INL/CON-21-62668-Revision-0

Radiolytic transformation of AHA under single-cycle conditions

May 2021

Changing the World's Energy Future

Gregory P Horne, Jacy Kathleen Conrad, Stephen P. Mezyk, Andrew R. Cook, Aliaksandr Baidak , Liam Isherwood, Daniel Whittaker, Andreas Wilden

Idaho National Laboratory

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Center for Radiation Chemistry Research

Radiolytic transformation of AHA and CDTA under single-cycle conditions

LRS Number: INL/CON-21-62668 Rev:000

The US/UK/German Team
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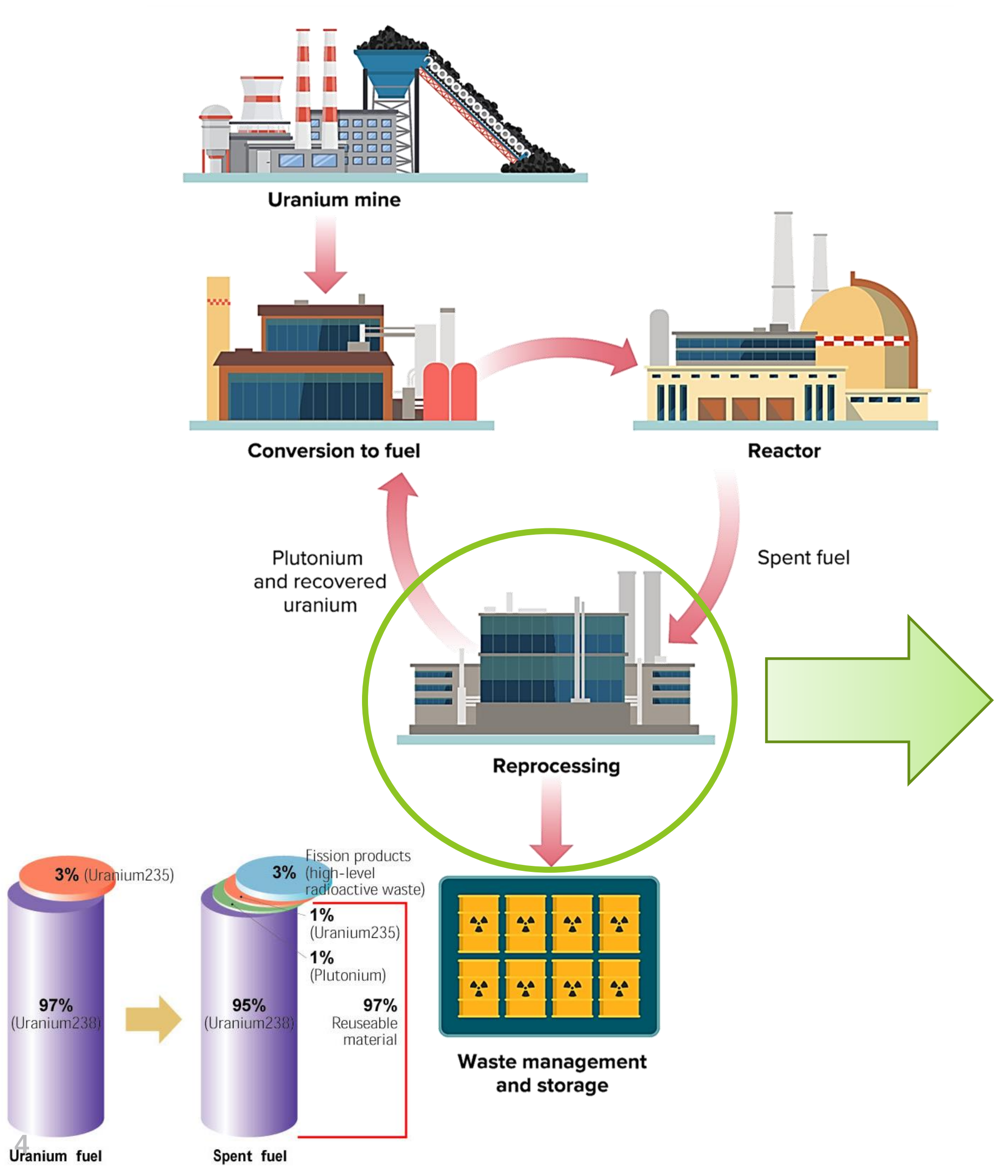
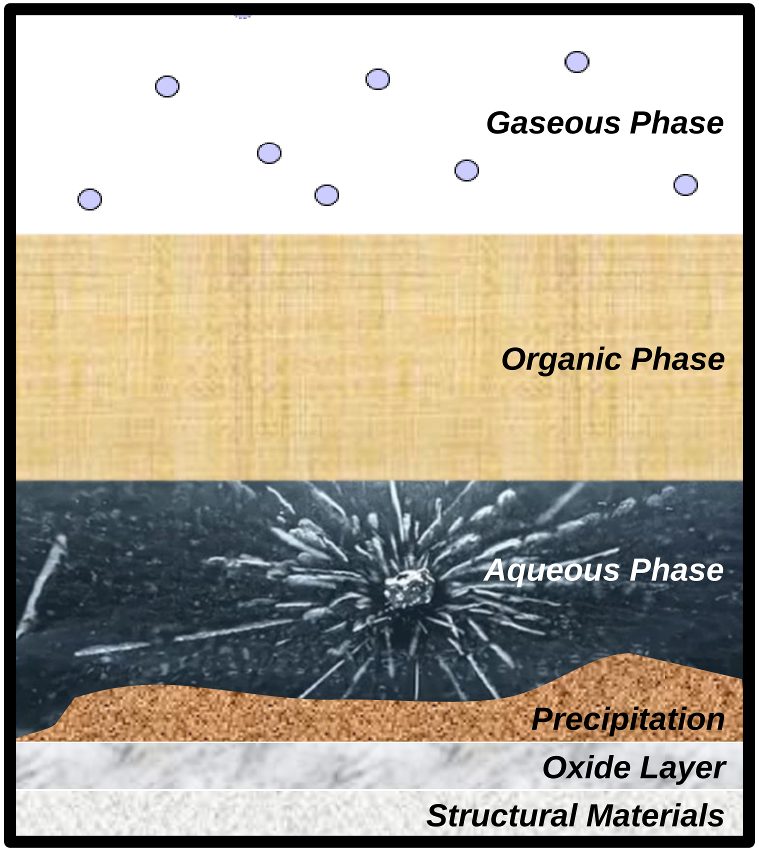
Nuclear Fuel Reprocessing and Radiation Chemistry



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



Radiation Chemistry of Reprocessing Solvents

Water Radiolysis

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

Indirect Radiation Effects

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

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

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

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

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

$N_2O_4 \rightarrow HNO_2 + HNO_3$

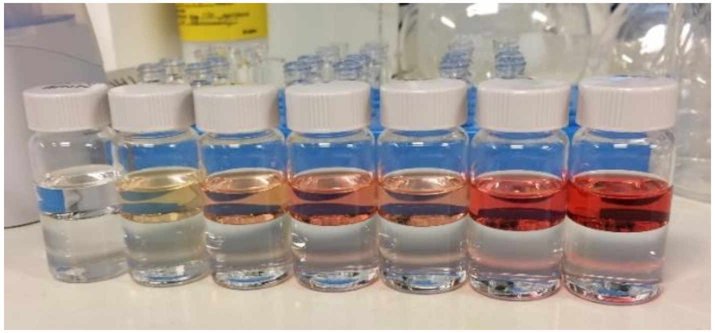
Direct Radiation Effects

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

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

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

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



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Radiation Chemistry of Reprocessing Solvents

Water Radiolysis

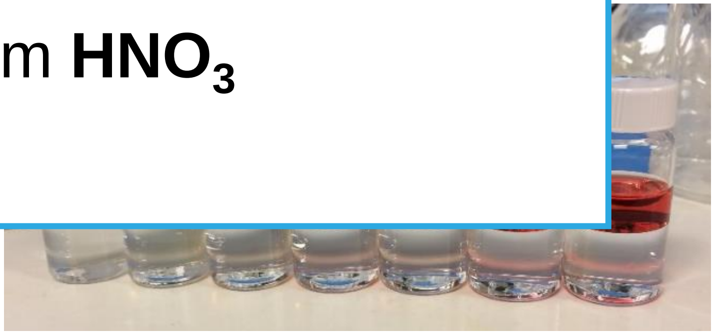
Direct Radiation Effects

Radiolysis Products of Concern in Reprocessing

$^{\bullet}$**OH** and **H_2O_2** from **H_2O**

$^{\bullet}$**NO_3** and **HNO_2** from **HNO_3**

$N_2O_4 \rightarrow HNO_2 + HNO_3$



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Acetohydroxamic Acid (AHA) Radiolysis

AHA Hydrolysis

$$\text{AHA} + \text{H}_{aq}^{+} \rightarrow \text{HA}(\text{H}_{aq}^{+}) + \text{AcOH}$$

AHA Radiolysis

$$\text{AHA} \rightsquigarrow {}^{\bullet}\text{CONHOH} + {}^{\bullet}\text{CH}_3$$

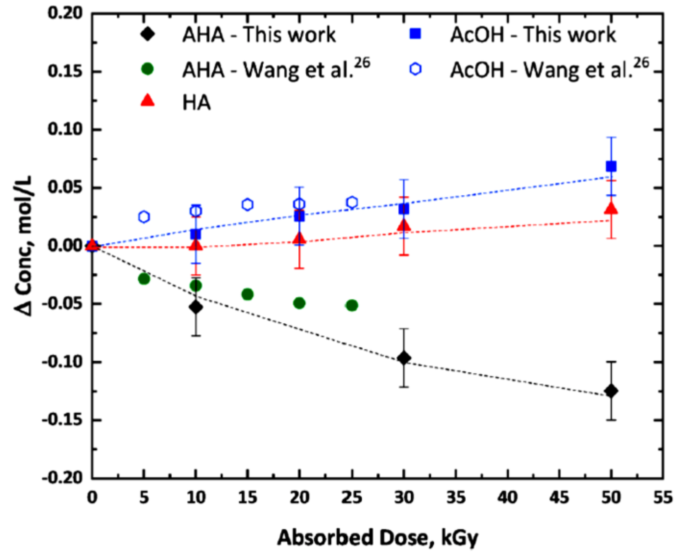
$$\text{AHA} + e_{aq}^{-} \rightarrow \text{AHA}^{\bullet -}$$

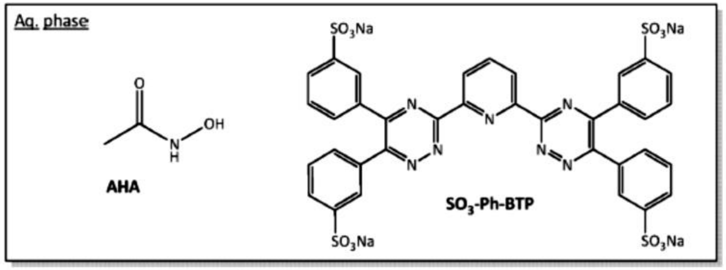
$$\text{AHA} + {}^{\bullet}\text{H} \rightarrow \text{AHA(-H)}^{\bullet} + \text{H}_2$$

$$\text{AHA} + {}^{\bullet}\text{OH} \rightarrow \text{AHA(-H)}^{\bullet} + \text{H}_2\text{O}$$

$$\text{AHA} + {}^{\bullet}\text{NO}_3 \rightarrow \text{AHA(-H)}^{\bullet} + \text{HNO}_3$$

Concentration of **AHA**, **HA**, and **AcOH** *vs.* gamma dose for 2 h of **AHA** hydrolysis.





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- 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.

Acetohydroxamic Acid (AHA) Radiolysis

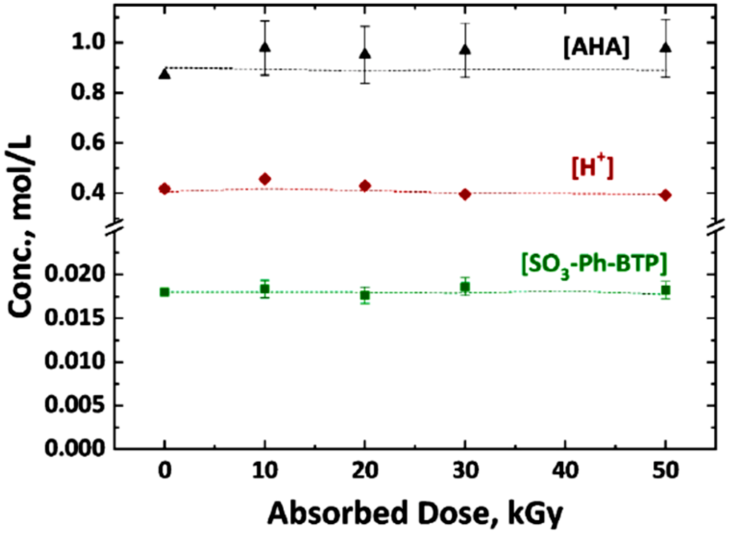
"…***concentrations for both molecules (AHA and SO_3-Ph-BTP) are practically invariable with dose***…"

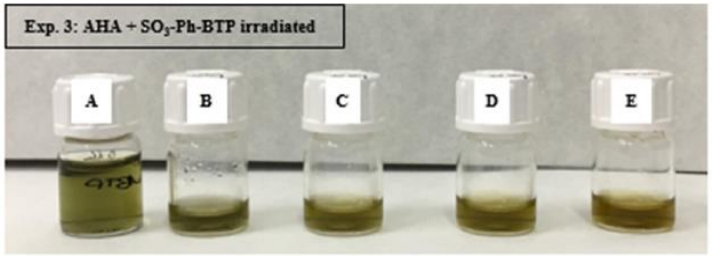
"…***the separation factor between Eu and Am to remain essentially unchanged***."

"…***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***…"

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





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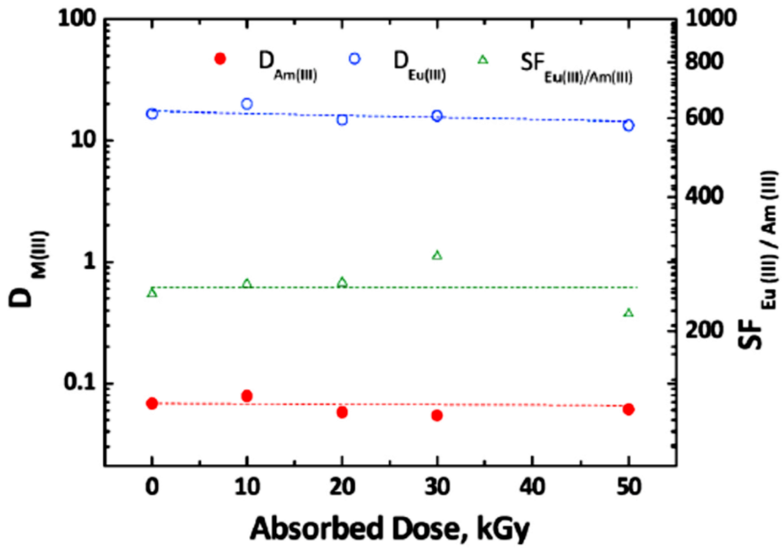
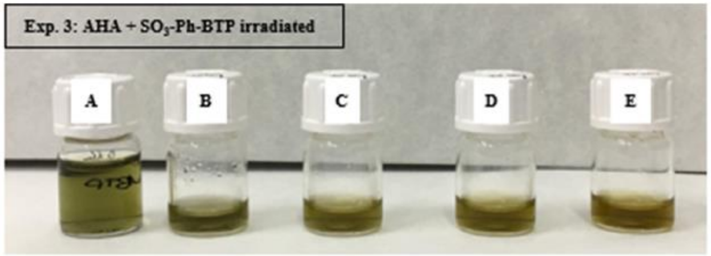
Distribution ratios of **Am(III)** and **Eu(III)** vs. absorbed dose received by *1 M AHA/18 mM SO_3-Ph-BTP/0.5 M HNO_3:0.2 M TODGA/0.5 M DMDOHEMA.*





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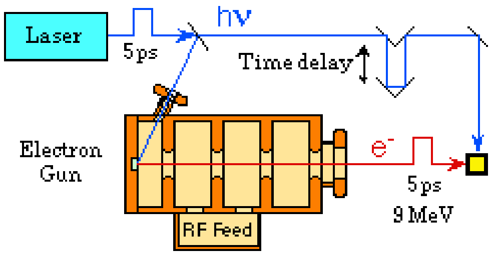
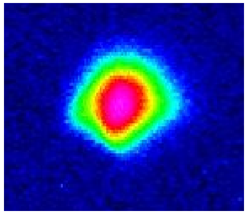
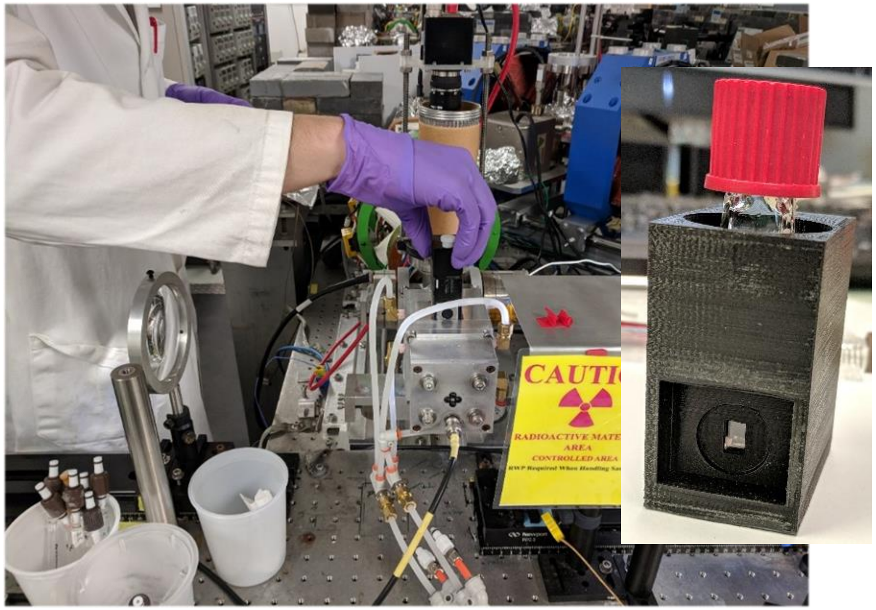
Experimental Methodology

Steady-State Gamma Radiolysis

Time-Resolved Pulsed Electron Radiolysis







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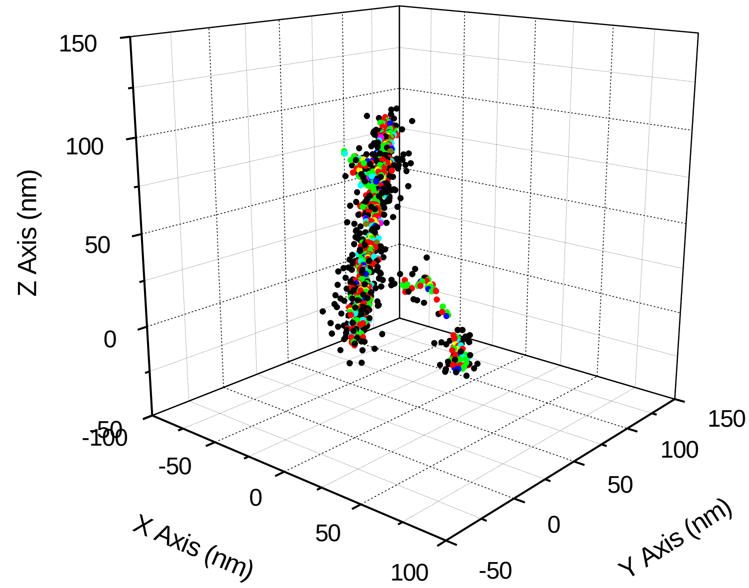
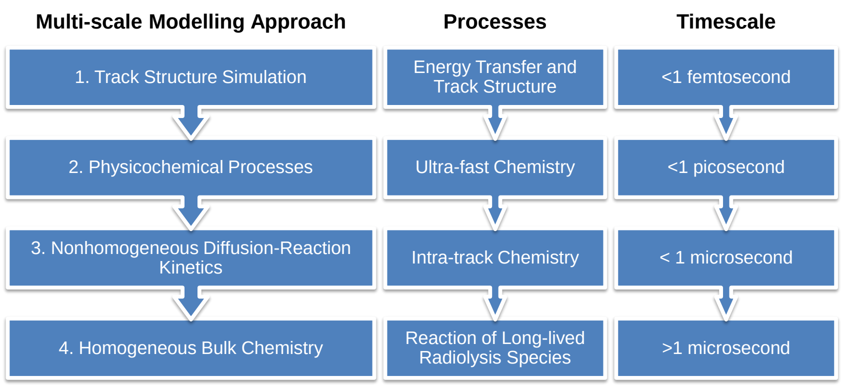
Computational Methodology

- Monte Carlo calculations to simulate the evolution of a radiation chemical track, from the point of initial energy transfer right up to the point of complete spatial relaxation of the radiation chemical track.
- Experimentally determined rate coefficients, diffusion coefficients, and liquid phase collision cross sections.
- Chemistry data files reflecting experimental chemical reaction compilations.





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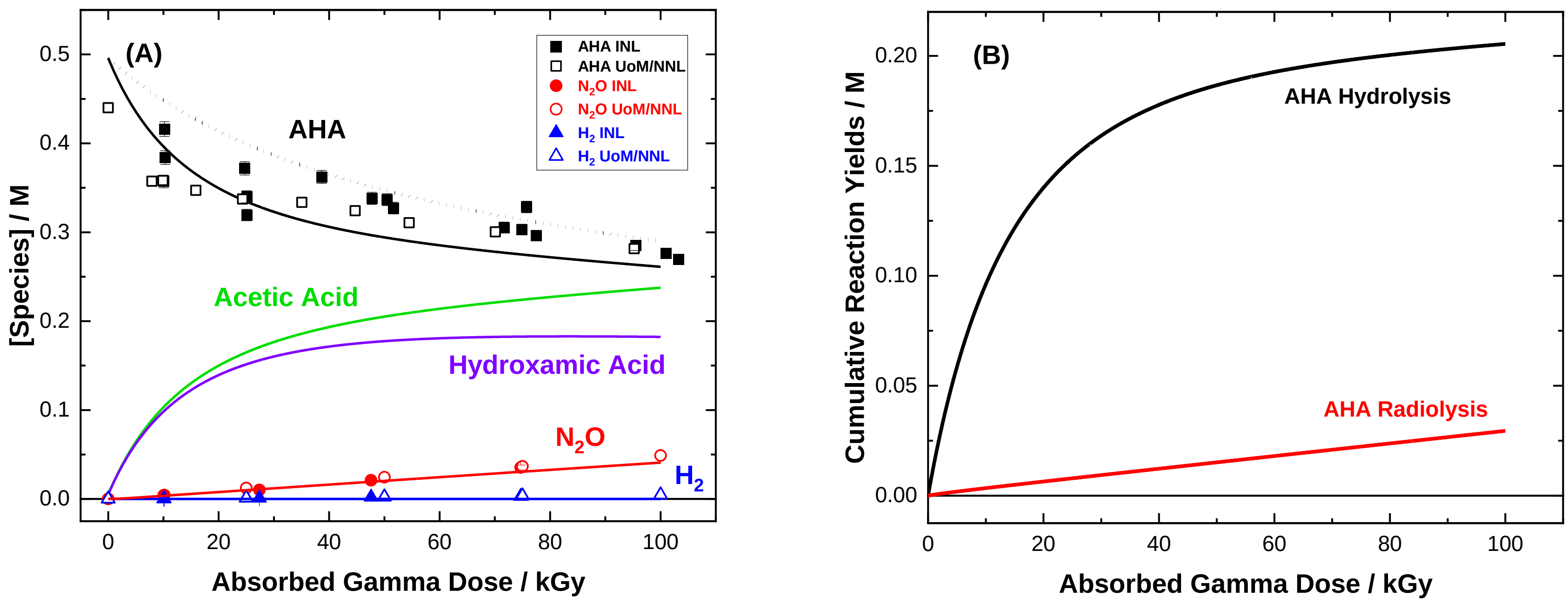
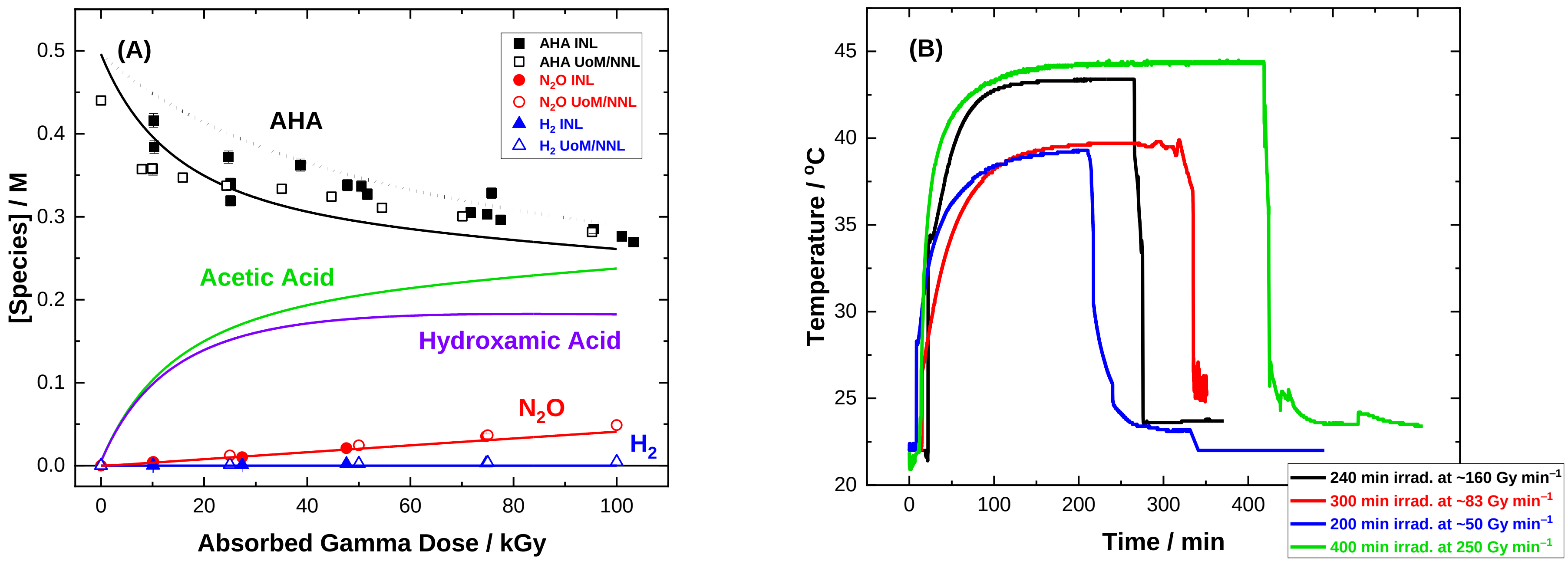
Acetohydroxamic Acid (AHA) Radiolysis



- *Settings:* **0.5 M AHA in 0.2 M HNO_3, 48 Gy min^{-1} at 36 °C.**
- 0.23 M loss of AHA within 100 kGy: 87% by hydrolysis and 13% by radiolysis.

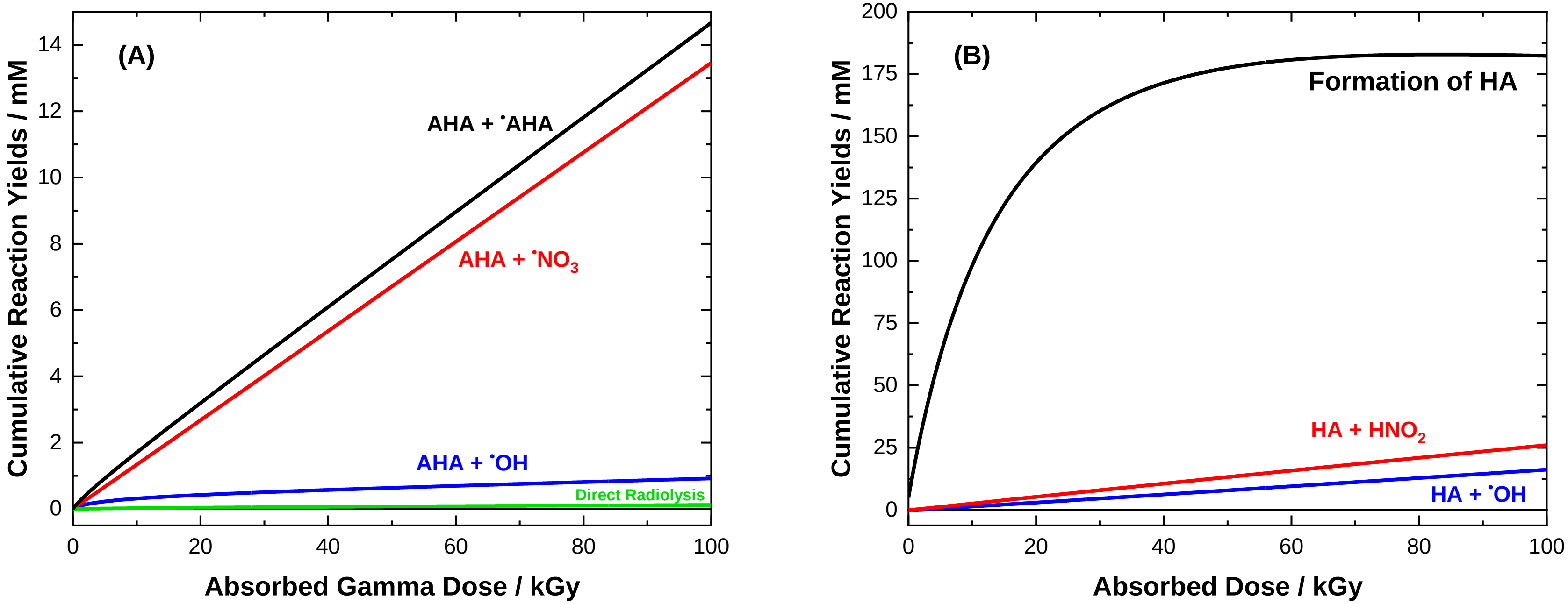
F.P.L. Andrieux, C. Boxall, H.M. Steele, and R.J. Taylor, *J. Sol. Chem.*, **2014**, *43*, 608.

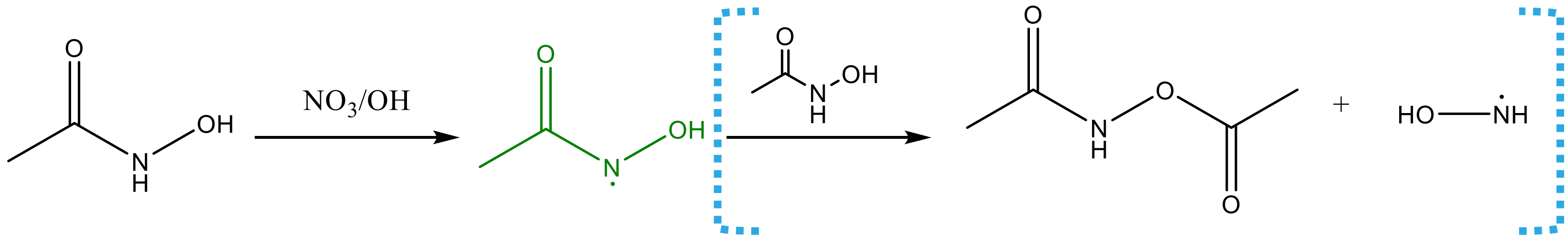
Acetohydroxamic Acid (AHA) Radiolysis



- *Settings:* **<u>0.5 M AHA in 0.2 M HNO_3, 250 Gy min^{-1} at 42 °C.</u>**
- Temperature and dose rate has a significant effect of loss of AHA.

Acetohydroxamic Acid (AHA) Radiolysis





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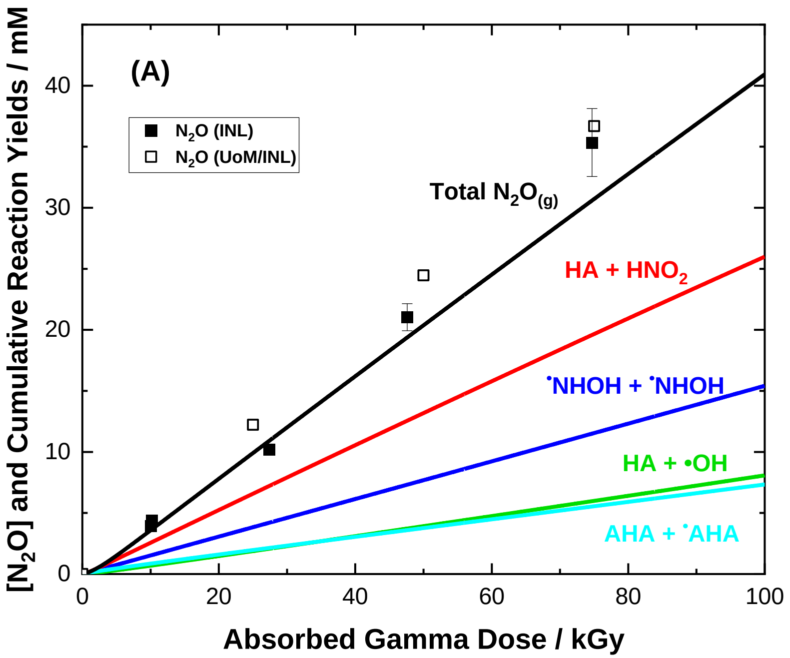
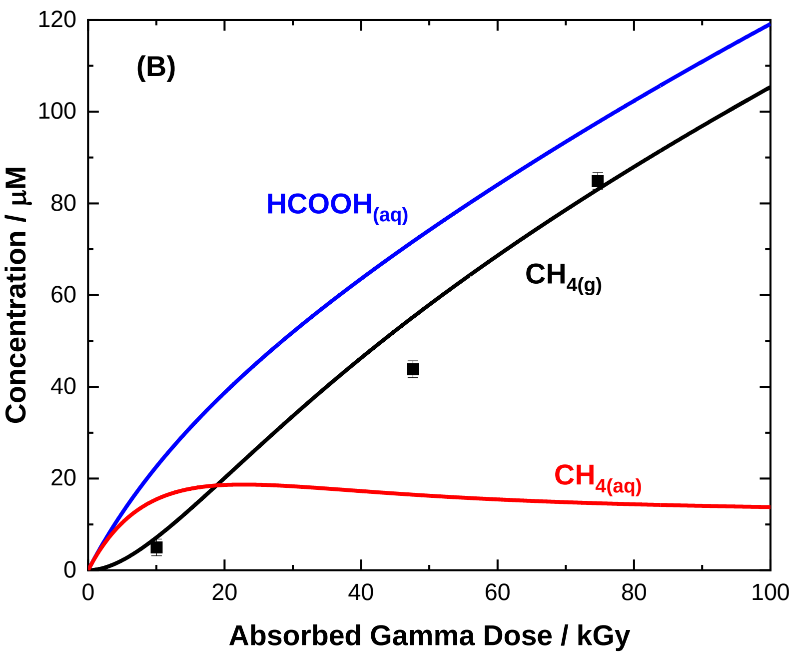
Generation of Gaseous Species

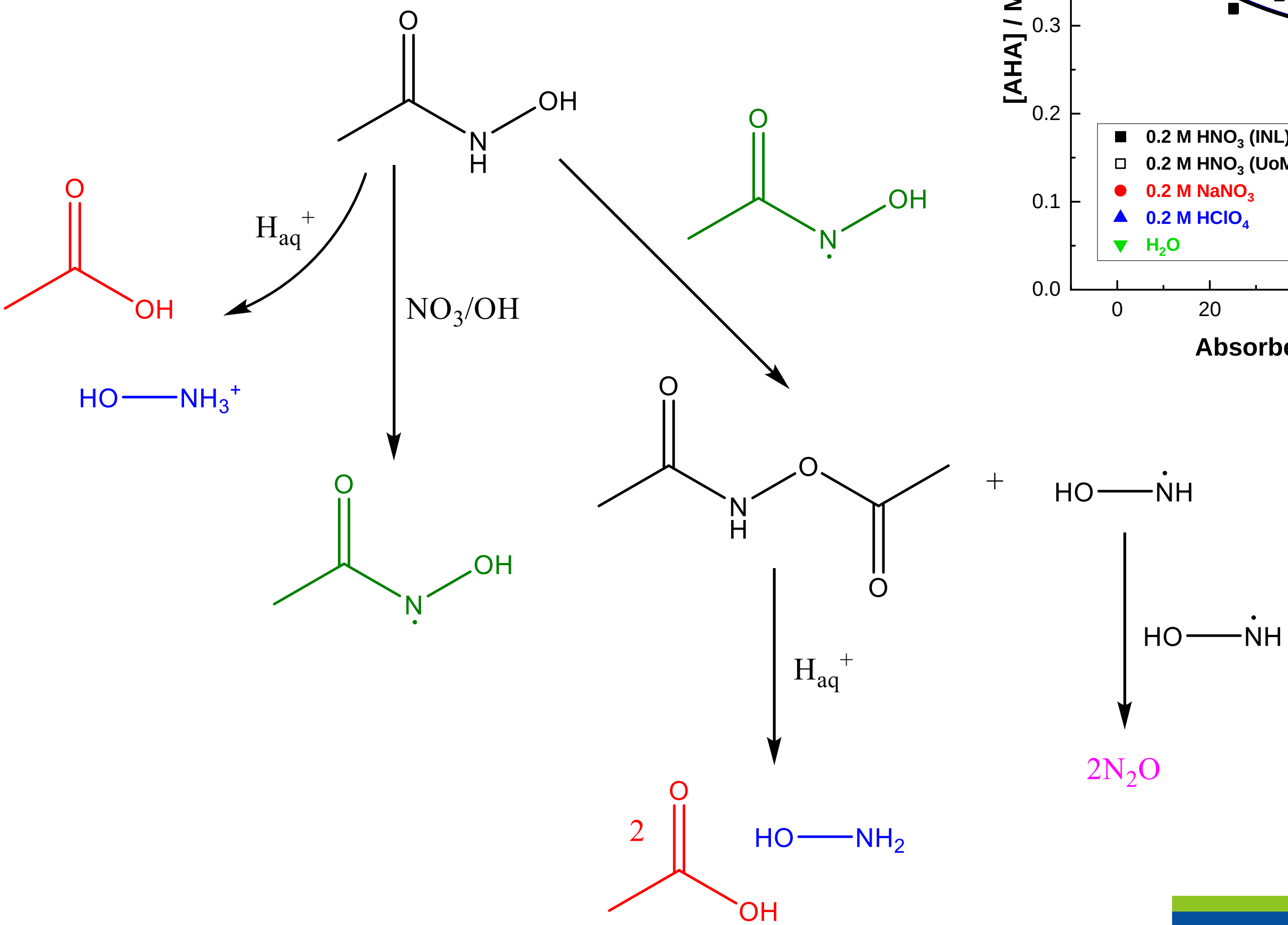


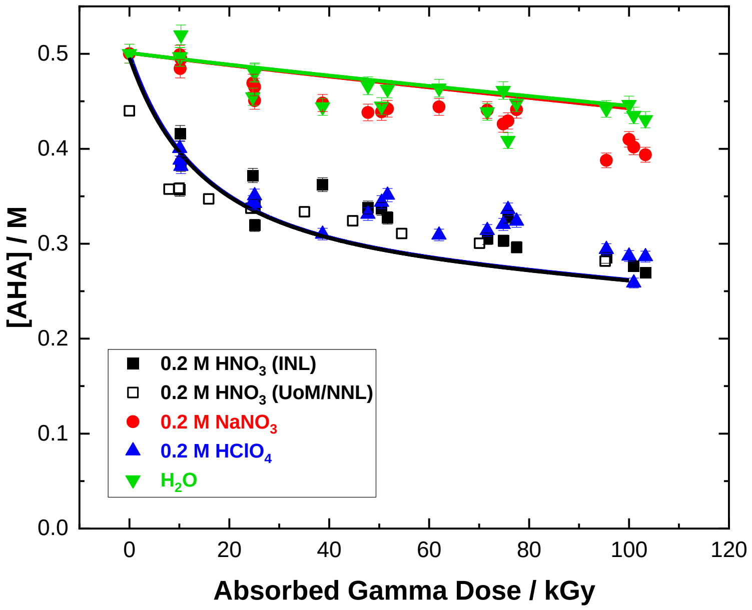


- $2\ HO\text{-}NH^{\bullet} \rightarrow N_2O + ?$
- $NH_2OH + HNO_2 \rightarrow NHOHNO + H_2O \rightarrow N_2O + 2H_2O$

- Y. Izato, K. Shiota, and A.Miyake, *Sci. Tech. Energetic Materials*, **2019**, *80(6)*, 212.

Preliminary Conclusions





Acknowledgements

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