INL/CON-22-68159-Revision-0

Radiolytic Studies of Single-Cycle Extraction Systems

July 2022

Changing the World's Energy Future

Gregory P Horne, Corey David Pilgrim, Jacy Kathleen Conrad, Peter R Zalupski, Travis S Grimes, Brian Rotermund, Stephen Mezyk, Andrew Cook

Idaho National Laboratory

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Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

July 19th 2022

Gregory P. Horne

Center for Radiation Chemistry Research

Radiolytic Studies of Single-Cycle Extraction Systems

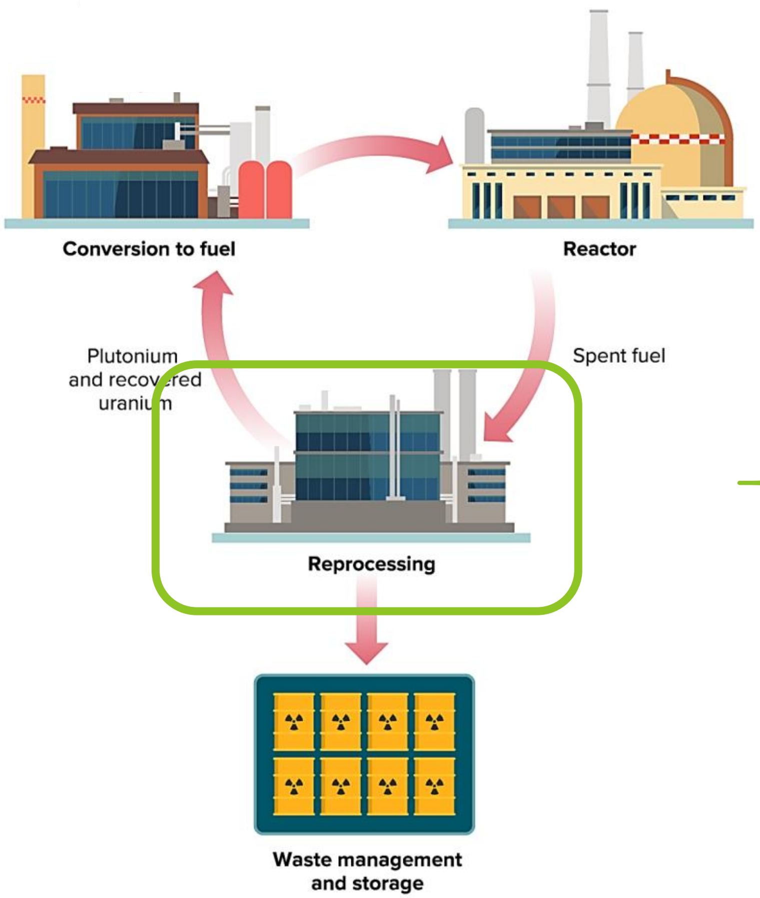
INL/CON-22-68159

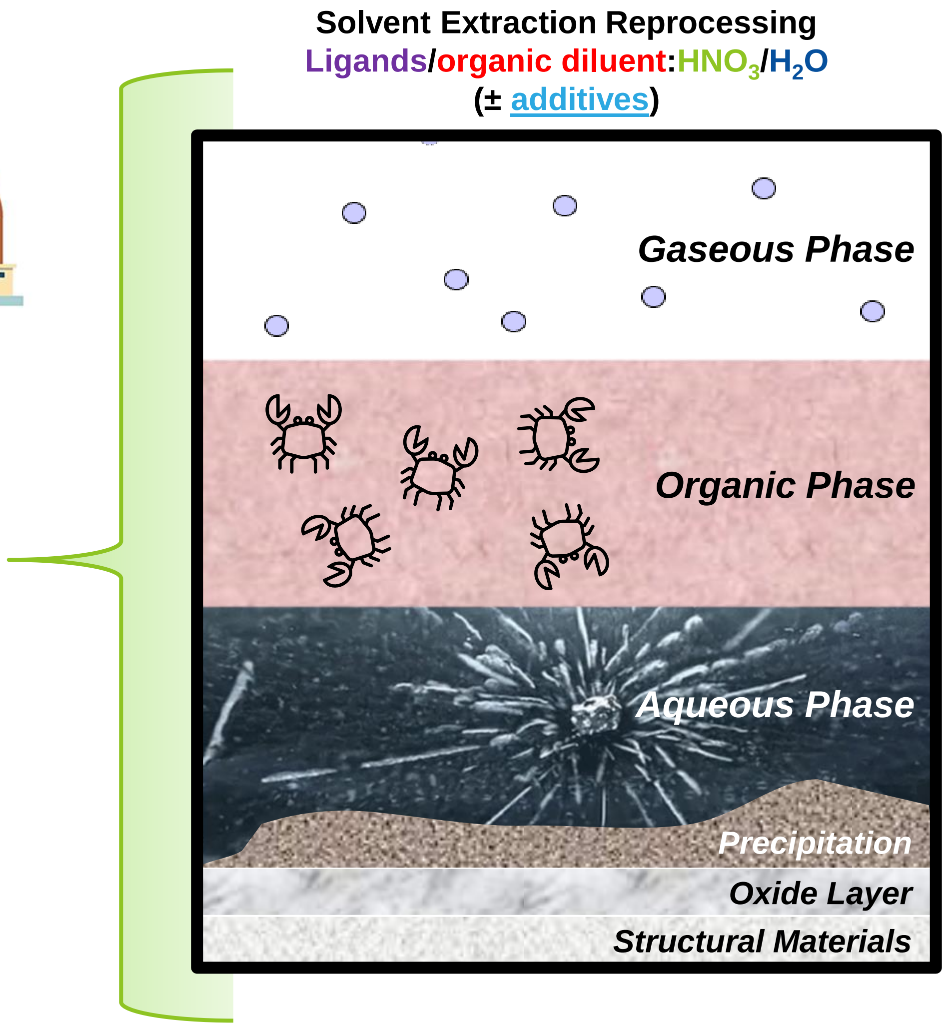
MATERIAL RECOVERY & WASTE FORM DEVELOPMENT

Summer Campaign Meeting 18-19 July 2022

Idaho National Laboratory

Single Cycle Processes & Innovative Aqueous Separations Radiation Chemistry





- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop: Science-Based Technology Directions for Accelerating Nuclear Fuel Recycle; Final workshop report to the US Department of Energy, Office of Nuclear Energy: Washington DC, **2022**.

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

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

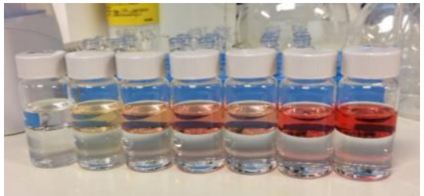
$$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$$

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

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

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**.

Reprocessing radiation chemistry

Water Radiolysis

Direct Radiation Effects

Key Transient Species

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

$^{\bullet}NO_3$ from HNO_3

$RH^{\bullet+}$ from *n*-dodecane

$N_2O_4 \rightarrow HNO_2 + HNO_3$

- 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**.

Reprocessing radiation chemistry

Water Radiolysis

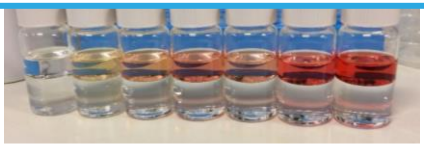
Direct Radiation Effects

Today's Research Focus

$RH^{\bullet +}$ from *n*-dodecane

H_2

$N_2O_4 \rightarrow HNO_2 + HNO_3$



- 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**.

Complexation effects

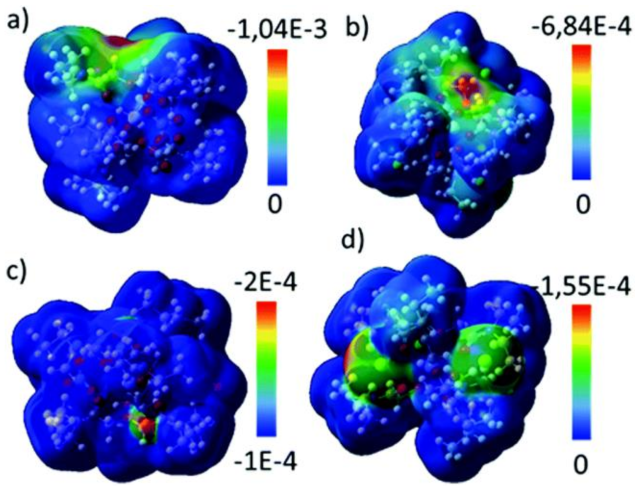
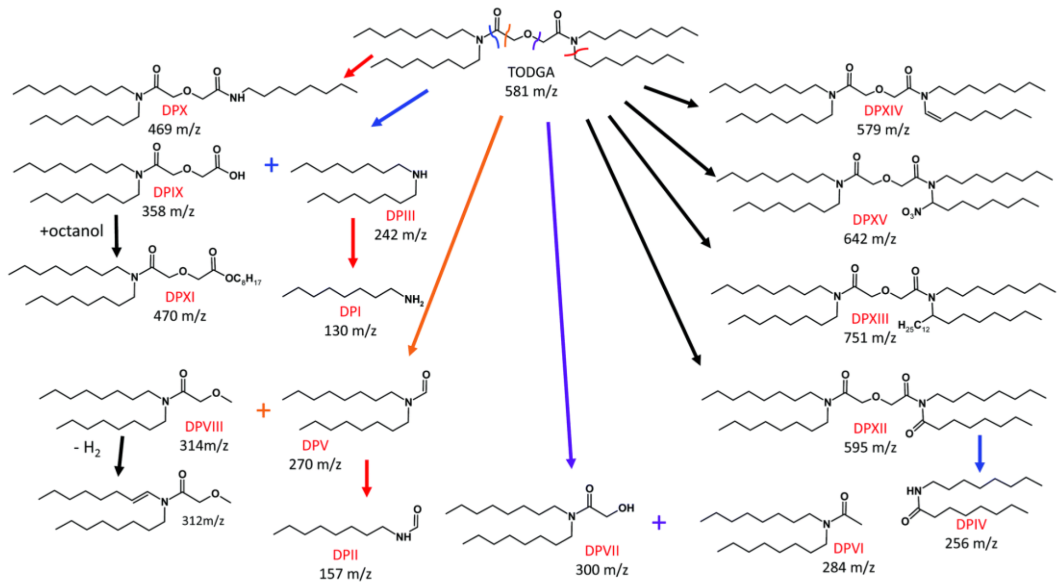
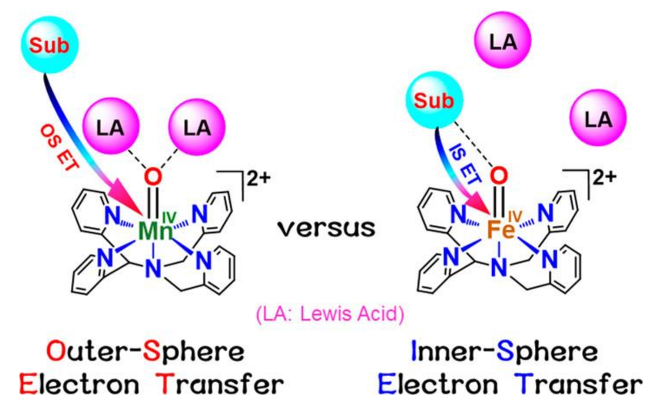


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



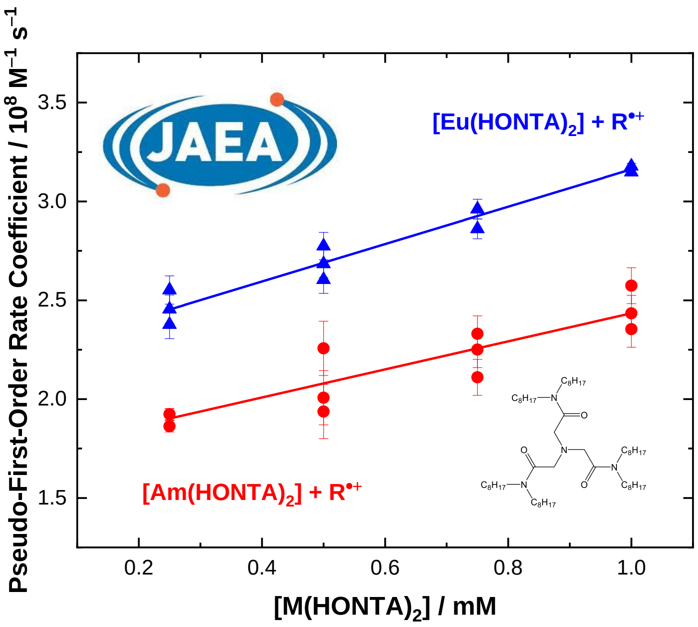


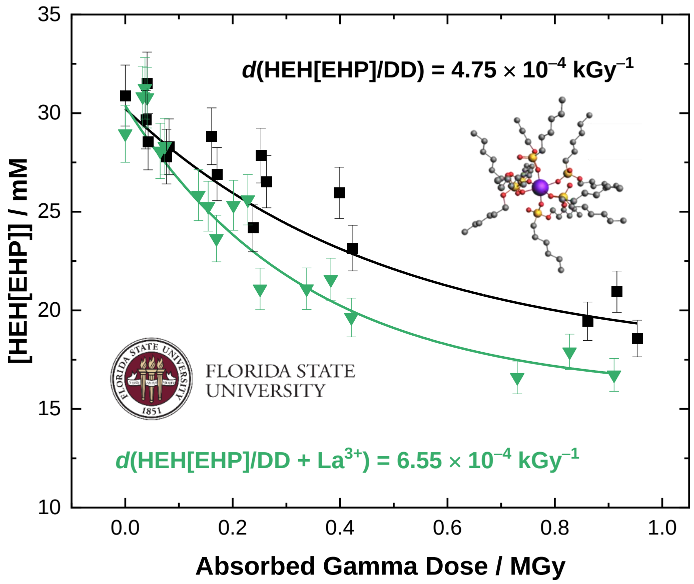
Sharma, Lee, Li, Nam, and Fukuzumi, *Inorg. Chem.*, **2019**, *58 (20)*, 13761.

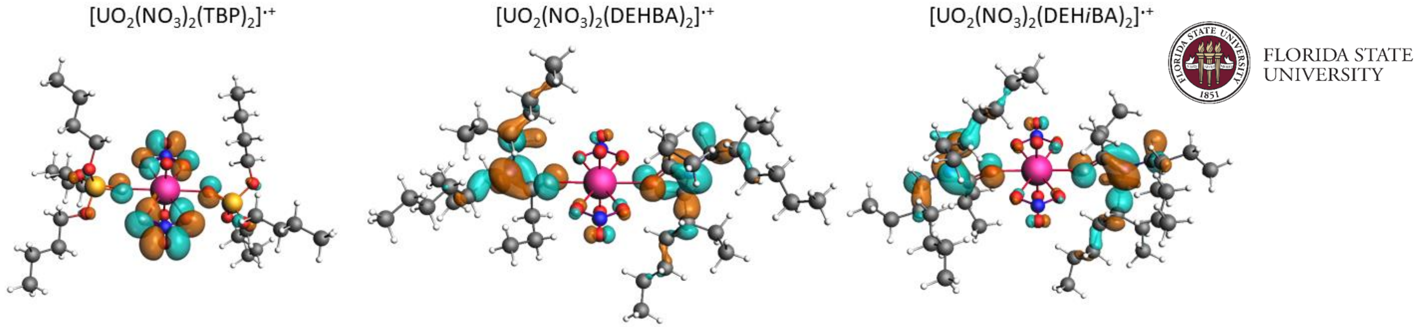
“…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products.” Kimberlin *et al.*, *PCCP,* **2022**.

- 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.
- Buettner, Doherty, and Patterson, *Fed. Euro. Biochem. Soc.*, **1983**, *158 (1)*, 143.
- Kimberlin, Saint-Loius, Guillaumont, Cames, Guilbaid, and Berthon, PCCP, **2022**, *24*, 9213.

Complexation effects under MRWFD

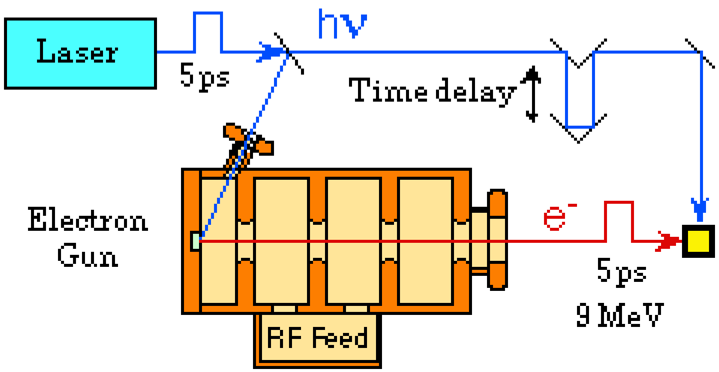




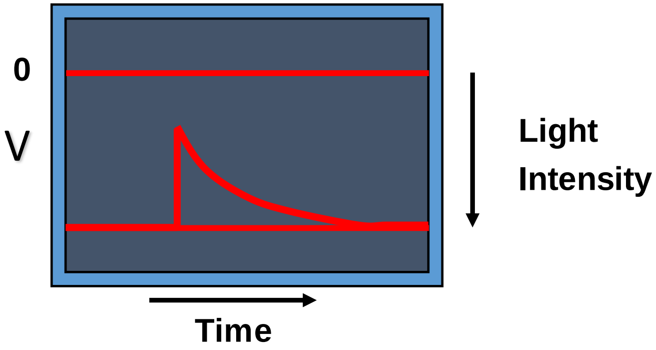


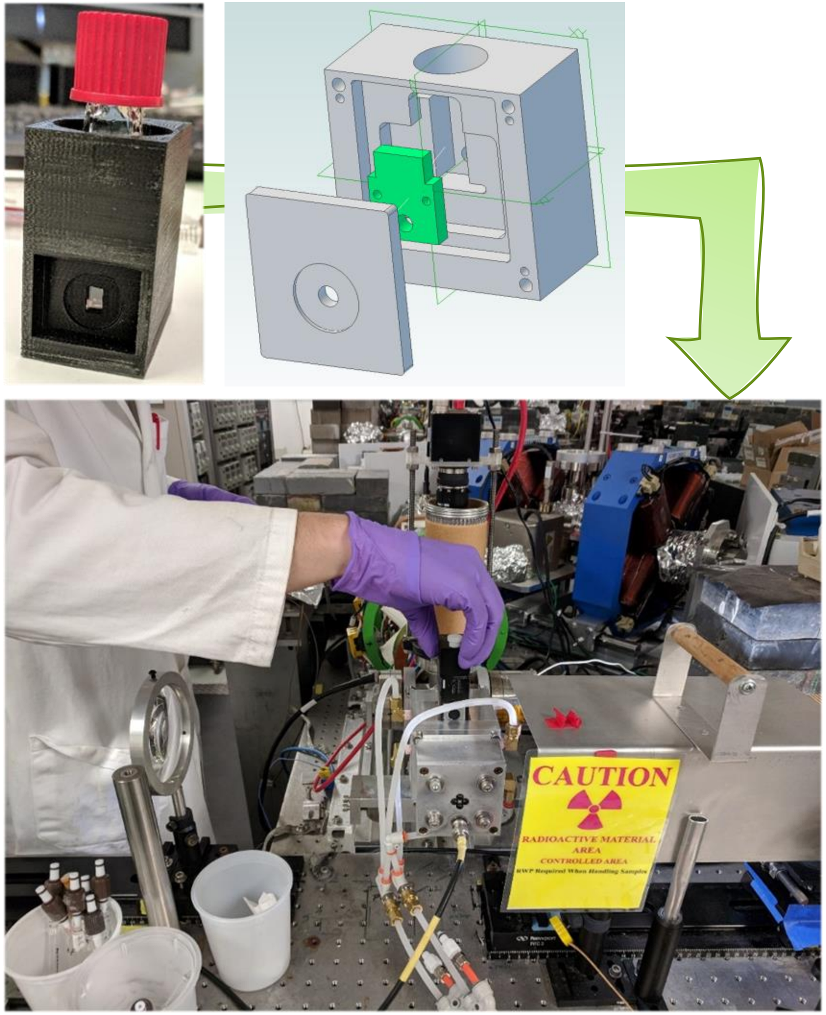
- Toigawa *et al., PCCP*, **2021**, *23*, 1343.
- Celis-Barros et al., *PCCP*, **2021**, *23*, 24589.
- Baxter *et al.*, *Dalton Trans.*, **2022**, *in preparation*.

Methodology



Transients are detected by optical absorption changes.





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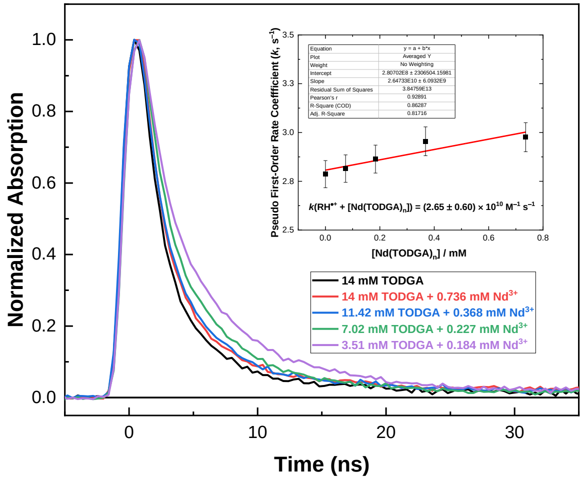
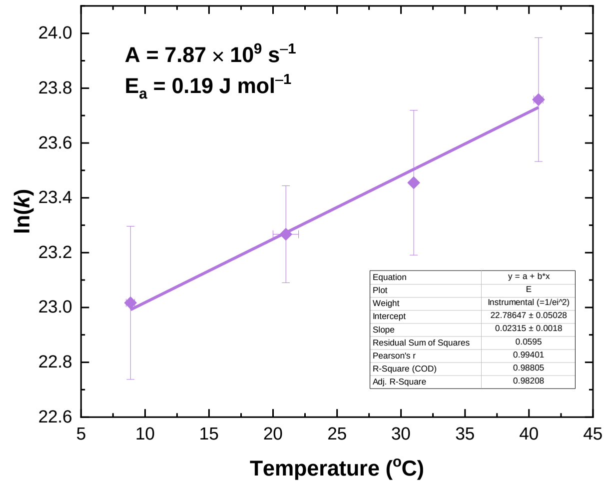
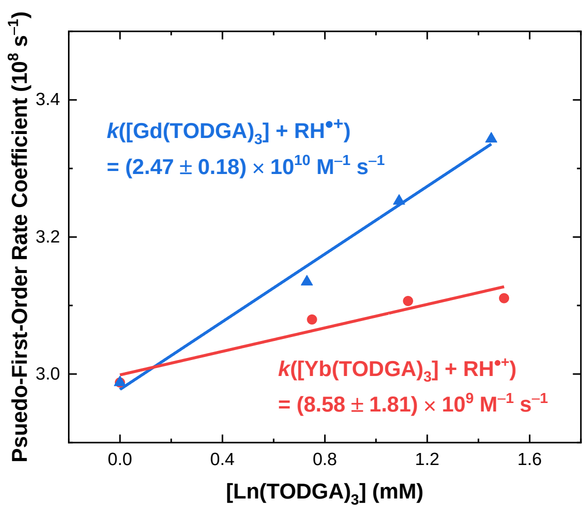
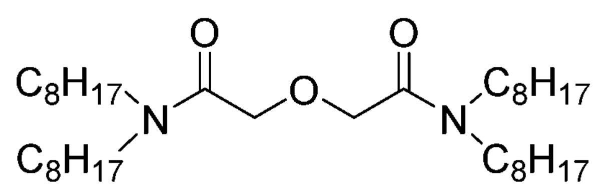
Lanthanide Complexed TODGA Radiolysis





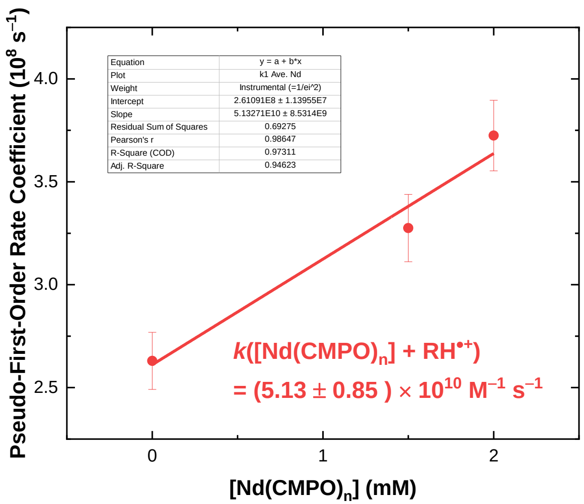


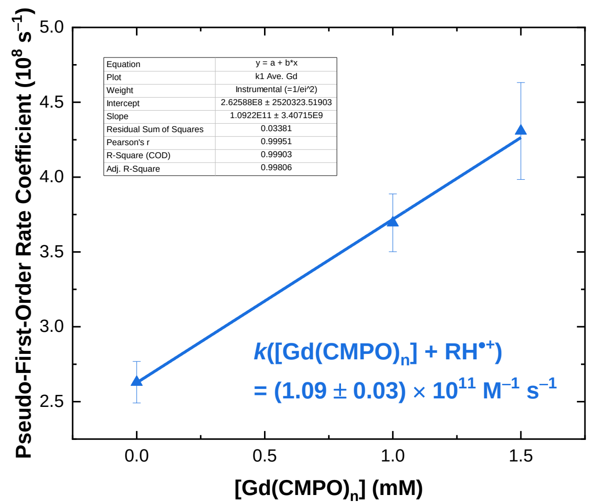


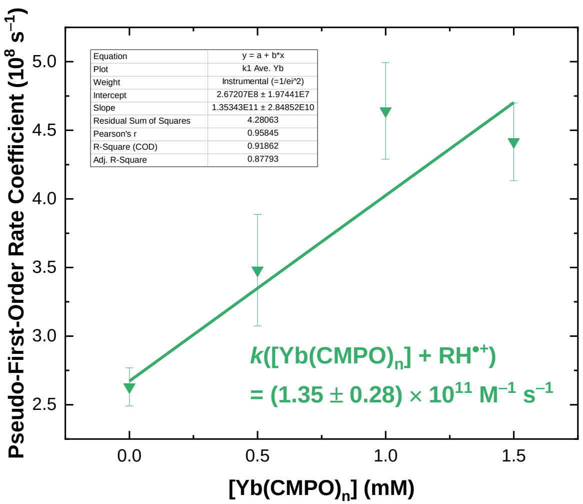
k(TODGA + $RH^{\bullet+}$)
$= (9.72 \pm 1.10) \times 10^9\ M^{-1}\ s^{-1}$

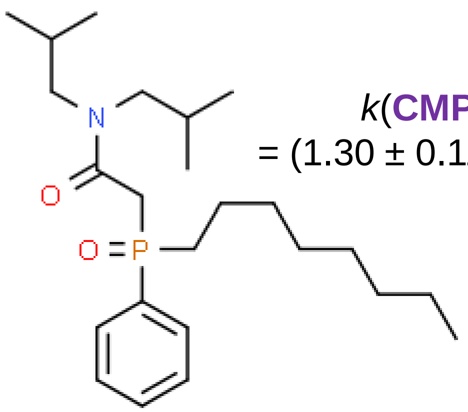
- Zarzana, Groenewold, Mincher, Mezyk, Wilden, Schmidt, Modolo, Wishart ,and Cook, *Solv. Extr. Ion Exch.*, **2015**, *33(5)*, 431.

Lanthanide Complexed CMPO Radiolysis









$k(\text{CMPO} + RH^{\bullet +})$
$= (1.30 \pm 0.11) \times 10^{10}\ M^{-1}\ s^{-1}$

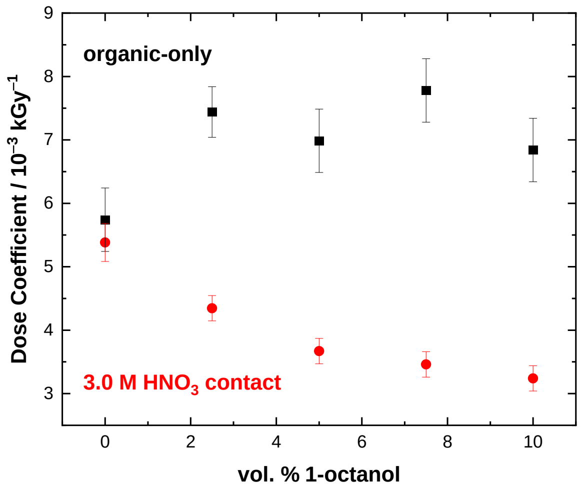
- Mezyk, Mincher, Dhiman, Layne, and J. W. Wishart, *J. Radioanal. Nucl. Chem.*, **2016**, *307*, 2445.

Conclusions

- Complexation has a profound effect on reaction kinetics, from changes in electron distribution to size.
- Understanding the impact of complexation on the radiation-induced degradation mechanisms of reprocessing ligands is essential for accurate estimates of process viability.
- *M4 milestone due September 30th 2022, draft manuscript*. On track.

Future Research

- Continued support in evaluating the radiation robustness of next generation ligands.
- Determine the impact of post-VOLOX direct dissolution formulations on metal-loaded ligand radiolysis behavior.



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- Horne *et al.*, Does Addition of 1-Octanol as a Phase Modifier Provide Radical Scavenging Radioprotection for N,N,N',N'-tetraoctyldiglycolamide (TODGA)? *PCCP*, **2020**, *22*, 24978.

Acknowledgements

U.S. DEPARTMENT OF ENERGY







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NTRD Nuclear Technology Research & Development

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