Safeguarding Protactinium through Surrogate Niobium Chemistry

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Nuclear Science & Security Consortium

Objective & Mission Relevance

Objective

Gain insight on **the redox and coordination chemistry** of thorium fuel cycle intermediate **protactinium (Pa)** by studying the electrochemical behavior and oxidation state of **surrogate Niobium (Nb)** while complexed with biologically-inspired chelators with the purpose of applying this knowledge for **improved safeguards** considerations and **aqueous reprocessing**.

Mission Relevance & Motivation

Safeguards requires:

- Increased knowledge of Pa separation behavior.
- More comprehensive safeguards practices for ^{233}Pa and ^{233}U.[1]

Group V chemistry is underdeveloped due to:

- A high tendency towards hydrolysis & stable oxide products.[2,3,4]
- For Pa: radioactivity and scarcity of material as well.

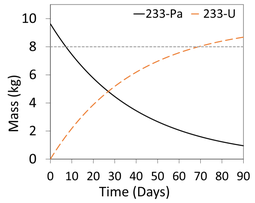


Figure 1: Mass evolution of 200 MCi pure ^{233}Pa (~10kg) decaying into ^{233}U over the course of 3 months.

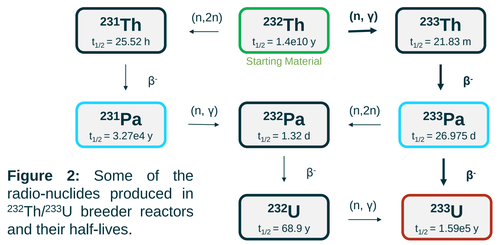


Figure 2: Some of the radio-nuclides produced in ^{232}Th/^{233}U breeder reactors and their half-lives.

Background: Group V Chemistry

Physical Properties

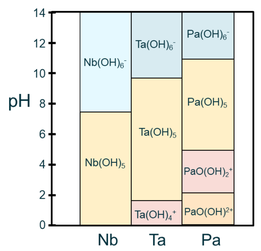
Commonly **5+ or 4+** in aqueous solution. **Hydrolysis** occurs readily in non-complexing media, decreasing in the order:[2,3,4,5]

Nb > Ta >> Pa

Thus, conditions that allow successful complexation of Nb (vs. hydrolysis) should work for Ta & Pa with less issue.

Nb_2O_5 and Pa_2O_5 are highly **insoluble** in all but HF, and slightly in oxalic acid.[3,4,5]

Figure 3: Predominance diagram for mononuclear species of pentavalent Nb, Ta, and Pa in non-complexing media, highlighting the effects of hydrolysis on speciation.[4]



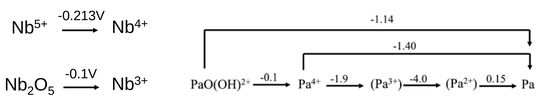


Figure 4: Redox potentials for Nb and Pa.
(a) Single electron reduction potential (V/SHE) of Nb(V) in 10.75 M HCl w/ a mercury-pool working electrode.[6]
(b) Two electron reduction potential (V/SHE) of Nb(V) in aqueous solution.[7]
(c) Latimer Diagram for Pa in aqueous solution (V/SHE).[7]

Surrogate Niobium Chemistry with Biologically-Inspired Chelators

The "Niobium – 3,4,3-LI(1,2,-HOPO)" Complex

Synthesis of a niobium complex with biologically-inspired chelator 3,4,3-LI(1,2-HOPO) aka HOPO (Figure 5).

Aqueous Synthesis: 100 µM $NbCl_5$ in 10 M HCl added to 1 eq. of HOPO

- **UV-Vis** in 1 M HCl (Figure 6) suggests complexation. The complex is a bright yellow in solution, as evidence by absorption of blue wavelengths.
- **Cyclic Voltammetry (CV)** (Figure 7) shows the Nb(V/IV) potential in 10 M HCl performed under Argon.

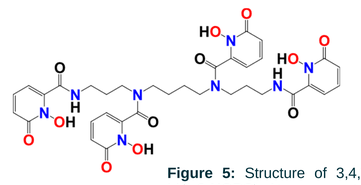


Figure 5: Structure of 3,4,3-LI(1,2-**HOPO**). Atoms expected to coordinate to metal centers are shown in red.

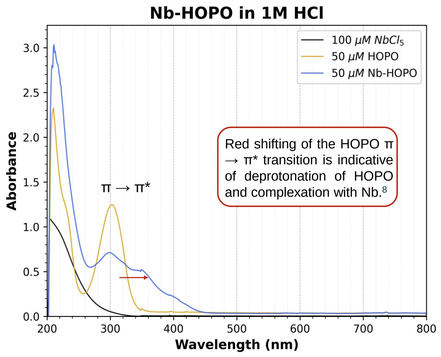
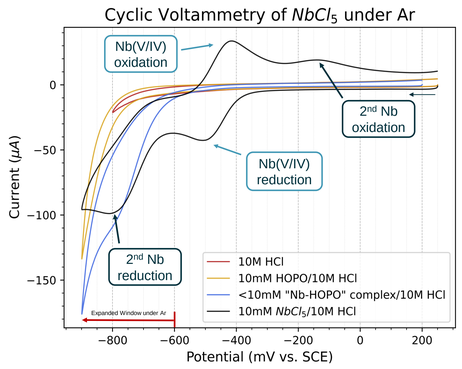


Figure 6 (left):
UV-Vis spectra of $NbCl_5$ (black), HOPO (yellow), and the "Nb-HOPO" complex (blue) in 1M HCl. Spectra taken in VWR Spectrosil quartz cuvettes. Note the source changes at 350nm.

Figure 7 (right):
Cyclic voltammogram of $NbCl_5$ (black), HOPO (yellow), and the "Nb-HOPO" complex (blue) in 10M HCl. Working electrode: glassy carbon, Counter electrode: Pt, reference electrode: Hg/Hg_2Cl_2,. Scan rate of 50 mV/s used. Performed under Ar.



Next: *Organic, air/moisture free, synthesis intended to reduce hydrolysis of $NbCl_5$ to increase synthetic yield, explore the solubility of HOPO in organic media, and to apply to future air-free protactinium-HOPO synthesis.*

Protactinium Purification Plans

Anion-exchange columns were used to remove ^{233}Pa from ^{237}Np. Procedure adapted from Mounce et al.[9] The resin was characterized by high purity germanium (HPGe) gamma spectroscopy (Figure 10).

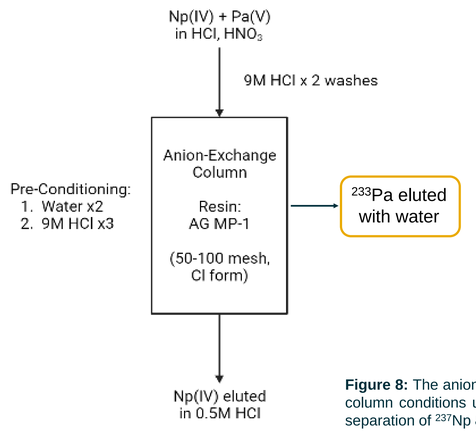


Figure 8: The anion exchange column conditions used in the separation of ^{237}Np & ^{233}Pa.

A legacy oxide source containing ^{231}Pa will be purified via base precipitation. This procedure is based on previous work done by Brown and Whittaker[10] and Wilson et al.[11]

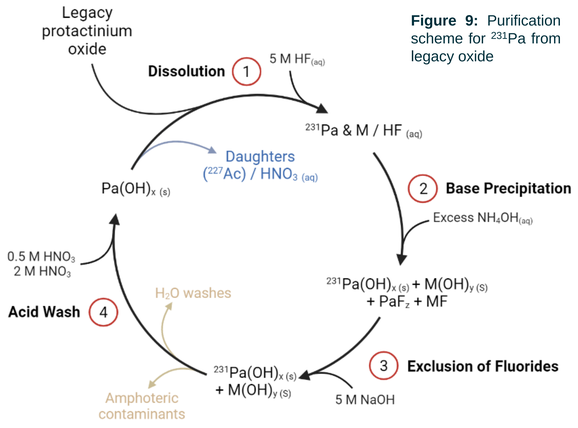


Figure 9: Purification scheme for ^{231}Pa from legacy oxide

^{233}Pa Characterization

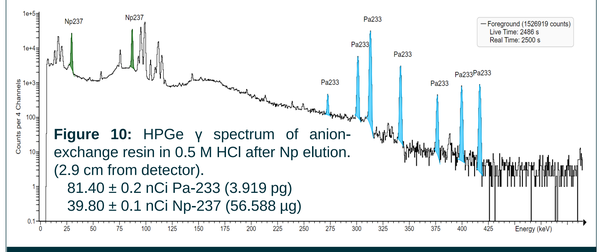


Figure 10: HPGe γ spectrum of anion-exchange resin in 0.5 M HCl after Np elution. (2.9 cm from detector).
81.40 ± 0.2 nCi Pa-233 (3.919 pg)
39.80 ± 0.1 nCi Np-237 (56.588 µg)

Future Direction

Niobium HOPO Complex

- Further optimization of Nb-HOPO synthesis, in aqueous and organic media
- Explore ligand variations
- Characterize via NMR, XRD and XAS (XANES/EXAFS)

Protactinium Chemistry

- Purification of ^{231}Pa from daughters via precipitation
- Based on optimized conditions from Nb-HOPO synthesis, complex Pa with HOPO.
- Characterize via NMR, UV-Vis, XRD, XAS, etc.

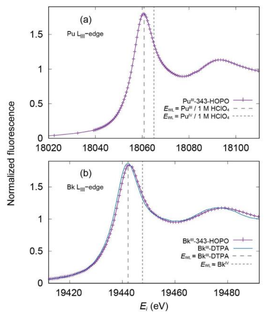


Figure 11: Example XANES spectra showing the oxidation states of Pu (a) and Bk (b) when complexed to HOPO.[12]

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