Electrochemical Manipulation and Radiolytic Evaluation of Organic Phase Neptunium

December 2021

Gregory P Horne
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Gregory P Horne

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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U.S. Department of Energy
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Electrochemical Manipulation and Radiolytic Evaluation of Organic Phase Neptunium

INL/MIS-21-65194
Advanced Used Nuclear Fuel Reprocessing

Solvent Extraction Reprocessing
Ligands/organic diluent: HNO₃/H₂O (± additives)

Gaseous Phase

Organic Phase

Aqueous Phase

Precipitation
Oxide Layer
Structural Materials

Figure 1. Concentration of NpO₂⁺ (■) and NpO₂²⁺ (●) ions as a function of absorbed gamma dose for formally 2 mM NpO₂²⁺ in 0.5 M HNO₃.

Np⁴⁺/NpO₂²⁺ → Extractable

NpO₂⁺ → Inextractable


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Electrochemical Manipulation of Neptunium

Figure 2. Americium speciation as a function of electrolysis time in 0.1 M HNO₃ and 0.9 M NaNO₃ using a p-tpy–derivatized ITO electrode at an applied potential of 2.25 V.
Research Methodology

Material Source (INL)
- On hand Ce/U/Np stocks at INL Radiochemistry Laboratory (RCL).

Electrochemical Manipulation (INL/FSU)
- Apply a series of novel functionalized electrodes to biphasic solutions of complexed Ce/U/Np to manipulate the oxidation state.
- Measure Ce/U/Np redox distributions and lifetimes with a combination of on hand in-situ optical and electrical techniques.

$^{60}$Co-Gamma Irradiations (INL)
- Irradiate novel electrodes in the absence of Ce/U/Np to evaluate their radiolytic stability.
- Irradiate electrochemically manipulated solutions to determine the lifetime of non-traditional Ce/U/Np oxidation states in organic media.

Pulsed Electron Irradiations (BNL)
- Ce/U/Np samples – prepared in custom-made, electrochemically modified, sealed cuvettes – will be shipped to BNL to perform reaction kinetic measurements to support the development of predictive models.

Research Team

Gregory P. Horne (INL)

Jacy K. Conrad (INL)

Jeffrey R. McLachlan (FIU)

Christopher J. Dares (FIU)

Benefits

Products
- Peer-reviewed journal manuscript with the intention of submission to either *JACS* (IF 15.42, 2020) or *Inorganic Chemistry* (IF 5.165, 2020).
- Process feasibility assessment.
- Talent pipeline investment through *Office of Science Graduate Student Research* internship.

Harvest Strategy
- **DOE Office of Nuclear Energy – Fuel Cycle Technologies – Separations and Waste Forms**: “developing innovative processes to recover uranium and other materials from UNF while improving proliferation resistance, reducing losses, and minimizing waste.”
- **DOE Office of Science Basic Energy Sciences - Heavy Element Chemistry** program: “understand the underlying chemical and physical principles that determine actinide behavior.”
- **Office of Science - Early Career Research Program** to “bolster the nation’s scientific workforce by providing support to exceptional researchers during the crucial early career years.” *This has been applied for by the PI.*
Addressing Queries

Reviewer #1

• “This is an excellent scientific proposal that merits funding.”

Reviewer #2

• “It is not clear to me why the proposal focuses on "identify the accessible electrochemical Np complexes in the organic phase" if the oxidation process is done in the organic phase, this can among other things lead to the decomposition of the extractant.”

• “The redox electrochemistry of Np(V) to Np(VI) in aqueous media has been well studied for nuclear waste separation and for applications like flow batteries.”

• “Why not focus on a tandem process to oxidize the Np in the aqueous phase and then extracted, with some degree of aqueous phase recirculation?”

• “There are several concepts that are pushed together which may complicate the execution of the project considering the limiting budget. i.e., the selection of the molecule to modify the electrode surface.”
Budget and Risks

A: Research Tasks

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<th>Task Description</th>
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<th>FY-23 ($k)</th>
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<td>Task 2: Gamma Radiolysis of Electrochemically Manipulated Neptunium Solutions</td>
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<td>Total Task budget</td>
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<td>41</td>
<td>125</td>
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B: Budget by researcher

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<th>Researcher</th>
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<tr>
<td>Gregory P. Horne (0.19 FTE)</td>
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<td>13</td>
<td>41</td>
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<td>Jacy K. Conrad (0.34 FTE)</td>
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<td>Radiological Control Coverage (0.03 FTE)</td>
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<td>Total INL labor</td>
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C: Non-labor

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<tr>
<td>Total Budget Request (B+C)</td>
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<td>41</td>
<td>125</td>
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</tbody>
</table>

Resource Availability Risk

- All equipment and expertise are readily available at INL.

Technical Risk

- Project continuation barrier is dependent upon whether solution formulations are compatible with current reprocessing constraints.
Project Overview

- **Customer:** Various DOE offices, including NE and BES.

- **Opportunity:** Novel and effective Np management, reduced reprocessing cycles, and increased cost-effectiveness.

- **Solution:** Application of novel functionalized electrodes for electrochemical manipulation of Ce/U/Np in reprocessing media.

- **Team:** 2 members of the INL *Center for Radiation Chemistry Research* – including a Russell L. Heath Distinguished Postdoc – and 2 university collaborators with significant combined experience in radiation, actinide, and electrochemistry.

- **Advantage:** Pre-existing expertise and capabilities at both institutions.

- **Results:** (i) process feasibility assessment; (ii) a high-impact factor peer-reviewed journal publication; (iii) talent pipeline investment; and (iv) preliminary data for the pursuit of follow-on funds from organizations such as *DOE NE* and *BES.*