INL/MIS-20-60519-Revision-0

US-UK Single Cycle Flow Sheet Initiative - Radiation Chemistry

January 2020

Gregory P Horne

Changing the World's Energy Future

Idaho National Laboratory

INL is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance, LLC

INL/MIS-20-60519-Revision-0

US-UK Single Cycle Flow Sheet Initiative - Radiation Chemistry

Gregory P Horne

January 2020

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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

January 20th, 2020

Gregory P. Horne
Center for Radiation Chemistry Research

US-UK Single Cycle Flow Sheet Initiative – Radiation Chemistry

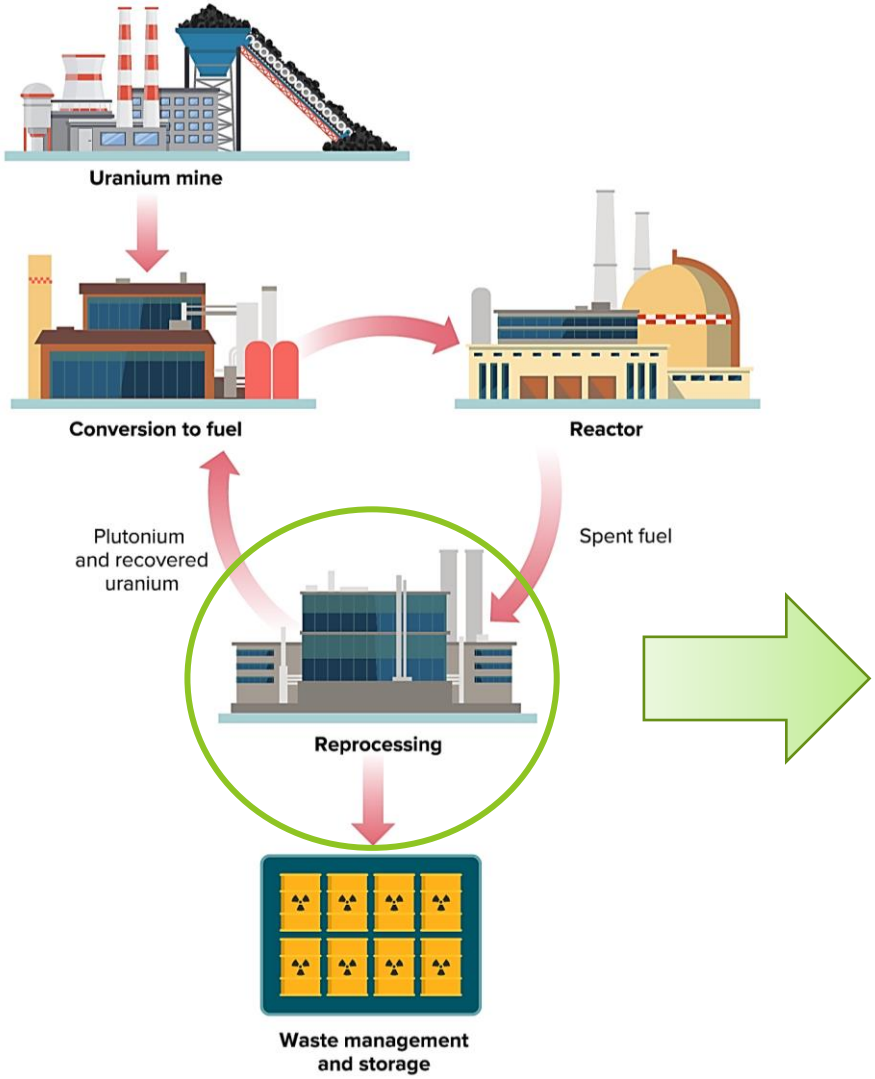
LRS Number: INL/MIS-20-60519Rev:000

The US/German Team

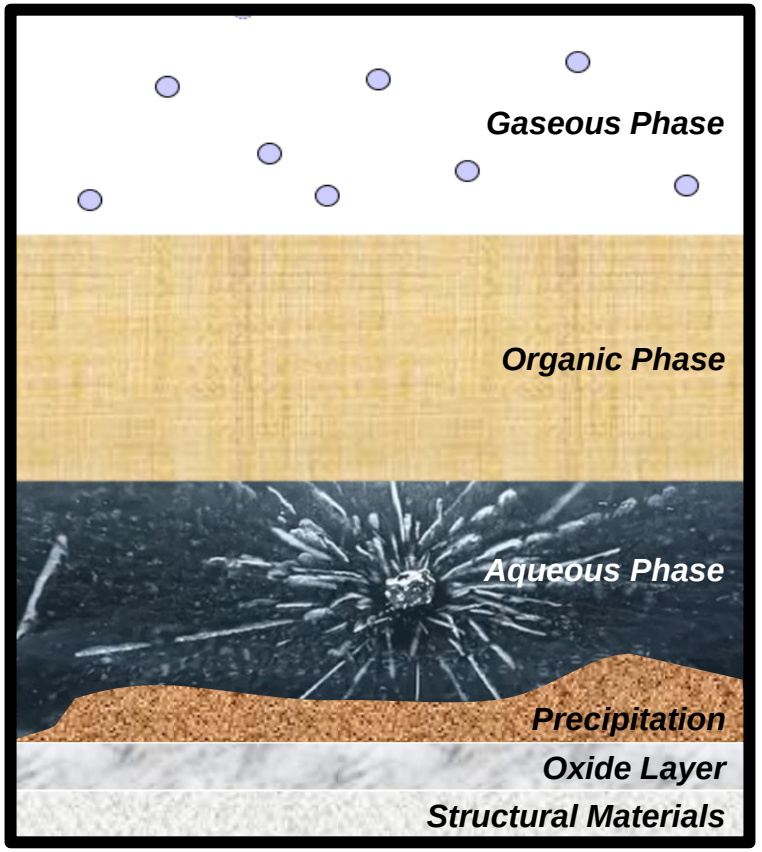
Jacy Conrad (INL), *Corey D. Pilgrim* (INL), *Andrew R. Cook* (BNL), *Andreas Wilden* (FZJ), *Stephen P. Mezyk* (CSULB), and *Bruce J. Mincher*

Idaho National Laboratory

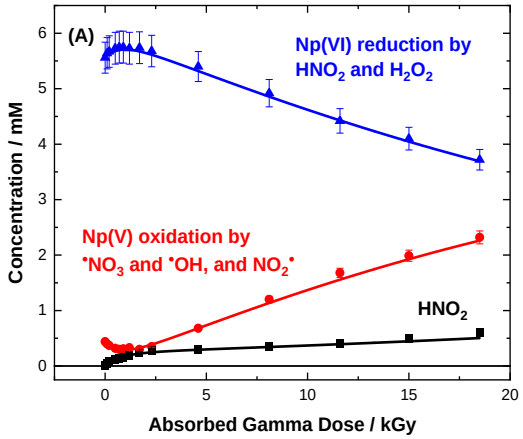
Reprocessing Radiation Chemistry

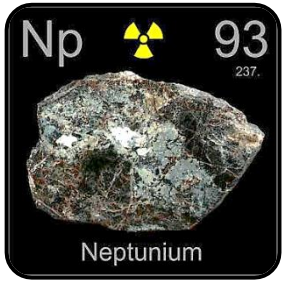


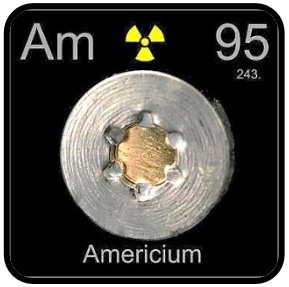
Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O (± additives)

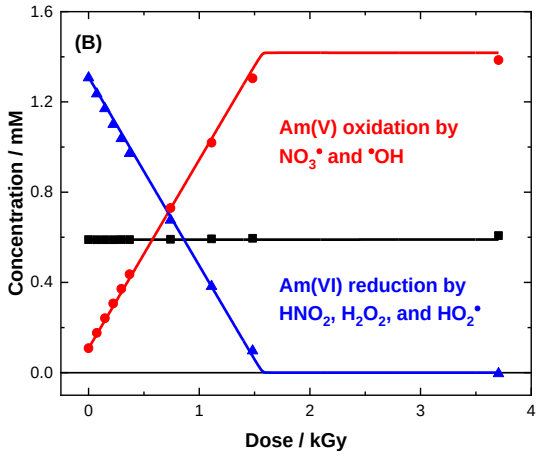


Metal Ion Redox Distributions

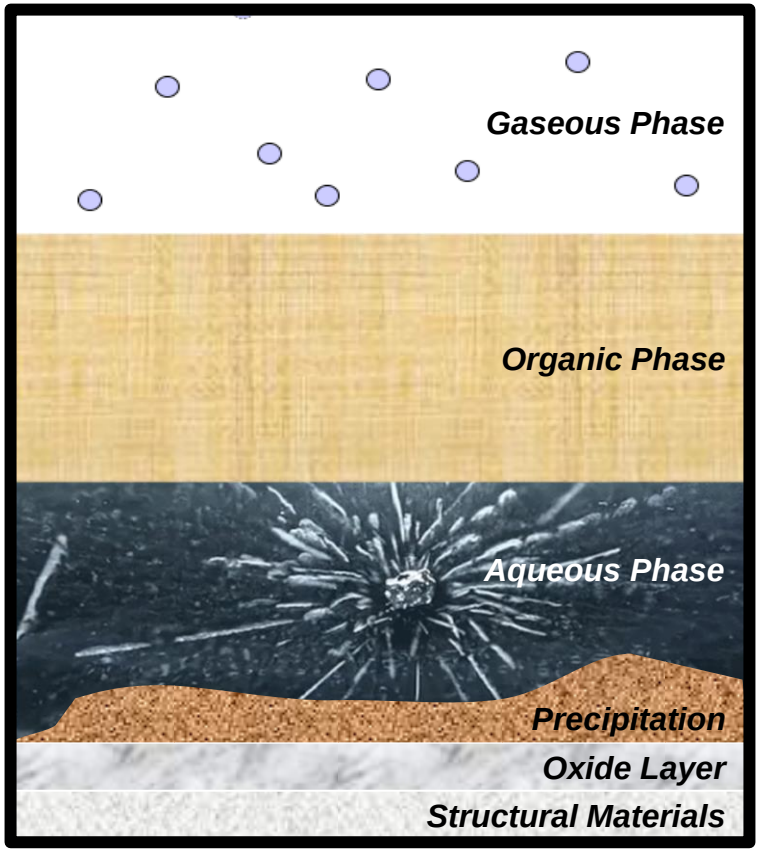






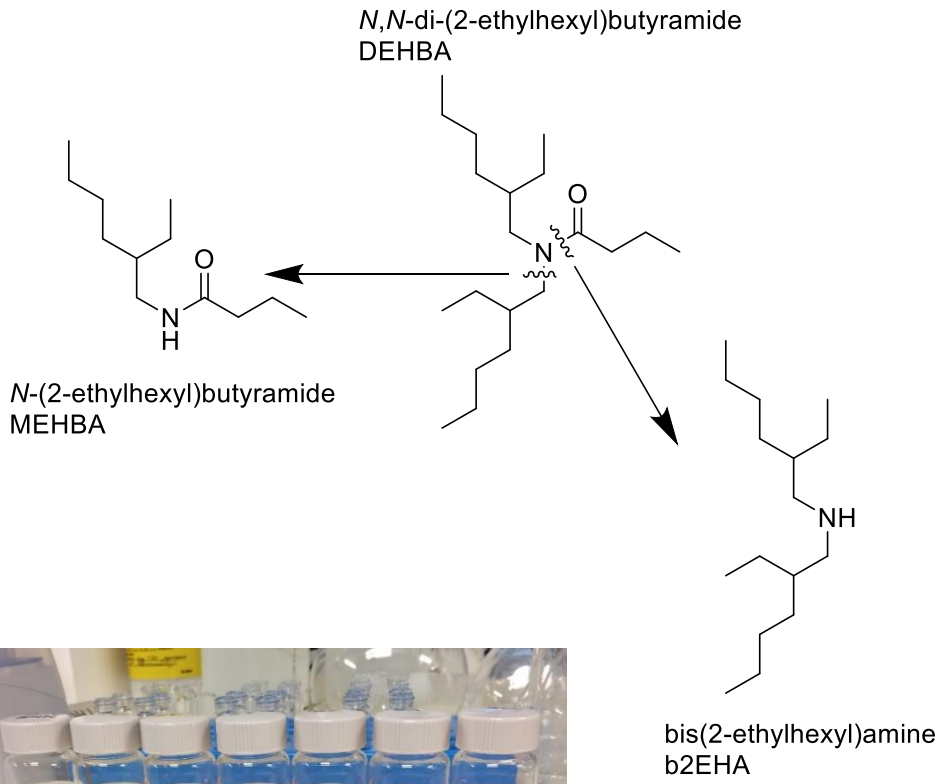


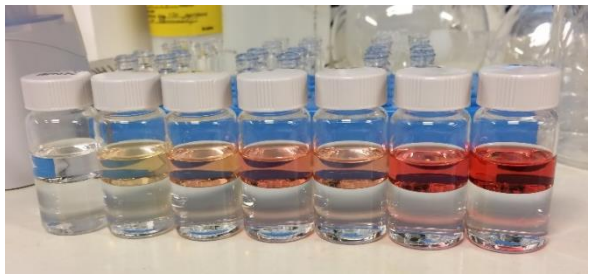
Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O
(± additives)



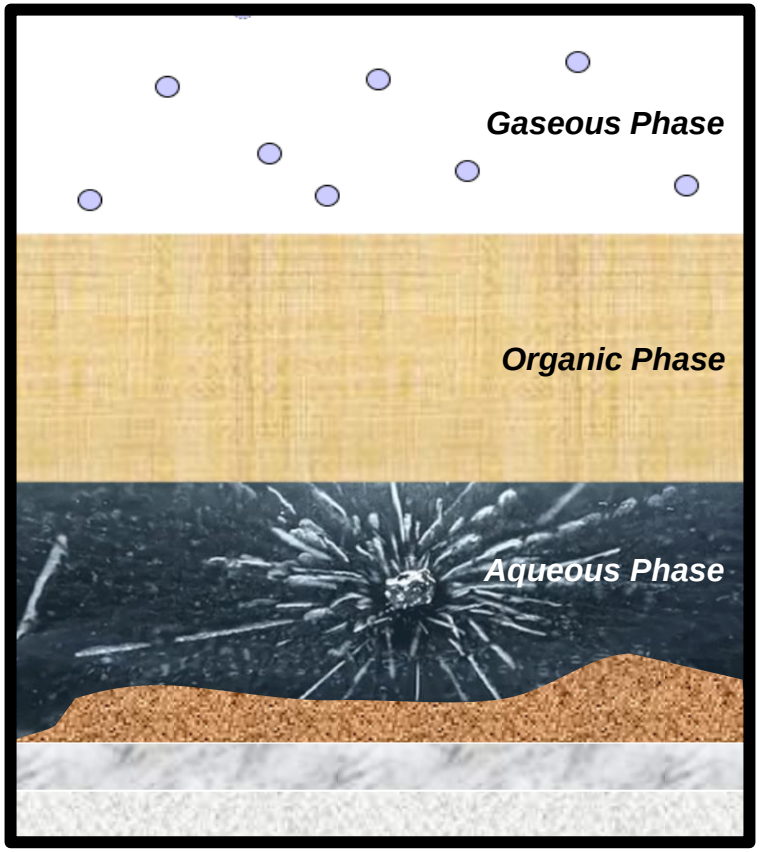
- Horne, G.P., Grimes, T.S., Mincher, B.J., Mezyk, S.P., *Journal of Physical Chemistry B*, **2016**, *120 (49)*, 12643.
- Horne, G.P., Grimes, T.S., Bauer, W.F., Dares, C.J., Pimblott, S.M., *et al.*, *Inorganic Chemistry*, **2019**, *58*, 8551.

Destruction of Active Molecules





Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O
(± additives)



- Horne, G.P., Zarzana, C.A., Grimes, T.S., Rae, C., Ceder, J., *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, G.P., Mezyk, S.P., Mincher, B.J., Zarzana, C.A., Rae, C., *et al.*, *Rad. Phys. Chem.*, **2019**, 170, 108608.

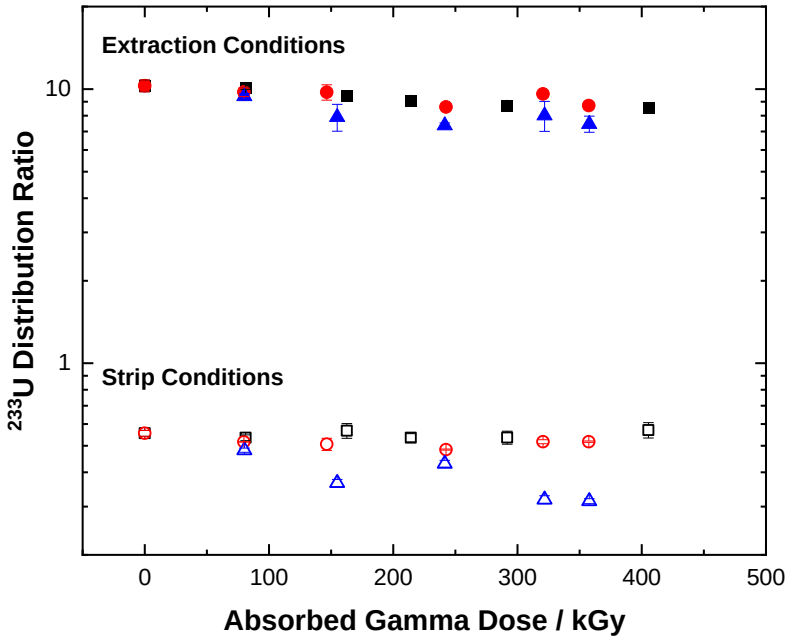
Destruction of Active Molecules

$D_U = [U]_{org}/[U]_{aq}$

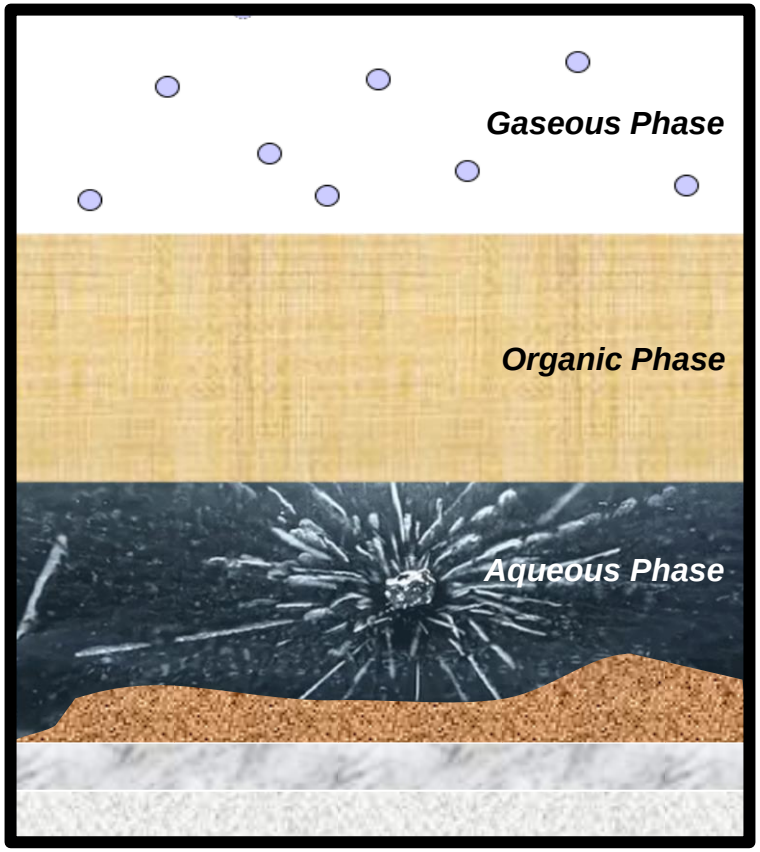
Organic-only (■/□)

0.1 M HNO_3 contact (●/○)

3.0 M HNO_3 contact (▲/△)



Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O
(± additives)



- Horne, G.P., Zarzana, C.A., Grimes, T.S., Rae, C., Ceder, J., *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, G.P., Mezyk, S.P., Mincher, B.J., Zarzana, C.A., Rae, C., *et al.*, *Rad. Phys. Chem.*, **2019**, 170, 108608.

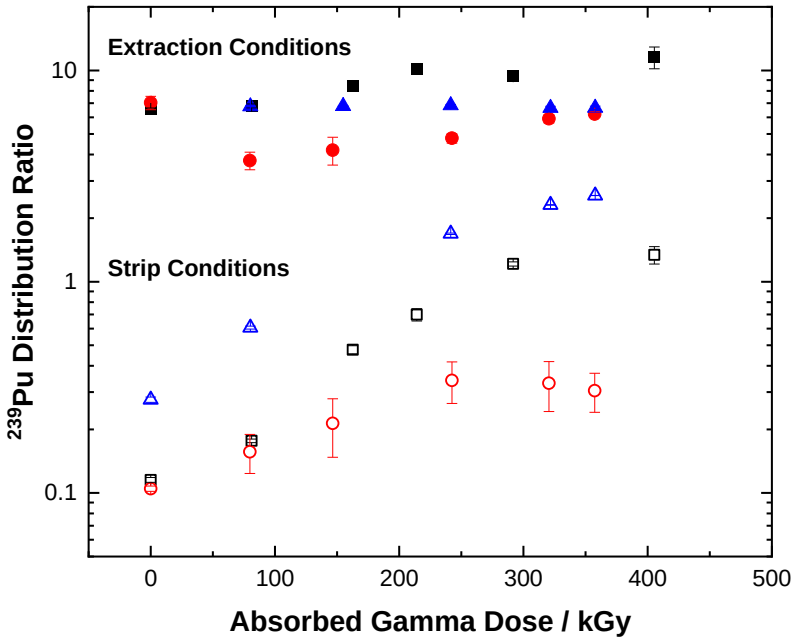
Destruction of Active Molecules

$D_{Pu} = [Pu]_{org}/[Pu]_{aq}$

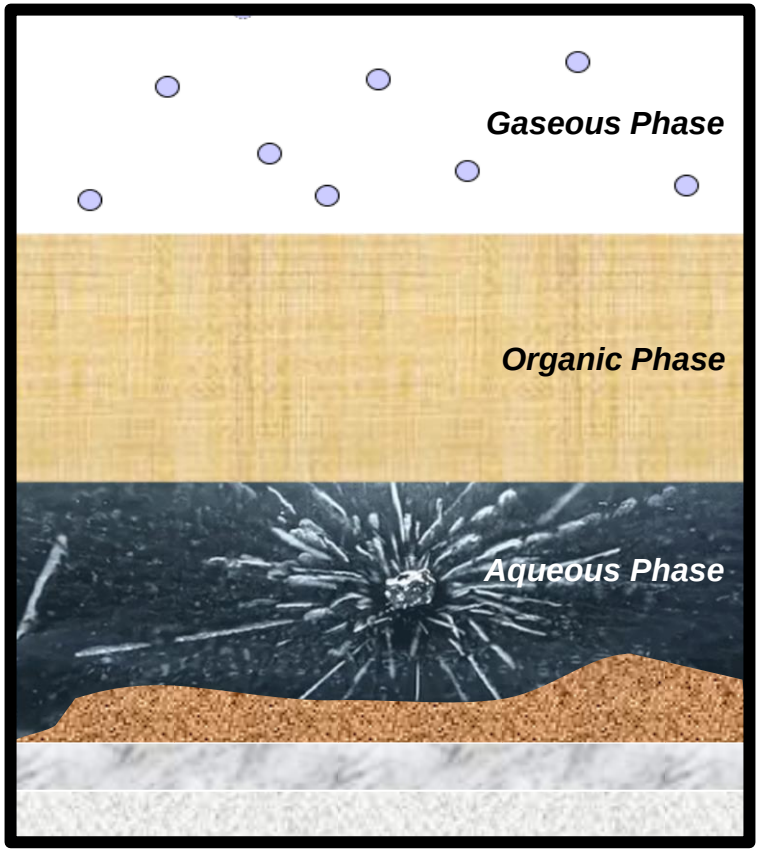
Organic-only (■/□)

0.1 M HNO_3 contact (●/○)

3.0 M HNO_3 contact (▲/△)



Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O
(± additives)



- Horne, G.P., Zarzana, C.A., Grimes, T.S., Rae, C., Ceder, J., *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, G.P., Mezyk, S.P., Mincher, B.J., Zarzana, C.A., Rae, C., *et al.*, *Rad. Phys. Chem.*, **2019**, 170, 108608.

Effect of Additives on Radiation Robustness

[1]

Table 2
The values of a dose constant (d) and an electron fraction of n-dodecane (ε_d) for γ-radiolysis of 0.1 M TODGA in different components of diluent

Diluent	d (Gy^{-1})	ε_d
n-dodecane (80)–1-octanol (20)	3.1×10^{-6}	0.715
n-dodecane (60)–1-octanol (40)	3.1×10^{-6}	0.512
1-octanol (100)	3.1×10^{-6}	0
n-dodecane (75)–benzene (25)	2.0×10^{-6}	0.664
n-dodecane (50)–benzene (50)	1.3×10^{-6}	0.413
Benzene (100)	8.0×10^{-7}	0

[2]

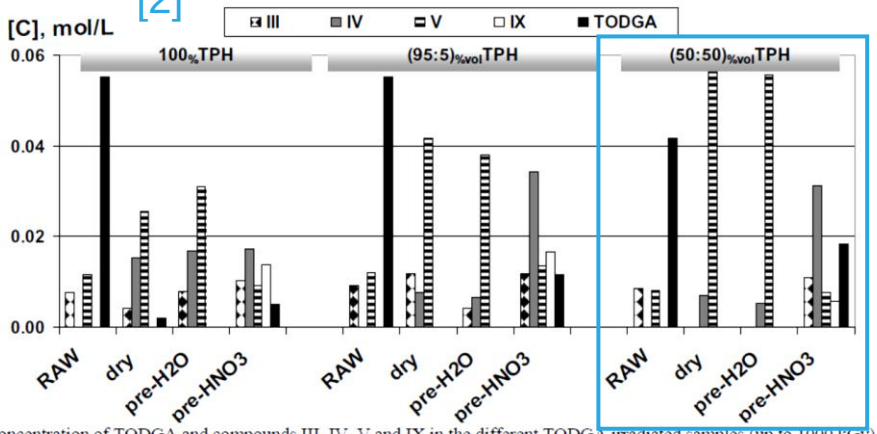


Fig. 3. Concentration of TODGA and compounds III, IV, V and IX in the different TODGA irradiated samples (up to 1000 kGy) and the corresponding D_M values. Samples 1: $100_{\%vol}$ TPH. Samples 2: $(95:5)_{\%vol}$ TPH/octanol. Samples 3: $(50:50)_{\%vol}$ TPH/octanol.

[3]

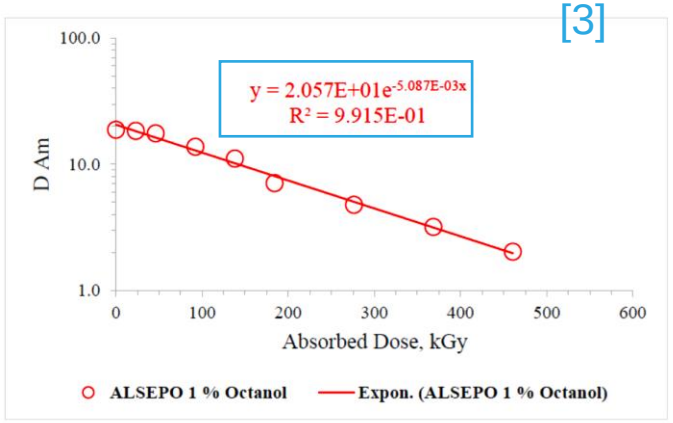


Figure 7. Plot of the americium extraction distribution ratios determined as a function of absorbed dose for the static irradiation of the ALSEPO solvent containing 1 % octanol in contact with 3 M HNO_3.

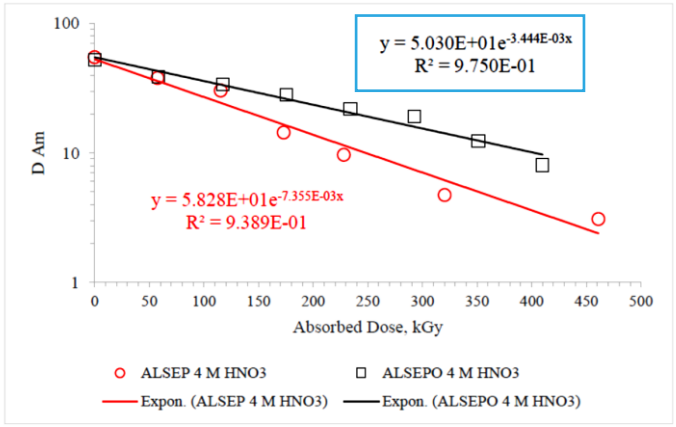
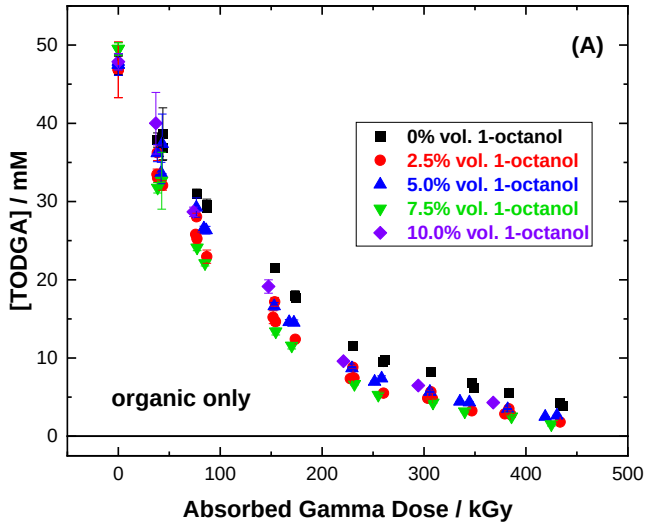
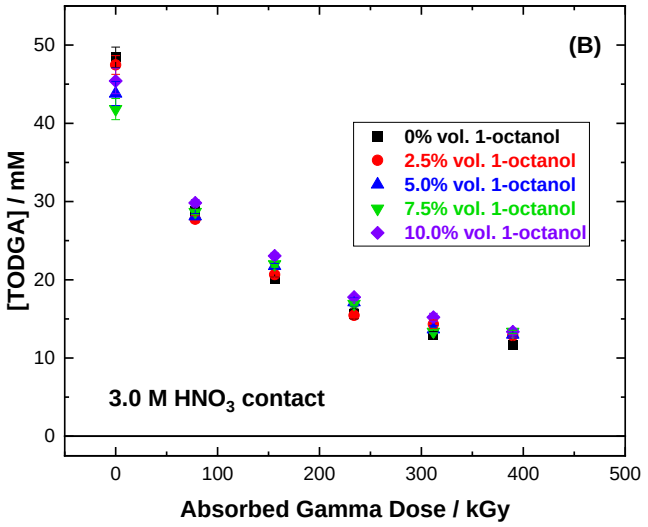


Figure 3. Plot of the americium distribution ratios determined as a function of absorbed dose for the static irradiation of the ALSEP and ALSEPO solvents in contact with 4 M HNO_3.

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

Effect of Additives on Radiation Robustness



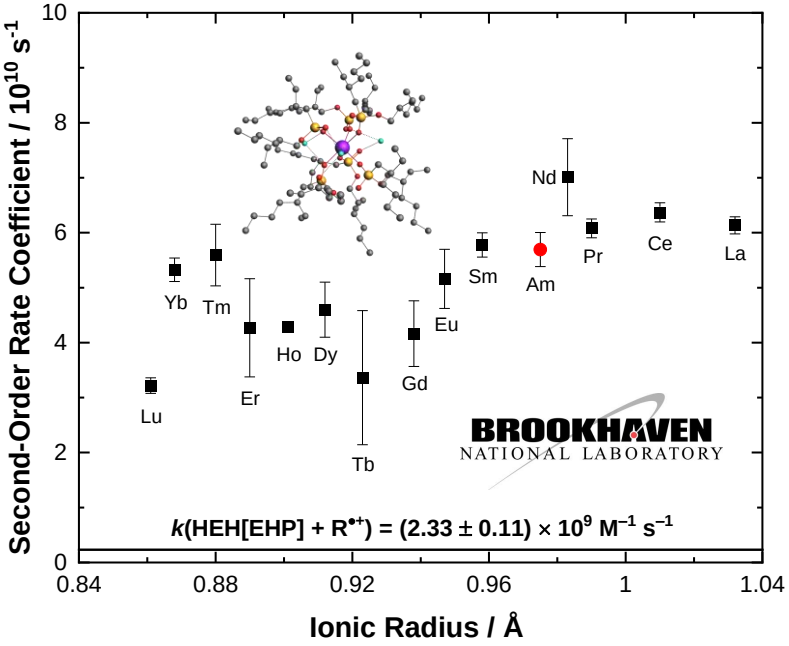


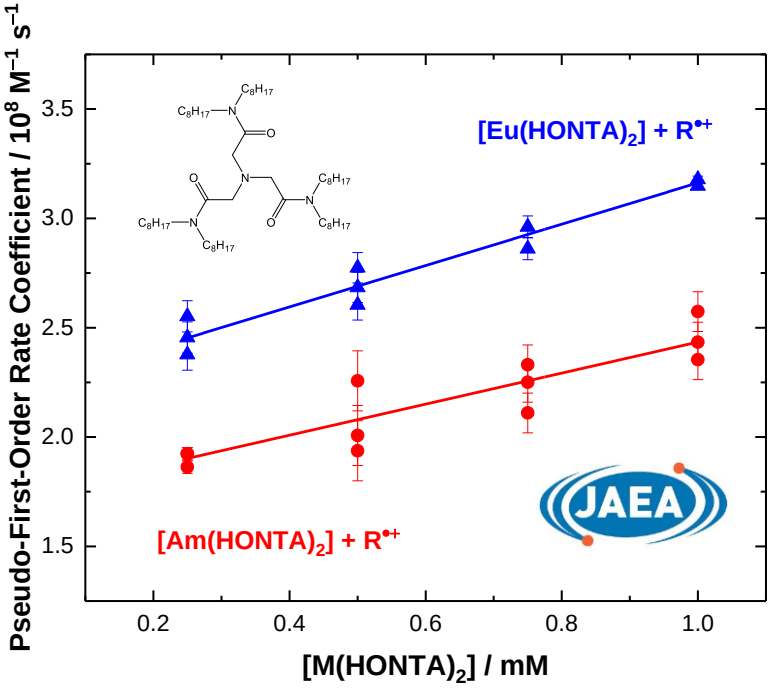
Addition of **1-octanol** to:

- ***Organic only*** **TODGA/*n*-dodecane** solutions ***increases*** the rate of **TODGA** radiolysis, d > = 0.0057 kGy^{-1}.
- ***Biphasic*** **TODGA/*n*-dodecane/3.0 M HNO_3** solutions ***decreases*** the rate of **TODGA** radiolysis, d < = 0.0057 kGy^{-1}.

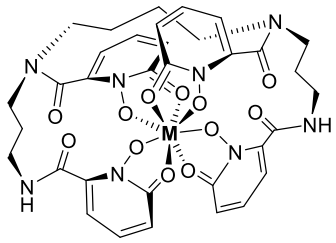
- Horne, G.P., Zarzana, C.A., Rae, C., Cook, A.R., Mezyk, S.P., Zalupski, P.R., Wilden, A., Mincher, B.J., *Phys. Chem. Chem. Phys.*, **2020**, https://doi.org/10.1039/D0CP04310A.

Effect of Complexation on Radiation Robustness





Radical	Rate coefficient (k, M^{-1} s^{-1})	
	HOPO	[Nd(HOPO)]
e_{aq}^- (10^{10})	3.17 ± 0.04	19.0 ± 0.1
$H^\bullet$ (10^9)	5.50 ± 0.20	2.92 ± 0.10
$^\bullet OH$ (10^{10})	1.66 ± 0.06	0.47 ± 0.03
$^\bullet NO_3$ (10^9)	3.79 ± 0.10	5.18 ± 0.17



Berkeley UNIVERSITY OF CALIFORNIA

IDAHO NATIONAL LABORATORY

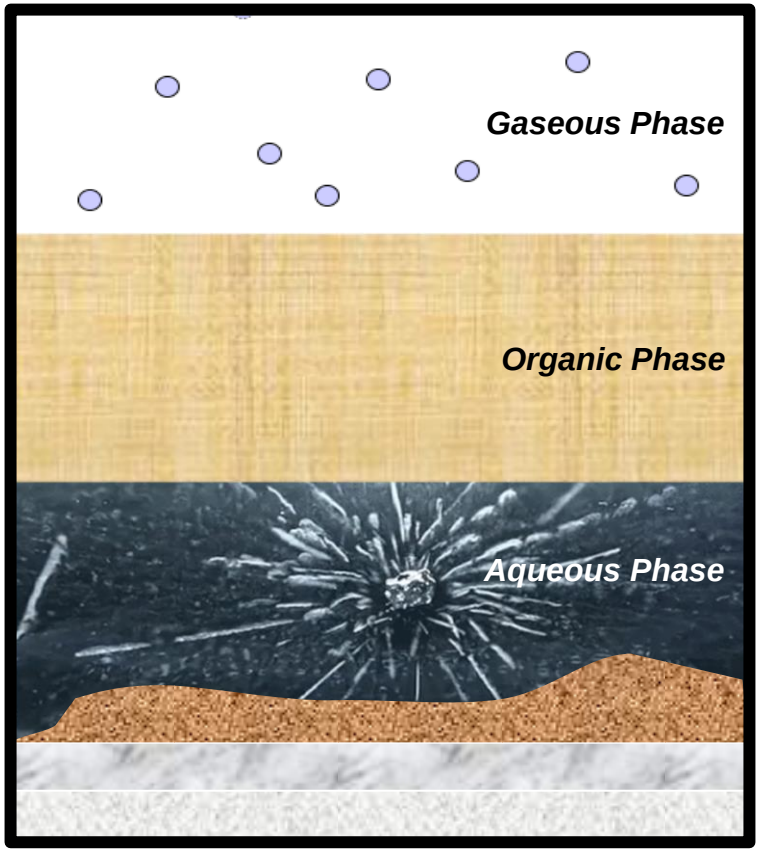
Single Cycle Concepts and Radiation Chemistry

How does *ionizing radiation* effect:

1. the integrity and function of **ligands** and **additives**?
2. single phase *vs.* biphasic system performance?
3. the redox distribution of *free* and **ligand**/**additive** *complexed* metal ions, and ultimately their mass transport?

And why?

Single Cycle Used Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O
(± additives)



Radiation Chemistry in Nitrate and Nitric Acid Solutions

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

$R\text{-}CH_3 \rightsquigarrow e^-, R\text{-}CH_3^{\bullet +}, R\text{-}CH_2^\bullet, {}^\bullet CH_3, H^\bullet, H_2$

Radiation Chemistry in Nitrate and Nitric Acid Solutions

Water Radiolysis

Direct Radiation Effects

Radiolysis Products of Concern in Reprocessing

$^{\bullet}OH$, H_2O_2, and H_2 from H_2O

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

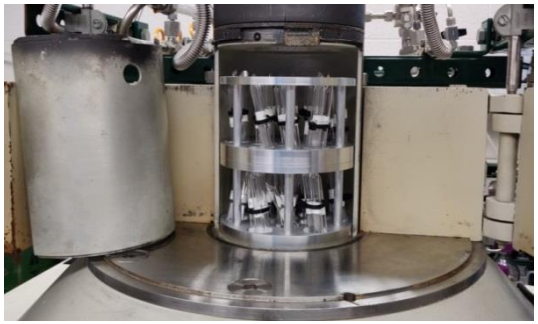
e^-, $R\text{-}CH_3^{\bullet+}$, $R\text{-}CH_2^{\bullet}$, and $H^{\bullet}$ from **organic diluent**

H_3, $H^{\bullet}$, H_2

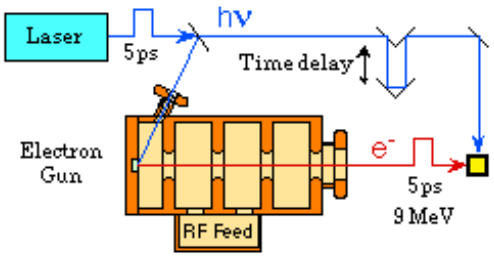
$N_2O_4 \rightarrow HNO_2 + HNO_3$

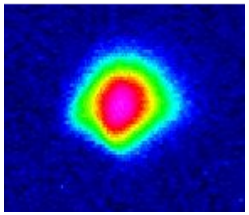
Radiation Chemistry Techniques

Gamma Radiolysis

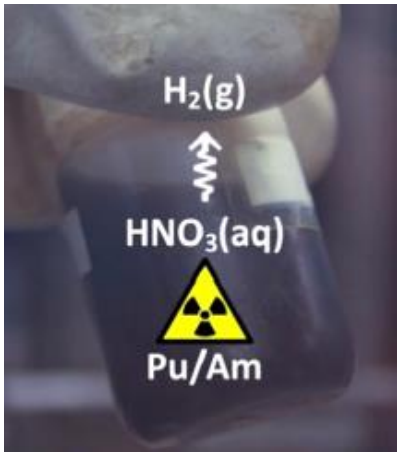


Pulsed Electron Radiolysis



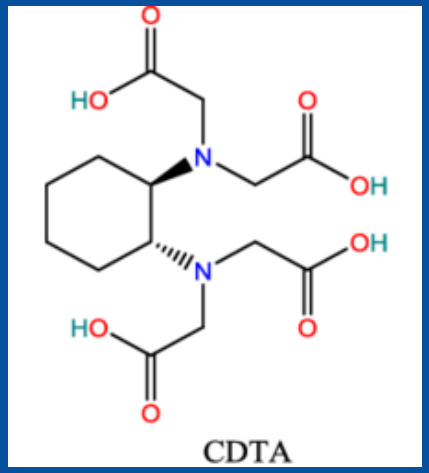


Self-Radiolysis

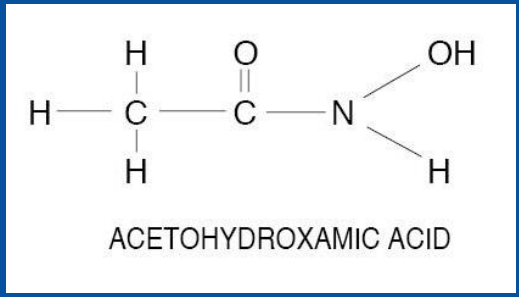


- Spinks, J.W.T., Woods, R.J., An Introduction to Radiation Chemistry; Third Edition; Wiley-Interscience: New York, **1990**.

Radiolytic Evaluation of Proposed Single-Cycle Used Nuclear Fuel Recycle Additives AHA and CDTA



CDTA



ACETOHYDROXAMIC ACID

AHA Radiolysis – What's Been Done?

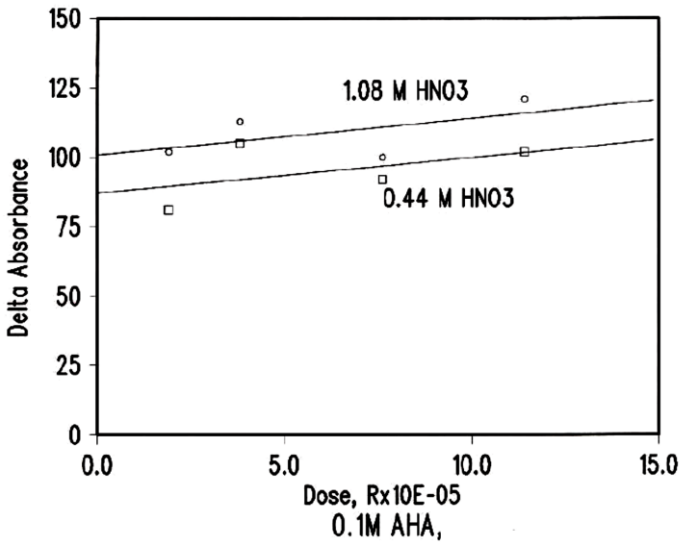


Fig. 4. Dose dependence of radiation damage [1].

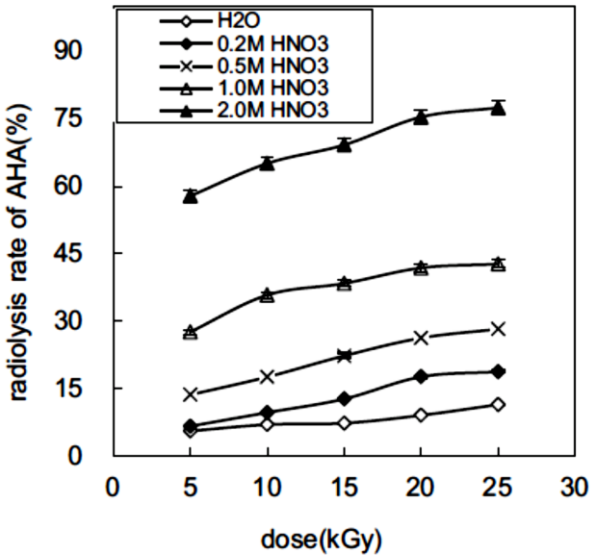


Fig. 1. Radiolysis rate of AHA as a function of dose [2].

- Main degradation products in solution were found to be ***acetate/acetic acid*** and **HNO_2**.
- *No investigation into the underlying mechanisms nor impact of radiation of AHA performance.*

1. Karraker, D.G., Radiation Chemistry of Acetohydroxamic Acid in the Urex Process, WSRC-TR-2002-00283, **2002**), 1.
2. Wang, J.-H., Li, C., Li, Q., Wu, M-H., Zheng, W.-F., He, H., *Nucl. Sci. Tech.*, 2018, 29 (27), 26

CDTA Radiolysis – What's Been Done?

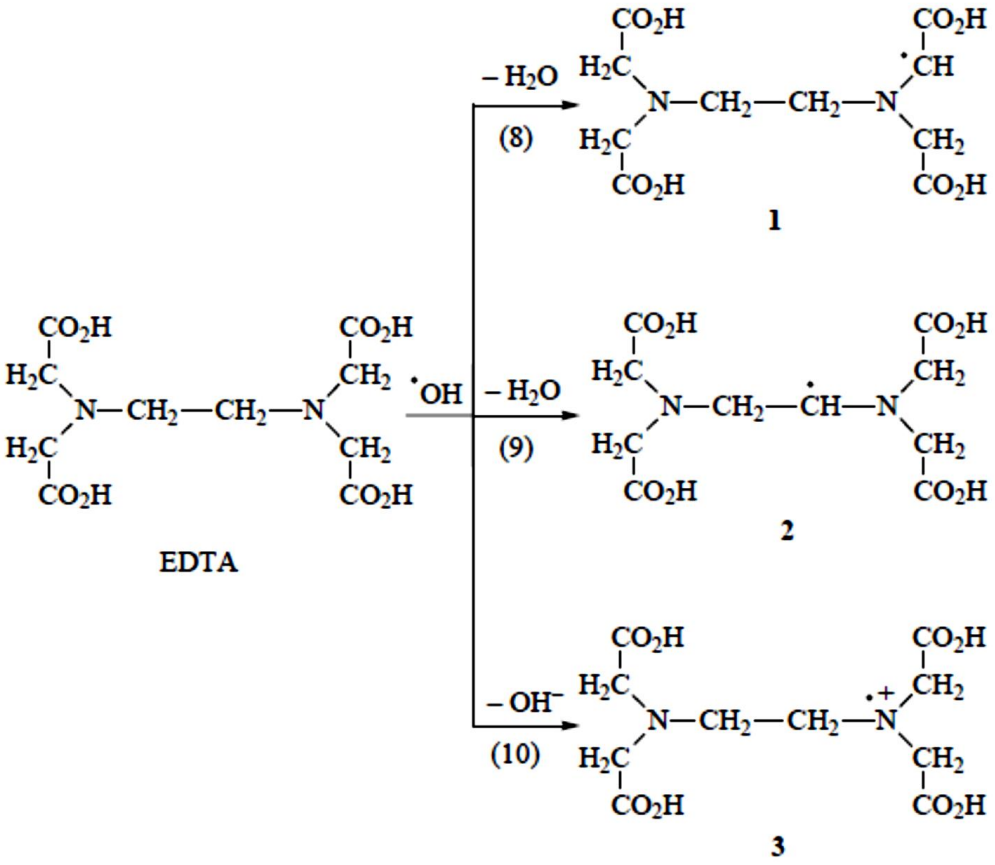


Table 2 γ-Radiolysis of EDTA (2×10^{-3} mol dm^{-3}) in N_2O-saturated and N_2O–O_2-saturated aqueous solutions. Products and their G values (in units of 10^{-7} mol J^{-1}). The yields of ethylenediaminetriacetic acid could not yet be quantified.

Product	N_2O	N_2O–O_2
Formaldehyde	0.2	1.6
Carbon dioxide	3.4	2.5
Formic acid	absent	0.7
Glyoxylic acid	0.5	3.6
Iminodiacetic acid	1.3	2.1
Ethylenediaminetriacetic acid	not determined	present
EDTA consumption	5.4	5.4

- Hobel, B., von Sonntag, C., *J. Chem. Soc. Oerkin Trans.*, **1998**, 2, 509.

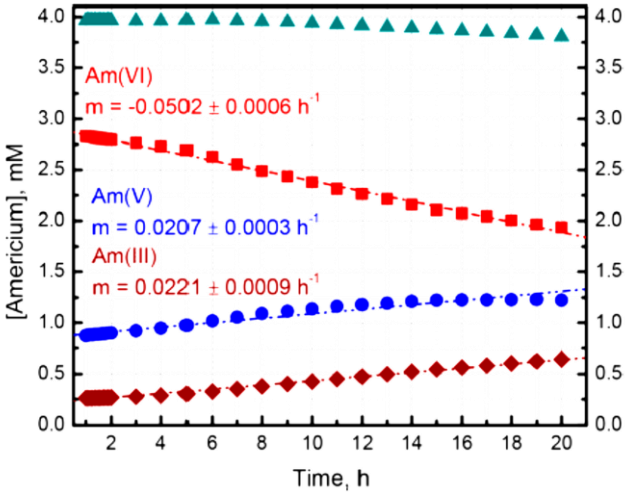
AHA and CDTA Radiolysis – Where Are We Going?

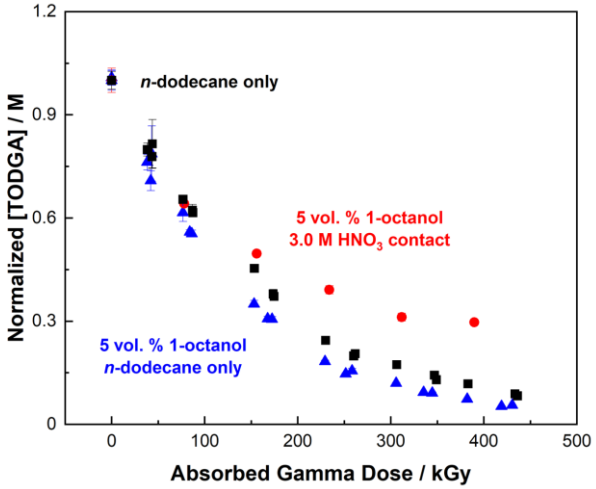
FY21

- Complimentary *biphasic* **AHA**/**CDTA** *γ*-irradiations using single cycle ligand systems: **TBP**, **DEHBA**, and **DEH*i*BA**.
- Pulse electron radiolysis reaction kinetic measurements for **AHA** and **CDTA**.

FY22

- Steady-state (*α* and *γ*) and time-resolved irradiations of metal (e.g., *Zr, Pd, U, Np, and Pu*) loaded solvent systems.





- Grimes, T.S., Horne, G.P., Dares, C.J., Pimblott, S.M., Mezyk, S.P., Mincher, B.J., *Inorg. Chem.*, **2017**, *56 (14)*, 8295.
- Horne, G.P., Zarzana, C.A., Rae, C., Cook, A.R., Mezyk, S.P., Zalupski, P.R., Wilden, A., Mincher, B.J., *Phys. Chem. Chem. Phys.*, **2020**, https://doi.org/10.1039/D0CP04310A.

Calculations for Single Phase AHA/CDTA Radiolysis

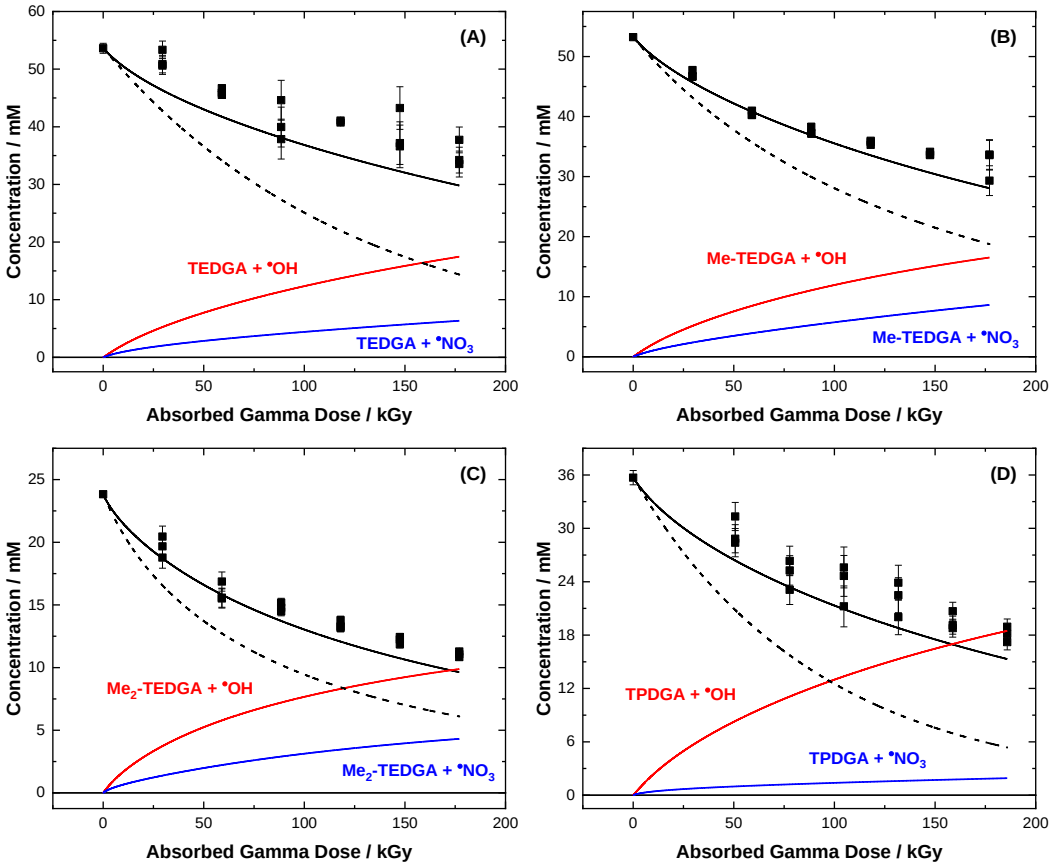


Fig. 5. Gamma radiolysis of hydrophilic DGAs in concentrated, aqueous nitrate solution as a function of absorbed dose: (A) TEDGA; (B) Me-TEDGA; (C) Me_2-TEDGA; and (D) TPDGA. Curves are from multi-scale calculations predicting DGA decay without secondary degradation product reactions (**dashed black**) and with secondary degradation product reactions (**solid black**) and corresponding accumulated reaction kinetics for •OH (**red**) and $•NO_3$ (**blue**).

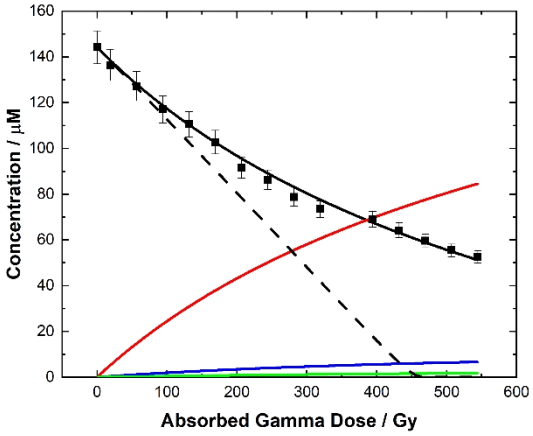
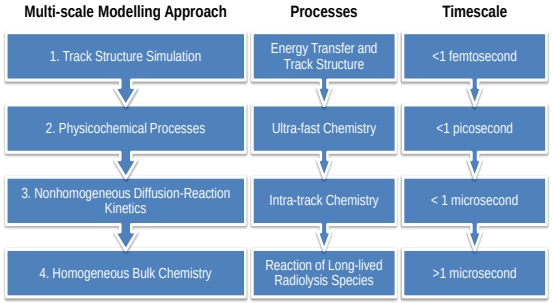


Fig. 3. Gamma radiolysis of BTP(S) (■) as a function of absorbed gamma dose. Curves are from deterministic reaction kinetics calculations predicting the change in concentration of: BTP(S) without secondary degradation product reactions with •OH (**Dashed Black**); and with secondary degradation product reactions with •OH (**Solid Black**) and the cumulative reaction concentrations of BTP(S) with •OH (**Solid Red**), e_{aq}^- (**Solid Blue**), and H• (**Solid Green**).



- Horne, G.P., Donoclift, T.A., Sims, H.E., Orr, R.M., Pimblott, S.M., *J. Phys. Chem. B*, **2016**, 120 (45), 11781.
- Horne, G.P., Wilden, A., Mezyk, S.P., Twight, L., et al., *Dalton Trans*., **2019**, 48, 17005
- Horne, G.P., Mezyk, S.P., Moulton, N., Peller, J.R., Geist, A., Dalton Trans., **2019**, 48, 4547..

Expected Deliverables

- Insight into the radiolytic working limit for both additives under process envisioned conditions.
- 1 joint manuscript on AHA radiolysis for ***PCCP*/*Dalton Transactions*** (*FY21*).
- 1 joint manuscript on CDTA radiolysis for ***PCCP*/*Dalton Transactions*** (*FY21*).
- 1 joint manuscript of modeling calculations for ***PCCP*** (*FY22*).
- **Postdoctoral research associate exchange?**

Acknowledgements

U.S. DEPARTMENT OF ENERGY






CALIFORNIA STATE UNIVERSITY LONG BEACH 1949

BROOKHAVEN NATIONAL LABORATORY

JÜLICH Forschungszentrum

Idaho National Laboratory