INL/CON-21-65479-Revision-0

Multiscale Evaluation of Acetohydroxamic Acid (AHA) Radiolysis Under Used Nuclear Fuel Reprocessing Solvent System Conditions

January 2022

Changing the World's Energy Future

Gregory P Horne

Idaho National Laboratory

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Gregory P. Horne
Center for Radiation Chemistry Research

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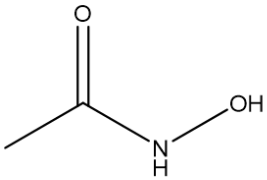
INL/CON-21-01844



16th DAE-BRNS Biennial Trombay Symposium on Radiation & Photochemistry (TSRP-2022)

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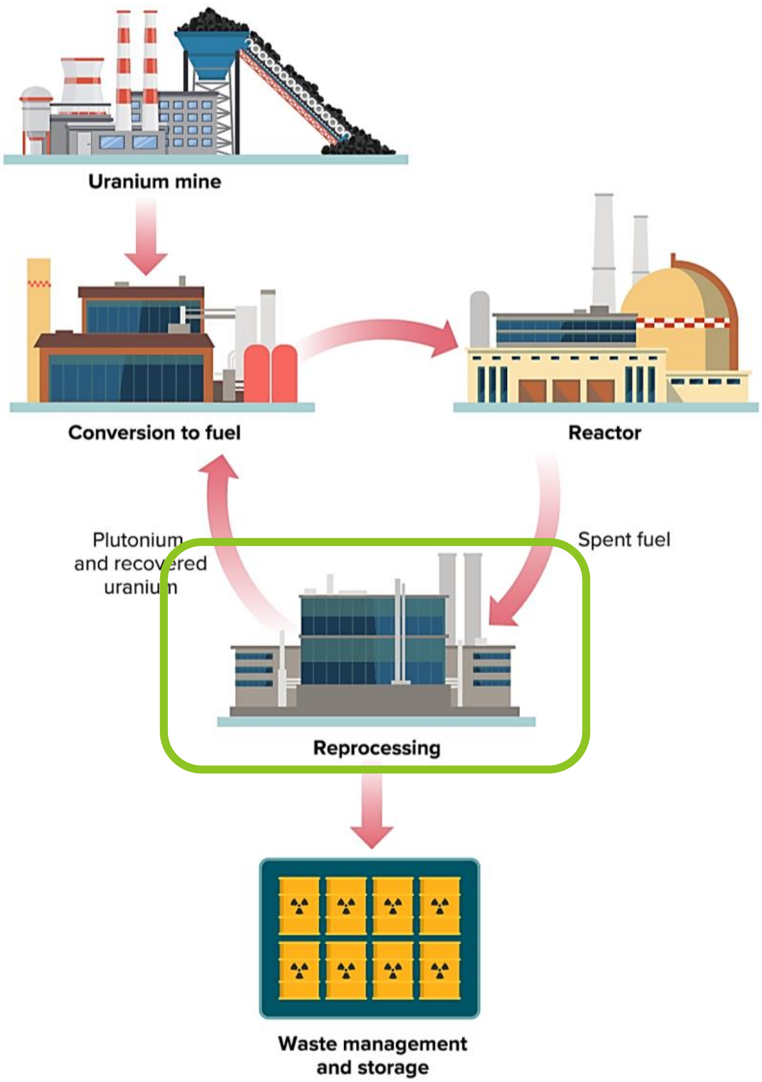
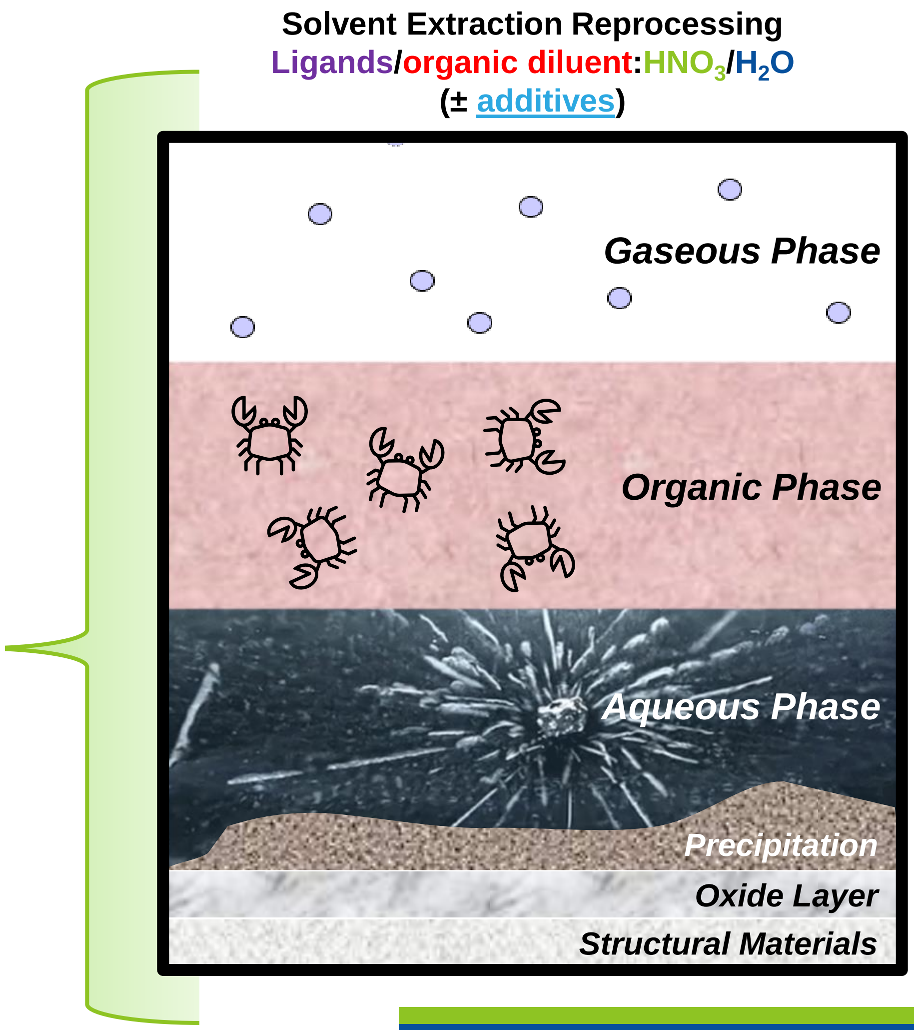
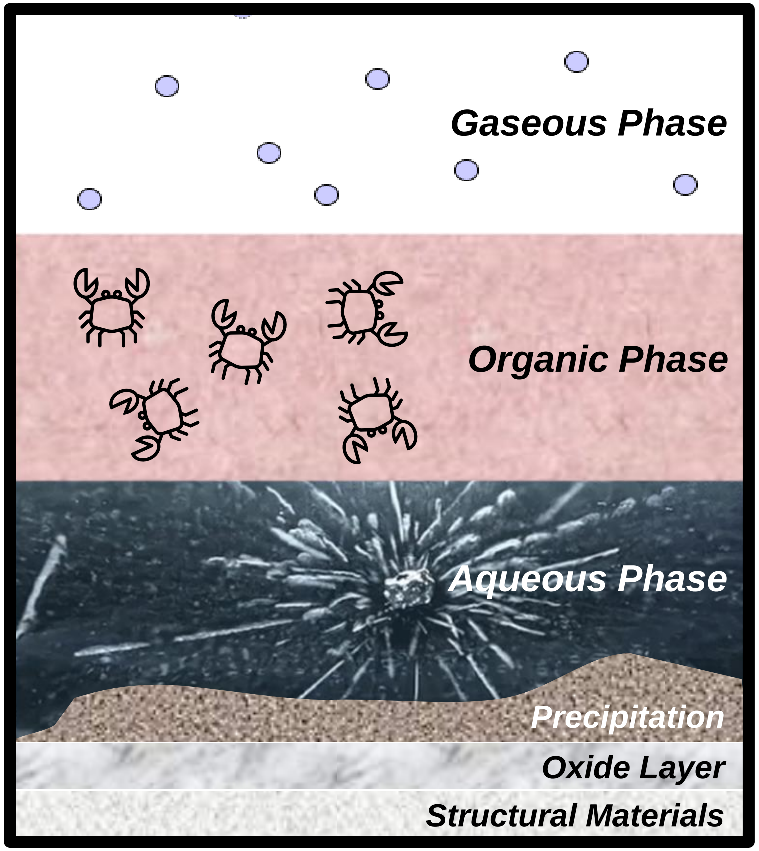
Radiation Chemistry and Used Nuclear Fuel Reprocessing

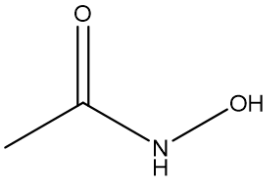




Advanced Used Nuclear Fuel Reprocessing

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





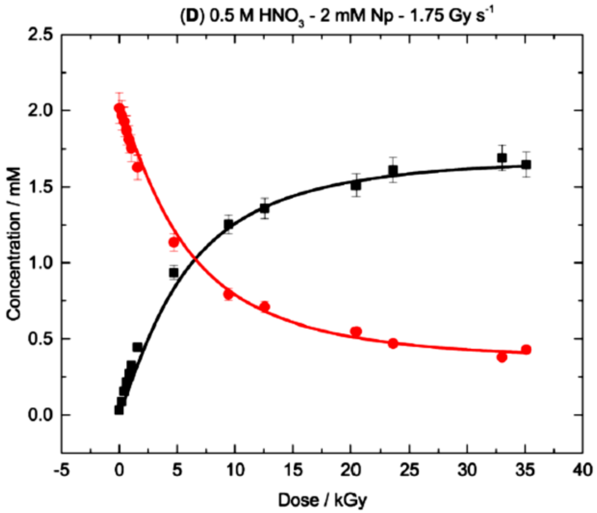


Figure 1. Concentration of NpO_2^+ (■) and NpO_2^{2+} (●) ions as a function of absorbed gamma dose for formally 2 mM NpO_2^{2+} in 0.5 M HNO_3.

Np^{4+}/NpO_2^{2+} → Extractable

NpO_2^+ → Inextractable

- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- G.P. Horne, T.S. Grimes, B.J. Mincher, S.P. Mezyk, *J. Phys. Chem. B* **2016**, *120*, 12643.

Radiation Chemistry in Nitrate and Nitric Acid Solutions

Water Radiolysis

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

Indirect Radiation Effects

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

$NO_3^{-} + e_{aq}^{-} \rightarrow NO_3^{\bullet 2-}$

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

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

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

$N_2O_4 \rightarrow HNO_2 + HNO_3$

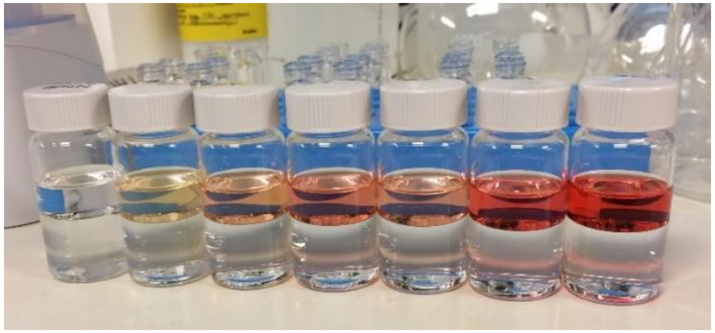
Direct Radiation Effects

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

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

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

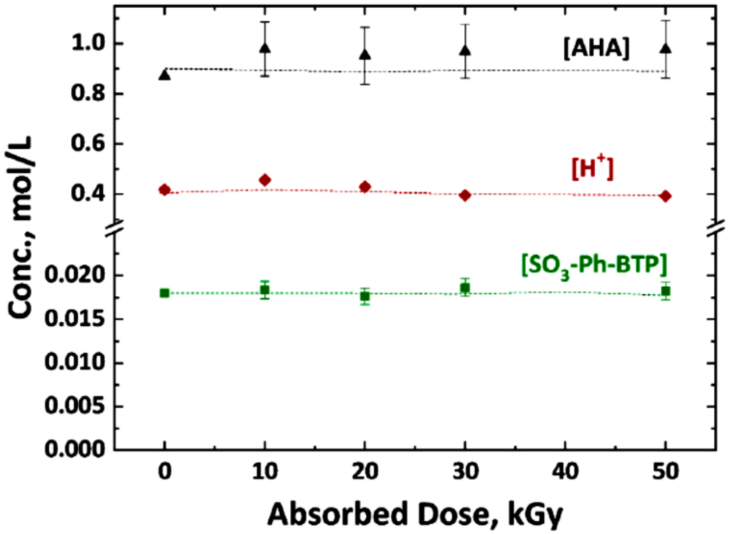
$HNO_3 \rightsquigarrow {}^{\bullet}NO_3 + H^{\bullet}$

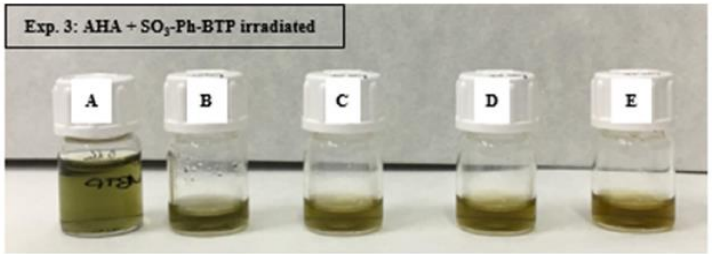


- G.V. Buxton, C.L. Greenstock, W.P. Helman, and A.B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Y. Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

The Role of AHA and its Radiolytic Behavior

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





"…***concentrations for both molecules (AHA and SO_3-Ph-BTP) are practically invariable with dose***…"

"…***the separation factor between Eu and Am to remain essentially unchanged.***"

"…***to scale up these kind of processes an in-depth knowledge of their resistance and long-term behavior is still required***…"

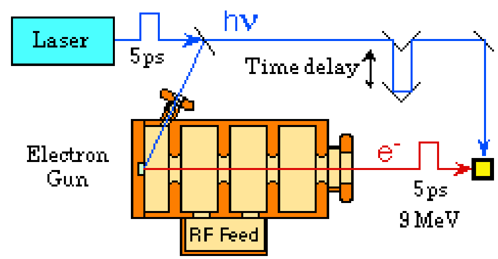
"…***it is essential to design reliable simulating strategies to predict the long-term performance of extraction systems***…"

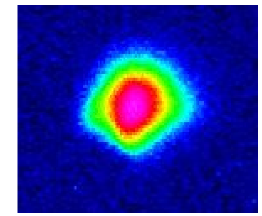
- D.G. Karraker, Radiation Chemistry of Acetohydroxamic Acid in the Urex Process, WSRC-TR-2002-00283, 2002), 1.
- J.-H. Wang, C. Li, Q. Li, M.-H. Wu, W.-F. Zheng, and H. He, *Nucl. Sci. Tech.*, **2018**, *29*, 26.
- I. Sánchez-García, L.J. Bonales, H. Galán, J.M. Perlado, and J. Cobos, *Rad. Phys. Chem.*,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

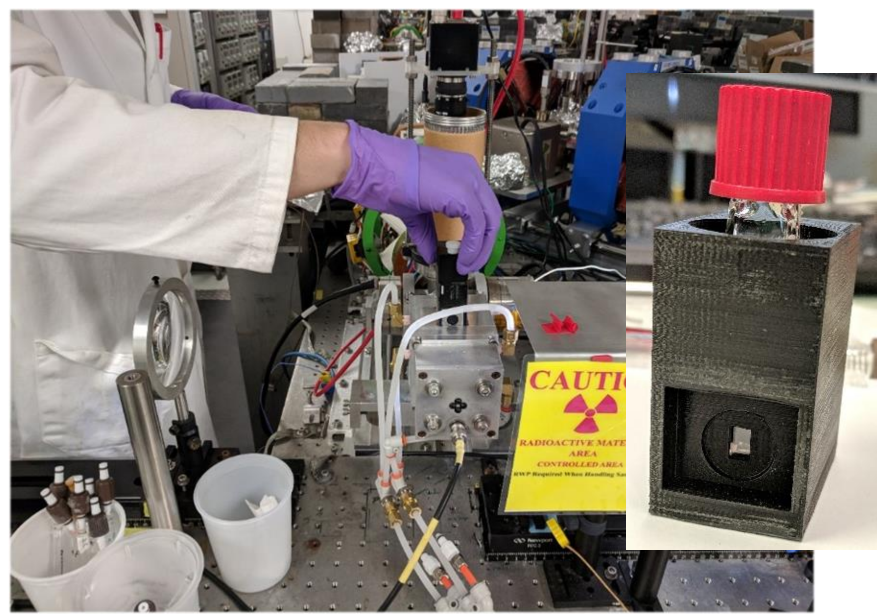
Experimental Methodology

Steady-State Gamma Radiolysis

Time-Resolved Pulsed Electron Radiolysis

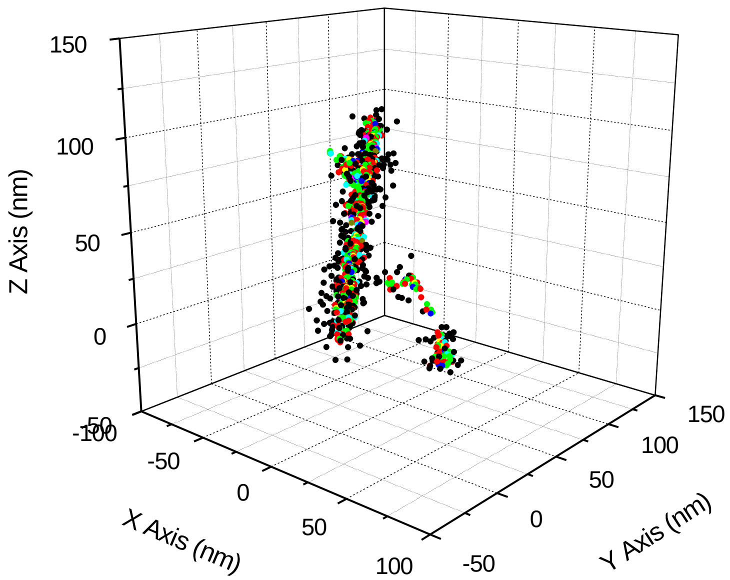






- J.F. Wishart, A.R. Cook, and J.R. Miller, *Rev. Sci. Instrum.*, **2004**, *75 (11)*, 4359.

Multiscale Modeling Irradiated Solutions

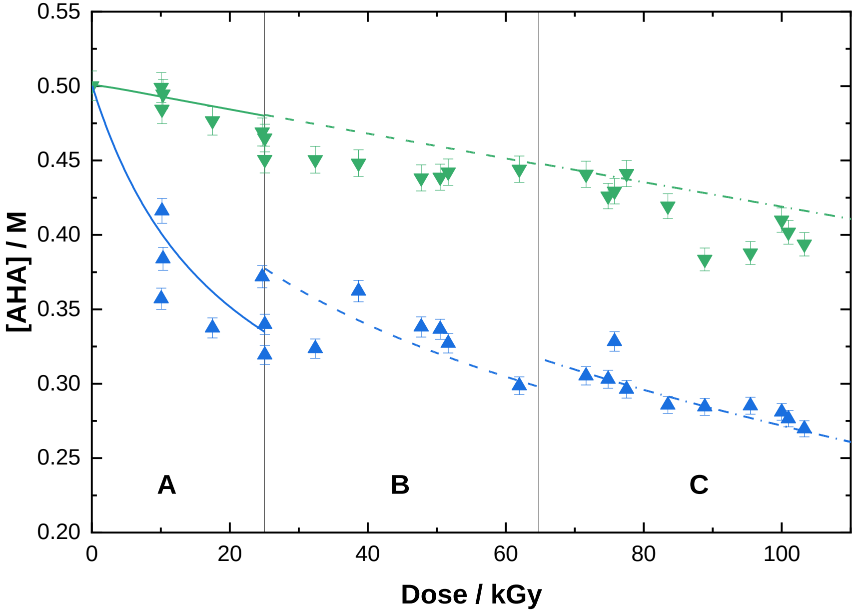


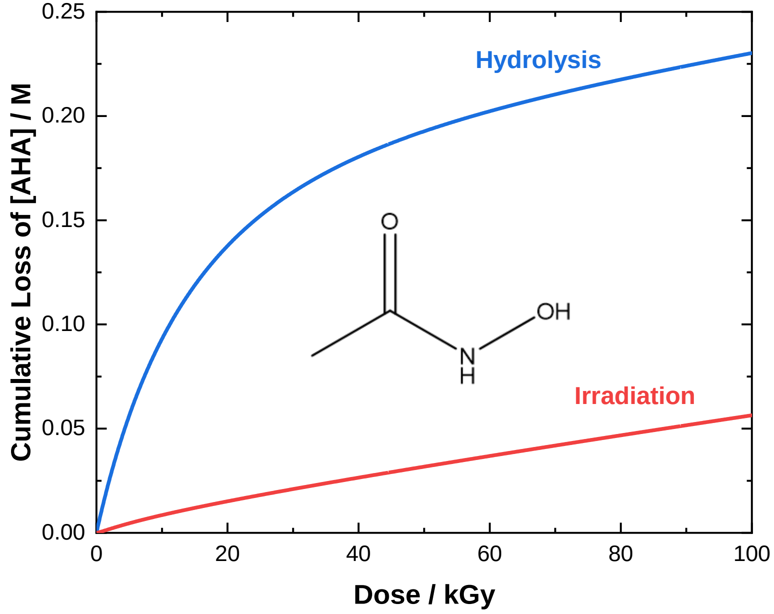
100 ps

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

- P. Clifford, N.J.B. Green, M.J. Oldfield, M.J. Pilling, S.M. Pimblott, *J. Chem. Soc., Faraday Trans.*, **1986**, *82*, 2673.
- S.M. Pimblott, J.A. LaVerne, A. Mozumder, *J. Phys. Chem.*, **1996**, *100*, 8595.
- G.P. Horne, T.A. Donoclift, H.E. Sims, R.M. Orr, and S.M. Pimblott, *J. Phys. Chem. B.*, **2016**, *120*, 11781.

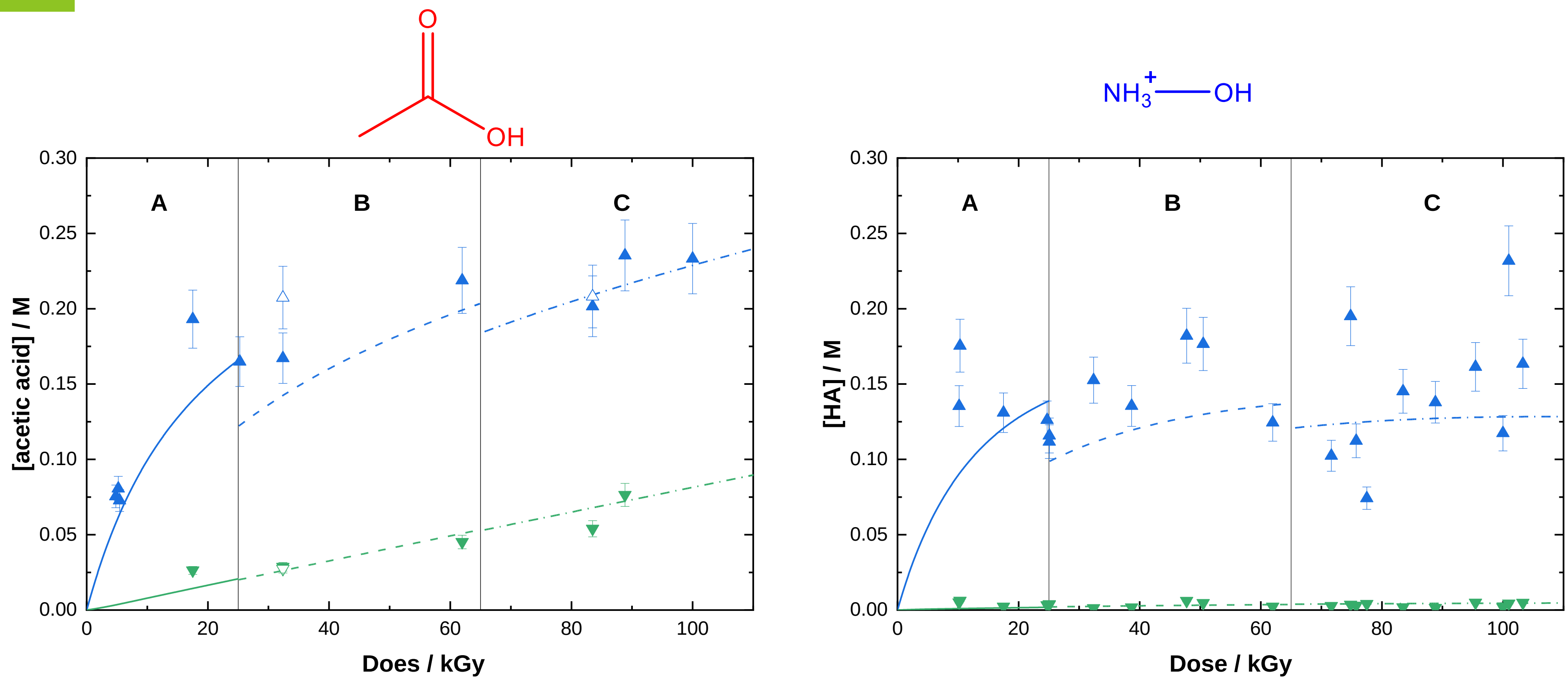
Acetohydroxamic Acid (AHA) Radiolysis





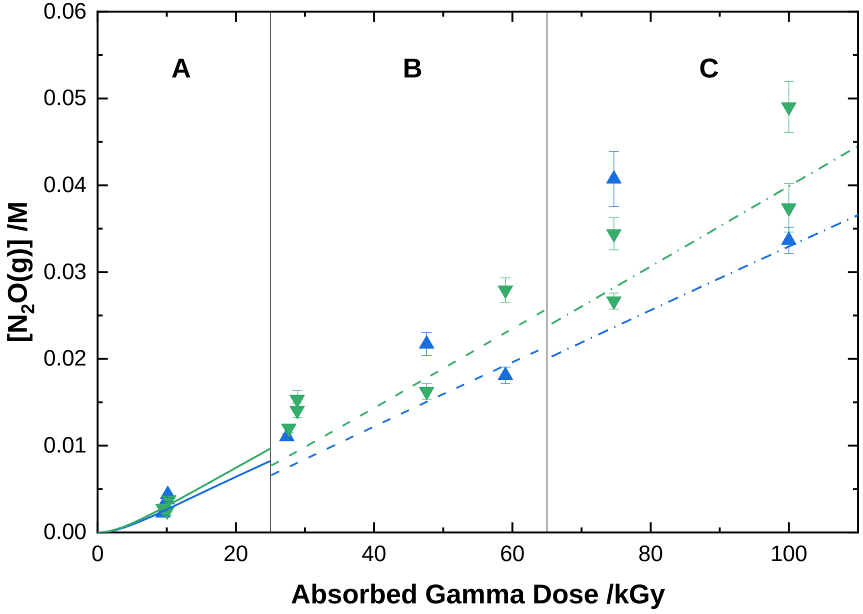
- Loss of **AHA** by *radiolysis* and *hydrolysis* processes from the irradiation of 0.5 M AHA in 0.2 M $NaNO_3$ (▼) and HNO_3 (▲): **(A)** 51 Gy min^{-1} at 36 °C; **(B)** 150 Gy min^{-1} at 40 °C; and **(C)** 250 Gy min^{-1} at 42 °C.

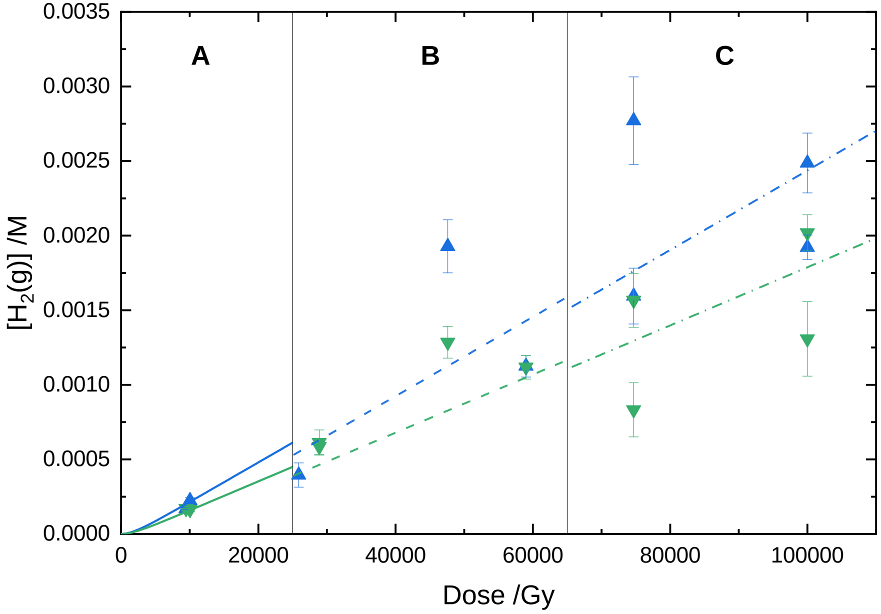
Dissolved Degradation Product Formation



- Yields of **Acetic Acid** and **HA** from the irradiation of 0.5 M AHA in 0.2 M $NaNO_3$ (▼) and HNO_3 (▲): **(A)** 51 Gy min^{-1} at 36 °C; **(B)** 150 Gy min^{-1} at 40 °C; and **(C)** 250 Gy min^{-1} at 42 °C.

Gaseous Degradation Product Formation

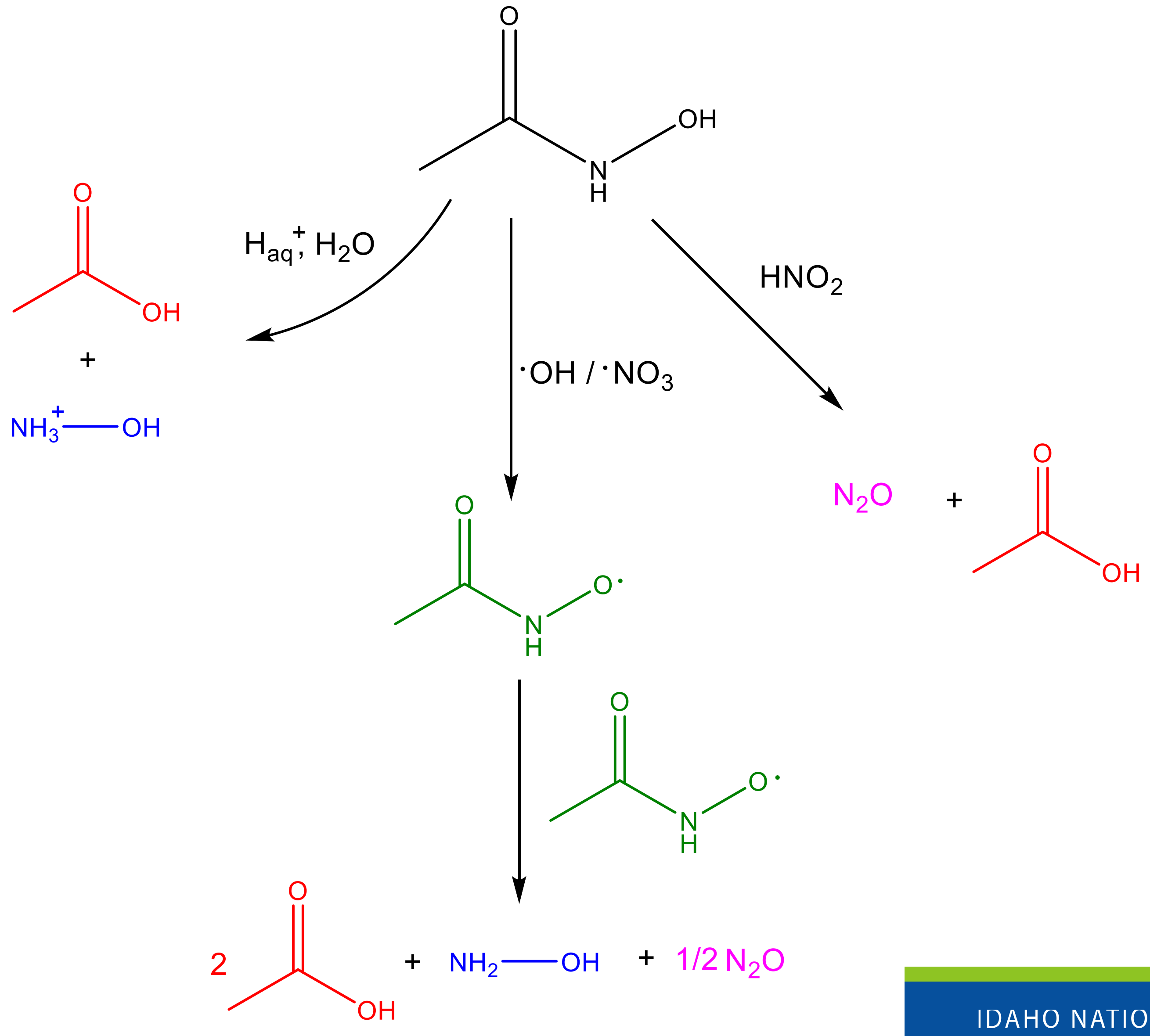




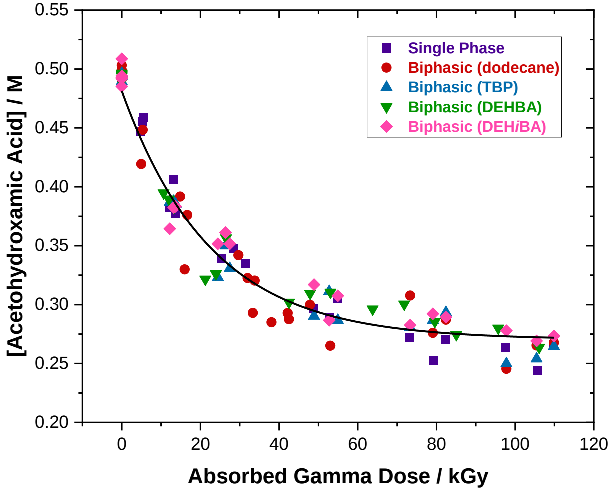
- Yields of **N_2O** and **H_2** from the irradiation of 0.5 M AHA in 0.2 M $NaNO_3$ (▼) and HNO_3 (▲): **(A)** 51 Gy min^{-1} at 36 °C; **(B)** 150 Gy min^{-1} at 40 °C; and **(C)** 250 Gy min^{-1} at 42 °C.

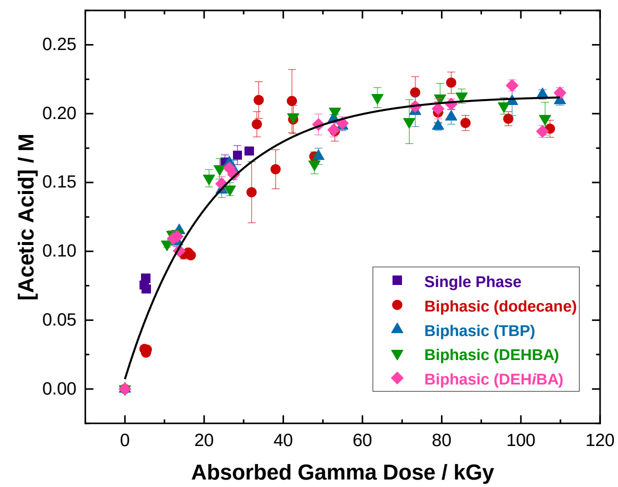
- G.P. Horne, S.M. Pimblott, and J.A. LaVerne, *J. Phys. Chem. B*, **2017**, *121 (21)*, 5385.
- C.R. Gregson, G.P. Horne, R.M. Orr, S.M. Pimblott, H.E. Sims, R.J. Taylor, and K.J. Webb, *J. Phys. Chem. B*, **2018**, 122, 2627.
- J.-H. Wang, C. Li, Q. Li, M.-H. Wu, W.-F. Zheng, and H. He, *Nucl. Sci. Tech.*, **2018**, *29*, 26.

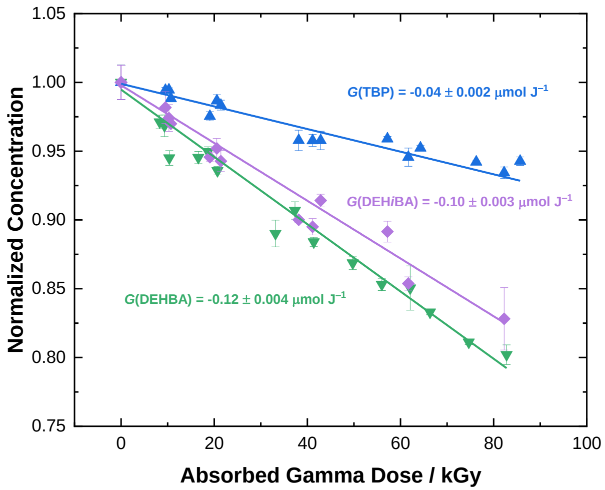
Dominant Reaction Mechanisms

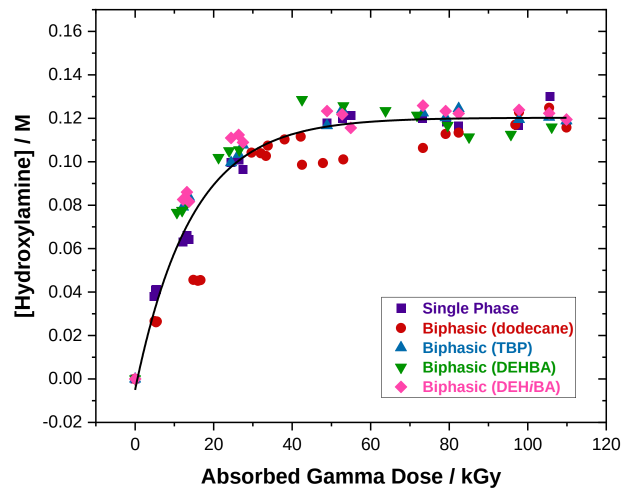


Biphasic Solution Effects





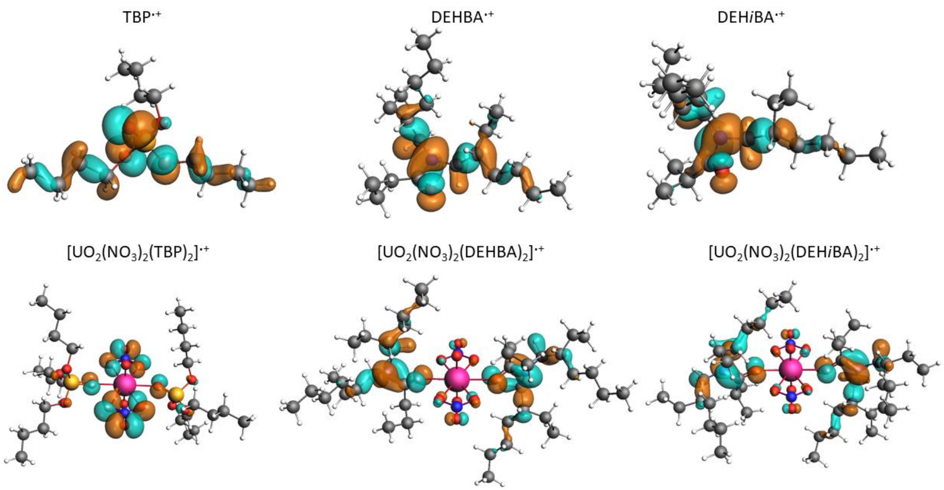




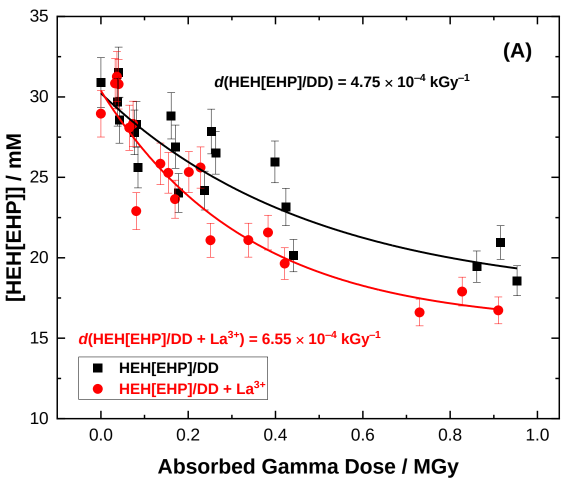
Conclusions and Future Research

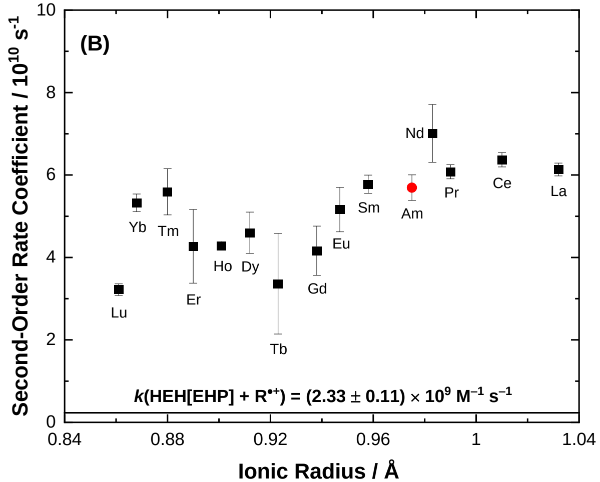
- Loss of **AHA** by hydrolysis > radiolysis.
- Radiolysis of **AHA** predominantly by oxidizing radicals (**$^{\bullet}OH$**, **$NO_3^{\bullet}$**, and **$AHA^{\bullet}$**).
- Multiscale model accurately predict loss of AHA in representative single cycle aqueous phase conditions.
- Biphasic conditions promote negligible changes in **AHA** and ligand (**TBP**, **DEHBA**, and **DEH*i*BA**) radiation chemistry.
- **What is the impact of metal ions?**

Impact of Metal Ions



Sample	**RH•+ Rate Coefficient** (10^{10} M^{-1} s^{-1})
TBP	1.36 ± 0.07
$[UO_2(NO_3)_2(TBP)_2]$	-
DEHBA	0.93 ± 0.02
$[UO_2(NO_3)_2(DEHBA)_2]$	2.49 ± 0.06
DEH*i*BA	1.14 ± 0.04
$[UO_2(NO_3)_2(DEH\textit{i}BA)_2]$	1.59 ± 0.08





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Acknowledgements

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