Benzotriazolium Metallate for ^{99}Tc Immobilization and Remediation

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Affiliated Lab: Los Alamos National Laboratory

NSSC3 Kickoff Meeting and Advisory Board Review
April 19-20, 2022

Introduction

Department and University: Chemistry, Radiochemistry Program, University of Nevada Las Vegas

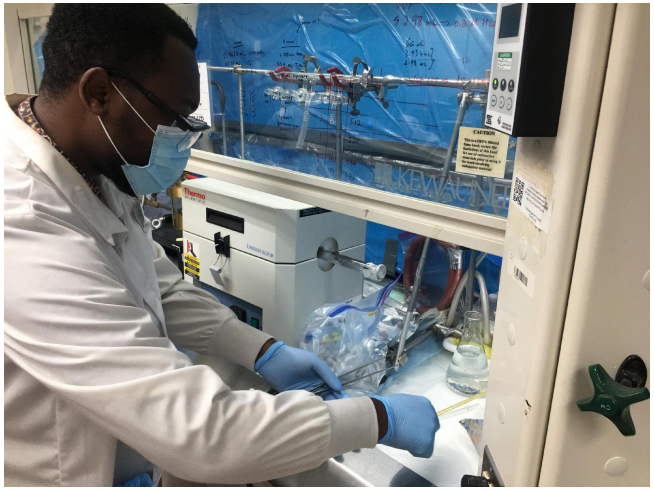
Academic Advisor: Dr. Frederic Poineau

NSSC Research Focus Areas: Materials science

Planned Graduation Date: Summer 2022

Lab Mentor and Partner Laboratory: Dr. Jeremy 'Jez' Inglis, LANL

Mission Relevance of Research: Supports the development of nuclear technology; trains and develops nuclear experts; characterizes nuclear materials



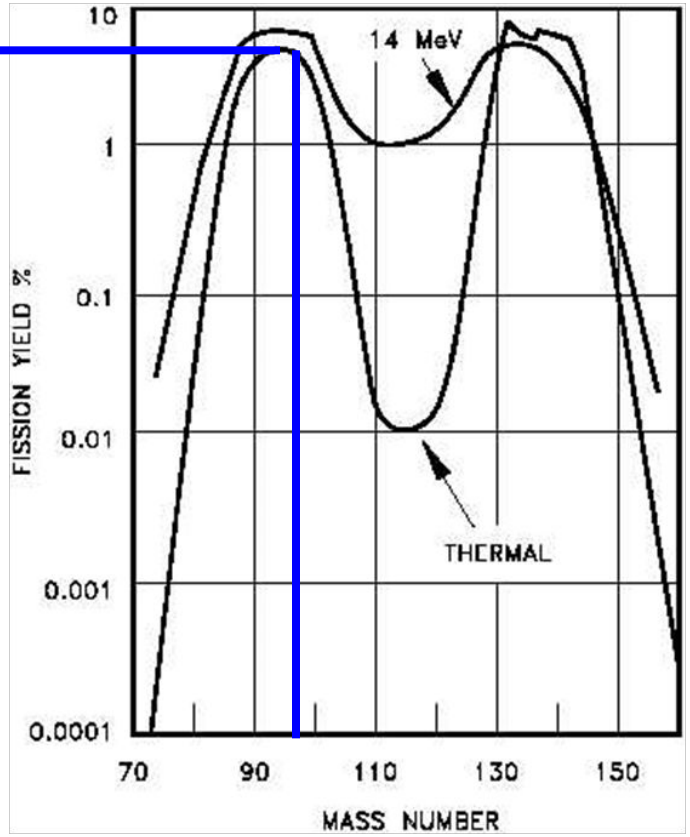
Outline

1. Introduction
    - 1.1. Nuclear fuel cycle
    - 1.2. Technetium behavior
2. Experimental methods
    - 2.1. Benzotriazole
    - 2.2. Precipitation of $[MO_4]^-$
3. Results and Discussion
    - 3.1. Structural characterization
    - 3.2 Spectral and thermal studies
4. Summary
    - 4.1. Future work

Formation of ^{99}Tc

- Nuclear fuel cycle of U/Pu
  - Fission of ^{235}U/^{239}Pu
    - Fission products
      - A = 99 isobar (^{99}Tc)
- Spent nuclear fuel
  - ^{99}Tc dominant specie
  - Alloyed with Mo–Ru–Pd–Rh
    - ^{99}Tc metallic
  - One ton (MT) of spent fuel contains 0.8 kg of ^{99}Tc
    - 2 tons of ^{99}Tc/year from nuclear industry

^{99}Tc

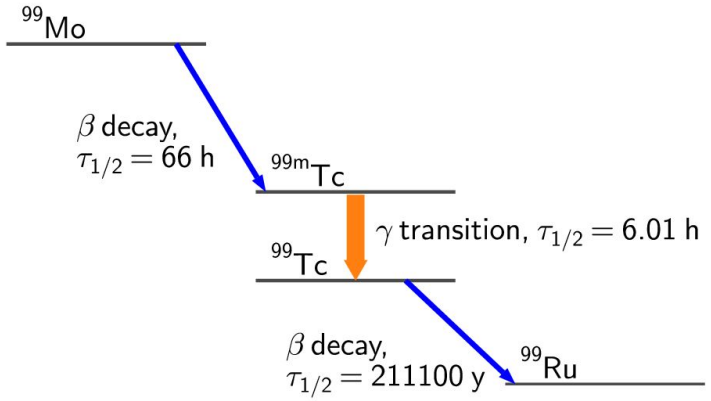


Nuclear fuel cycle

- **Nuclear fuel reprocessing**
  - Dissolution of spent fuel in nitric acid
  - Extraction of U along with Tc
    - Nitrato-pertechnetato-TBP complex of UO_2^{2+}
  - $[UO_2(NO_3)_2 \cdot 2TBP]_{(org)} + [TcO_4]^-_{(aq)} \longleftrightarrow [UO_2(NO_3)(TcO_4) \cdot 2TBP]_{(org)} + NO_3^-{}_{(aq)}$
  - Enrichment of U
    - Conversion of UO_2 to UF_6
    - Extracted Tc converted to TcF_6
  - In 35 tons of recovered U
    - 0.14 kg of Tc returns to the fuel
    - 30 kg of Tc enters high level waste

Occurrence of ^{99}Tc

- **Environmental occurrence**
  - **Nuclear industry**
    - **Hanford site tanks**
      - **1310 ± 220 Kg (^{99}Tc)**
  - **Radiopharmaceutical**
    - **Imaging agent (^{99m}Tc)**

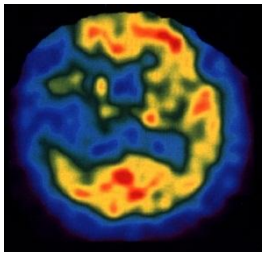


^{99}Tc

- β-Emitter
- E_{max} = 294 keV
- $t_{1/2} = 2.1 \cdot 10^5$ a
- fission yield : 6.1% from ^{235}U
- 0.8 kg/ Metric ton of spent fuel

^{99m}Tc

- pure γ-Emitter
- E_{max} = 140 keV
- $t_{1/2}$ = 6 h
- available from ^{99}Mo
- nanomolar scale



Motivations

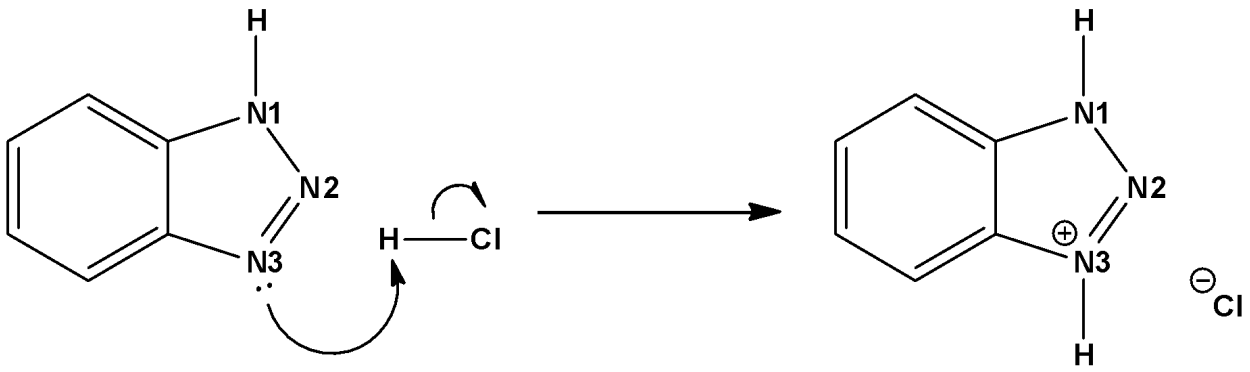
- **Problems**
  - **High mobility $[^{99}TcO_4]^-$**
    - **Migration to geological environment**
  - **Highly soluble under oxidizing conditions**
    - **Hanford tanks**

GOAL

Immobilize $[^{99}TcO_4]^-$ anions and propose avenue for nuclear waste remediation

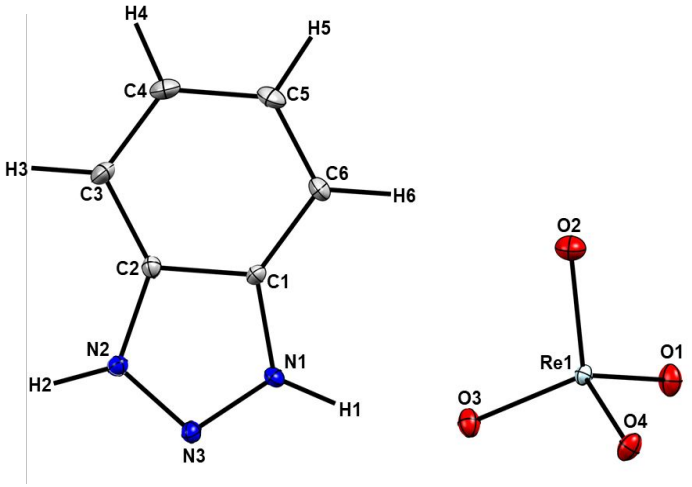
Methods

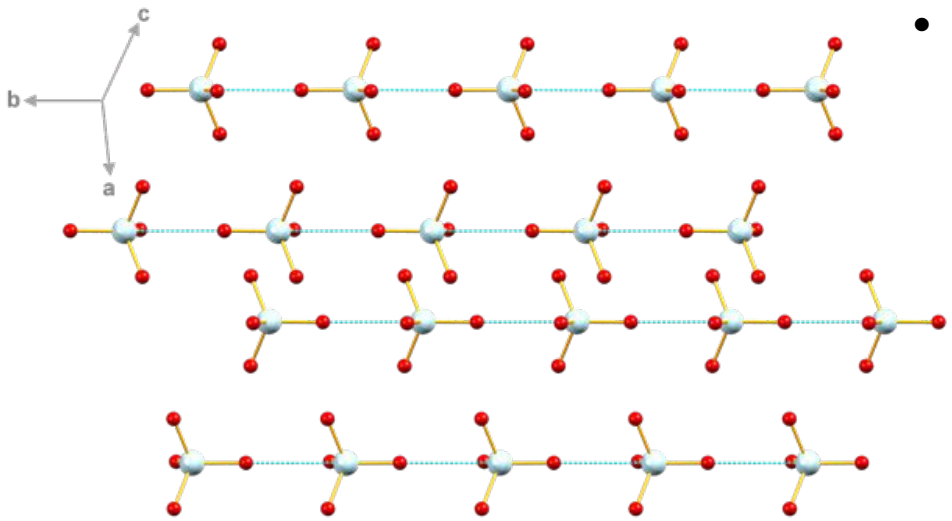
- Tc and Re often form analogues composition compounds
  - Group (VII) transition metal (Mn, Tc, Re)
- Precipitation of $[^{99}TcO_4]^-$ anions
  - Studied with organic and inorganic cations
- This study: 1H-benzotriazole (BTA)
  - Neutral compound
  - Extensively studied for its anticorrosion properties



Structural analysis

- Structure description: $[C_6H_6N_3][ReO_4]$
- Monoclinic space group $P2_1/c$
- Distorted tetrahedral (T_D) $[ReO_4]^-$ anion
  - Short Re-$O_{1\&2}$ bond: 1.725(3) Å & 1.730(2) Å
  - Long Re-$O_{3\&4}$ bond: 1.740(2) Å & 1.739(2) Å

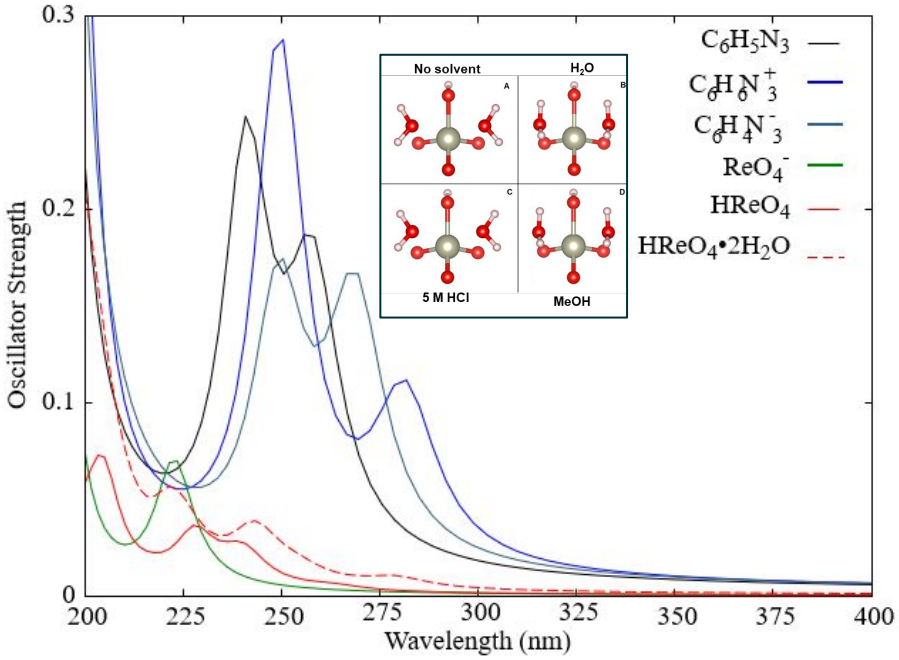


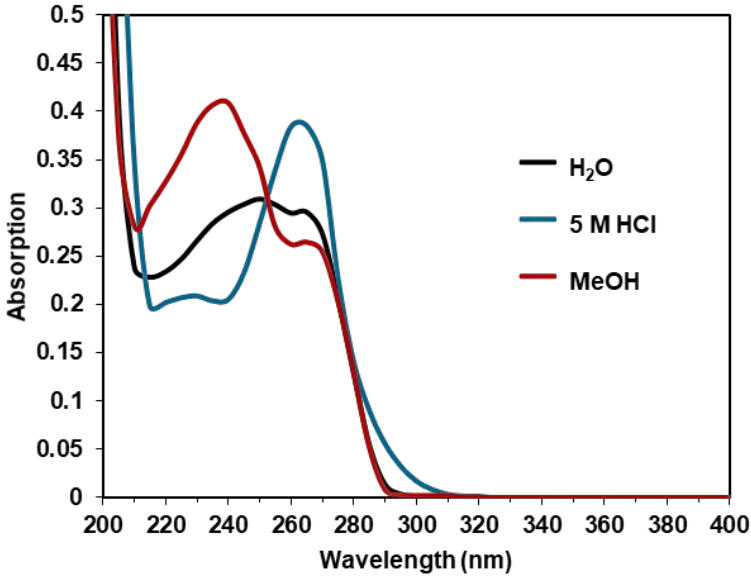


- Hydrogen bond interactions
  - $[C_6H_6N_3]^+$ cation and $[ReO_4]^-$ anion
    - C6-H6···O2 and N1-H1···O3
  - Neighboring $[ReO_4]^-$ anion
    - Re-O1···Re-O1 contacts: 3.188 Å

Spectroscopic analysis

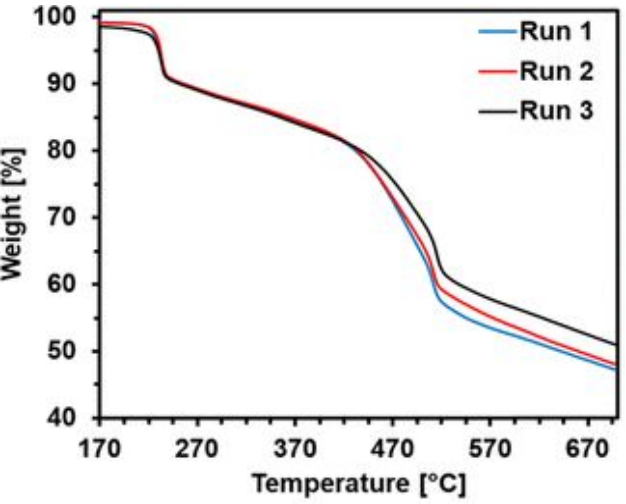
- **UV-Vis measurements**
  - **Solvent dependency**
  - **Wavelength shifts**

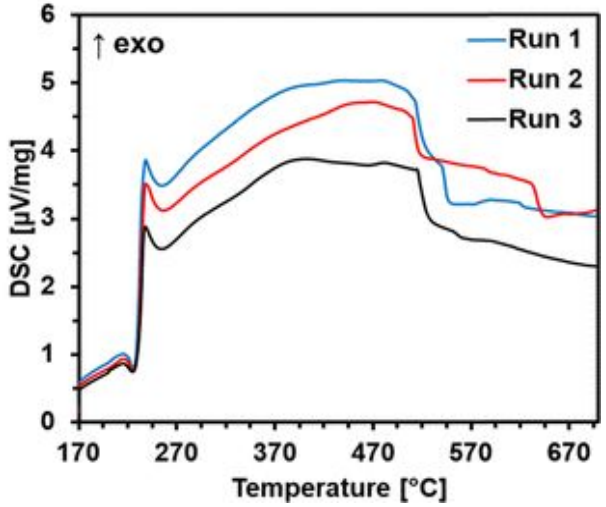




- **UV-Vis measurements: DFT**
  - **Absorption maxima are solvent dependent**
    - **Based on BTA / $[ReO_4]^-$ species in solution and pKa**
    - **Neutral BTA, protonated and deprotonated species**

Thermal analysis: TGA



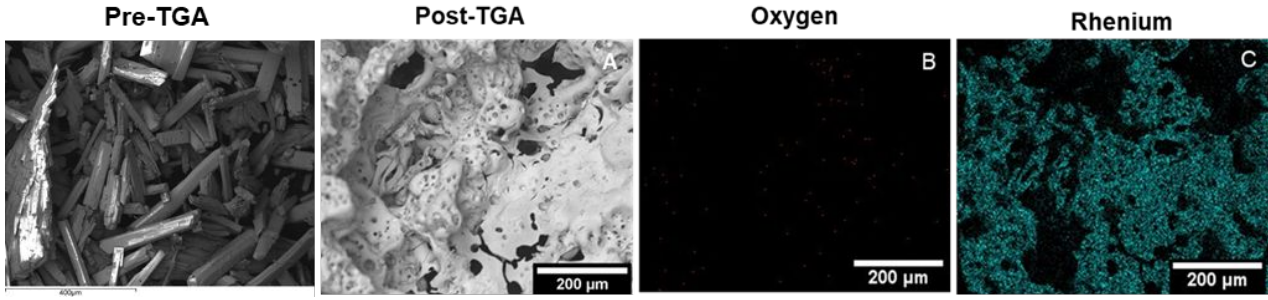


- **Thermal analysis: TGA/DSC**
  - **Studied under argon at 10 K/min**
  - **Temp: 20 to 700 °C**
    - **Two stage decompositions**

Step 1: Reduction of $[ReO_4]^-$ to ReO_2

Step 2: $ReO_{2(s)} + 2\,CO \rightarrow Re_{(s)} + 2\,CO_{2(g)}$

$ReO_{2(s)} + 2\,H_{2(g)} \rightarrow Re_{(s)} + 2\,H_2O_{(g)}$



Thermal studies

Re Metal	Composite	Temp [°C]	Time [min]	Atmosphere	Note
	$C_6H_6N_3[ReO_4]$	700	40	O_2	–
1	$C_6H_6N_3[ReO_4]$	700	40	Ar	Crystalline
1a	$C_6H_6N_3[ReO_4]$	900	30	Ar	Crystalline
1b	$C_6H_6N_3[ReO_4]$	900	240	Ar	Crystalline
2	$C_6H_5N_3:Re_2O_7$	350	30	Ar	Amorphous
2a	$C_6H_5N_3:Re_2O_7$	900	120	Ar	Crystalline
3	$C_6H_5N_3:NH_4ReO_4$	500	40	Ar	ReO_2
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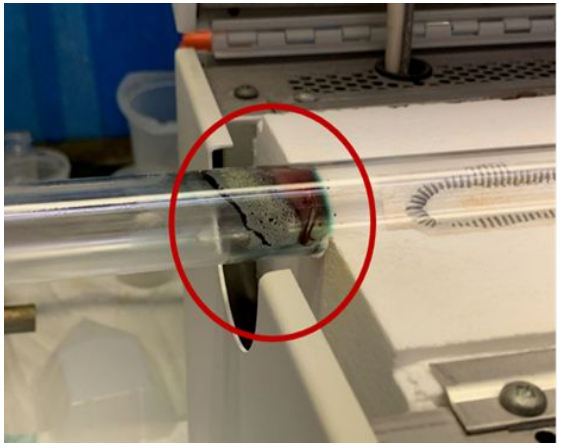
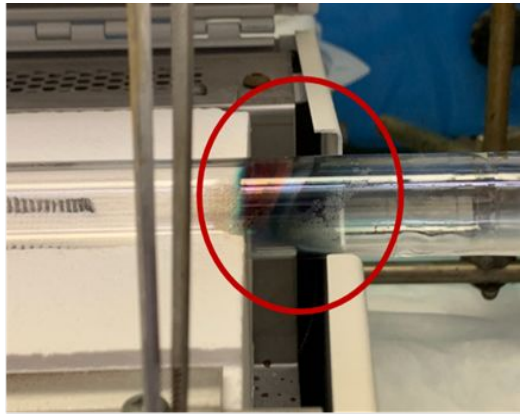
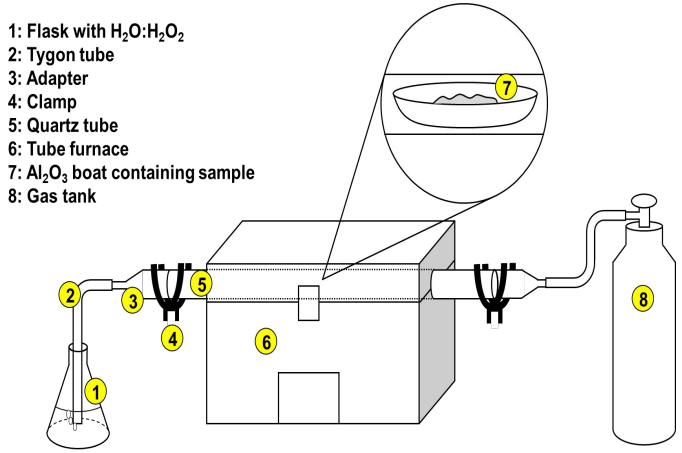
- **Tube furnace**
  - **Volatilization in O_2 atm**
  - **Formation of Re oxides**







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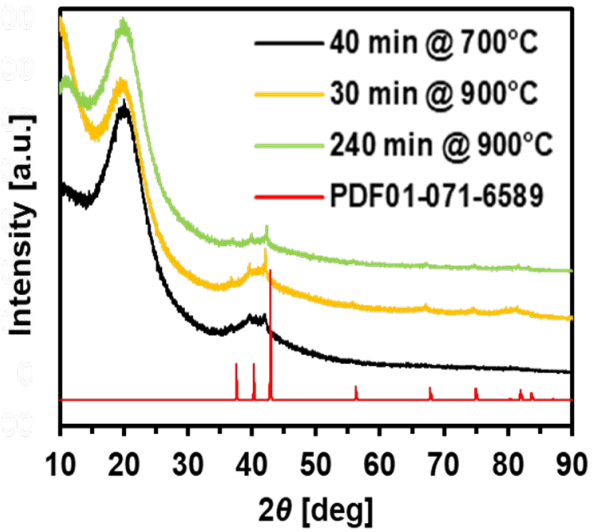

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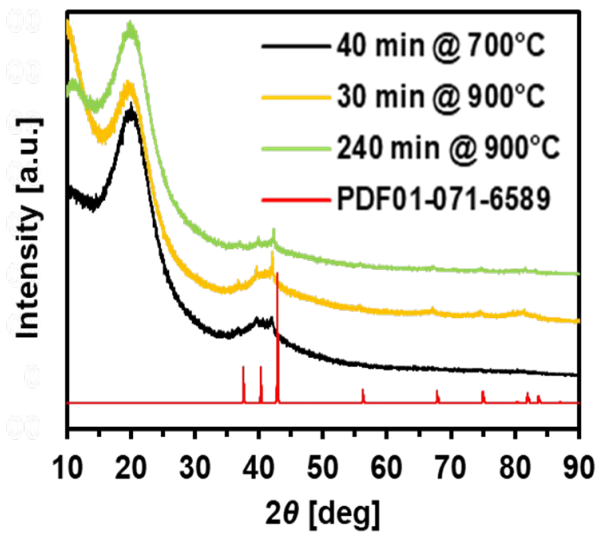

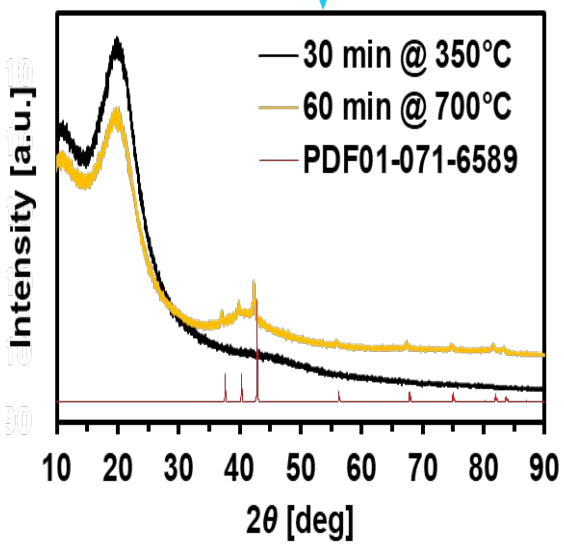

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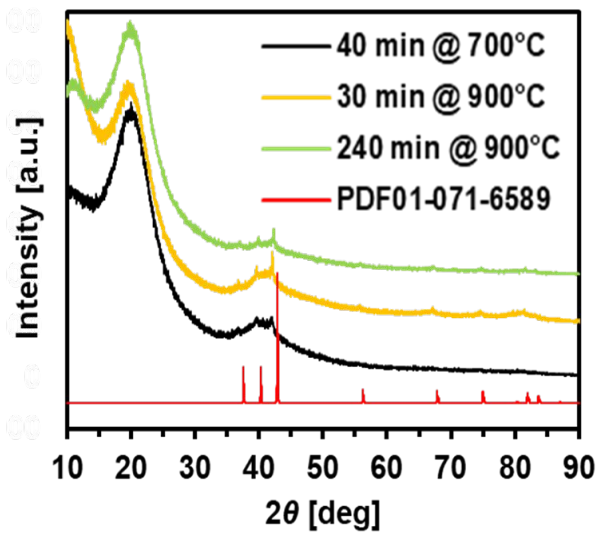

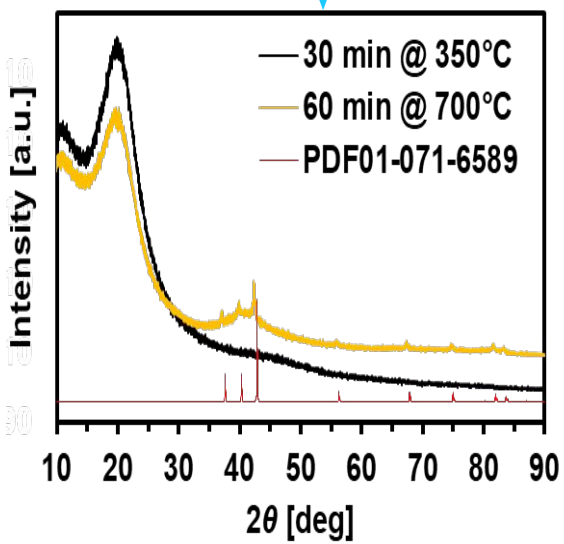

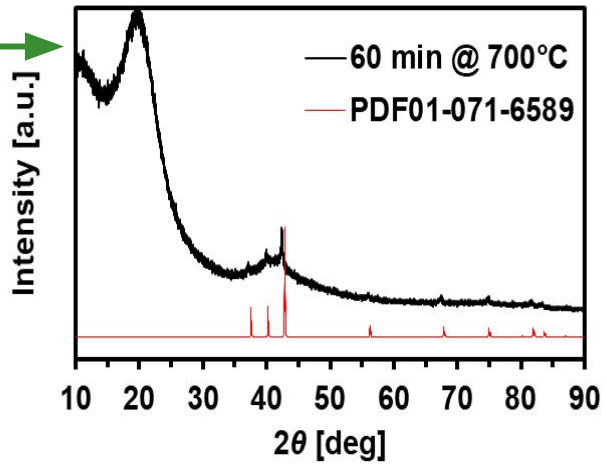

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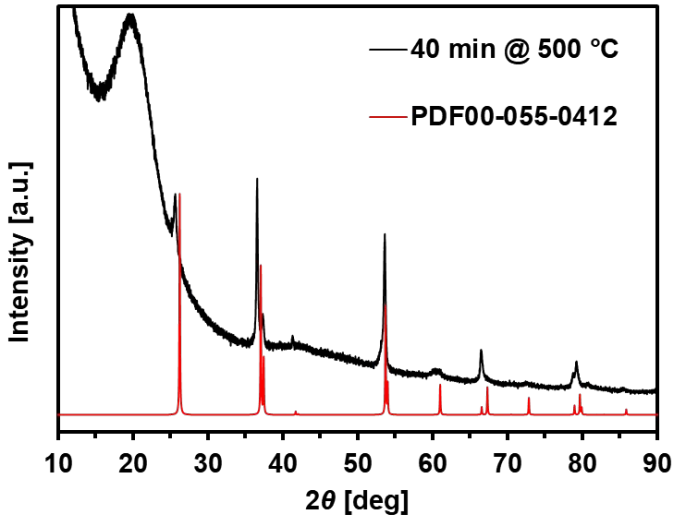

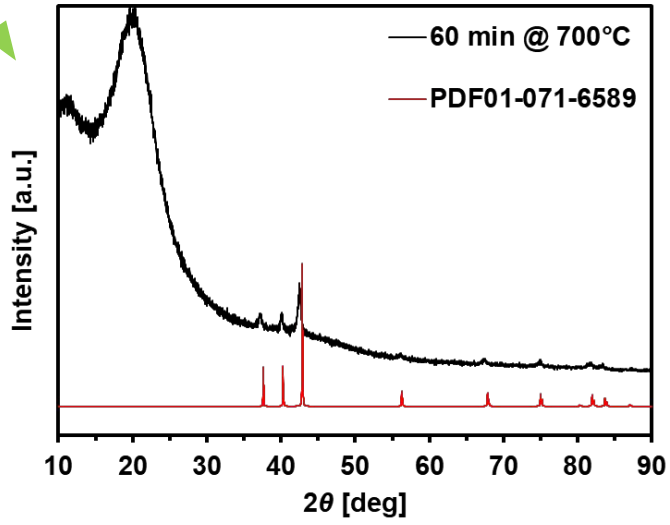

- **Tube furnace: mixed materials**
  - **$NH_4[ReO_4]:C_6H_5N_3$**
  - **Formation of ReO_2 (1:1 mol)**
  - **Formation of Re metal (1:5 mol)**

Summary

- **Expand the use of benzotriazole (anticorrosive)**
  - **Precipitate and immobilize $[MO_4]^-$ (M = 99Tc, Re) ions**
  - **Potential application for nuclear waste**
    - **Recall: ~1310 ± 220 Kg of 99Tc in Hanford tanks**
  - **Effort to convert HBTA$[MO_4]$ to metallic species**
    - **Various atmospheres: 350-900 °C**
    - **Provide the first use of BTA as reducing agent for metal production**

Future work:

- **Report the study on ^{99}Tc**
  - **COVID-19 slows the progress**
- **Study the chemistry of BTA in simulated tanks environment**

The NSSC Experience

- **NSSC-LANL interactions**
  - Nuclear safeguards summer school – Summer 17
  - Keepin nonproliferation program – summer 17
  - G.T. Seaborg Summer Fellowship – summer 18-19

- **NSSC-GWU interactions**
  - Nuclear Security and Policy Boot Camp – summer 2019

- **DOE Innovations in Nuclear Technology R&D Awards - 2020**
  - 1st place in Material Recovery % Waste Form Development

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