INL/MIS-21-62592-Revision-0

Radiolytic Study of Single-Cycle Extraction Systems

May 2021

Changing the World's Energy Future

Gregory P Horne

Idaho National Laboratory

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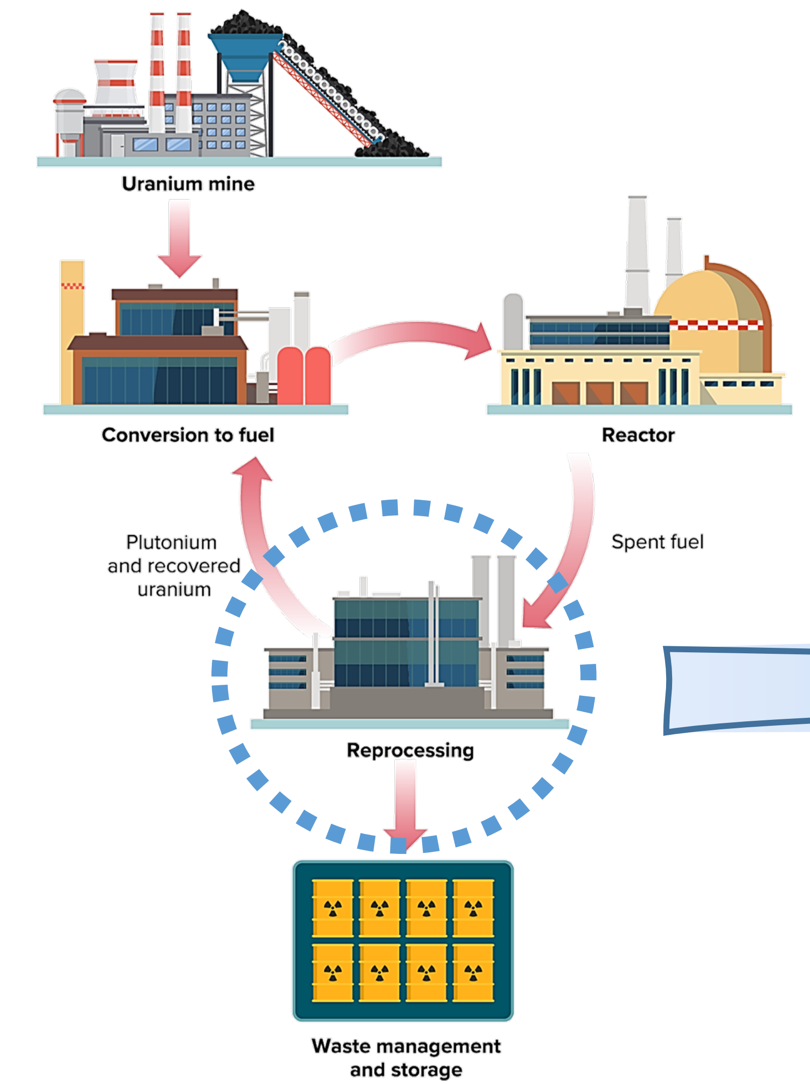
Radiolytic Study of Single-Cycle Extraction Systems

Gregory P. Horne

INL Center for Radiation Chemistry Research

U.S. DEPARTMENT OF ENERGY

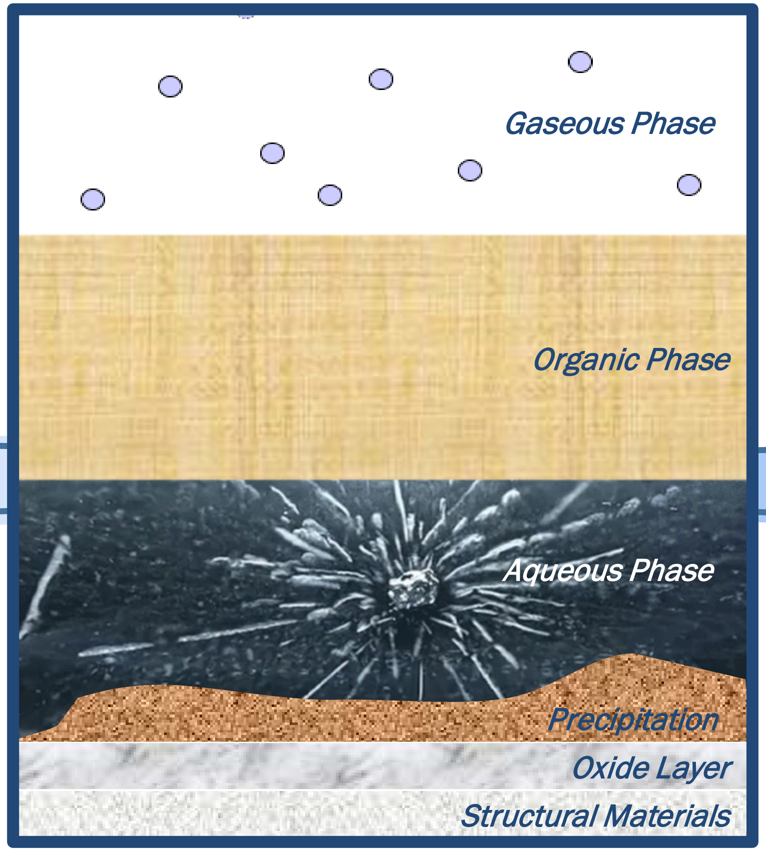
Nuclear Fuel Reprocessing and Radiation Chemistry

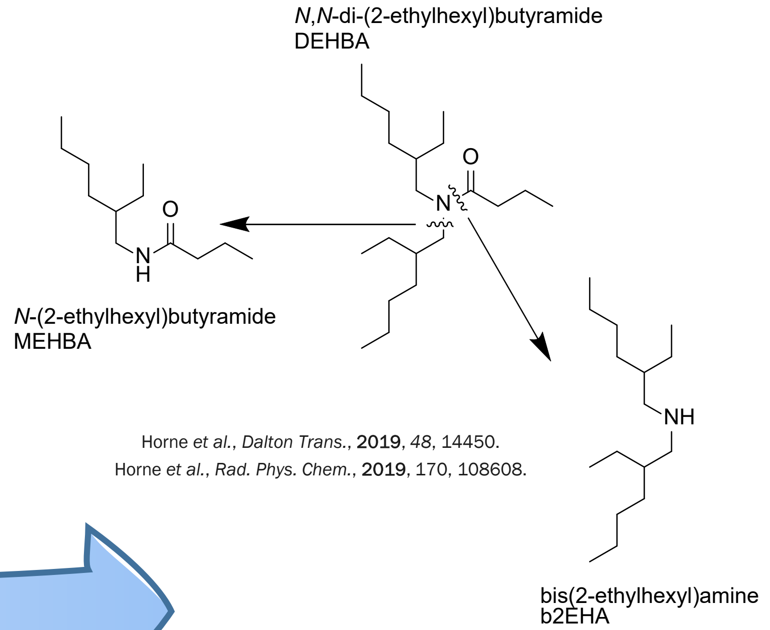


Solvent Extraction Reprocessing

Ligands/organic diluent:HNO_3/H_2O

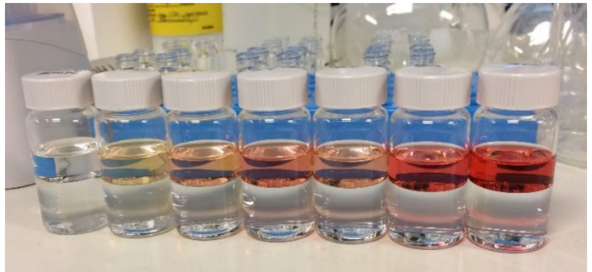
(± additives)





Horne et al., *Dalton Trans.*, **2019**, *48*, 14450.

Horne et al., *Rad. Phys. Chem.*, **2019**, 170, 108608.



Our (*the Fundamental Radiation Chemistry Group*) Goal

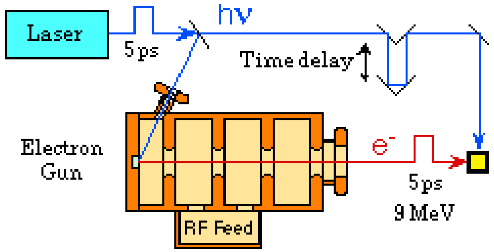
Provide quantitative mechanistic insight into radiation-induced processes to facilitate ***prediction*** of:

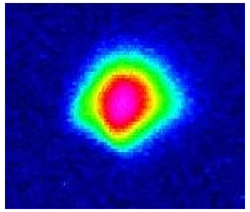
1. Actinide and other key element redox distributions
2. Solvent system component lifetimes and chemistry
3. Optimum ligand and solvent system design

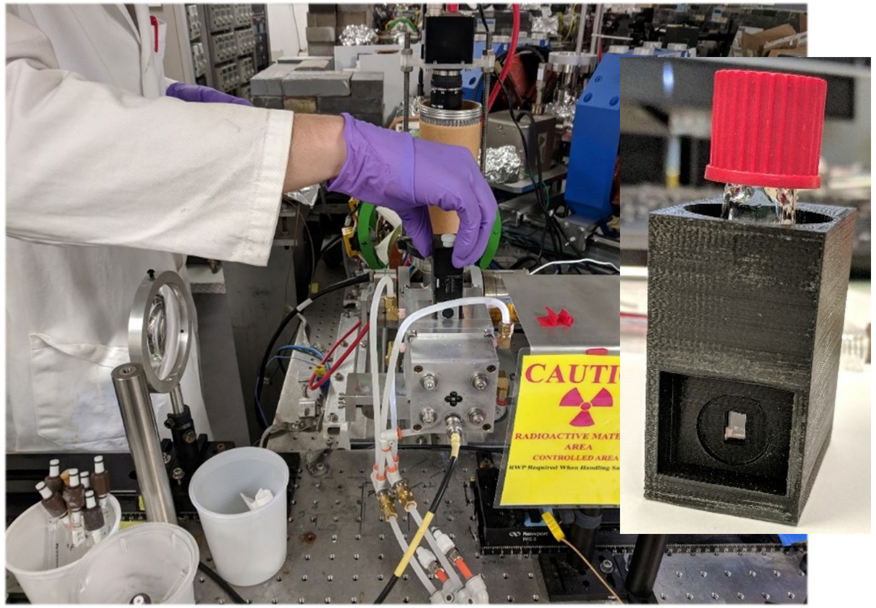
Methodology

Steady-State Alpha and Gamma Irradiations

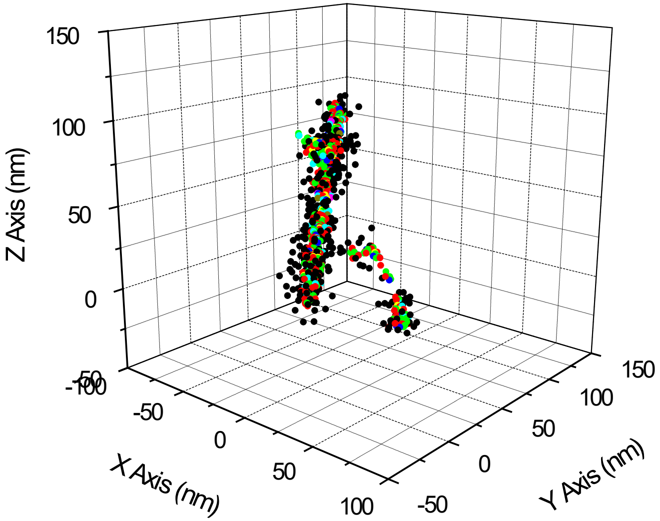
Time-Resolved Pulsed Electron Irradiations







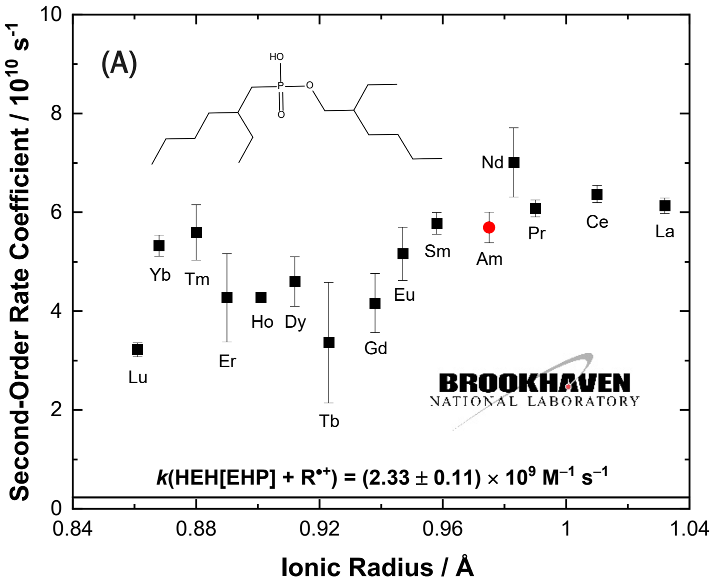
Multi-scale Modelling

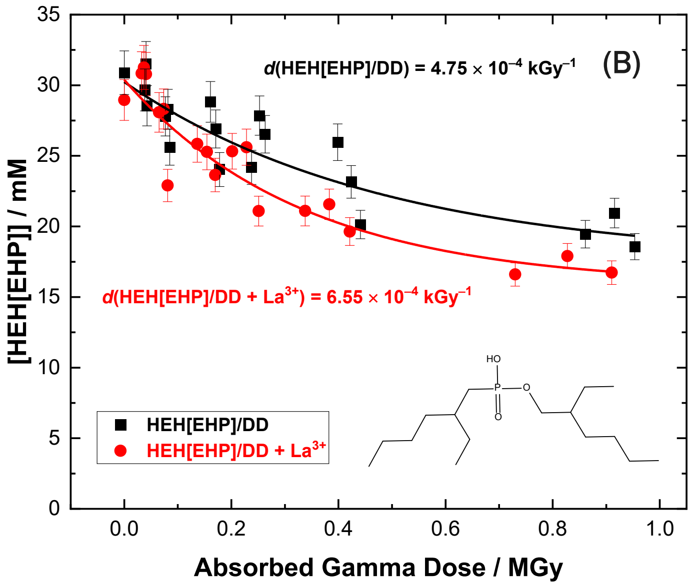


Multi-scale Modelling Approach	Processes	Timescale
1. Track Structure Simulation	Energy Transfer and Track Structure	<1 femtosecond
2. Physicochemical Processes	Ultra-fast Chemistry	<1 picosecond
3. Nonhomogeneous Diffusion-Reaction Kinetics	Intra-track Chemistry	< 1 microsecond
4. Homogeneous Bulk Chemistry	Reaction of Long-lived Radiolysis Species	>1 microsecond

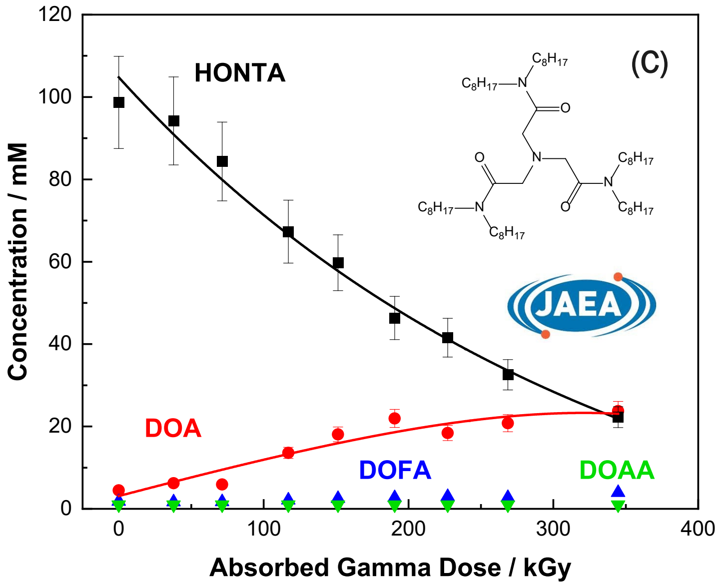
Effect of Complexation on Ligand Radiolysis (FY20-21)

Baxter *et al.*, *ChemComm,* **2021**, in preparation.





Toigawa *et al.*, *Physical Chemistry Chemical Physics,* **2021**, *23*, 1343.



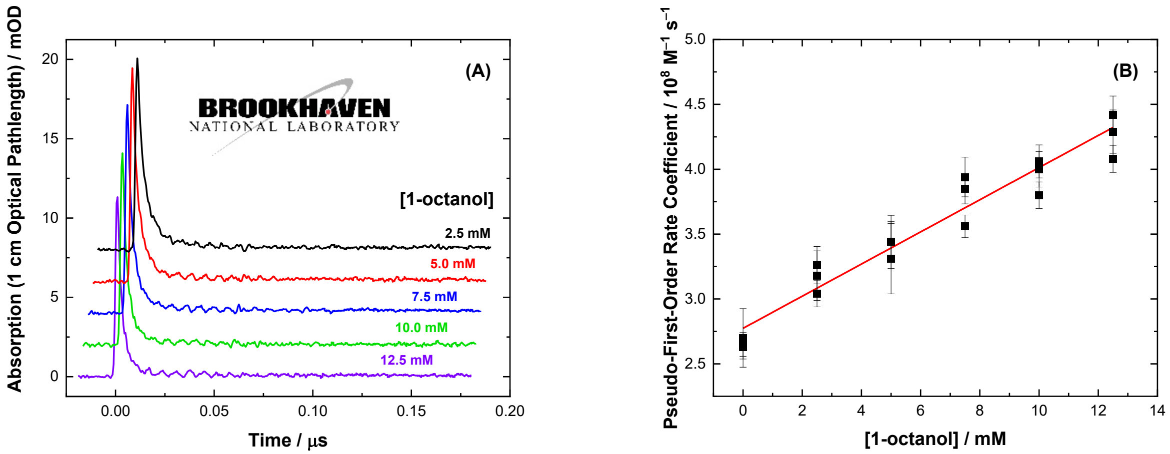
Metal ion complexation alters electron distribution and sterics, ultimately influencing ligand radiolysis!

• Toigawa, T.; Peterman, D.R.; Meeker, D.S.; Grimes, T.S.; Zalupski, P.R.; Mezyk, S.P.; Cook, A.R.; Yamashita, S.; Kumagai, Y.; Matsumura, T.; Horne, G.P., *PCCP*, **2021**, *23*, 1343.

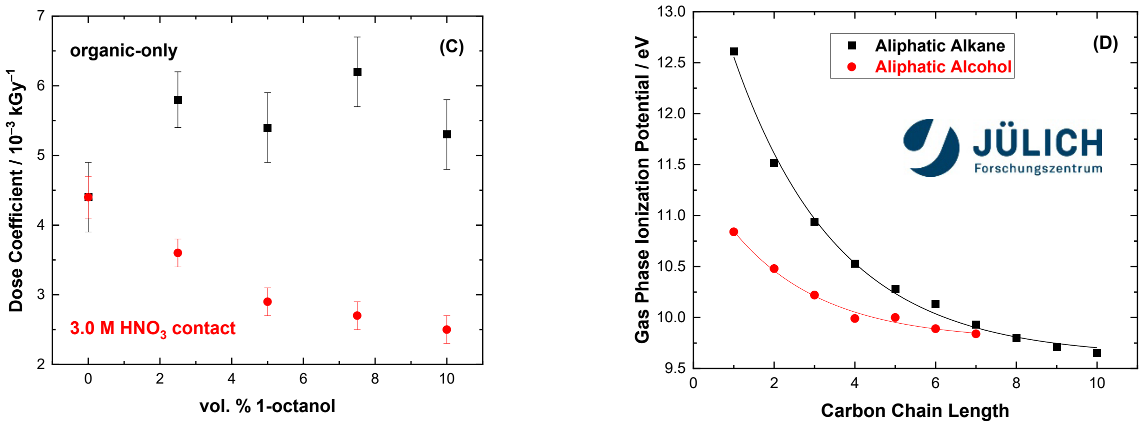
Effect of Additives – Octanol as a Phase Modifier (FY20-21)

- Octanol has been proposed as a phase modifier for TODGA based extraction systems, e.g., ALSEP.
- 3 conflicting radiolysis studies on the effect of octanol on TODGA degradation.
- **Octanol exhibits diametrically different effects depending on solvent system formulation.**

Additives play a significant role in altering the outcome of radiolytic processes!



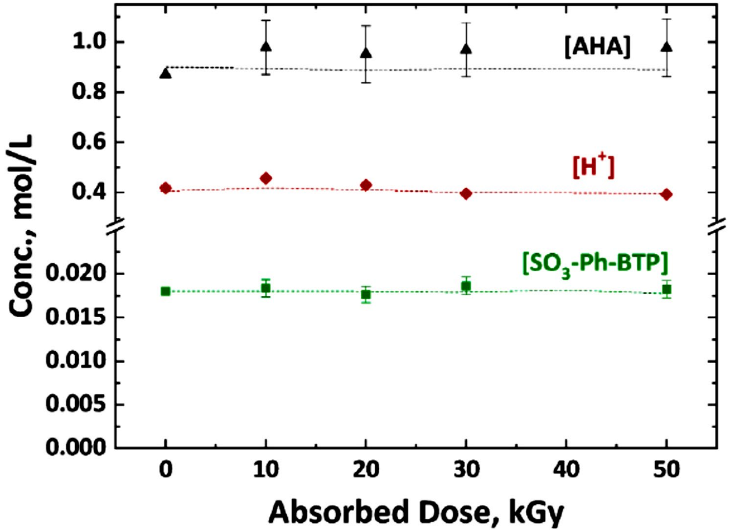
Horne *et al.*, *Physical Chemistry Chemical Physics*, **2020**, *22*, 24978.

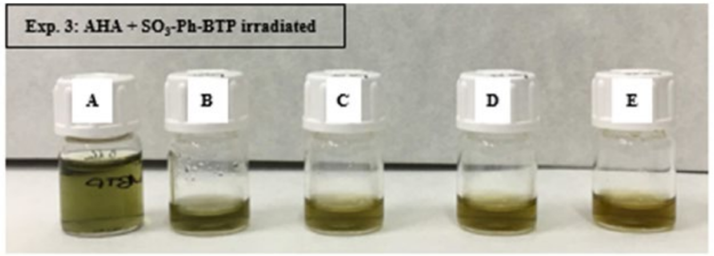


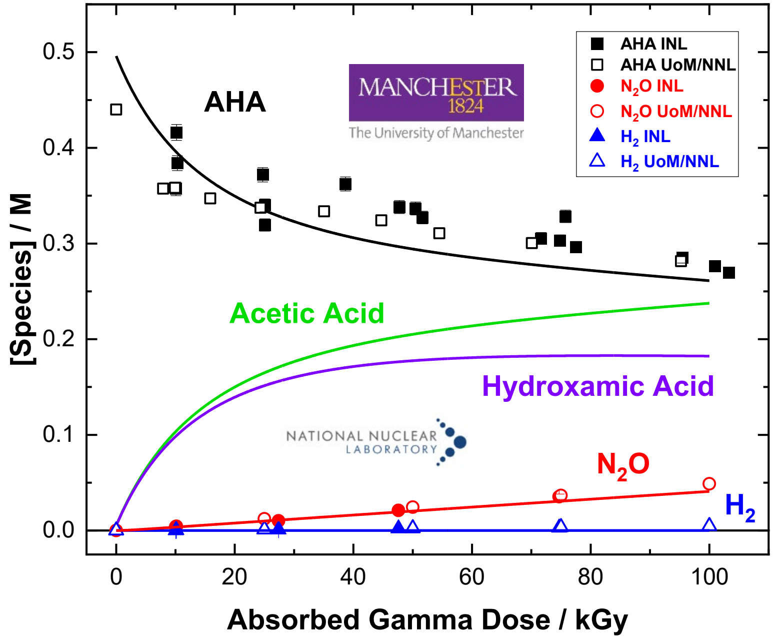
- Sugo, Y., Izumi, Y., Yoshida, Y., Nishijima, S., Sasaki, Y., *et al.*, *Radiat. Phys. Chem.*, **2007**, *76*, 794.
- Galán, H., Núñez, A., Espartero, A.G., Sedano, R., Durana, A., Mendoza, J.D., *Procedia Chem.*, **2012**, *7 (0)*, 195.
- Zalupski, P.R., Peterman, D.R., INL/EXT-17-43040 Technical Report, 2017, OSTI.gov, United States.

Effect of Additives – AHA for Pu/Np Reduction (FY21)

Concentration of AHA, BTPS, and H_{aq}^{+} *vs.* gamma dose for 2 h of AHA hydrolysis.



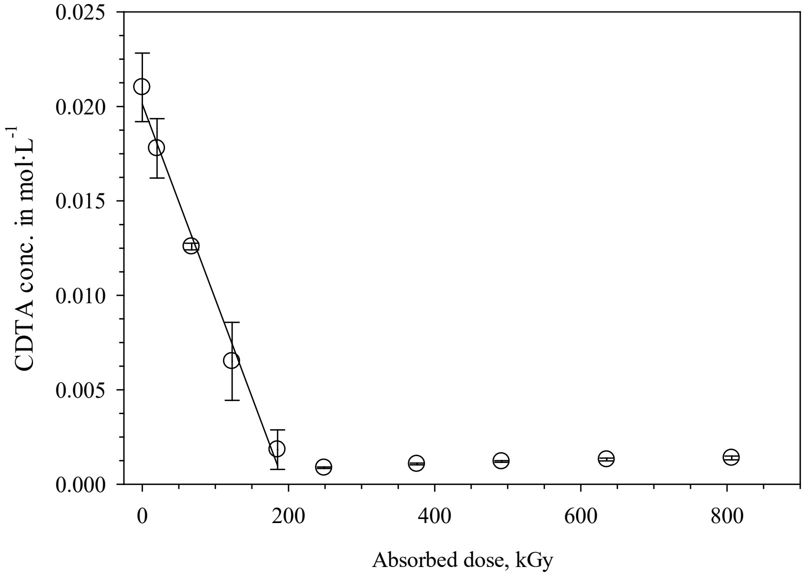




Understanding fundamental mechanisms is critical for designing innovative processes.

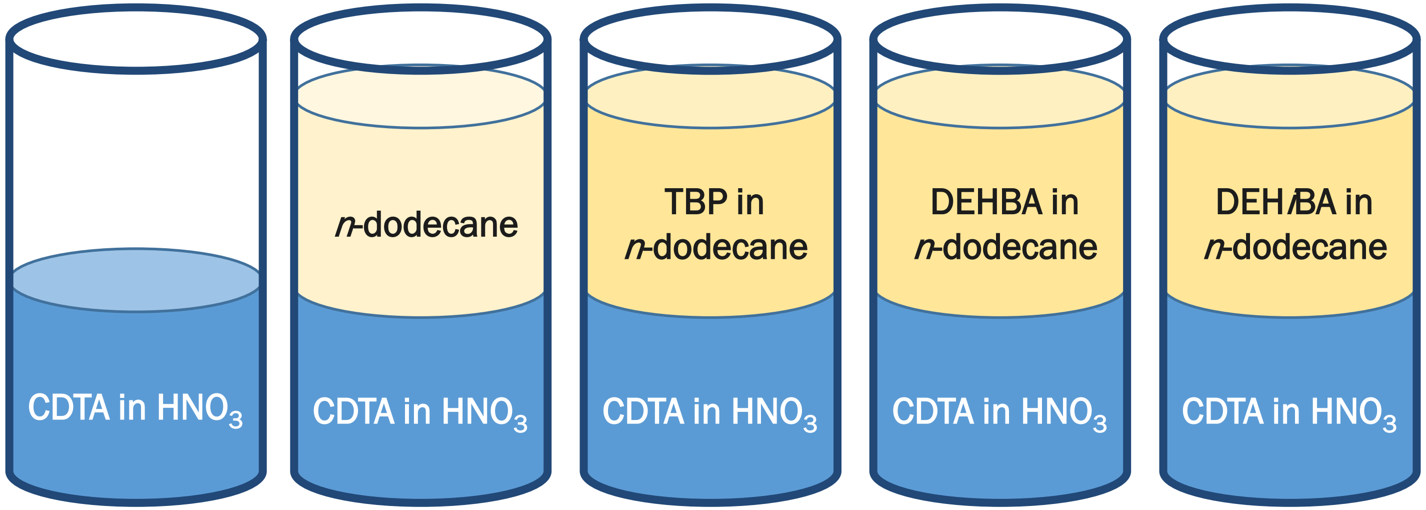
- Karraker, D.G., Radiation Chemistry of Acetohydroxamic Acid in the Urex Process, WSRC-TR-2002-00283, 2002), 1.
- Wang, J.-H., Li, C., Li, Q., Wu, M-H., Zheng, W.-F., He, H., Nucl. Sci. Tech., 2018, 29 (27), 26.
- I. Sánchez-García, L.J. Bonales, H. Galán, J.M. Perlado, and J. Cobos, *Rad. Phys. Chem.*, 2021, **183**, 109402.

Effect of Additives – CDTA for Zr Retention (FY21)



Concentration of **CDTA** *vs.* gamma dose from for the test loop irradiation of ALSEP solvent (*0.050 M T2EHDGA + 0.75 M HEH[EHP] in dodecane*) in contact with simulated feed solution adjusted to 3.0 M HNO_3.

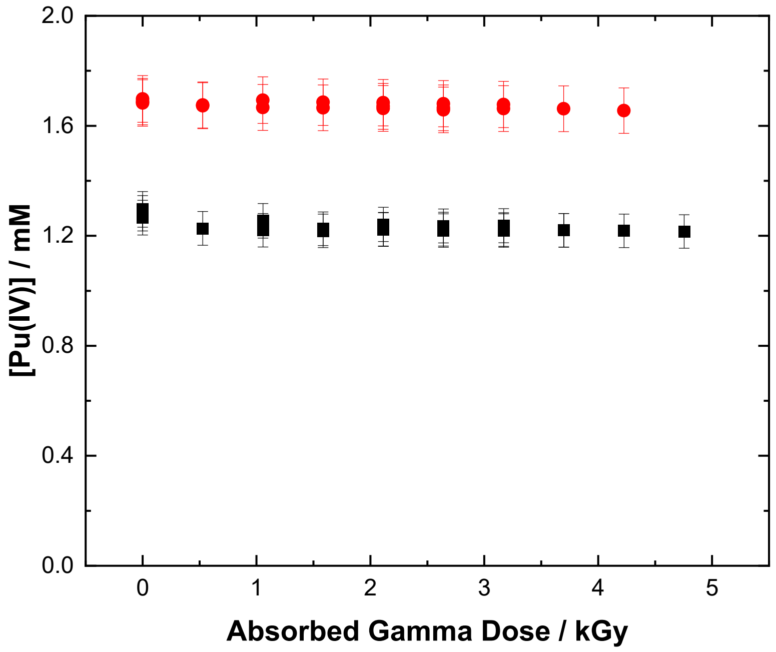
JÜLICH Forschungszentrum

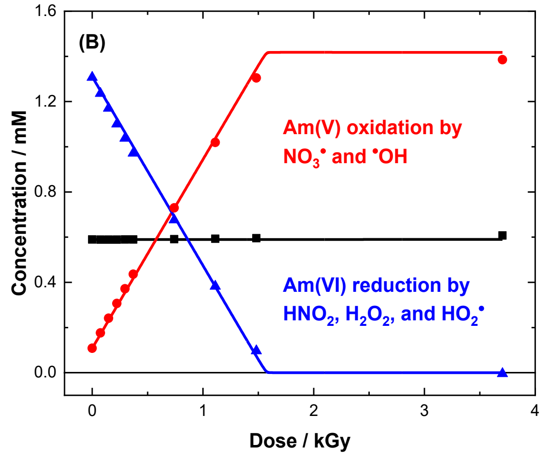


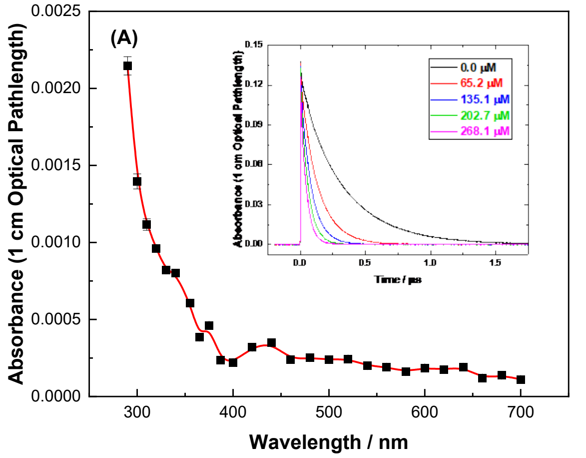
Understanding fundamental mechanisms is critical for designing innovative processes.

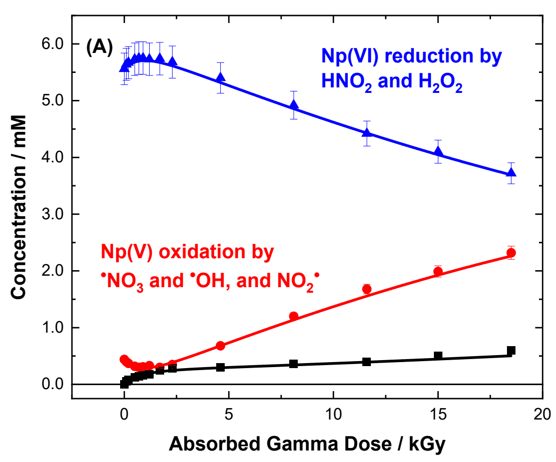
- Peterman, D. R. (**2018**). Completion of M4NT-18IN030102011 "Analysis of FY17 ALSEP Samples". Idaho Falls, ID, INL.

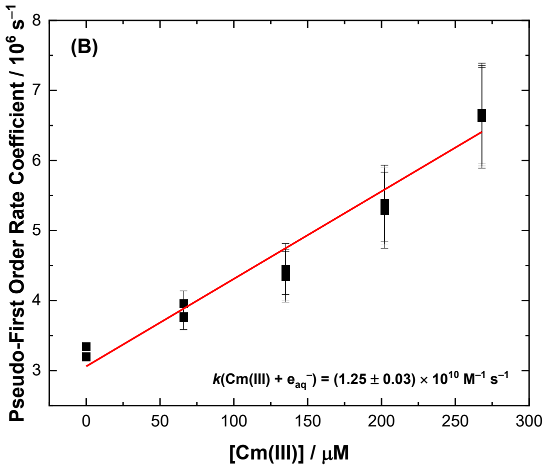
Radiation-Induced Actinide Redox Chemistry (FY21) - Pu











Actinide radiolysis alters oxidation state distributions and can yield exotic states with high redox potentials.

- Horne, G.P., Grimes, T.S., Mincher, B.J., Mezyk, S.P., *Journal of Physical Chemistry B*, 2016, *120 (49)*, 12643.
- Horne, G.P., Grimes, T.S., Bauer, W.F., Dares, C.J., Pimblott, S.M., *et al.*, *Inorganic Chemistry*, 2019, *58*, 8551.
- Horne, G.P.; Grimes, T.S.; Zalupski, P.R.; Meeker, D.S.; Albrecht-Schönzart, T.E.; Cook, A.R.; Mezyk, S.P., *Dalton Transactions*, 2021, in review.

Summary

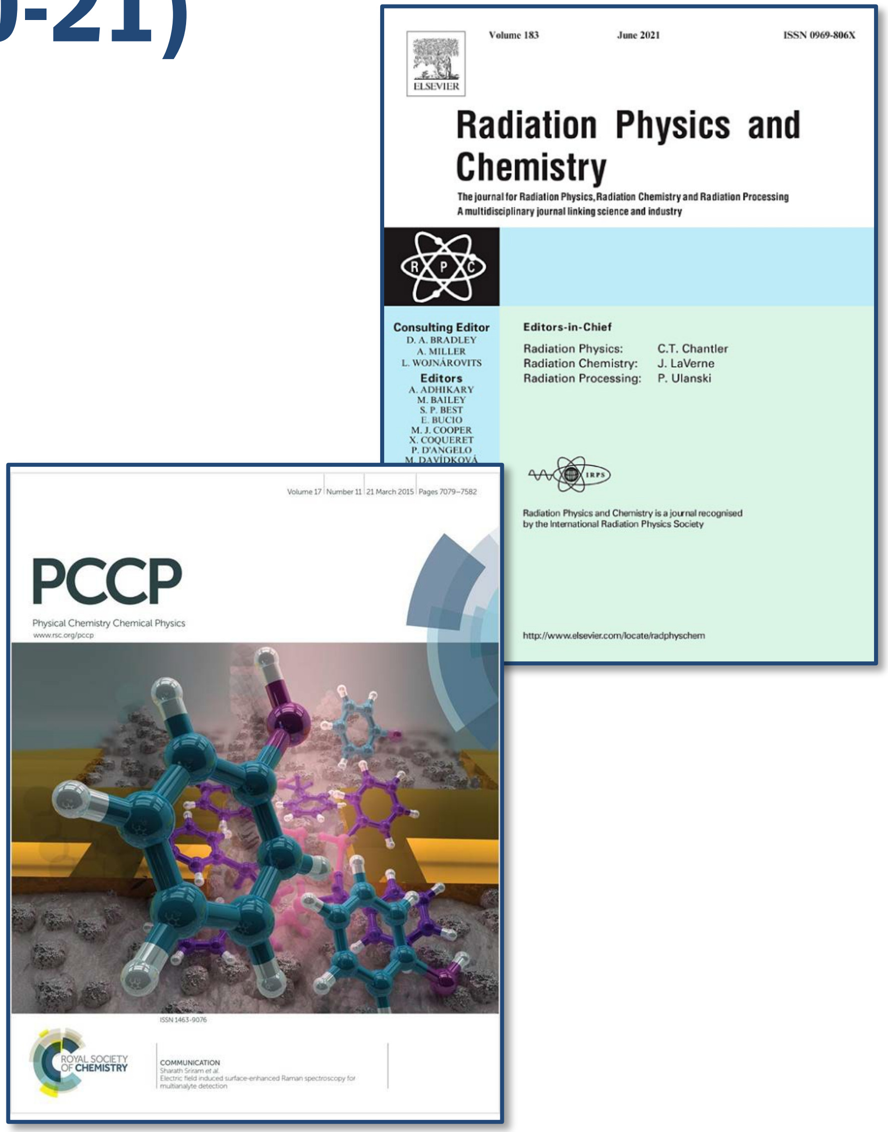
1. **The *Fundamental Radiation Chemistry Group* aims to provide predictive capabilities for process design.**
2. Metal ion complexation alters electron distribution and sterics, ultimately influencing ligand radiolysis.
3. Additives can play a significant role in altering the outcome of radiolytic processes.
4. Actinide radiolysis alters oxidation state distributions and can yield exotic states with high redox potentials.
5. Understanding fundamental mechanisms is critical for designing innovative processes.

Future Challenges and Innovative Research Avenues

- *Diluent Composition Effects on Ligand Radiolysis (e.g., n-dodecane, odorless kerosene, TPH, Isane-175/185)* – ionization potential, extraction efficiencies, variation sensitivity, etc.
- *Organic Phase Radiation-Induced Neptunium Redox Chemistry?*
- *Radiation-Induced Technetium Extraction Behavior?*
- *Voloxidation/Direct Dissolution Mediated Changes in Radiolysis?*
- *Tailored Ligand Degradation* – can ligands be designed so that their inevitable degradation products facilitate recycle goals, e.g., Tc stripping?

Deliverables (FY20-21)

1. Toigawa et al., *PCCP*, **2021**, *23*, 1343-1351. DOI: https://doi.org/10.1039/D0CP05720G.B.
2. Horne *et al.*, *PCCP*, **2020**, *22*, 24978-24985. DOI: https://doi.org/10.1039/D0CP04310A.
3. Horne *et al.*, *Rad. Phys. Chem.*, **2020**, *170*, 108636. DOI: https://doi.org/10.1016/j.radphyschem.2019.108636G.
4. Horne *et al.*, *Rad. Phys. Chem.*, **2020**, *170*, 108608. DOI: https://doi.org/10.1016/j.radphyschem.2019.108608.



Acknowledgements

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