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Radiation Chemistry and the Nuclear Fuel Cycle

January 2024

Gregory Peter Holmbeck

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Idaho National Laboratory

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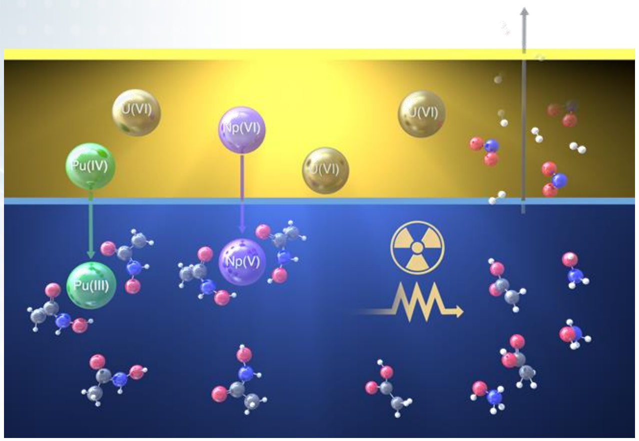
May 8th 2023

Gregory P. Horne
Center for Radiation Chemistry Research

Radiation Chemistry and the Nuclear Fuel Cycle

INL/MIS-23-03347



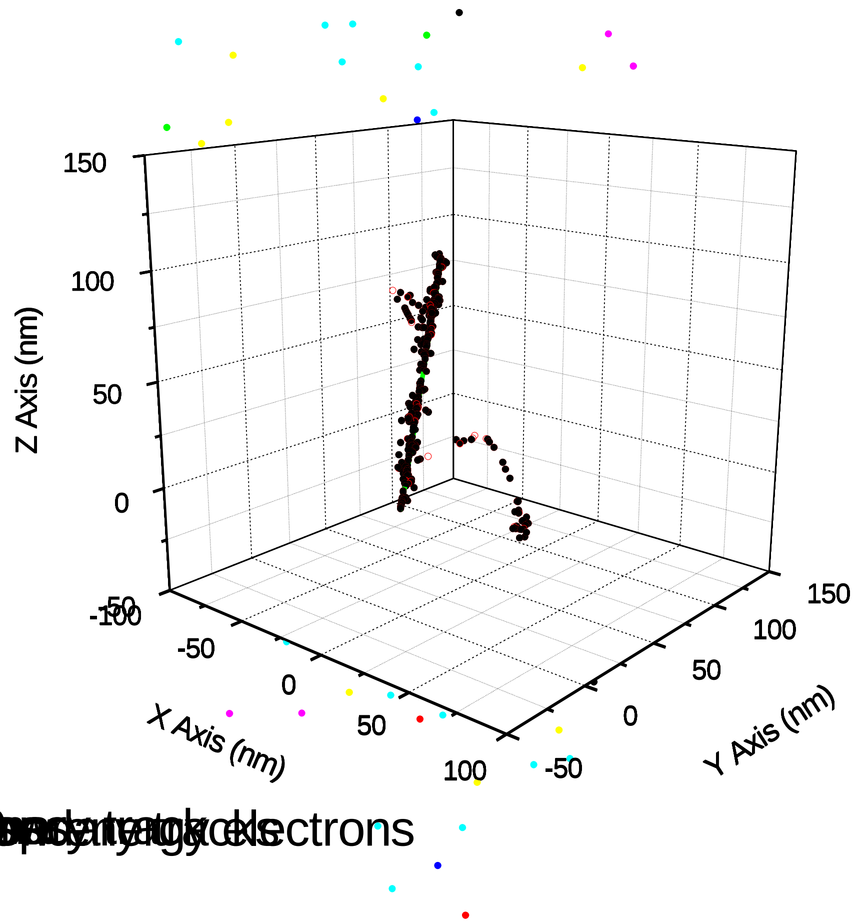
Conrad *et al.*, *ChemPhysChem* **2022**, e20220074

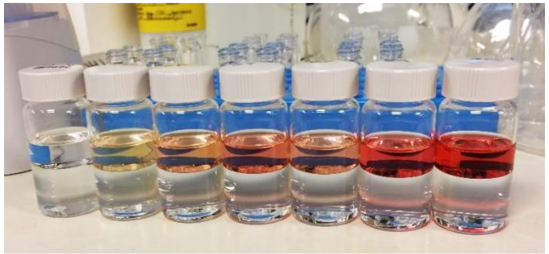
UK Professor and PhD Student Visit: Presentation on Separations and Waste Forms along with National Programs

Idaho National Laboratory

Radiation Chemistry

- The study of chemistry induced by the absorption of ionizing radiation.
- The passage of radiation through matter results in a series of energy transfer events.
- Radiolysis products propagate physical and chemical changes in the absorbing medium.





Increasing Gamma Dose

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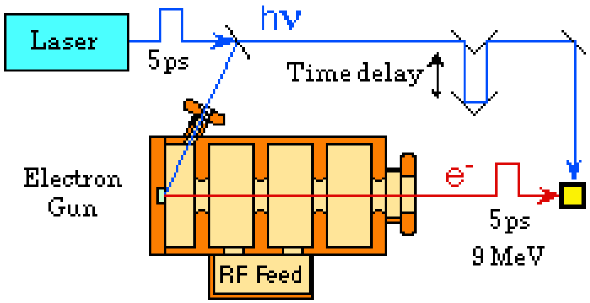
- Pimblott, LaVerne, and Mozumder, J. Phys. Chem. 1996, 100, 8595.
- Clifford, Green, Oldfield, Pilling, and Pimblott, J. Chem. Soc., Faraday Trans., 1986, 82, 2673.

Time-Resolve and Steady-State Irradiations

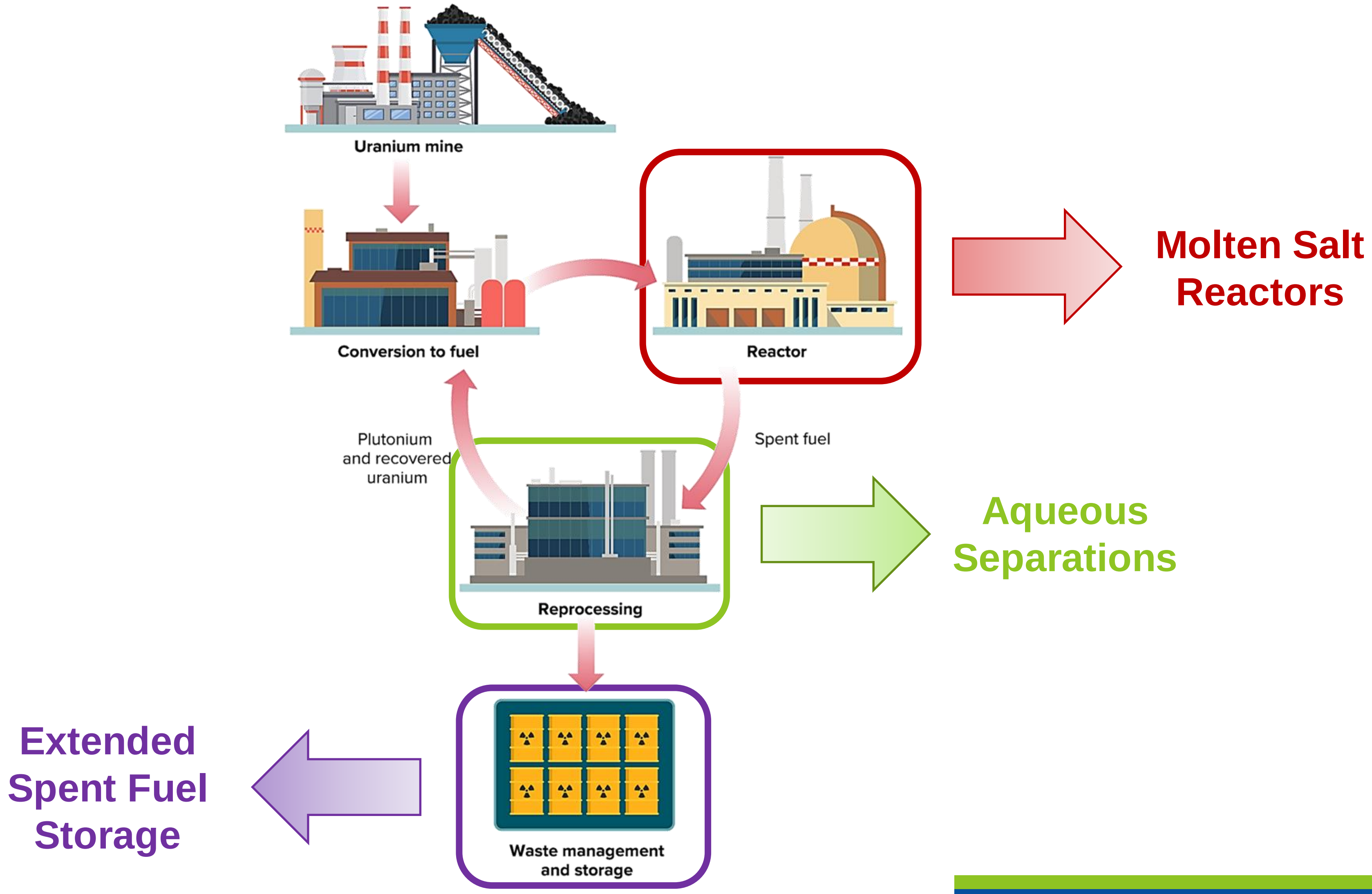
***Ex Situ* Gamma and *In Situ* Alpha Irradiations**



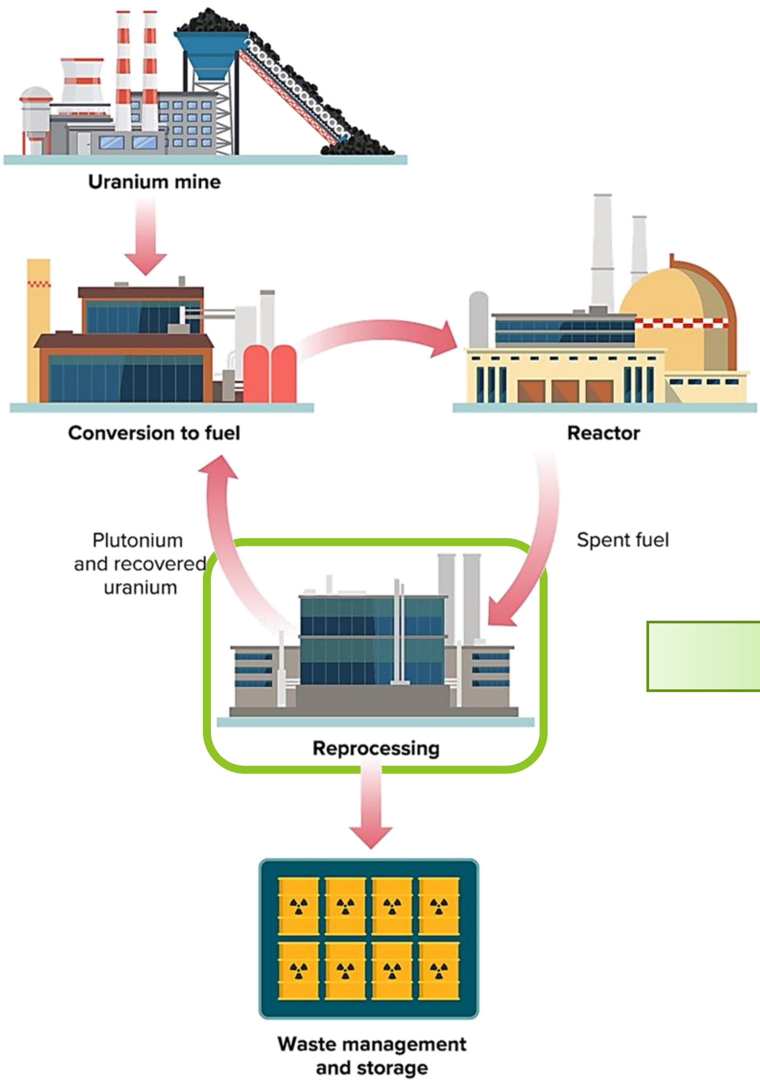
Electron Pulse Irradiations

- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

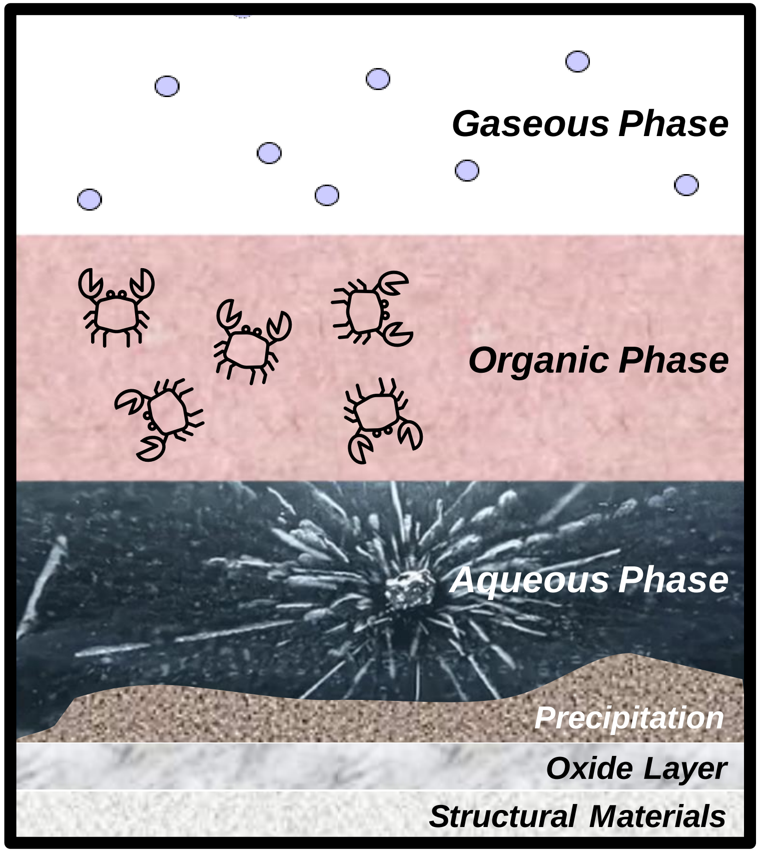
Radiation Challenges in the Fuel Cycle



Aqueous Separations



Solvent Extraction Reprocessing
Ligands/organic diluent:HNO_3/H_2O
(± additives)



Reprocessing radiation chemistry

Water Radiolysis

$$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$$

Indirect Radiation Effects

$$HNO_3 + {}^\bullet OH \rightarrow {}^\bullet NO_3 + H_2O$$

$$NO_3^- + e^- \rightarrow NO_3^{\bullet 2-}$$

$$NO_3^{\bullet 2-} + H_2O \rightarrow {}^\bullet NO_2 + 2OH^-$$

$$NO_3^- + H^\bullet \rightarrow HNO_3^- \rightarrow {}^\bullet NO_2 + OH^-$$

$${}^\bullet NO_2 + {}^\bullet NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 \rightarrow HNO_2 + HNO_3$$

Direct Radiation Effects

$$NO_3^- \rightsquigarrow NO_3^{-*} \longrightarrow NO_2^- + O$$

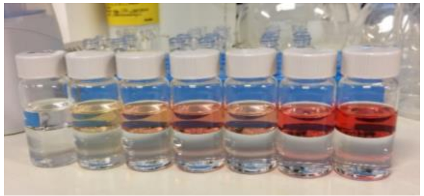
$$HNO_3 \rightsquigarrow HNO_3^* \longrightarrow HNO_2 + O$$

$$NO_3^- \rightsquigarrow {}^\bullet NO_3 + e^-$$

$$HNO_3 \rightsquigarrow {}^\bullet NO_3 + H^\bullet$$

Alkane Radiolysis

$$R\text{-}CH_3 \rightsquigarrow e^-, RH^{\bullet +}, RH^\bullet, {}^\bullet CH_3, H^\bullet, H_2$$



- 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**.

Impact of Actinide Complexation

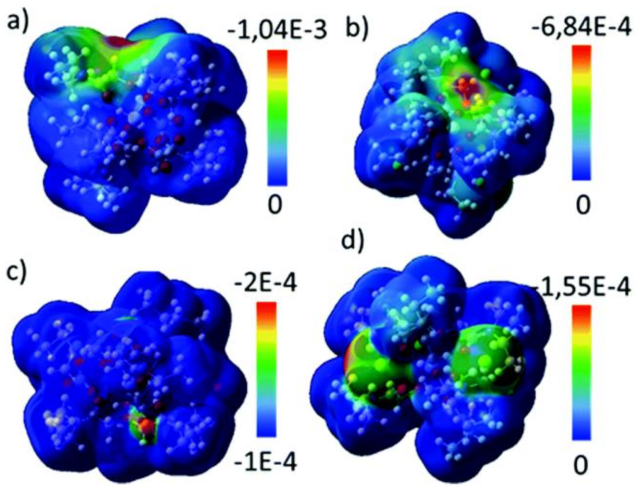
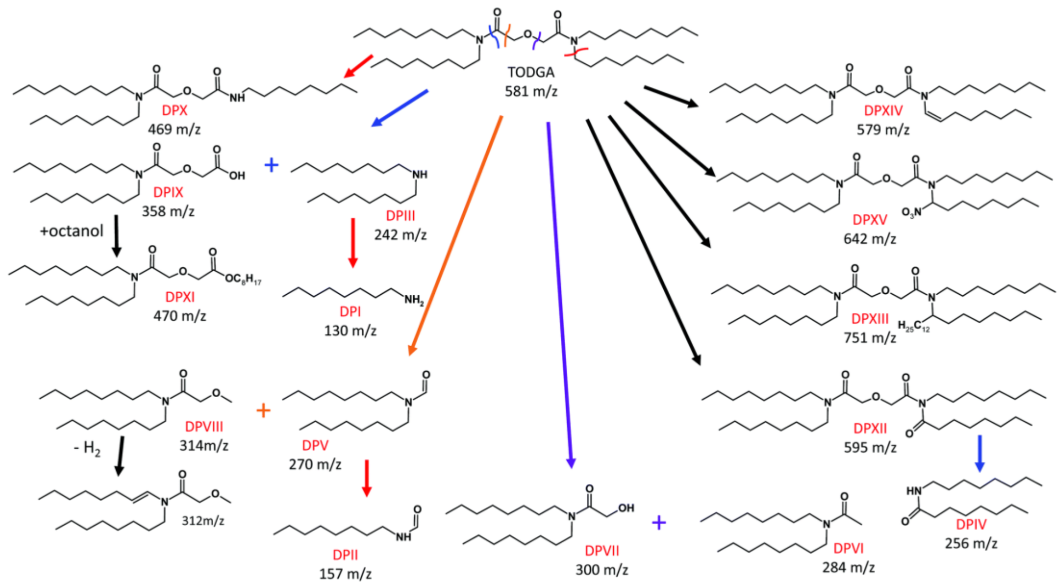


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



"…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.

- Bhattacharyya and Kundu, Int. *J. Radiat. Phys. Chem.*, **1971**, *3*, 1.
- Kundu and Matuura, *Int. J. Radiat. Phys. Chem.*, **1975**, *7*, 565.
- Ilan and Czapski, *Biochimica et Biophysica Acta*, **1977**, *498*, 386.
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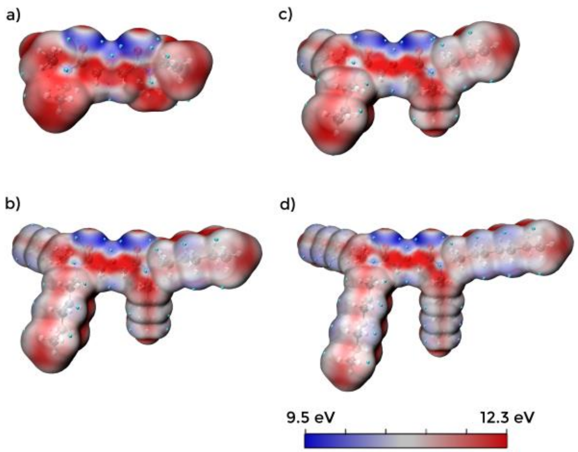
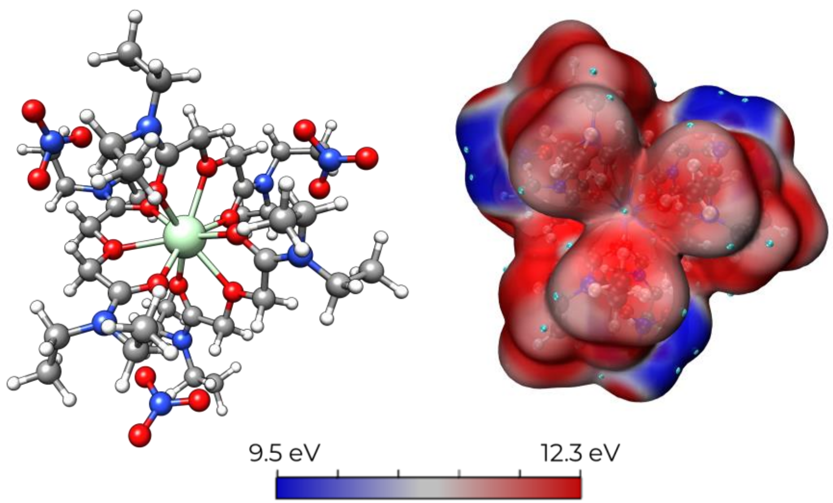
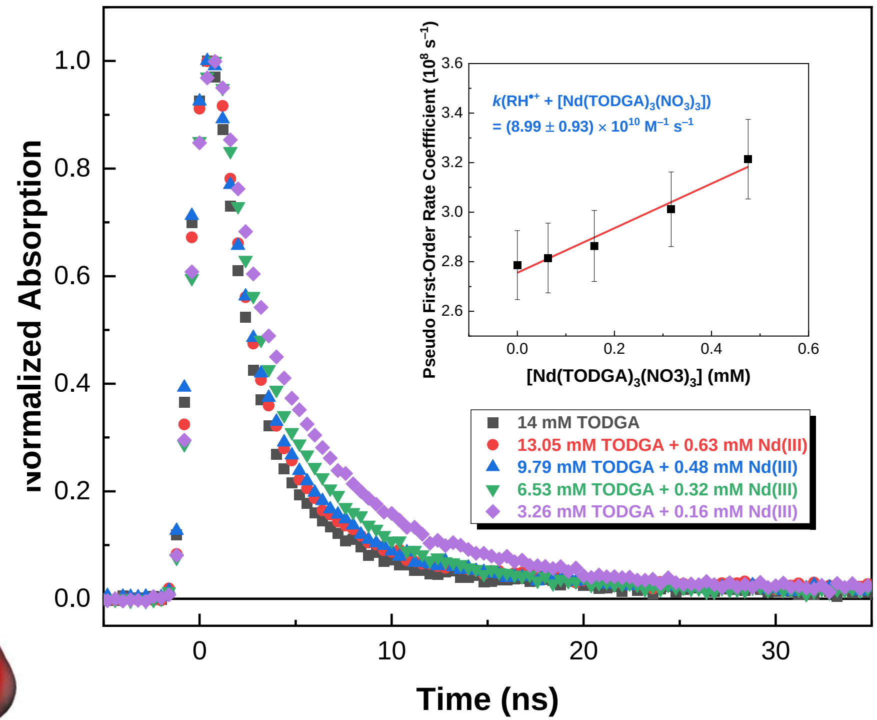
- Kimberlin, Saint-Louis, Guillaumont, Cames, Guilbaud, and Berthon, *PCCP*, **2022**, *24*, 9213.

Impact of Actinide Complexation



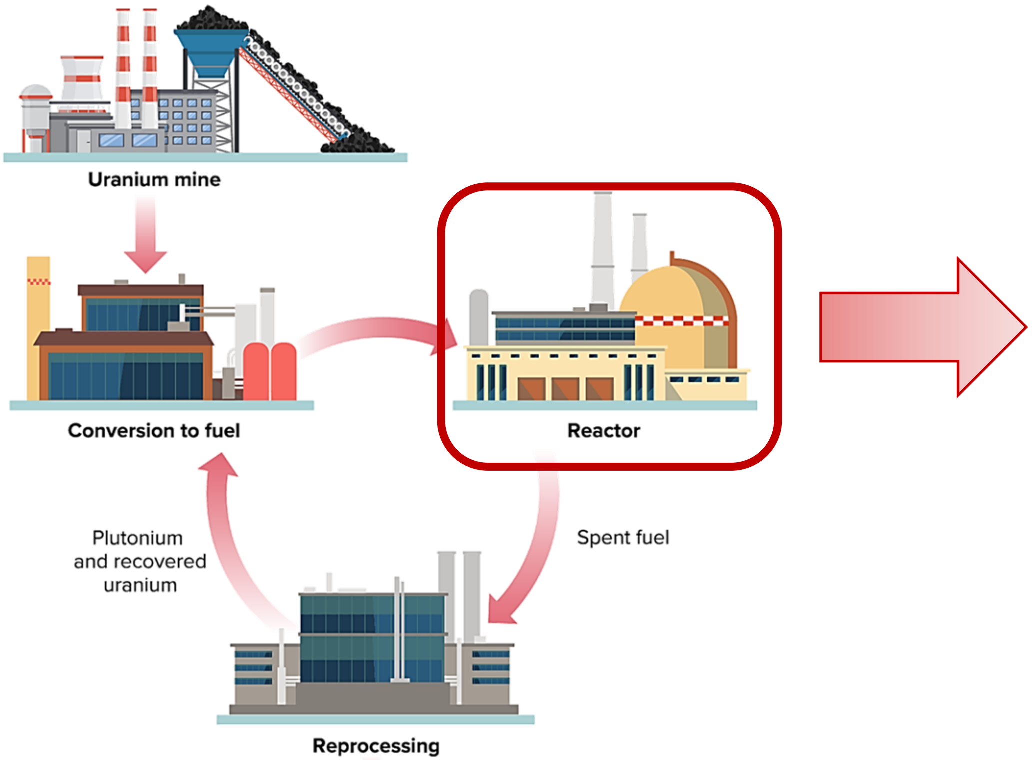


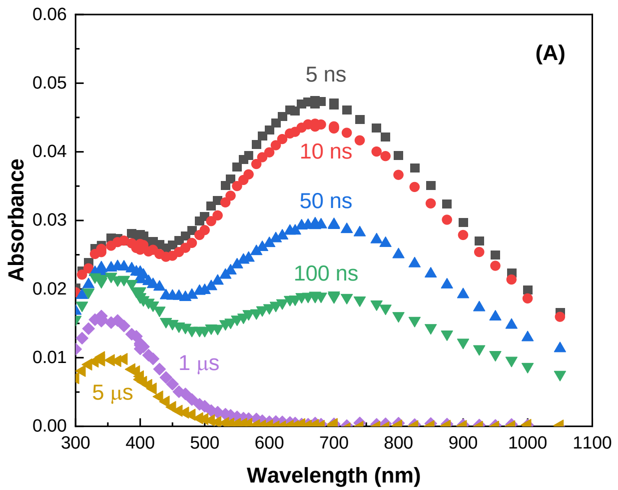


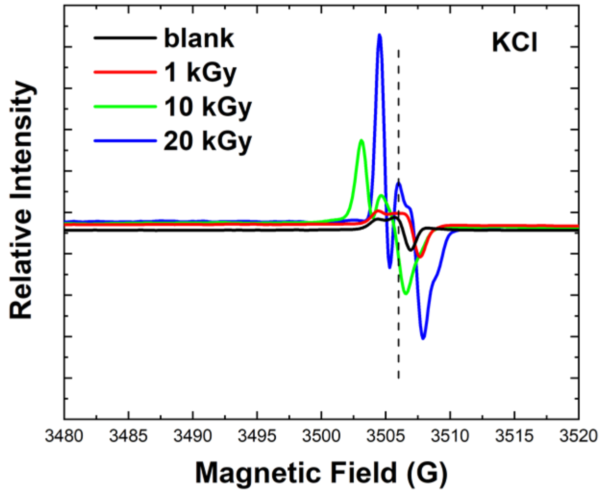
- **Computations:** average local ionization energy analysis highlights the sites of the molecule susceptible to a radical or electrophilic attack.

- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, Under Review.

Molten Salt Reactors







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- Ballesteros, Gakhar, Horne, Iwamatsu, Wishart, Pimblott, and LaVerne, *PCCP* **2021**, *23*, 10384.
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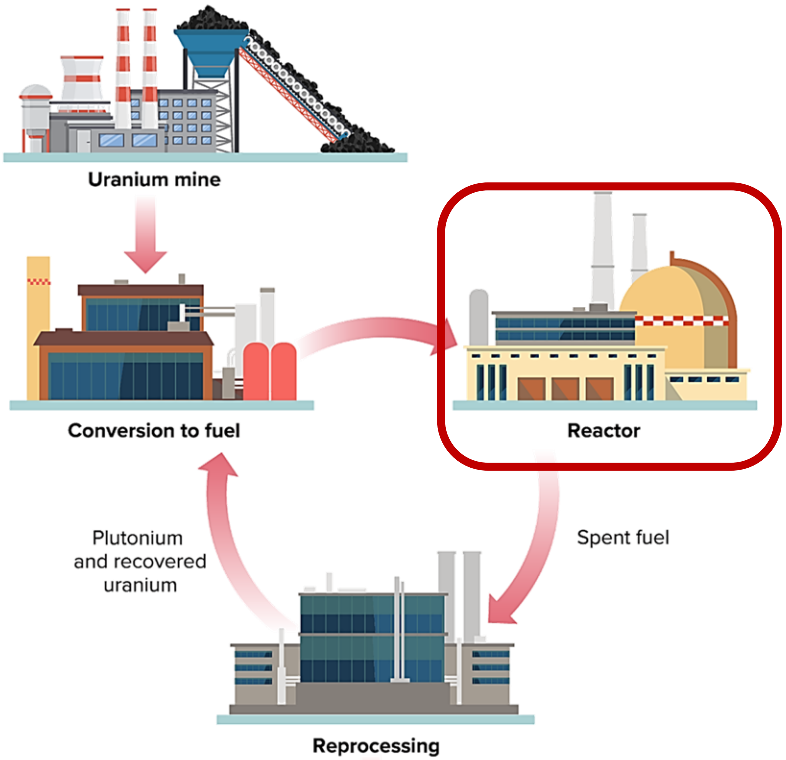
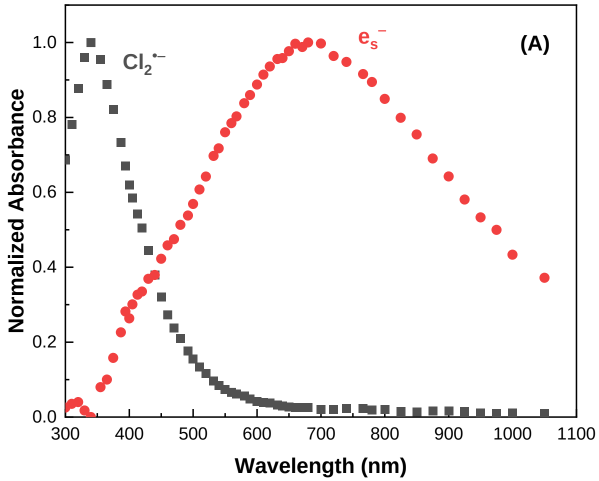
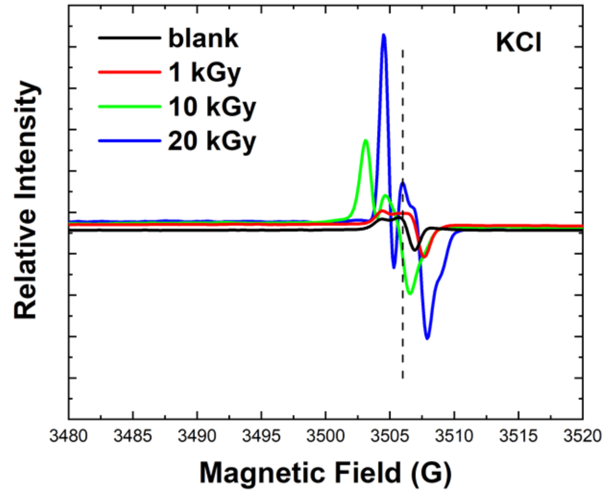
Molten Salt Reactors







- Phillips *et al.*, AIP Rev. Sci. Instrum. **2020**, *91 (8)*, 083105.
- Ballesteros, Gakhar, Horne, Iwamatsu, Wishart, Pimblott, and LaVerne, *PCCP* **2021**, *23*, 10384.
- Ballesteros, Gakhar, Woods, Horne, Iwamatsu, Wishart, Pimblott, and LaVerne, *J. Phys. Chem. C* **2022**, *126 (23)*, 9820.
- Iwamatsu, Horne, Gakhar, Halstenberg, Layne, Pimblott, and Wishart, *PCCP* **2022**, *24*, 25088.

Molten Salt Radiolysis

Molten Salt Radiolysis

$M^{n+}X_n^- \rightsquigarrow e^-, X^\bullet, M^{(n+1)+}$

$e_S^- + M^{n+} \rightarrow M^{(n-1)+} \rightarrow \rightarrow \rightarrow M_{clusters}$

$X^\bullet + X^- \rightarrow X_2^{\bullet -}$

$X_2^{\bullet -} + X_2^{\bullet -} \rightarrow X_3^- + X^-$

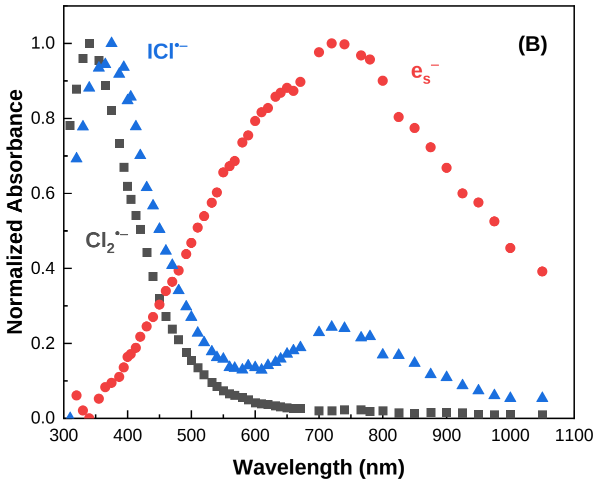
$X_3^- \rightleftharpoons X_2 + X^-$

Fission Product Iodine

$X^\bullet + I^- \rightarrow XI^{\bullet -}$

$XI^{\bullet -} + XI^{\bullet -}/X_2^{\bullet -} \rightarrow XI_2^-/X_2I^-/X_3^- + X^-/I^-$

$XI_2^-/X_2I^- \rightleftharpoons XI + I^-/X^-$



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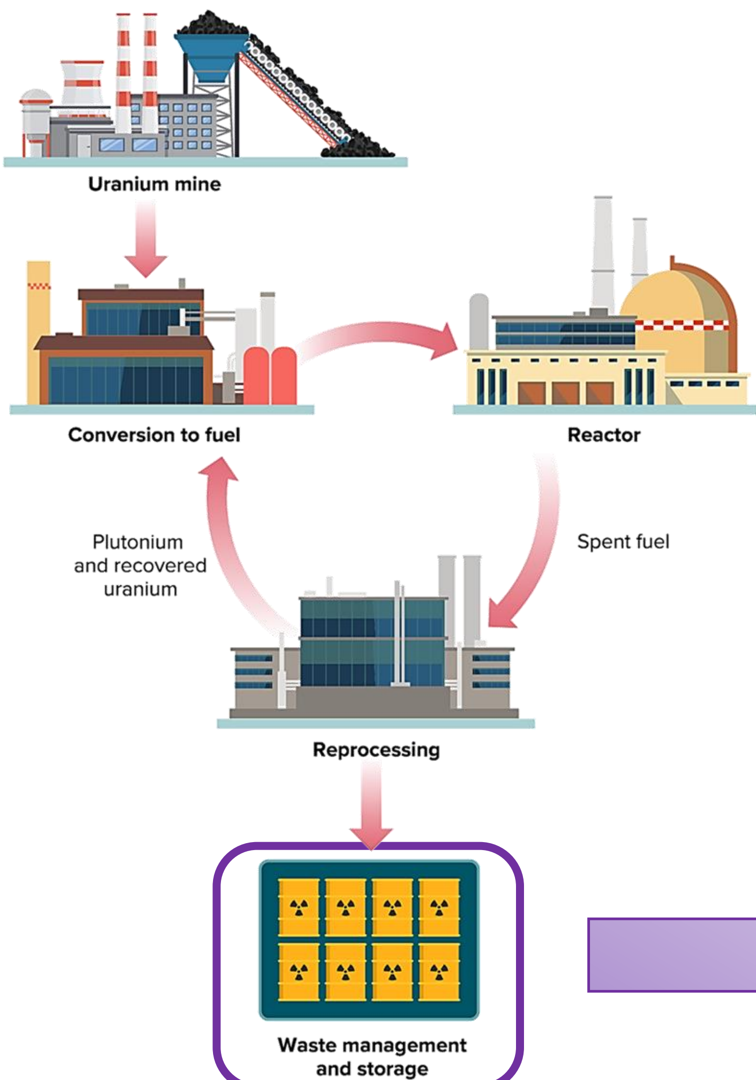
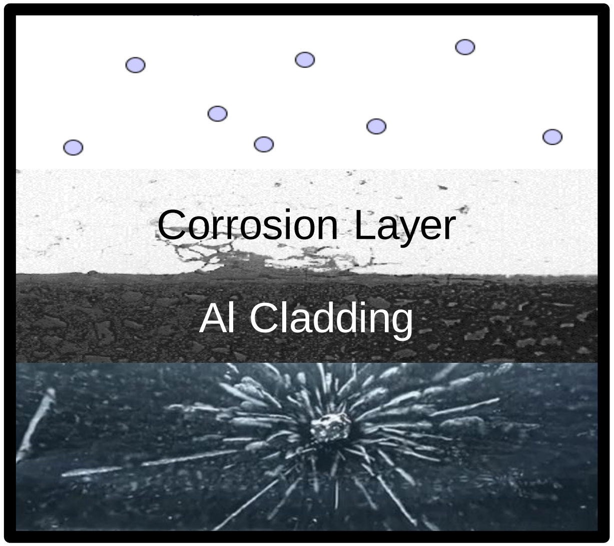
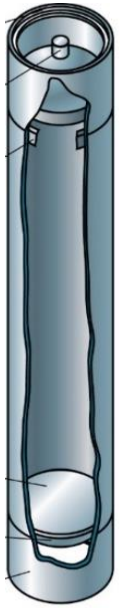
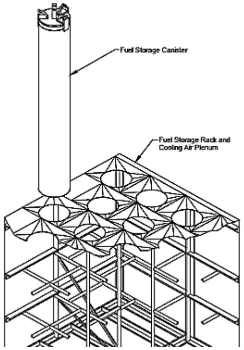
- Conrad, Iwamatsu, Woods, Gakhar, Layne, Cook, and Horne, *PCCP* **2023**, Under Review.

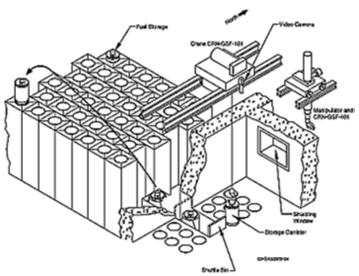
Extended Spent Fuel Storage











Radiation-Induced H_2 Production Pathways

Water Radiolysis

$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$

Surface Processes

$Al_{(s)} \rightsquigarrow h^+ + e^-$

H_2 Production Processes

$H_2O^* \rightarrow H_2 + O$

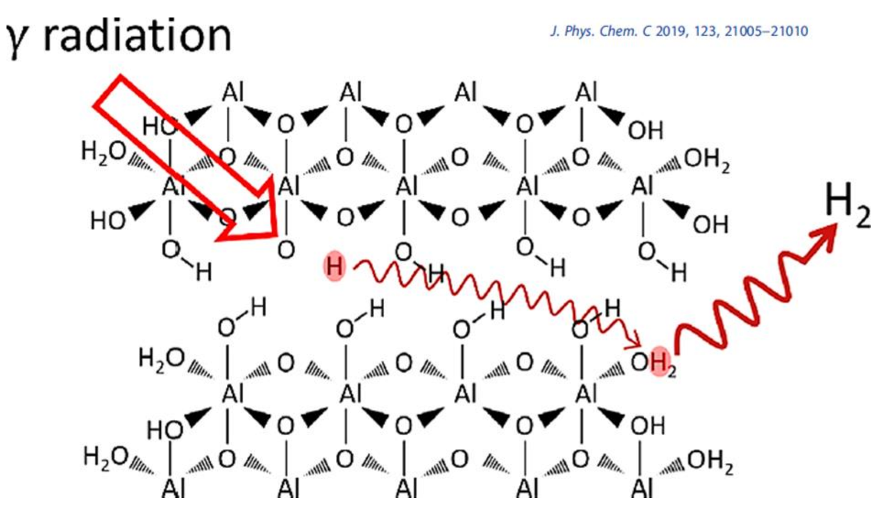
$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$

$e_{aq}^- + H^\bullet + H_2O \rightarrow H_2 + OH^-$

$e_{aq}^- + H_{aq}^+ \rightarrow H^\bullet$

$H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH$

$H^\bullet + H^\bullet \rightarrow H_2$



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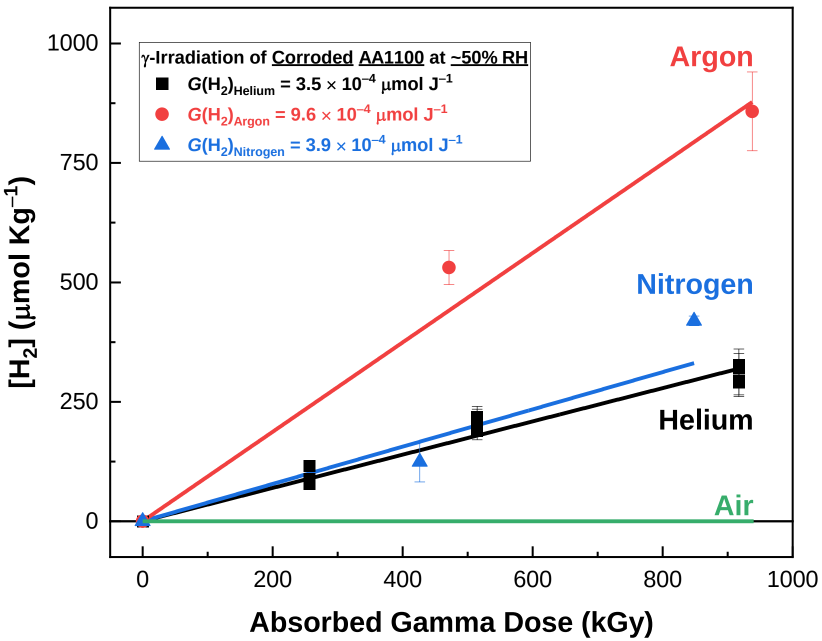
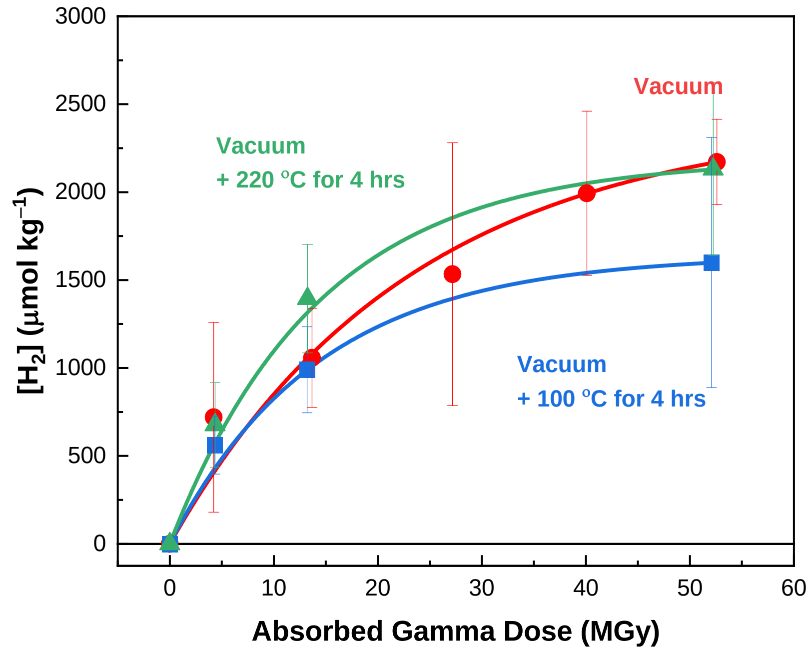
- Eidelpes, Jarrell, Sindelar, Lister, Horne, Parker-Quaife, Conrad, Pilgrim, Abboud, Winston, Smith, Randall, and d'Entremont, *J. Nucl. Mat.* **2023**, 154299.

Radiation-Induced H_2 Generation





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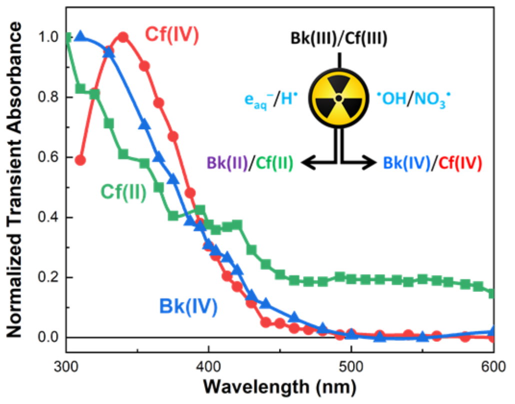
Summary and Acknowledgements

- Radiation chemistry is the study of phenomena induced by the absorption of ionizing radiation.
- Radiolysis products propagate physical and chemical changes in the absorbing medium (solids, liquids, and gases)
- Understanding the underlying chemistry is critical for the innovation of nuclear fuel cycle technologies



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