INL/CON-24-81320-Revision-0

Backend Nuclear Fuel Cycle Radiation Chemistry

October 2024

Changing the World's Energy Future

Gregory Peter Holmbeck

Idaho National Laboratory

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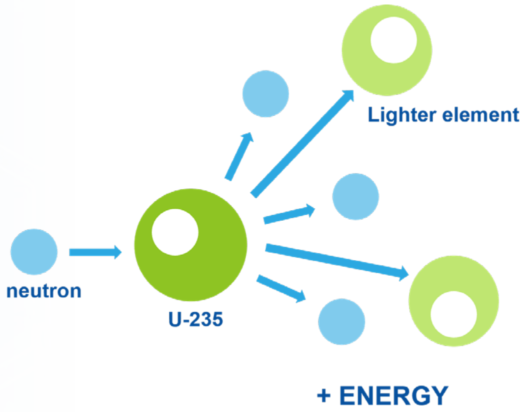

Backend Nuclear Fuel Cycle Radiation Chemistry

INL/CON-24-81320 Rev:000

BNL LEAF Workshop
October 21, 2024 | Brookhaven National Laboratory, NY, USA

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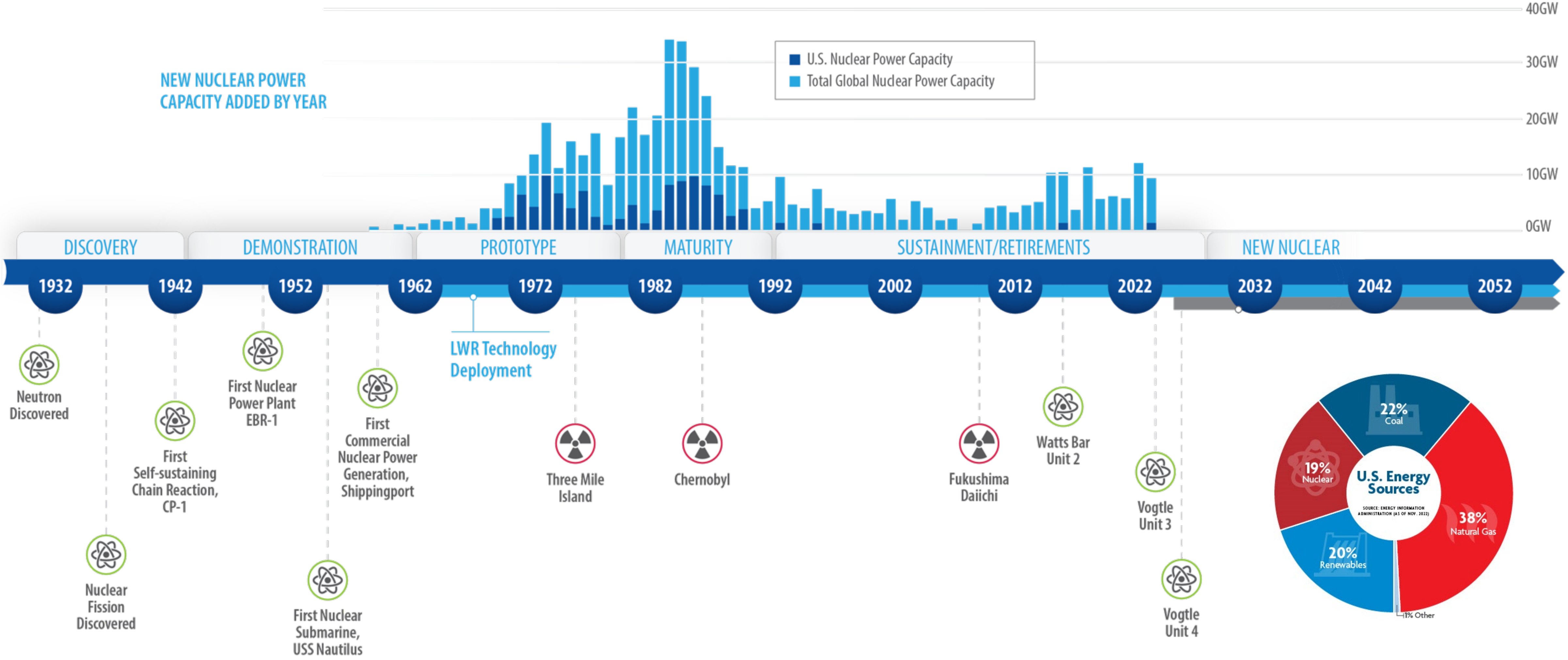
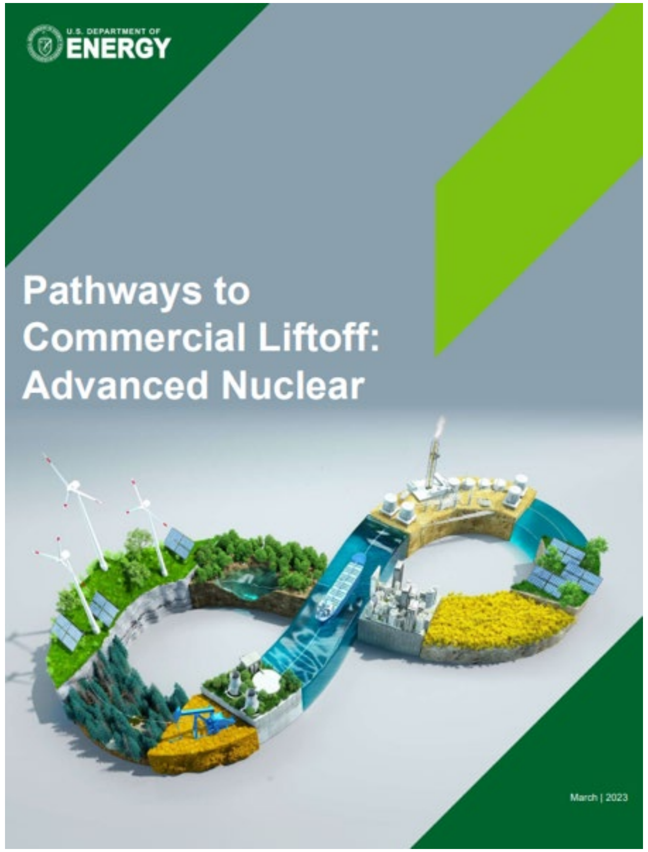
A brief history of nuclear power



- https://kclonline.com/wp-content/uploads/2023/03/US-Energy-Sources-Mix.jpg

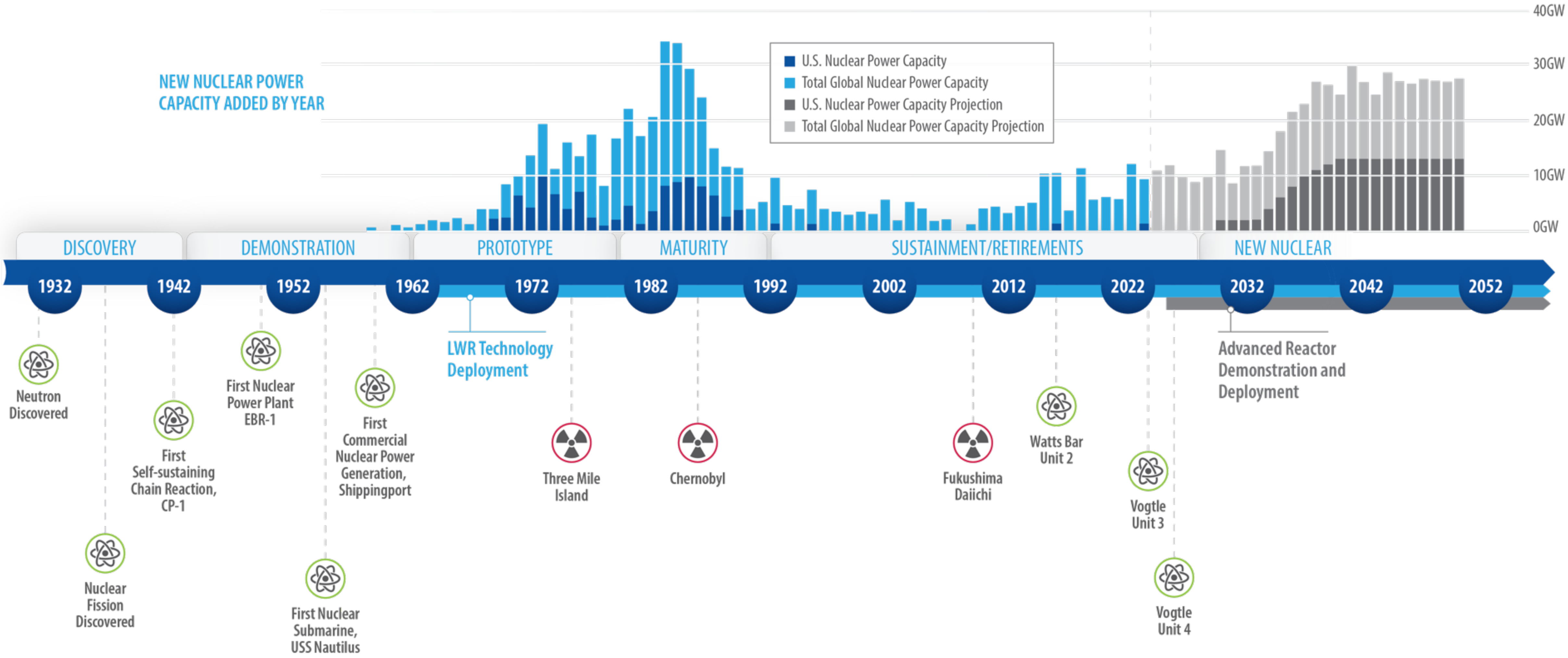
The future of nuclear power

- Countries participating in the international climate summit, the *28th Conference of the Parties* (**COP28**), commit to working together to triple nuclear capacity by 2050:
  - For the United States, this would mean going from **100 GWe to 300 GWe**
  - World-wide, this would mean going from **400 GWe to 1200 GWe**
- *"Power system decarbonization modeling, regardless of level of renewables deployment, suggests that the U.S. will need ~550–770 GW of additional clean, firm capacity to reach net-zero."*

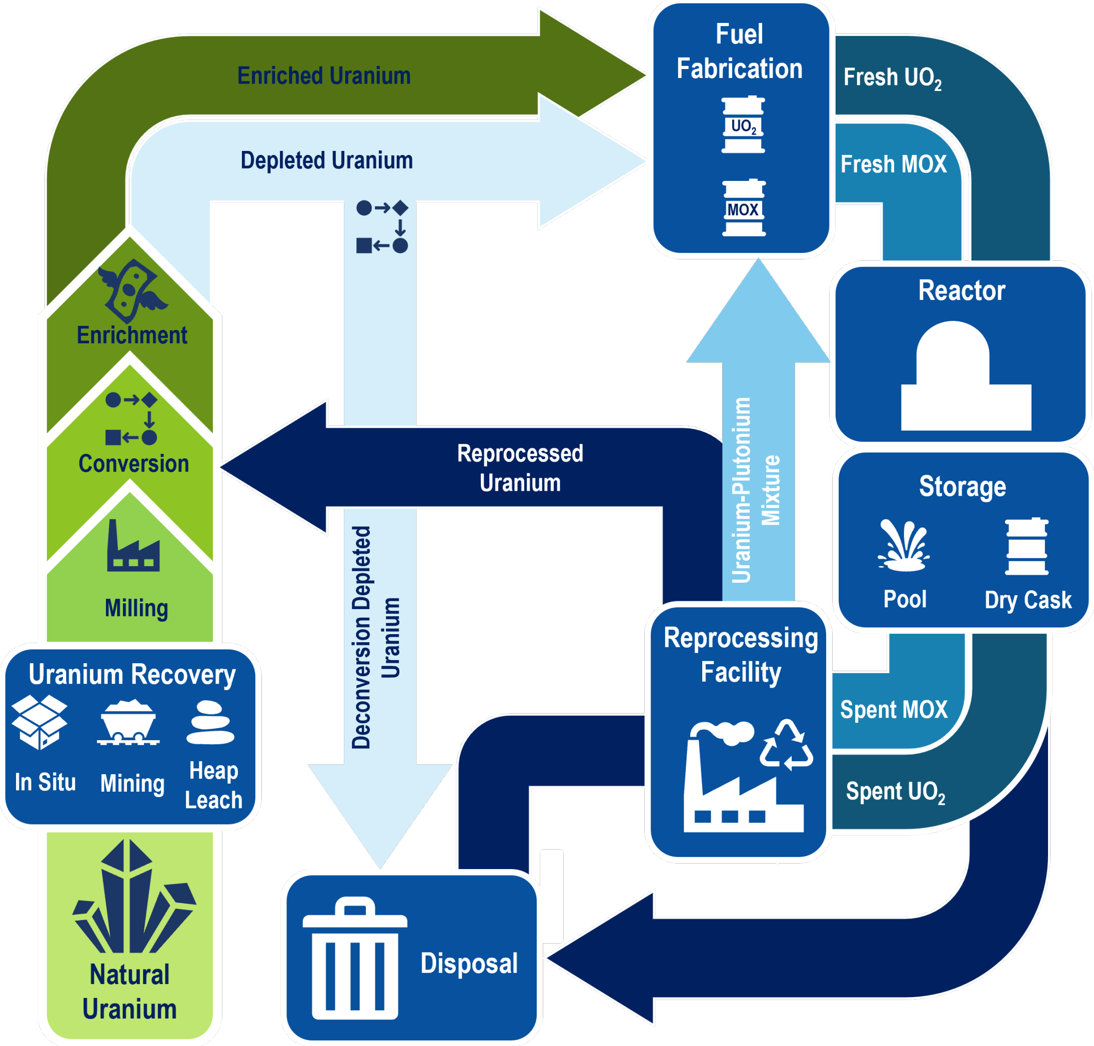


- COP28 declaration language: https://www.energy.gov/articles/cop28-countries-launch-declaration-triple-nuclear-energy-capacity-2050-recognizing-key .
- U.S. Department of Energy Pathways to Commercial Liftoff: Advanced Nuclear report, March **2023**, 1–62.

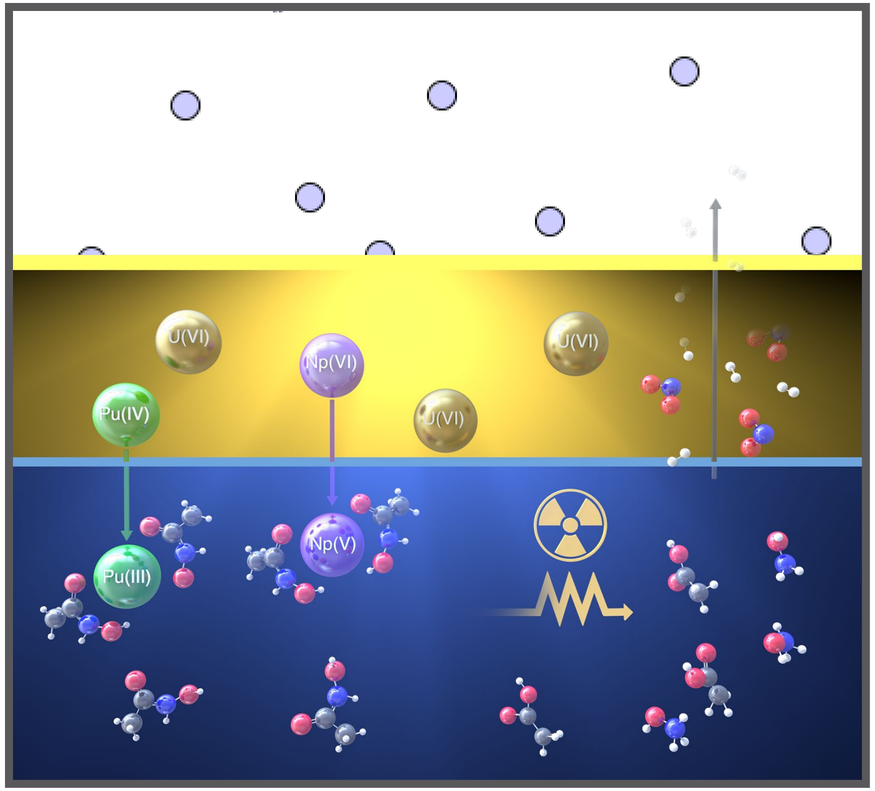
The future of nuclear power



The nuclear fuel cycle + backend challenges



A typical reprocessing solvent system is comprised of a concentrated HNO_3 aqueous phase contacted with an organic phase (organic extractants and diluent).



- Conrad, Mezyk, Isherwood, Baidak, Pilgrim, Whittaker, Orr, Pimblott, and **Horne**, ChemPhysChem **2022**, e20220074.

Reprocessing solvent system radiation chemistry

Water Radiolysis

$H_2O \rightsquigarrow e_{aq}^-$, ...

Direct Radiation Effects

Indirect Rad...

$HNO_3 + {}^\bullet OH$ ...

$NO_3^- + e^- \rightarrow$ ...

$NO_3^{\bullet 2-} + H_2O$ ...

$NO_3^- + H^\bullet \rightarrow$ ...

$NO_2^\bullet + NO_2^\bullet$ ...

$N_2O_4 \rightarrow HNO_2 + HNO_3$

..., H_2

Key Radiolysis Products

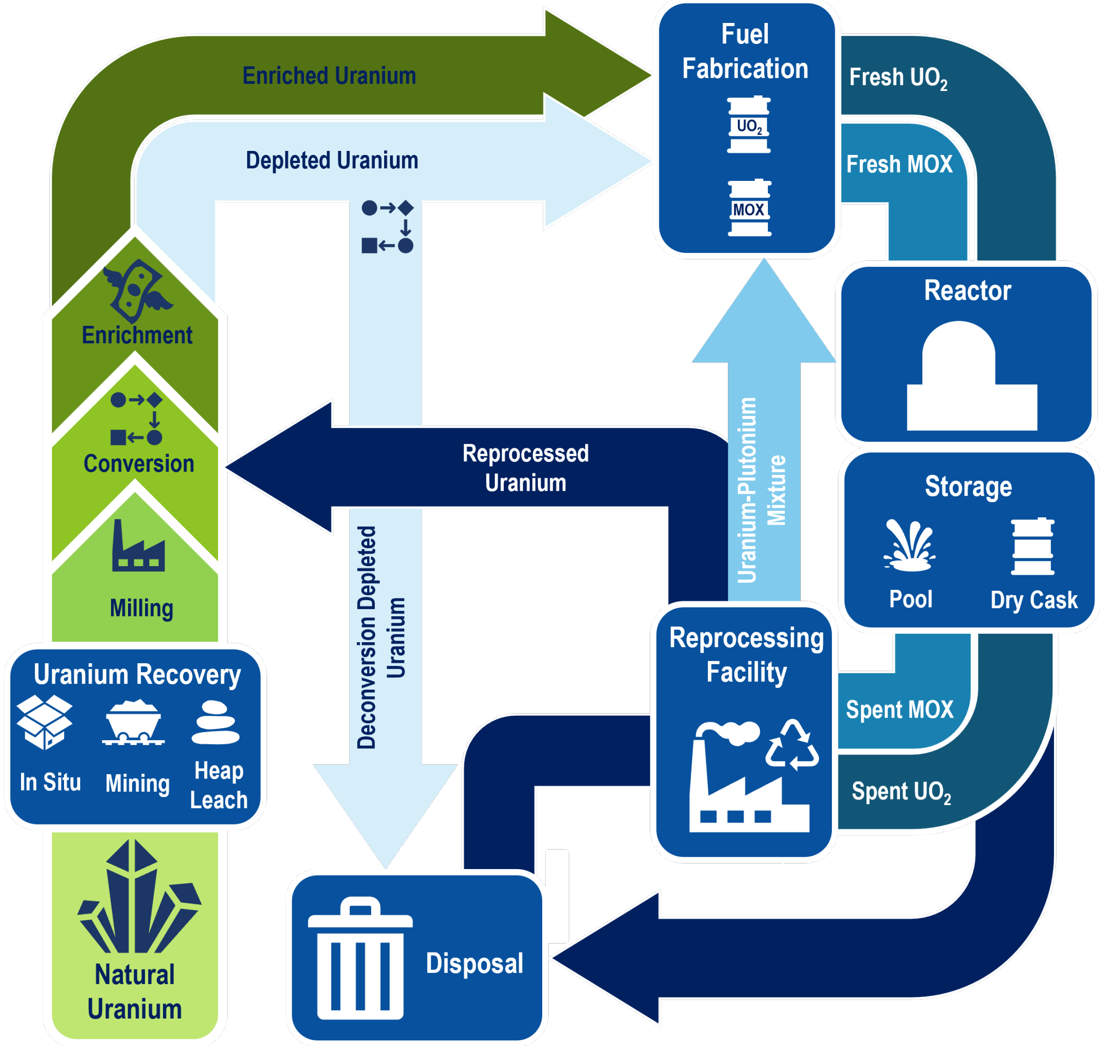
e_{aq}^-, $H^\bullet$, ${}^\bullet OH$, and H_2O_2 from H_2O

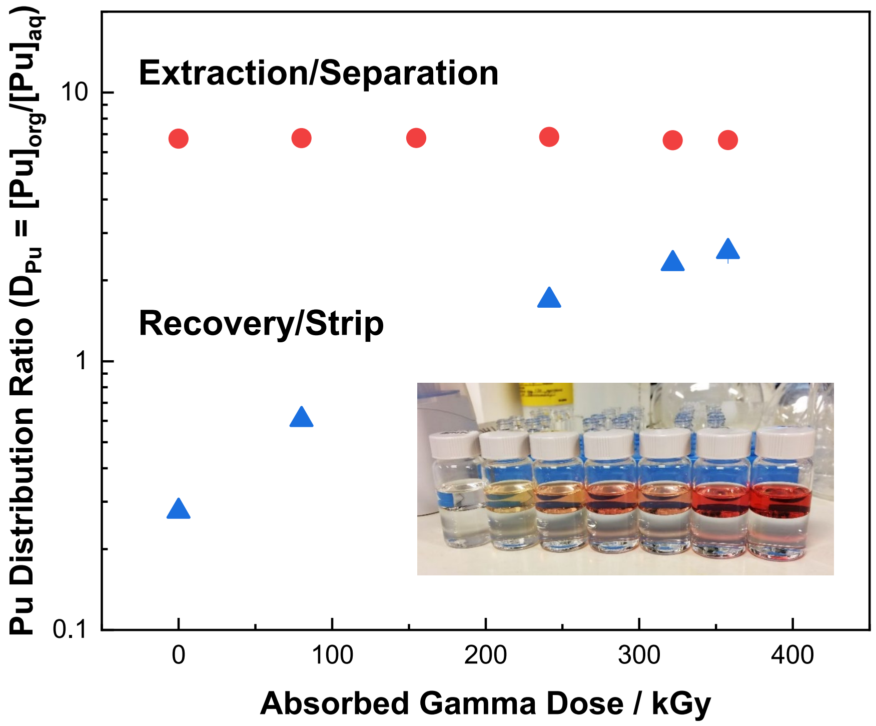
$NO_3^\bullet$ and HNO_2 from HNO_3

e_s^- and $RH^{\bullet +}$ from **organic diluent**

- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Ligand radiolysis and degradation product formation

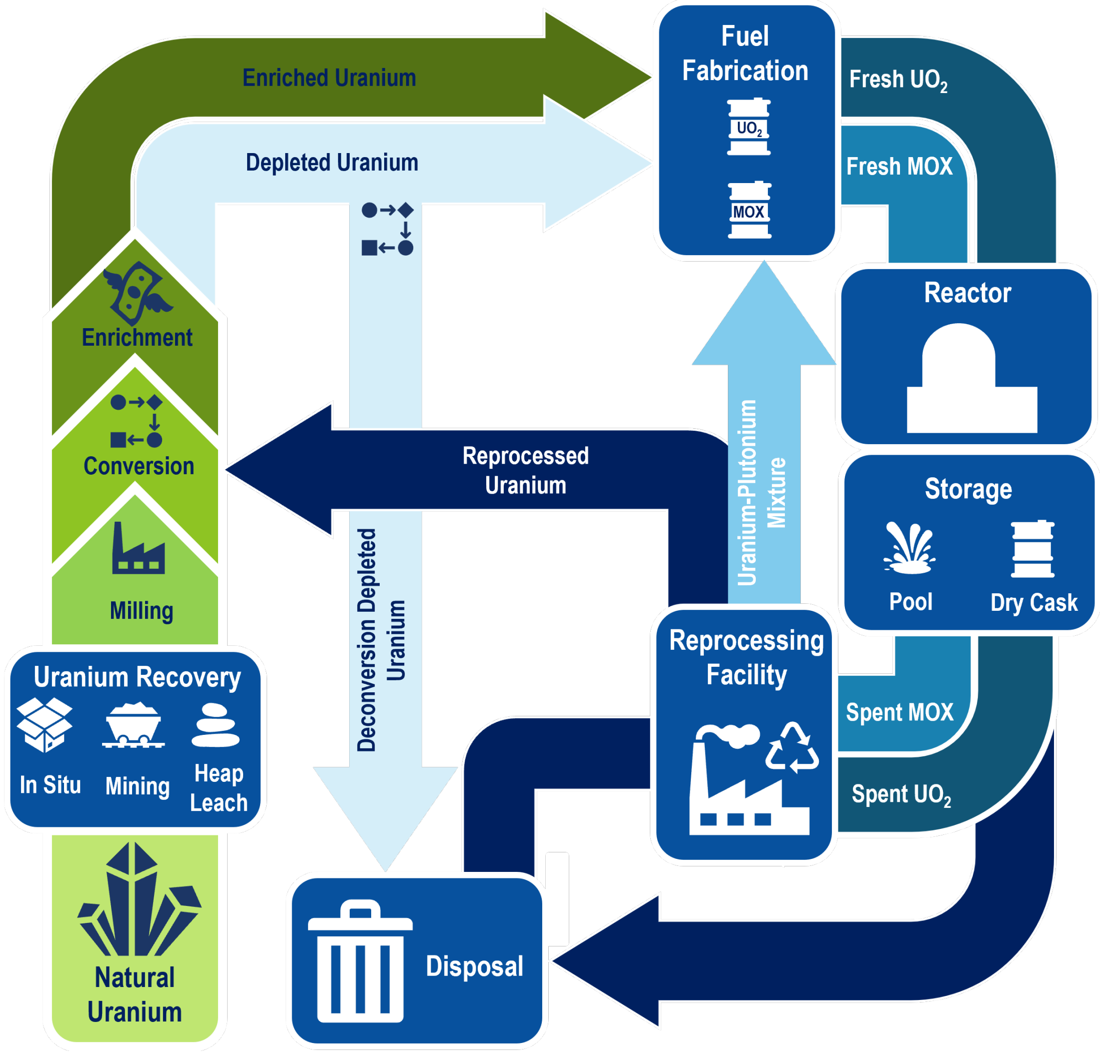


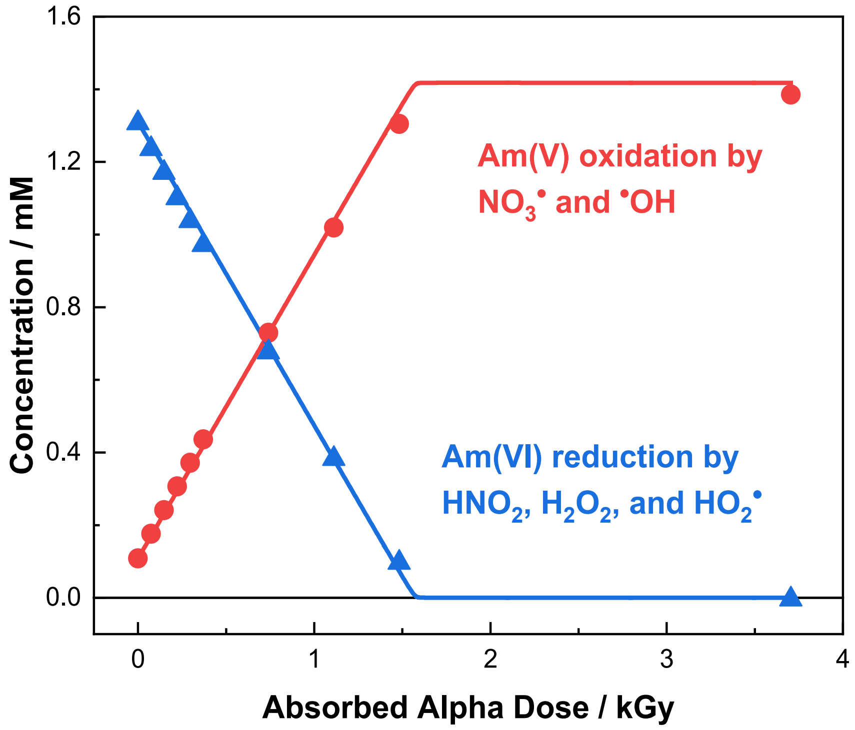


Pu distribution ratios for extraction (▲) and strip (●) conditions as a function of absorbed gamma dose for pre-irradiated DEHBA/n-dodecane contacted with 3 M HNO_3.

- **Horne**, Mezyk, Mincher, Zarzana, Rae, Tillotson, Schmitt, Ball, Ceder, Charbonnel, Guilbaud, Saint-Louis, and Berthon, *Rad. Phys. Chem.* **2020**, *170*, 108608.

Radiation-induced redox chemistry

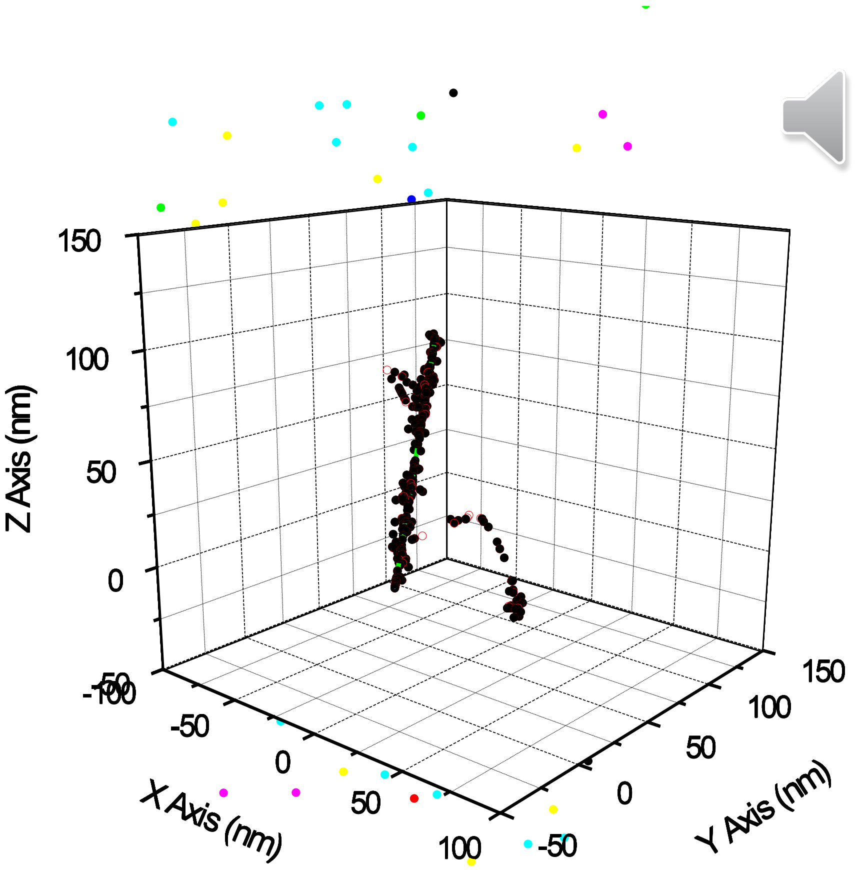


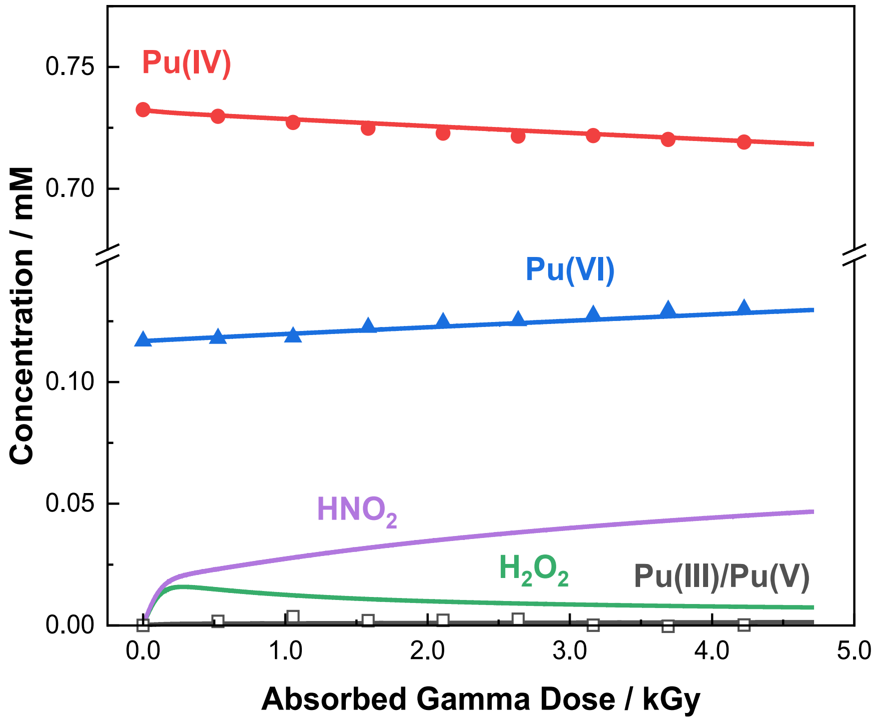


Concentration of Am(VI) (▲) and Am(V) (●) as a function of absorbed gamma dose from the irradiation of 2 mM Am in aerated 3.0 M HNO_3 solution.

- **Horne**, Grimes, Bauer, Dares, Pimblott, Mezyk, and Mincher, *Inorganic Chemistry* **2019**, *58*, 8551.

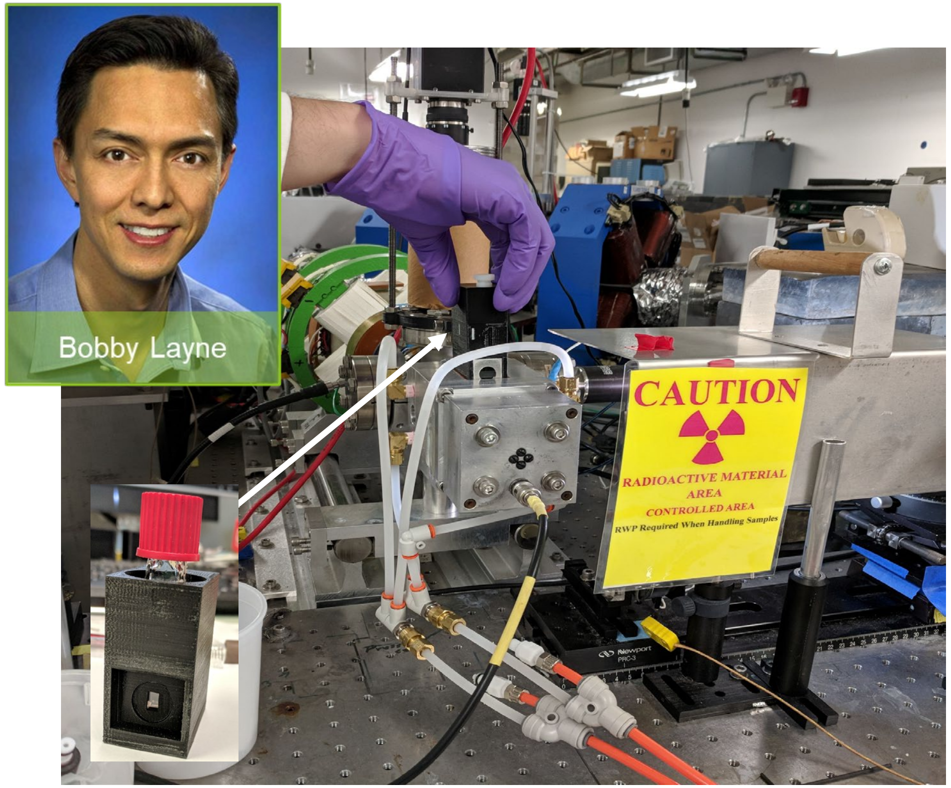
The dream: predictive models for engineer-scale processes



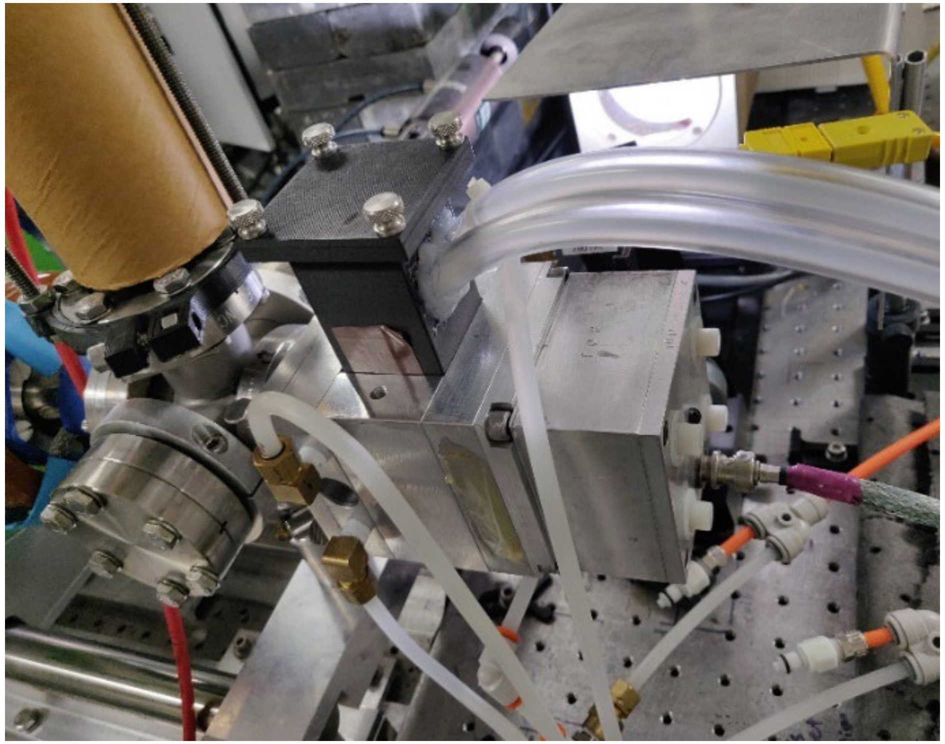


- Clifford, Green, Oldfield, Pilling, and Pimblott, *Journal of the Chemical Society, Faraday Transactions* **1986**, *82*, 2673.
- Pimblott, LaVerne, and Mozumder, *Journal of Physical Chemistry* **1996**, *100*, 8595.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**, *63(18)*, 8092.

Reaction mechanisms and activation parameters



LEAF actinide sample holder



New temperature-controlled holder

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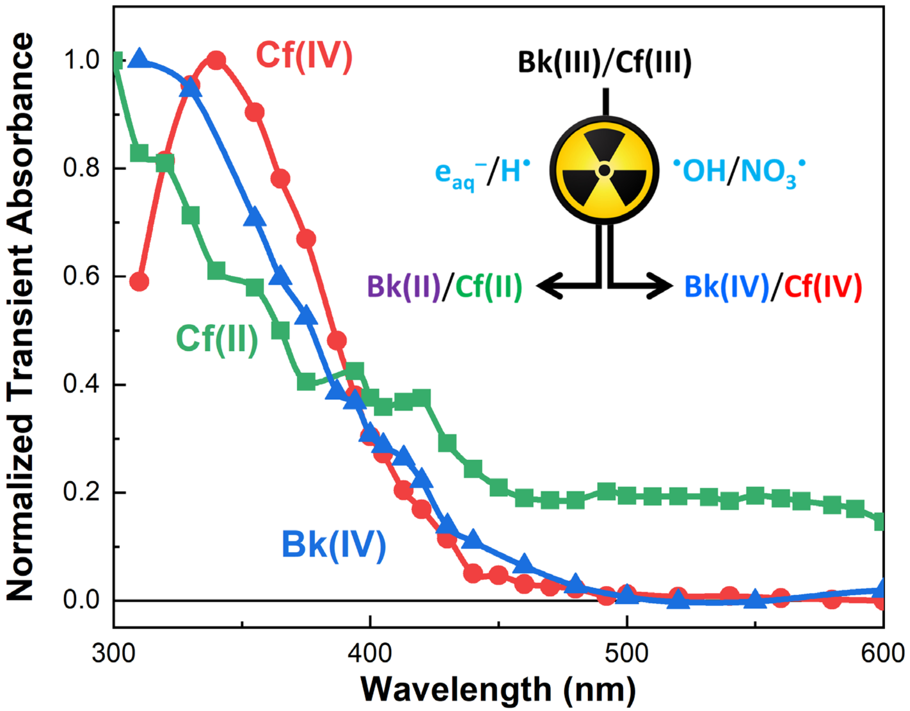
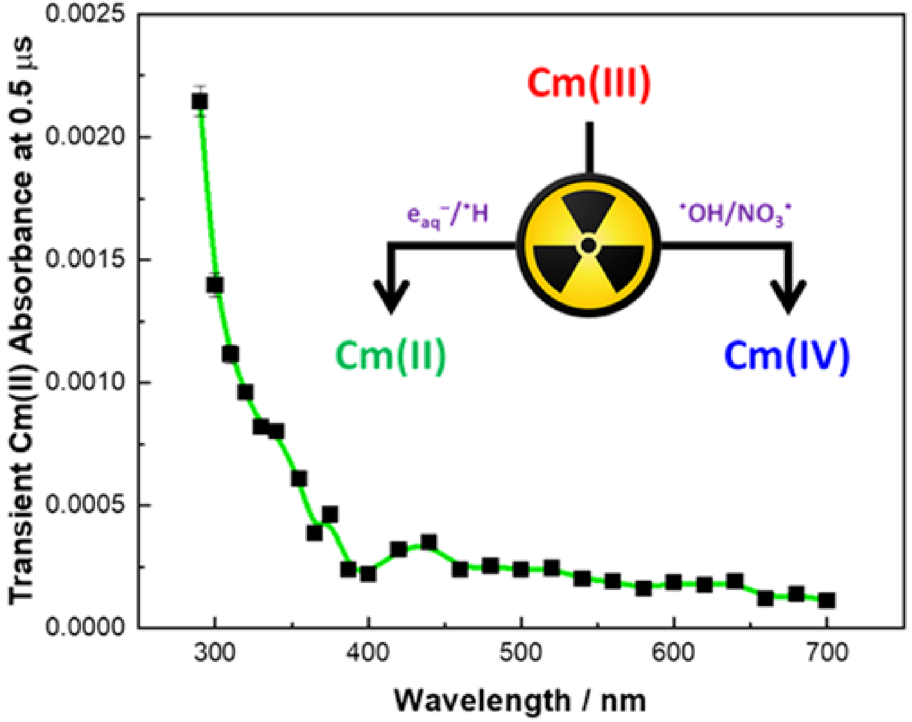
- Wishart, Cook, and Miller, *Review of Scientific Instruments* **2004**, *75(11)*, 4359.
- **Horne**, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Transactions* **2021**, 50, 10853.
- **Horne**, Rotermund, Grimes, Sperling, Meeker, Zalupski, Beck, Gomez Martinez et al., *Inorganic Chemisty* **2022**, *61(28)*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart, and **Horne**, *Journal Physical Chemistry A* **2024**, *128(3)*, 590.
- Kynman, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Transactions* **2024**, *53*, 9262.

Radiation-induced actinide redox chemistry





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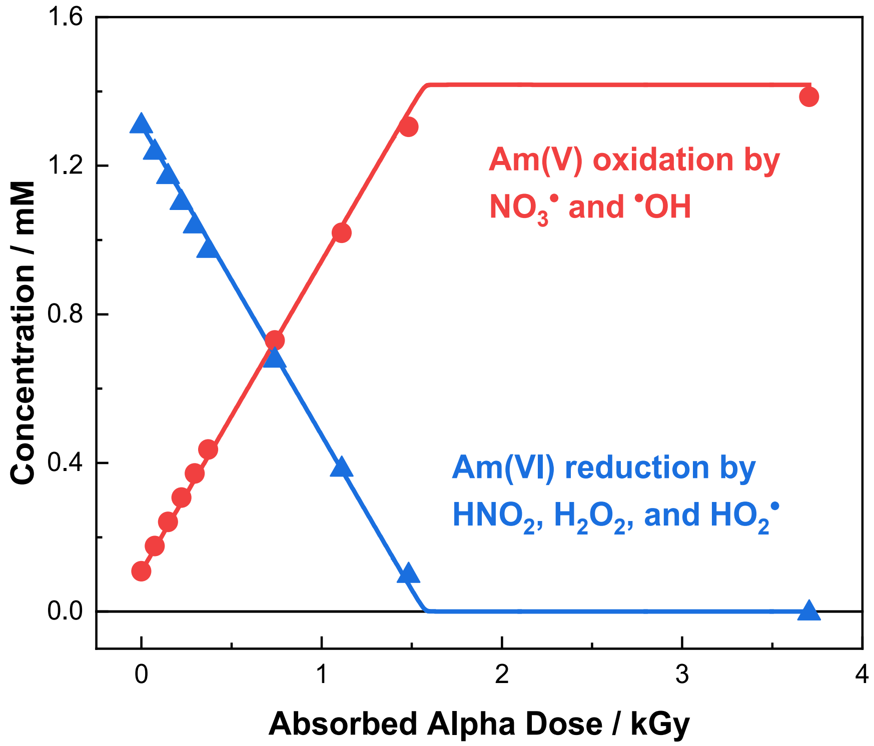
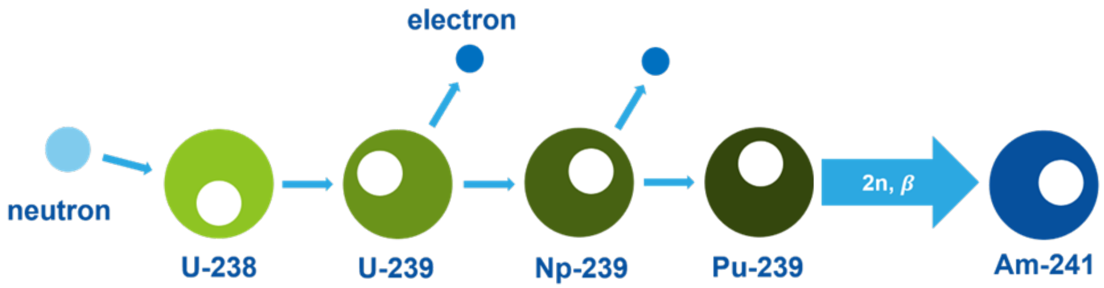
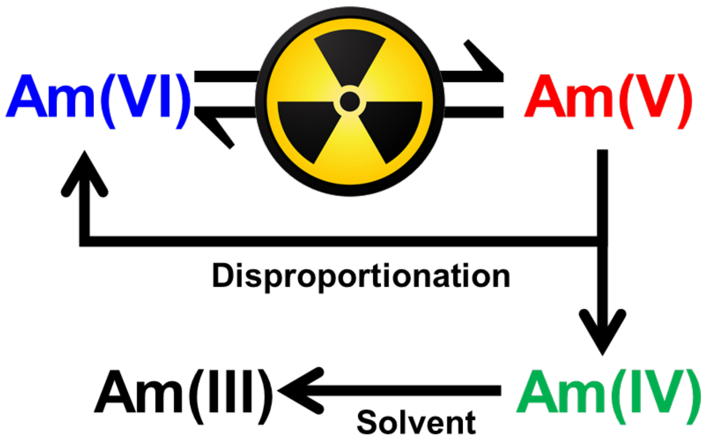
- Pikaev, Gogolev, and Shilov, *Isotopenpraxis* **1990**, 26, 465.
- **Horne**, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Transactions* **2021**, 50, 10853.
- **Horne**, Rotermund, Grimes, Sperling, Meeker, Zalupski, Beck, Gomez Martinez et al., *Inorganic Chemisty* **2022**, *61(28)*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart, and **Horne**, *Journal Physical Chemistry A* **2024**, *128(3)*, 590.

Radiation-induced americium redox chemistry





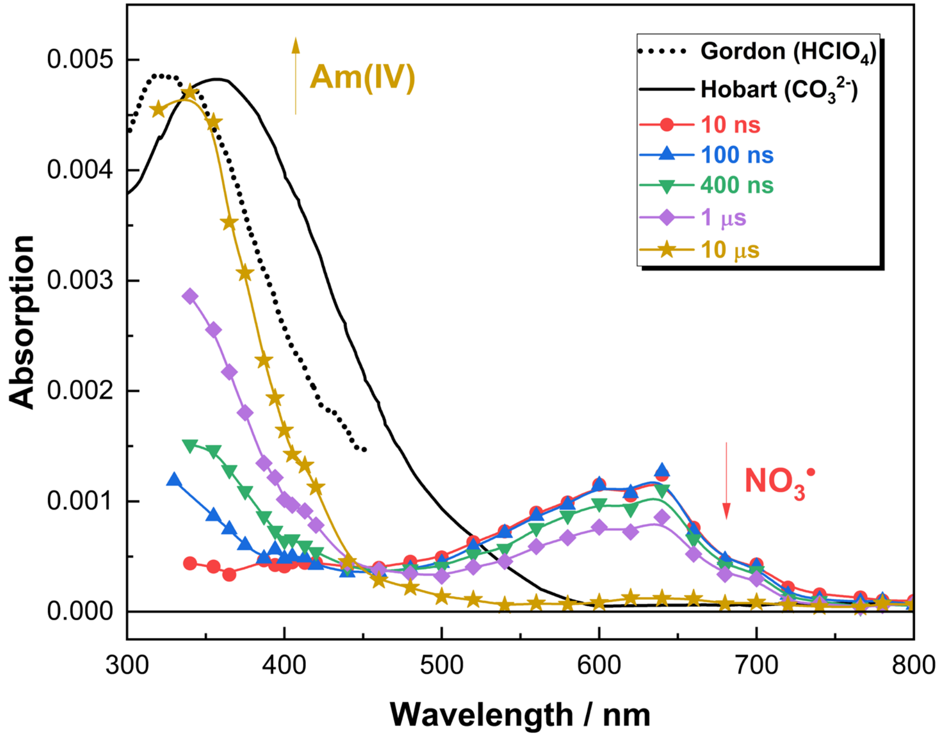


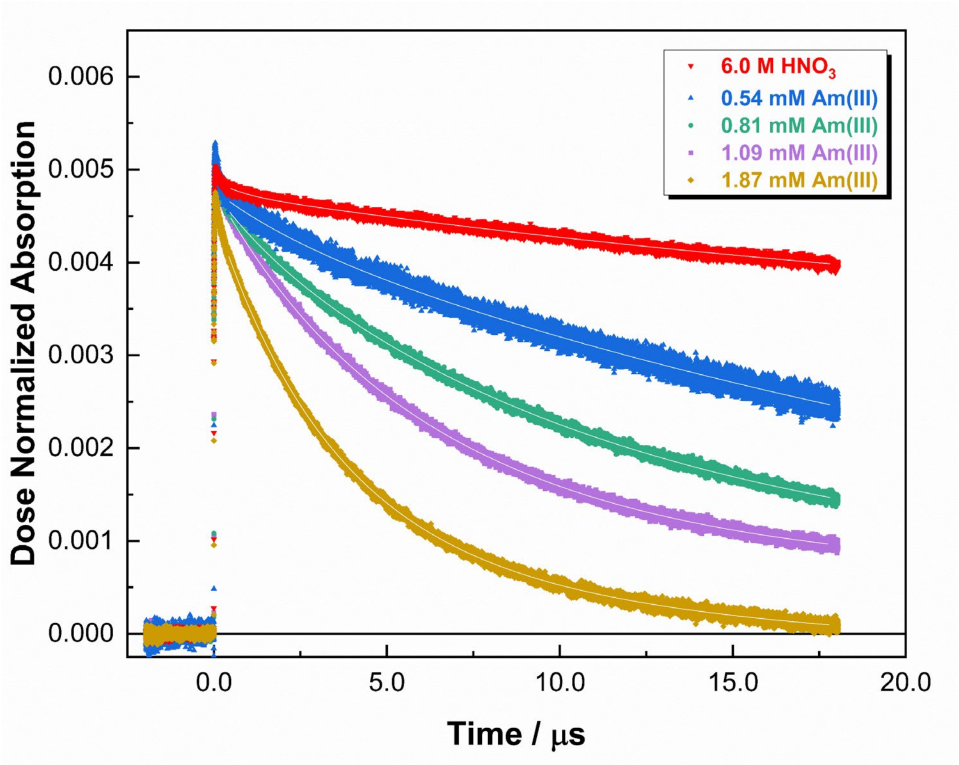
- **Horne**, Grimes, Bauer, Dares, Pimblott, Mezyk, and Mincher, *Inorganic Chemistry* **2019**, *58*, 8551.

Radiation-induced americium(IV) redox chemistry

Am(III) + $NO_3^{\bullet}$ → Am^{4+} + NO_3^-, $k = (1.35 \pm 0.05) \times 10^8\ M^{-1}\ s^{-1}$

Am(IV) lifetime in 6 M HNO_3 is approximately 16 μs





- Kynman, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Transactions* **2024**, *53*, 9262.

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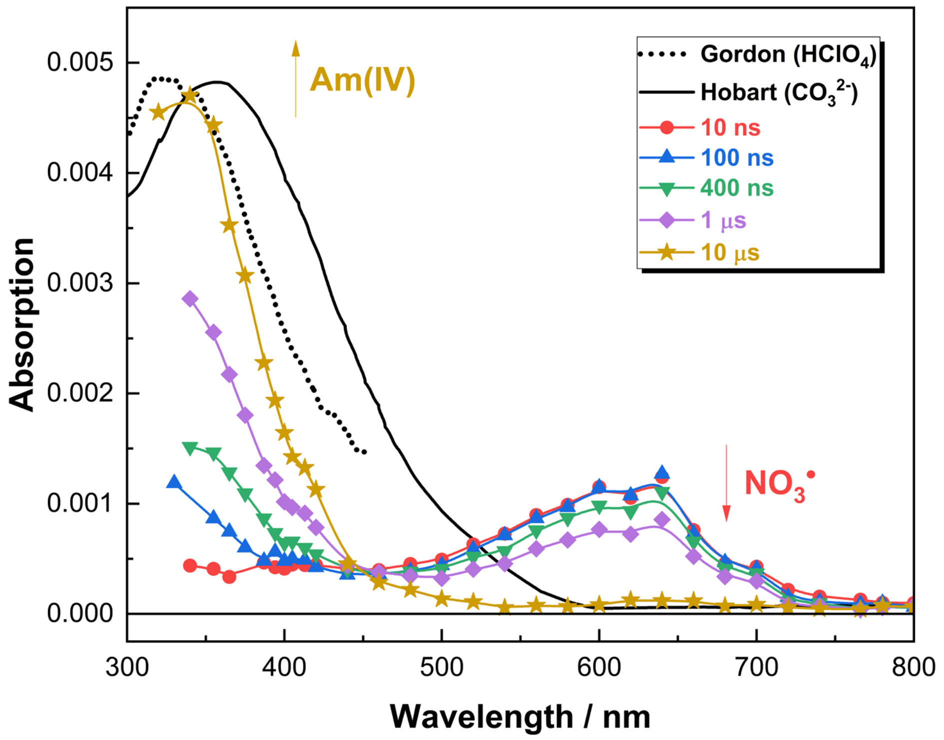
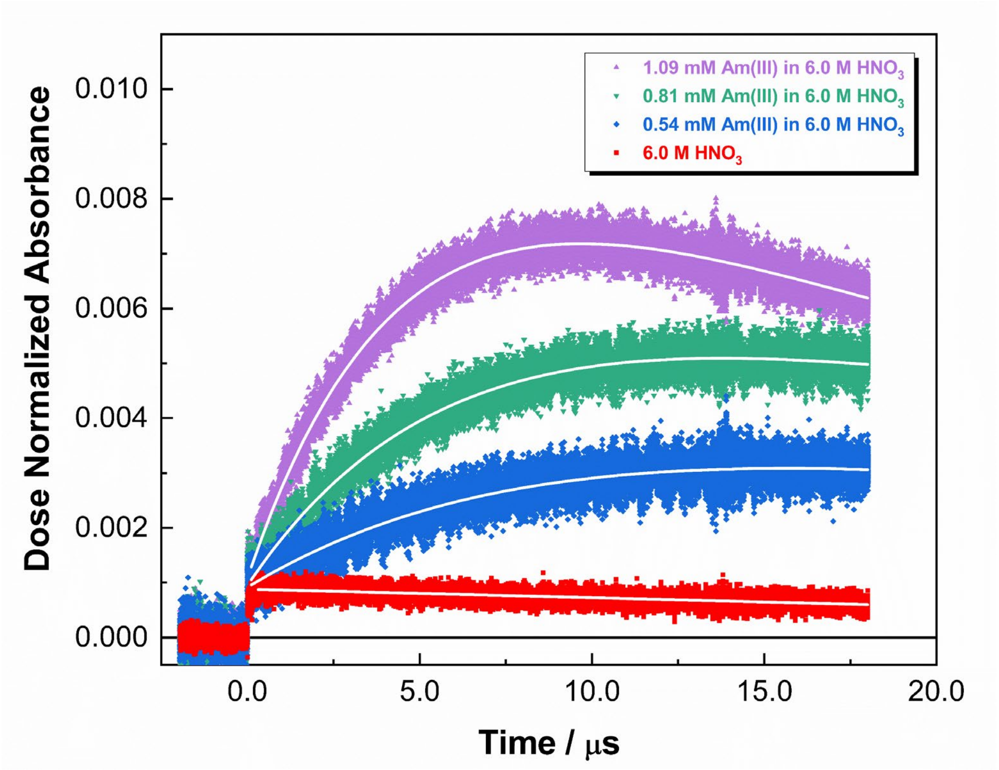


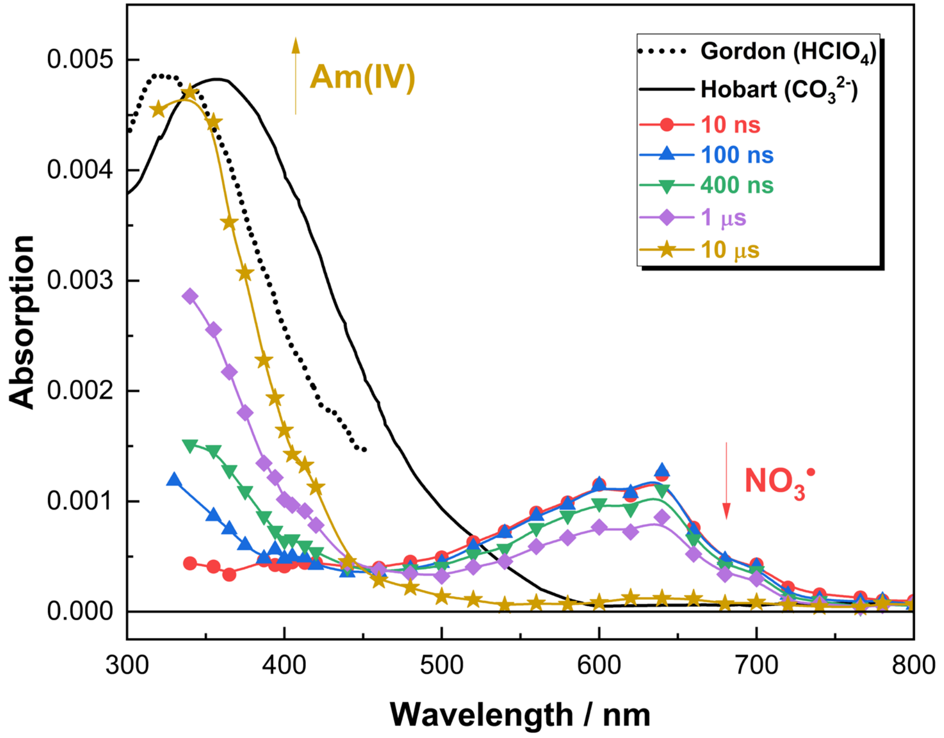


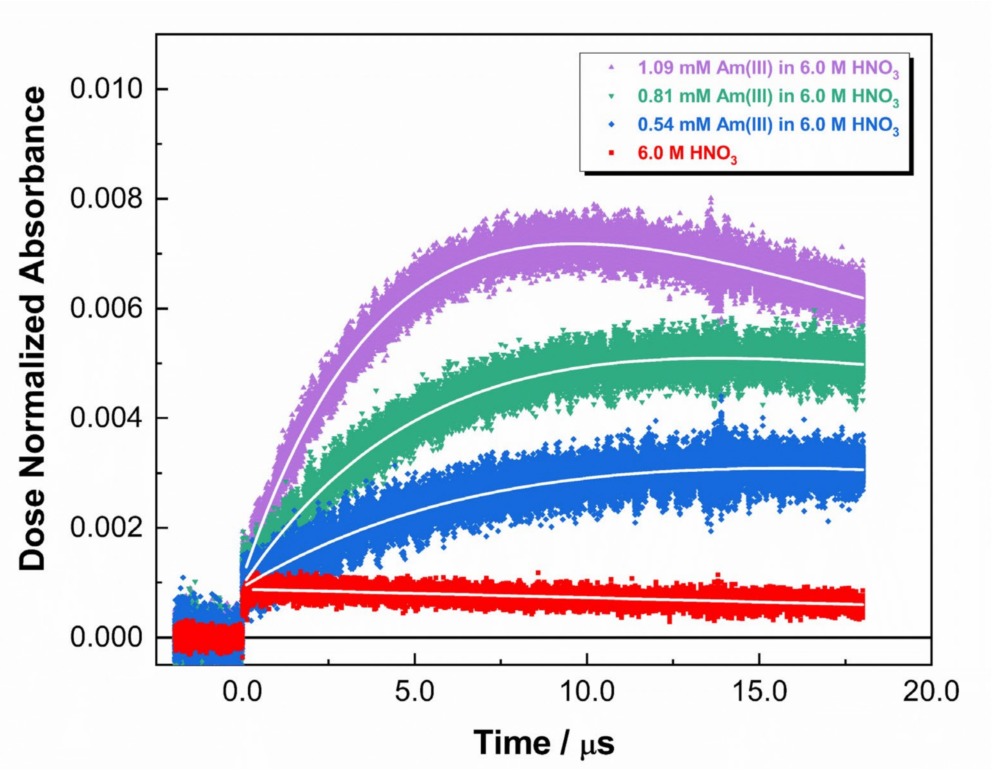
- Kynman, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Transactions* **2024**, *53*, 9262.

Radiation-induced americium(IV) redox chemistry

Arrhenius: E_a = 19.5 kJ mol^{-1} and A = 4.2 × 10^{11} s^{-1}

Eyring: $\Delta H^‡$ = 17 kJ mol^{-1} and $\Delta S^‡$ = -30.7 J mol^{-1} K^{-1}





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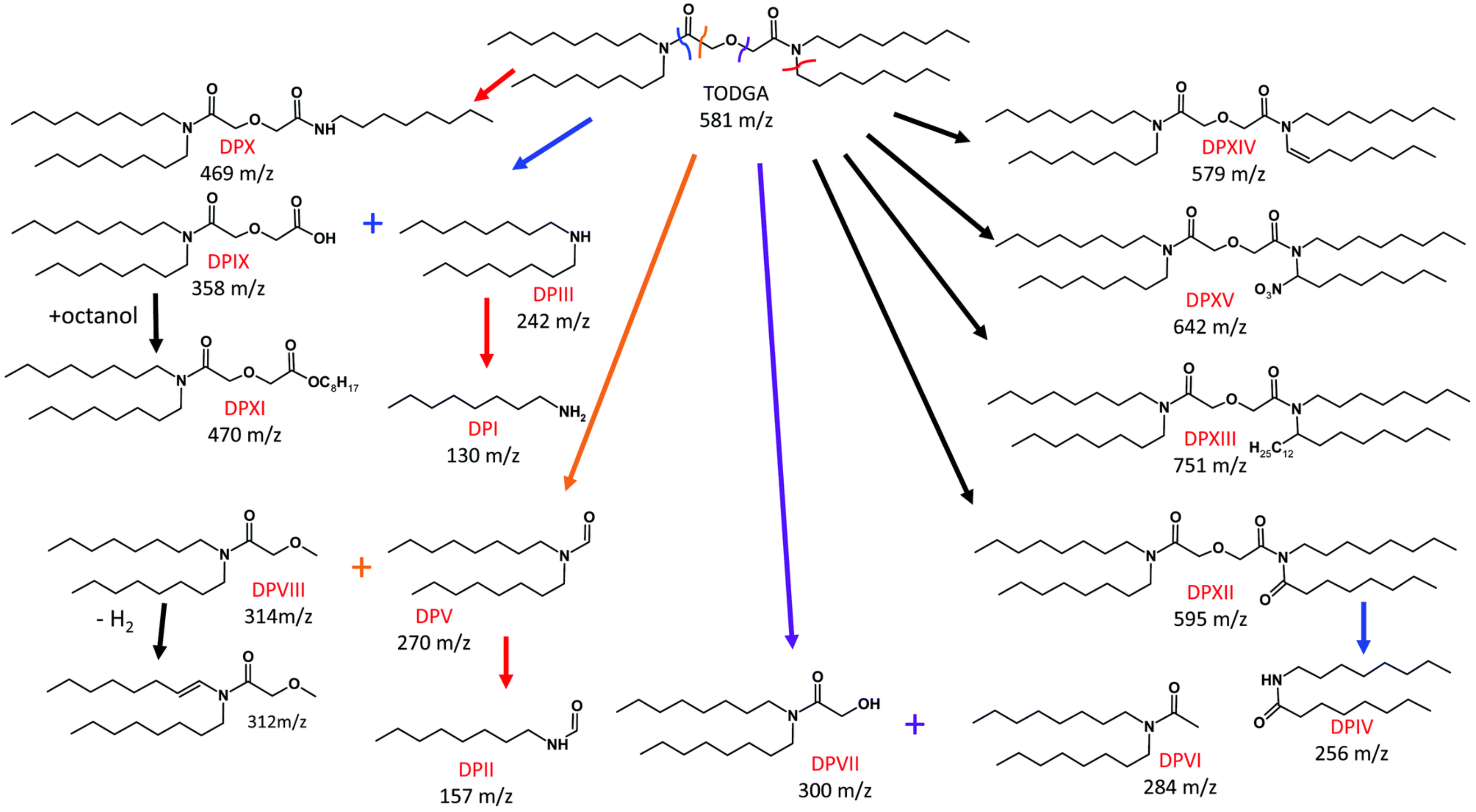
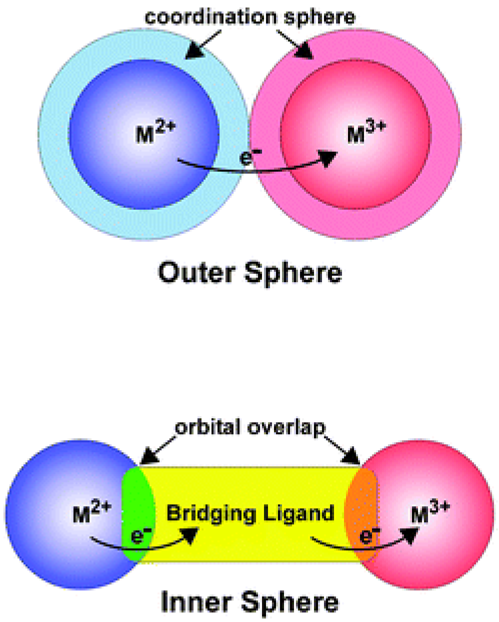
- Kynman, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Transactions* **2024**, *53*, 9262.

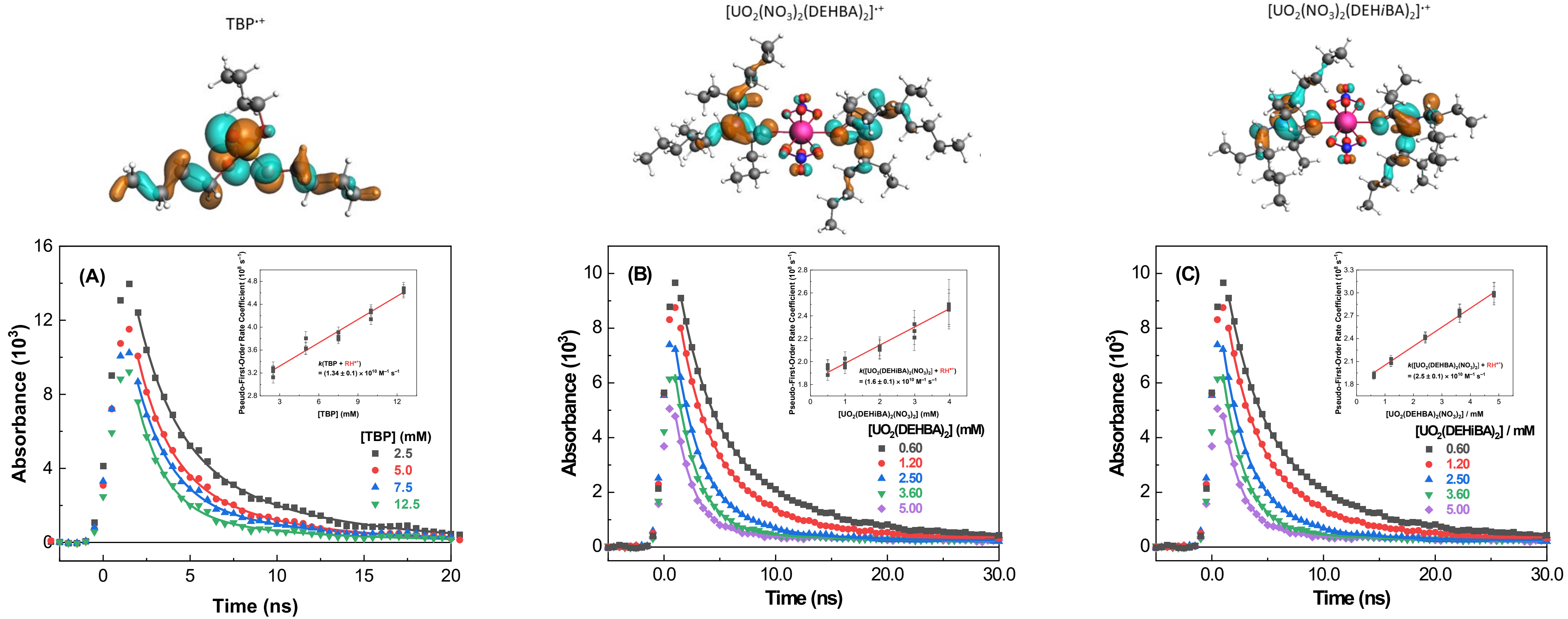
What about metal ion complexation effects?





- Kimberlin, Saint-Louis, Guillaumont, Cames, Guilbaud, and Berthon, *Physical Chemistry Chemical Physics* **2022**, *24*, 9213.
- https://pubs.rsc.org/image/article/2005/CC/b408479a/b408479a-f1.gif

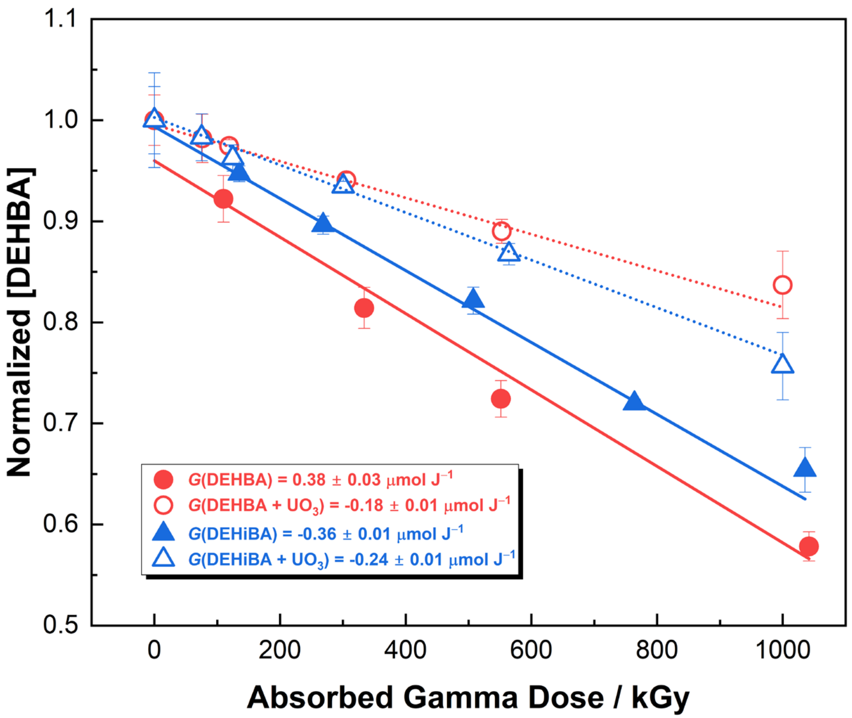
Uranium complexation effects



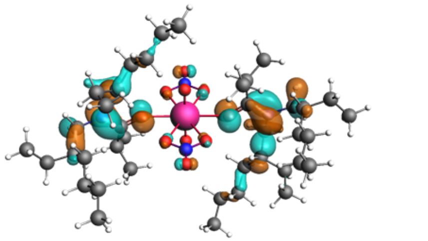
- **U(VI)** complexation had negligible effect on the reaction of **TBP** with **$RH^{\bullet+}$**, $k = (1.3 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$.
- For **DEHBA** and ***DEHiBA***, **U(VI)** complexation afforded a 2.6× and 1.4× increase in their respective rate coefficients.

- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and **Horne**, *Physical Chemistry Chemical Physics* **2021**, *23*, 24589.

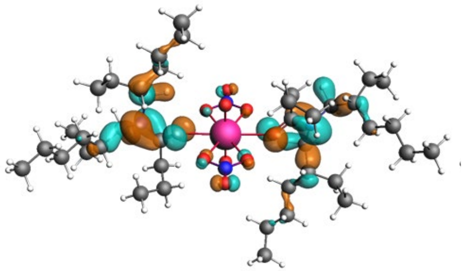
Gamma irradiation of uranium loaded solvent systems



$[UO_2(NO_3)_2(DEH\textit{i}BA)_2]^{\cdot +}$



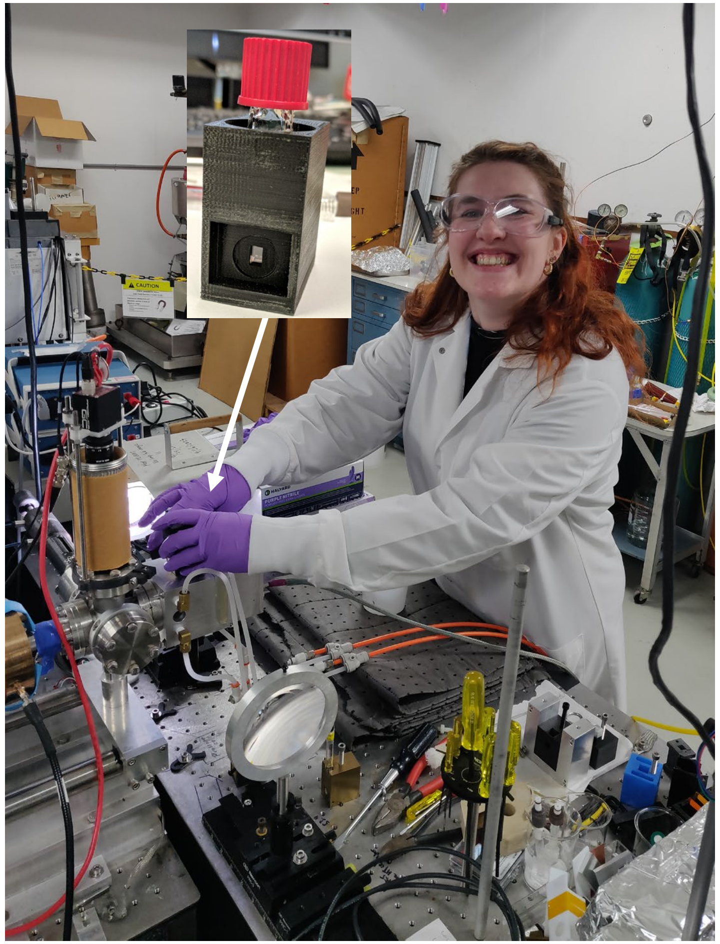
$[UO_2(NO_3)_2(DEHBA)_2]^{\cdot +}$

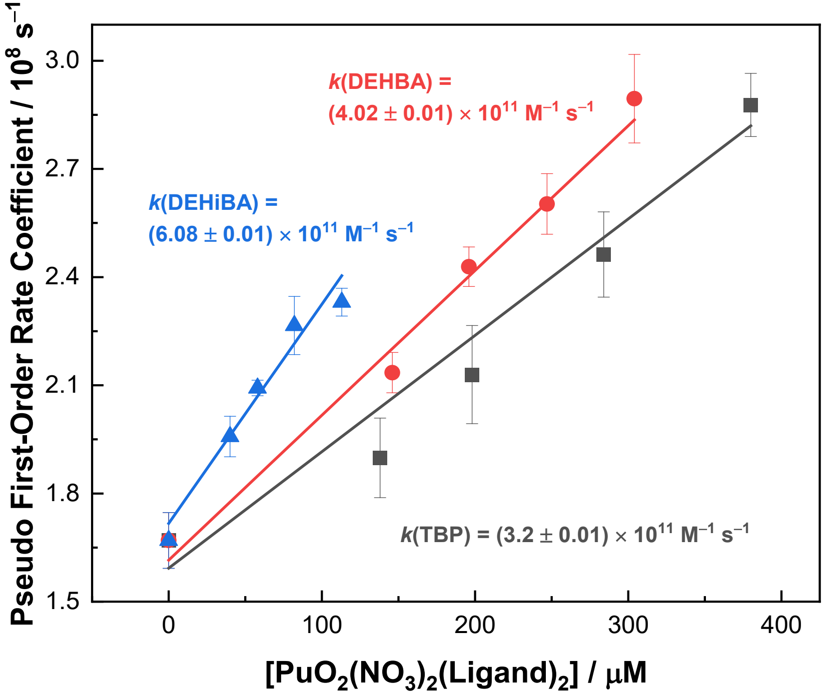


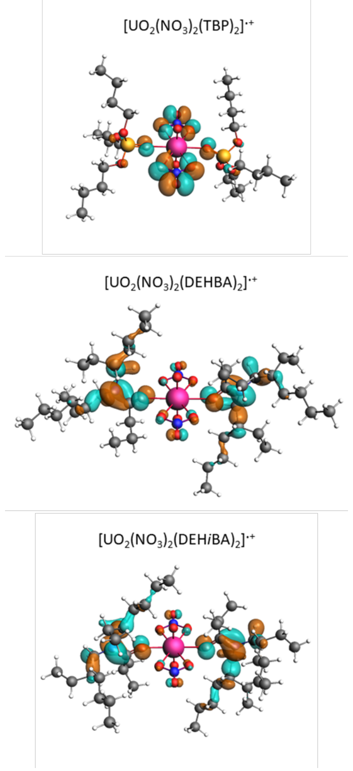
- Normalized loss of **DEHBA** (●/○) and **DEH*i*BA** (▲/△) in deaerated, 6.0 M HNO_3 pre-equilibrated *n*-dodecane solution in the presence and absence of **ε-UO_3** as a function of absorbed cobalt-60 gamma dose.

- Kynman, Dang, Grimes, Mezyk, Wilbanks, Zarzana, Deokar, Cook, Boglaienko, Hall, and **Horne**, *ACS Omega* **2024**, Under Review.

Electron pulse irradiation of plutonium loaded solvent systems







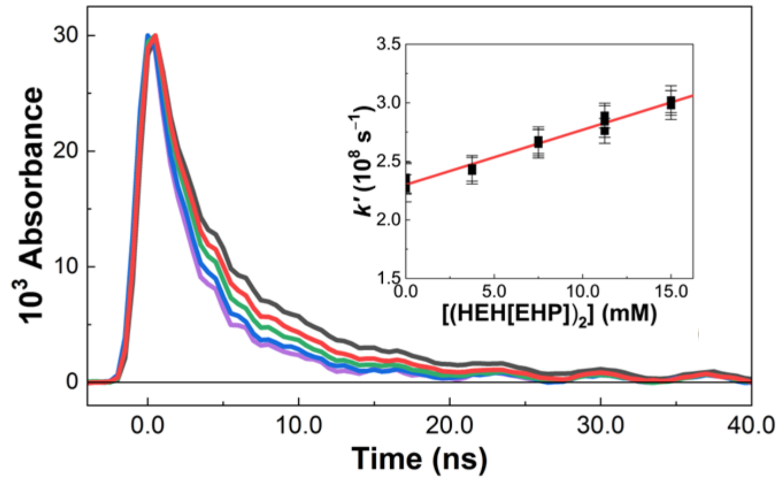
- **Pu(VI)** complexation afforded significantly faster rates for the reaction of **RH$^{•+}$** with [PuO_2(NO_3)$_2$(**L**)$_2$] as compared to the non-complexed ligands (~10^{10} M^{-1} s^{-1}).

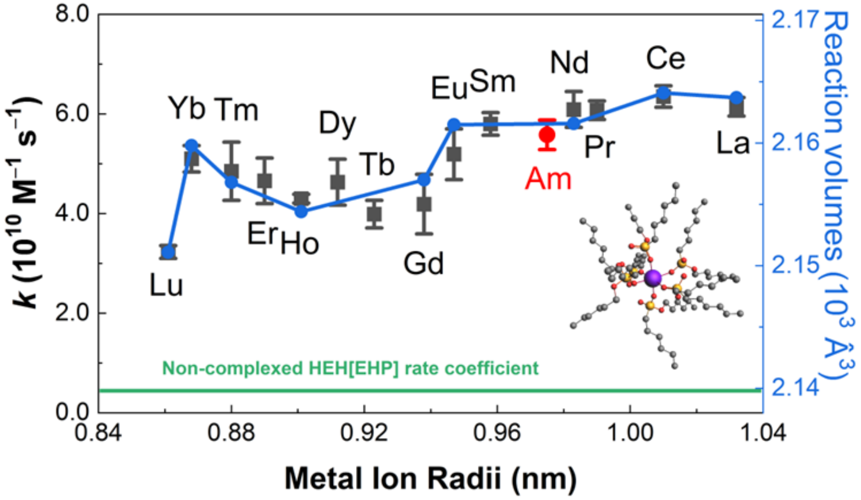
Brookhaven National Laboratory

- Culbertson, Celis-Barros, Pilgrim, McLachlan, Cook, Mezyk, and **Horne**, *Inorganic Chemistry* **2024**, In Preparation.

Overview

- Radiation-induced processes have the capacity to drive backend nuclear fuel cycle systems far from equilibrium, impacting their performance and longevity.
- Electron pulse radiolysis is an essential technique for elucidating complex reaction mechanisms, especially those involving short-lived transients.
- Metal ion complexation has profound effect on the chemical kinetics and radiation robustness of organic ligands.





- Mezyk, Baxter, Celis-Barros, Grimes, Zalupski, Rae, Zarzana, Cook, and **Horne**, *Dalton Transactions* **2024**, *53*, 6881.

Acknowledgements


Amy Kynman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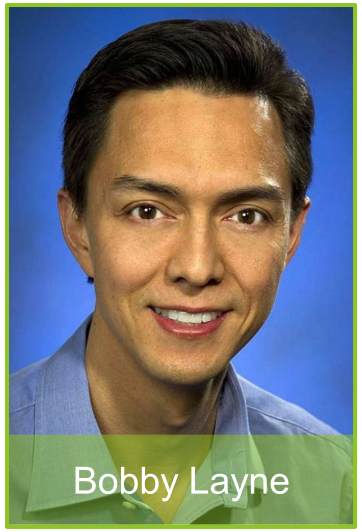
Bobby Layne


Andrew Cook


Stephen Mezyk


Thomas Schoenzart

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