Actinide Radiation Chemistry and Used Nuclear Fuel Reprocessing

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Gregory P Horne

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Gregory P. Horne
Center for Radiation Chemistry Research
Idaho National Laboratory

Holmbeck et al., The European Physical Journal A, 2023, 59 (28).
Reprocessing Used Nuclear Fuel

Solvent Extraction Reprocessing
Ligand(s)/organic diluent: HNO₃/H₂O


Plutonium Distribution Ratio

$D_{Pu} = \frac{[Pu]_{org}}{[Pu]_{aq}}$

DEHBA in 3.0 M HNO₃ contact

Increasing Gamma Dose → → →
Reprocessing Radiation Chemistry

Water Radiolysis

\[
\text{H}_2\text{O} \leftrightarrow \text{e}^-, \text{H}^+, \cdot\text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_{\text{aq}}\text{+}
\]

Indirect Radiation Effects

\[
\text{HNO}_3 + \cdot\text{OH} \rightarrow \text{NO}_3^\cdot + \text{H}_2\text{O}
\]
\[
\text{NO}_3^- + \text{e}^- \rightarrow \text{NO}_3^\cdot{2^-}
\]
\[
\text{NO}_3^\cdot{2^-} + \text{H}_2\text{O} \rightarrow \cdot\text{NO}_2 + 2\text{OH}^-
\]
\[
\text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3^- \rightarrow \text{NO}_2^\cdot + \text{OH}^-
\]
\[
\text{NO}_2^\cdot + \text{NO}_2^\cdot \Rightarrow \text{N}_2\text{O}_4
\]
\[
\text{N}_2\text{O}_4 \rightarrow \text{HNO}_2 + \text{HNO}_3
\]

Direct Radiation Effects

\[
\text{NO}_3^- \rightarrow \text{NO}_3^\cdot \rightarrow \text{NO}_2^- + \text{O}
\]
\[
\text{HNO}_3 \rightarrow \text{HNO}_3^\cdot \rightarrow \text{HNO}_2 + \text{O}
\]
\[
\text{NO}_3^- \rightarrow \text{NO}_3^\cdot + \text{e}^-
\]
\[
\text{HNO}_3 \rightarrow \text{NO}_3^\cdot + \text{H}^+
\]

Alkane Radiolysis

\[
\text{R-CH}_3 \leftrightarrow \text{e}^-, \text{RH}^+, \text{RH}^+, \cdot\text{CH}_3, \text{H}^+, \text{H}_2
\]
Radiation-Induced Actinide Redox Chemistry


Complexation Effects

Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in \( \text{Å}^{-3} \). (a) \([\text{Nd(TEDGA)}_3][\text{NO}_3]_6\), (b) \([\text{Nd(TEDGA)}_3]\text{Cl}_6\), (c) \([\text{Am(TEDGA)}_3][\text{NO}_3]_6\), and (d) \([\text{Am(TEDGA)}_3]\text{Cl}_6\).

“...in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products.”
Kimberlin et al., *PCCP*, 2022, 24, 9213.
Research Goals

1. Understand the basic radiation chemistry of the actinides in formally non-complexing media.

2. Elucidate the mechanisms underpinning the impact of actinide complexation on ligand radiolysis.

3. Develop multiscale modeling codes for the prediction of radiation-induced chemistry, speciation, and transport of the actinide series in any media.
Transients are detected by optical absorption changes.

**Research Techniques**

**Time-resolved Electron Pulse Radiolysis**

**Ex Situ Gamma and In Situ Alpha Radiolysis**
Radiation-Induced Actinide Redox Chemistry

Horne et al., Dalton Trans. 2021, 50, 10853.

Horne et al., Inorg. Chem. 2022, 61 (28), 10822.
Complexation Effects – HEH[EHP]

- **Methodology**: \( \Delta [\text{HEH[EHP]}]/[M(\text{HEH[EHP]})_2]_3 \) in 0.5 M DCM/\( n \)-dodecane; \( \text{RH}^+ \) decay measured at 800 nm over 200 ns using the BNL Laser Electron Accelerator Facility (LEAF).
Complexation Effects – HEH[EHP]

- **Steady-State Gamma Irradiations**: Cobalt-60 irradiation of 30 mM HEH[EHP] under organic only (■) and loaded with 2.5 mM La(III) from PIPPS/HNO₃ solution (●). Dose constants (d) were calculated from linear fits to $[[\text{La}([\text{HEH}[\text{EHP}]]_{2}3))]$ vs. absorbed gamma dose.
Complexation Effects – TBP, DEHBA, and DEHіBA

- **UO$_2^{2+}$** complexation had negligible effect on $k(TBP + RH^{+})$.
- For **DEHBA** and **DEHіBA**, **UO$_2^{2+}$** complexation afforded a $2.6\times$ and $1.4\times$ increase in their respective rate coefficients, respectively.

Celis-Barros et al., *PCCP* 2021, 23, 24589.
Complexation Effects – TBP, DEHBA, and DEH/iBA

- Coordinated $\text{NO}_3^-$ protect $[\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2]^+$ complexes.
- Most likely site of attack in DEHBA/DEH/iBA remains on the amide functionality in the complex.

Celis-Barros et al., PCCP 2021, 23, 24589.
Complexation Effects – TBP, DEHBA, and DEHiBA

- $\text{NpO}_2^{2+}$ and $\text{PuO}_2^{2+}$ complexation afforded significantly faster rates of reaction with $\text{RH}^+$, then for the non-complexed TBP, DEHBA and DEHiBA molecules.
- Evidence for electron transfer with the complexed metal center?
Complexation Effects – TODGA

- **Computations:** average local ionization energy analysis highlights the sites of the molecule susceptible to a radical or electrophilic attack.
- Horne *et al.*, *PCCP 2023*, under review.
Conclusions

• Understanding radiation chemistry is essential for innovating nuclear energy technologies.
• Non-traditional actinide oxidation states likely play a large role in redox cycling.
• Actinide complexation has significant effects on the fundamental radiation chemistry of their complexes, owing to steric effects, electron distribution differences, and the facilitation of inner vs. outer sphere mechanisms.
Acknowledgements
Questions?