O)

Magnitude of FT $k^3 \chi(k)$

R - φ (Å)

- L3 LTHH (2 yr)
- L3 HTHH (2 yr)
- L3 LTLH (2 yr)
- L3 HTLH (2 yr)
- L3 t=0
Morphology of L1 at all conditions after 0 and 2 years

$\text{T=2 yrs. LTLH-5^\circ C @ 25\% RH}$

$\text{T=2 yrs. HTHH-37^\circ C @ 89\% RH}$

$\text{L1 T=0 yrs.}$

$\text{20^\circ C}$  
$\text{800^\circ C}$  
$\text{UNH \rightarrow UO_4 \rightarrow U_3O_8}$  
$\text{pH 1}$  

$(UO_2(O_2)\cdot xH_2O)$

$\text{T=2 yrs. HTLH-37^\circ C @ 15\% RH}$
pXRD patterns of L1 U₃O₈ at all conditions after 3 years reveals hydration

\[
UNH \rightarrow UO_4 \rightarrow U_3O_8 \quad (UO_2(O_2) \cdot xH_2O)
\]
EXAFS of L1 U$_3$O$_8$ at all conditions after 0 and 3.5 years

20°C
UNH $\rightarrow$ UO$_4$ $\rightarrow$ U$_3$O$_8$  (UO$_2$(O$_2$)$_x$·xH$_2$O)
pH 1

Magnitude of FT $k^2 \chi(k)$

R - $\varphi$ (Å)

- L1 LTLH (3.5 yr)
- L1 HTLH (3.5 yr)
- L1 LTHH (3.5 yr)
- L1 HTHH (3.5 yr)
- L1 t=0
Conclusions

• Processing of uranium oxides is chemical in nature, providing opportunities for measurements of chemical signatures

• Results from an integrated approach rely upon synthesis, spectroscopy and morphologic characterization of a variety of materials

• Chemical speciation following aging under environmental conditions is providing insights into chemical transformations

• Speciation can be characterized, not only by \( \mu \)-XRD and \( \mu \)-XANES spectroscopy, but also via \( \mu \)-EXAFS measurements, an incisive technique for determining chemical speciation and changes in local structure
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