INL/PRO-20-60575-Revision-0

The Role of Fundamental Science in Innovating Nuclear Technology ? A Radiation Chemistry Perspective and Reprocessing Case Study

December 2020

Changing the World's Energy Future

Gregory P Horne

Idaho National Laboratory

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

December 7th, 2020

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Center for Radiation
Chemistry Research

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LRS Number: INL/PRO-20-60575 Rev:000

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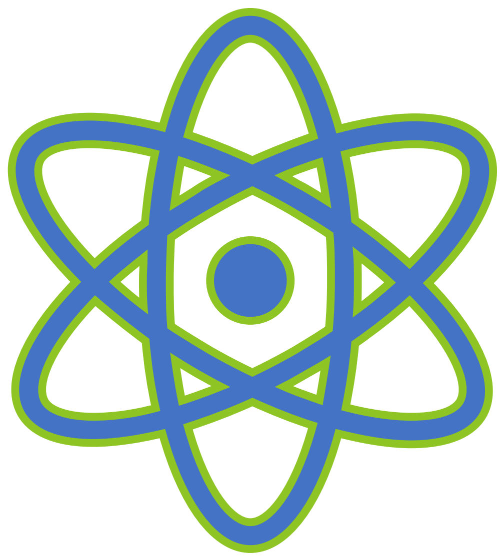
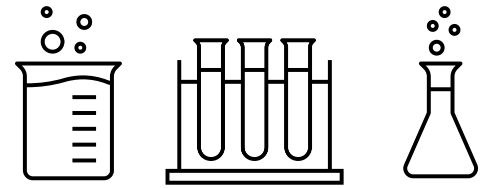
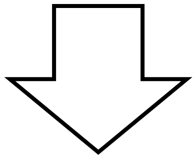
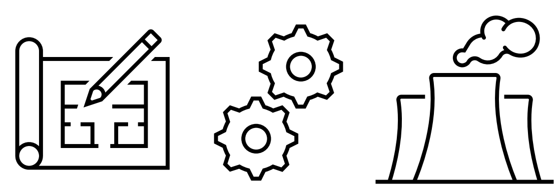


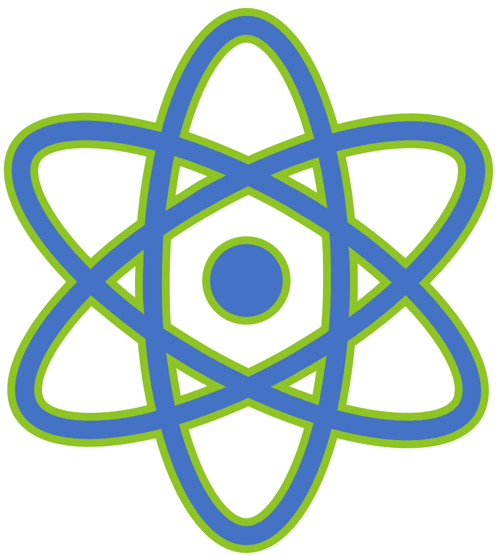


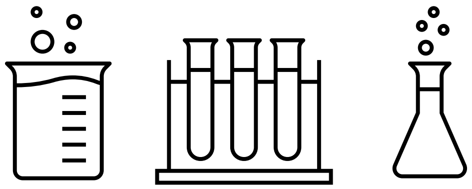
Fundamental Science



Applied Science







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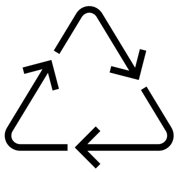

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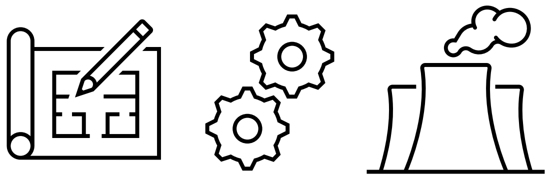
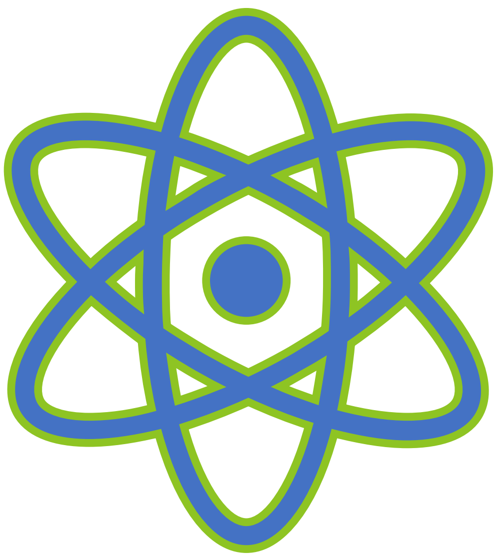
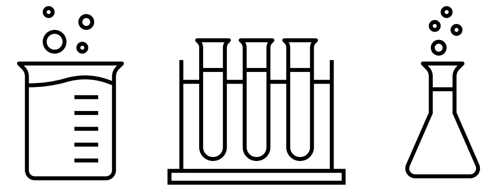


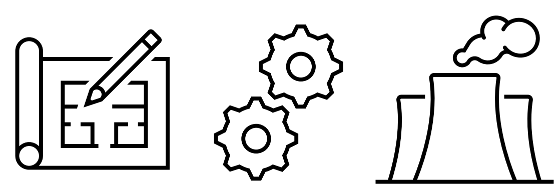




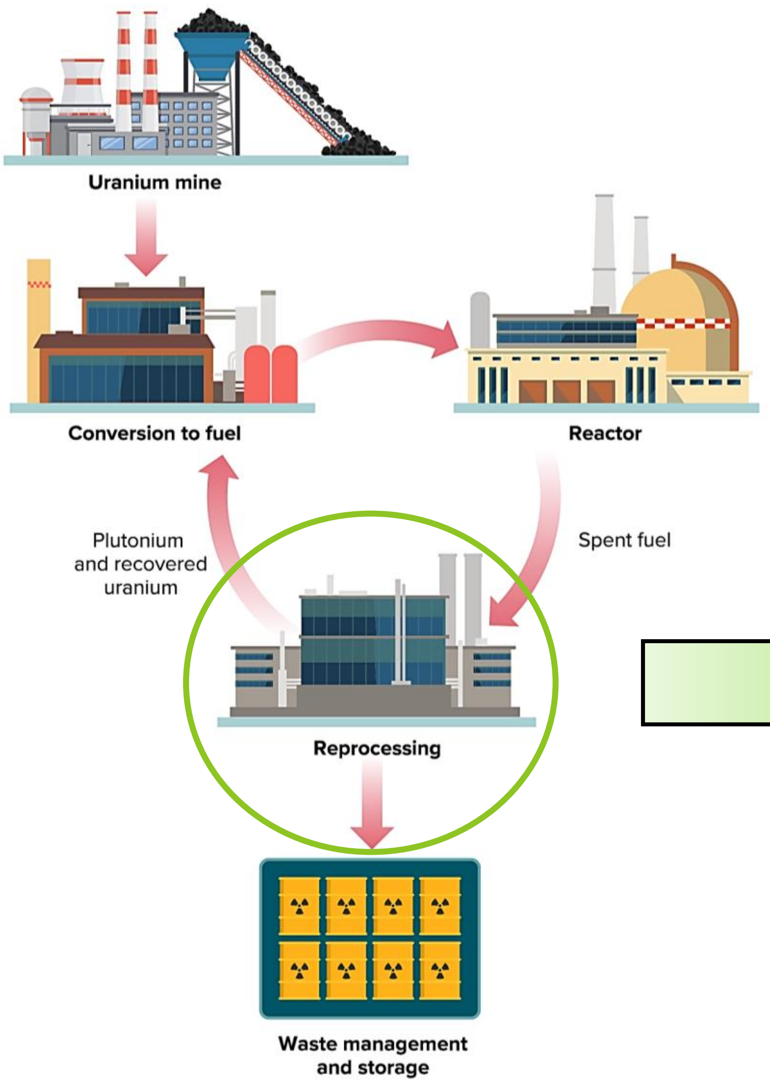
Fundamental Science

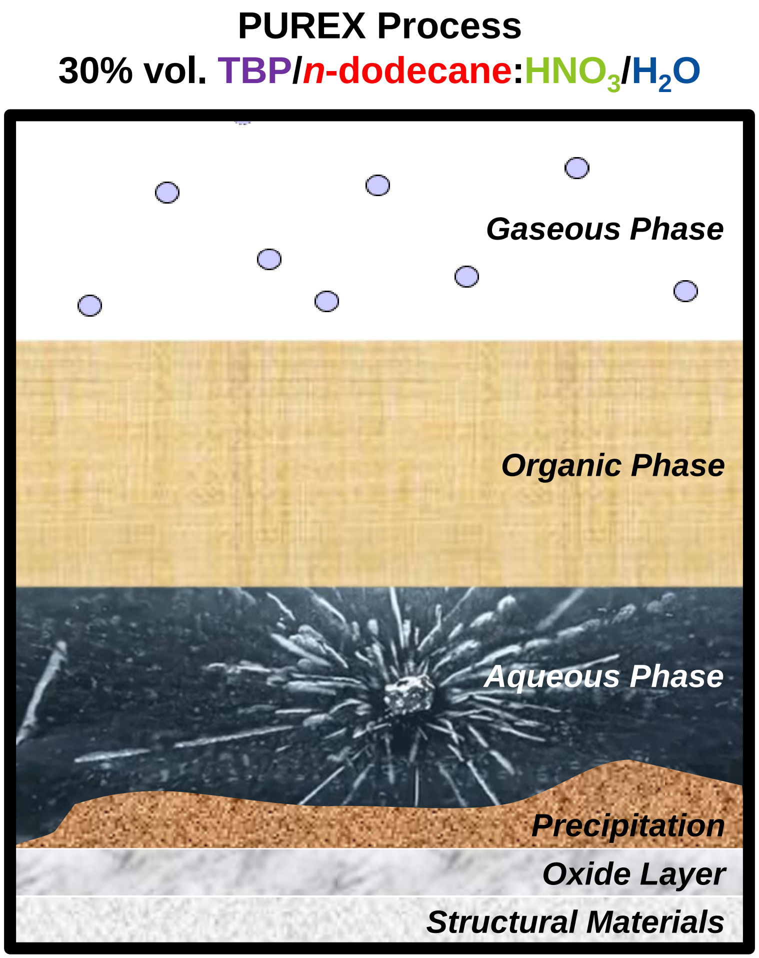
vs.

Applied Science



The Nuclear Fuel Cycle and Radiation Chemistry





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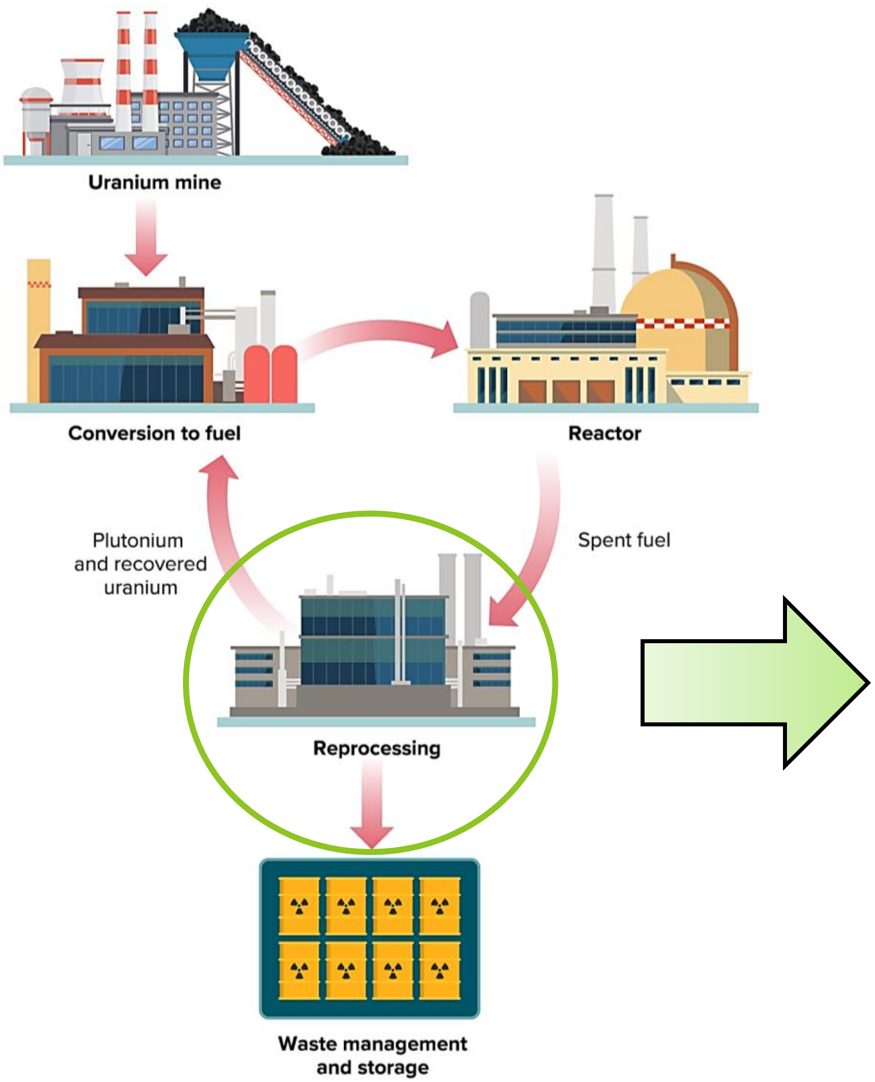
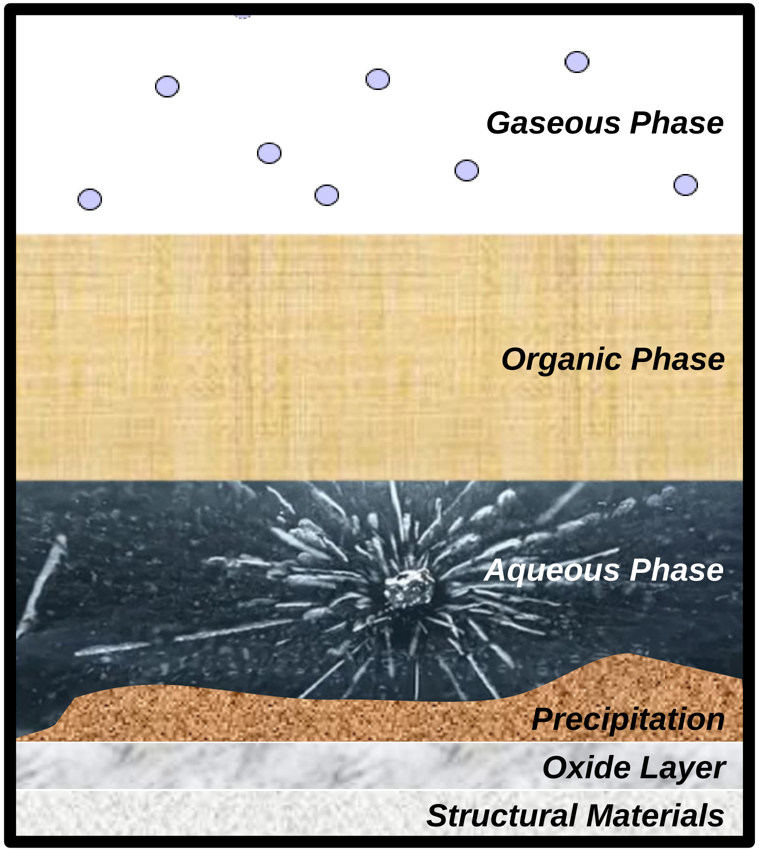


Advanced Used Nuclear Fuel Reprocessing Concepts

ligands/*n*-dodecane:HNO_3/H_2O



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

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

Radiation Chemistry in Nitrate and Nitric Acid Solutions

Water Radiolysis

Direct Radiation Effects

Radiolysis Products of Concern in Reprocessing

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

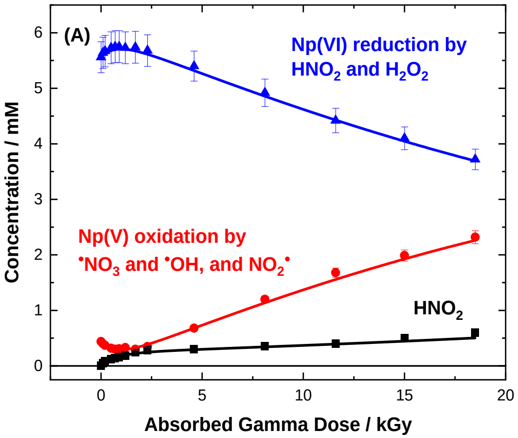
$^{\bullet}NO_3$ and HNO_2 from HNO_3

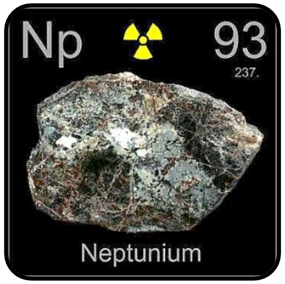
e^-, $R\text{-}CH_3^{\bullet +}$, $R\text{-}CH_2^{\bullet}$, and $H^{\bullet}$ from organic diluent

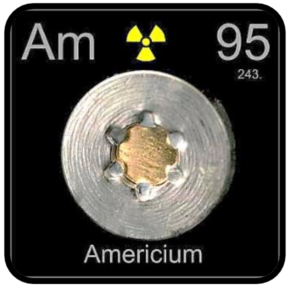
…$_3$, $H^{\bullet}$, H_2

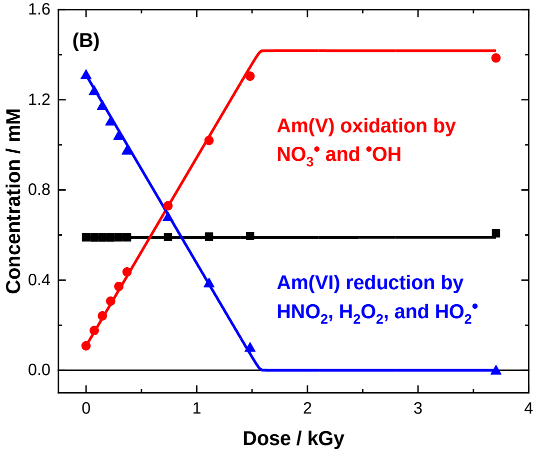
$N_2O_4 \rightarrow HNO_2 + HNO_3$

Radiation-Induced Redox Chemistry









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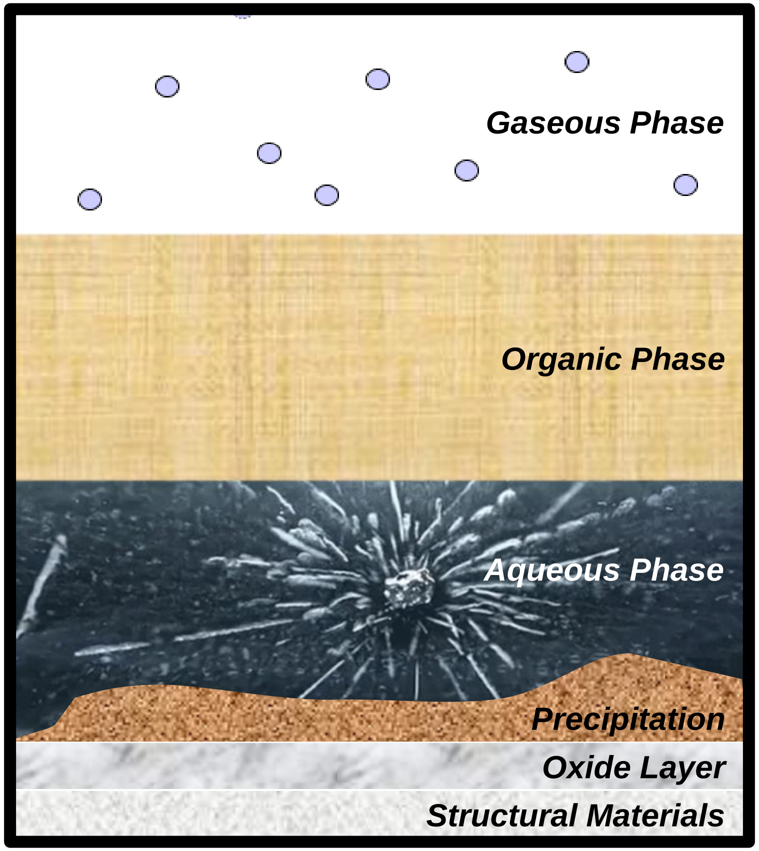
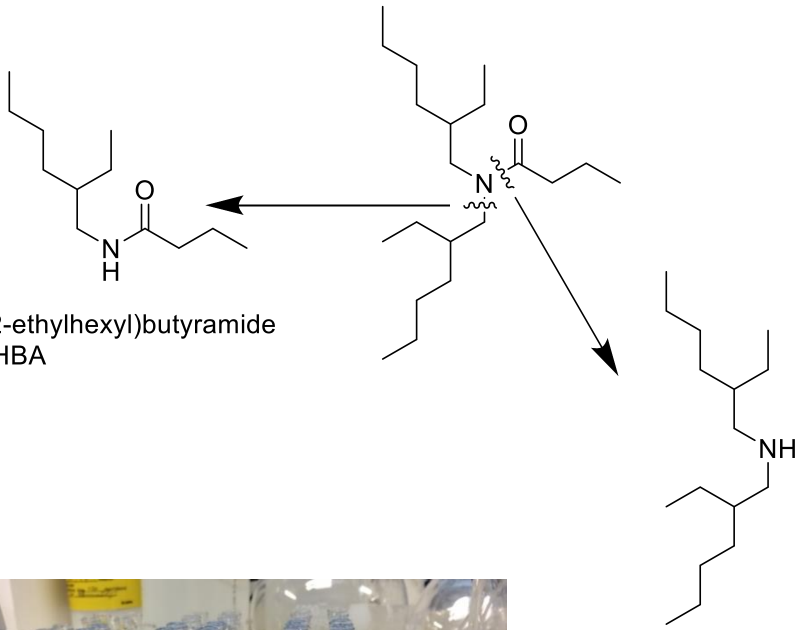


- Horne, G.P., Grimes, T.S., Mincher, B.J., Mezyk, S.P., *Journal of Physical Chemistry B*, **2016**, *120 (49)*, 12643.
- Horne, G.P., Grimes, T.S., Bauer, W.F., Dares, C.J., Pimblott, S.M., *et al.*, *Inorganic Chemistry*, **2019**, *58*, 8551.

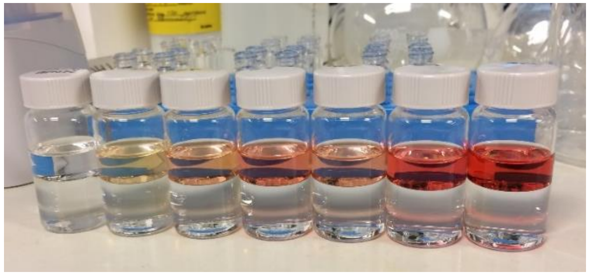
Destruction of Active Molecules

N,*N*-di-(2-ethylhexyl)butyramide
DEHBA

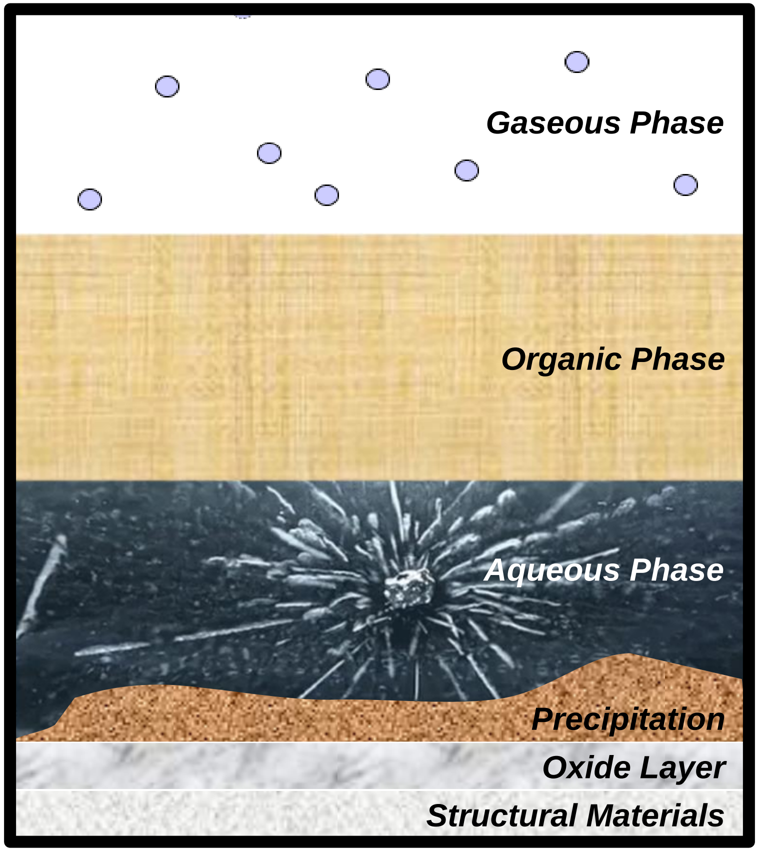


N-(2-ethylhexyl)butyramide
MEHBA

bis(2-ethylhexyl)amine
b2EHA



Advanced Used Nuclear Fuel Reprocessing Concepts
ligands/*n*-dodecane:HNO_3/H_2O

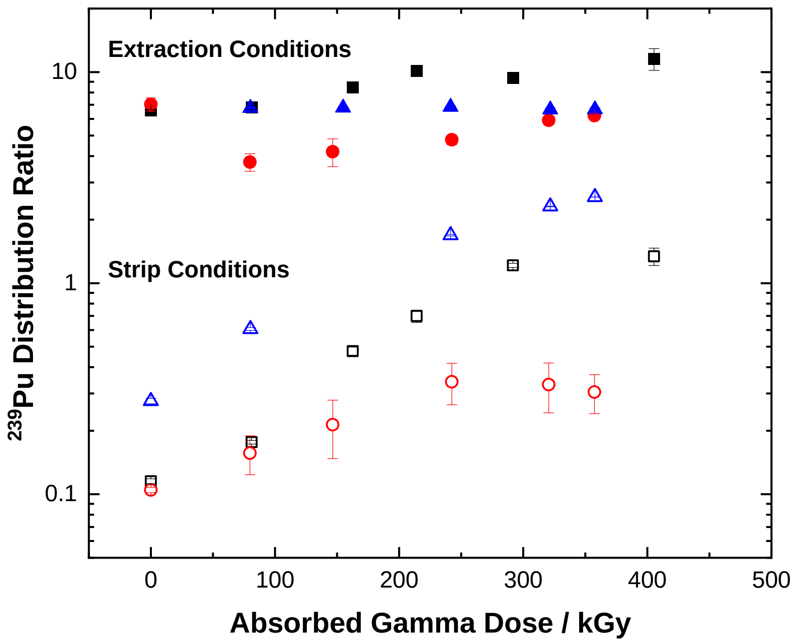


- Horne, G.P., Zarzana, C.A., Grimes, T.S., Rae, C., Ceder, J., *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, G.P., Mezyk, S.P., Mincher, B.J., Zarzana, C.A., Rae, C., *et al.*, *Rad. Phys. Chem.*, **2019**, 170, 108608.

Destruction of Active Molecules

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

Organic-only (■/□)
0.1 M HNO_3 contact (●/○)
3.0 M HNO_3 contact (▲/△)



Advanced Used Nuclear Fuel Reprocessing Concepts
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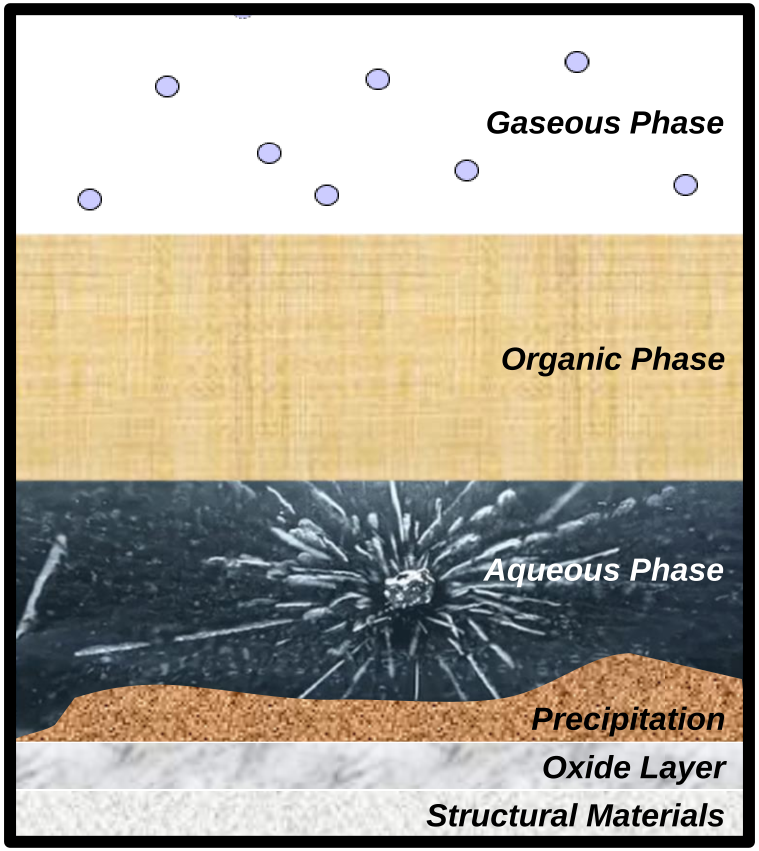
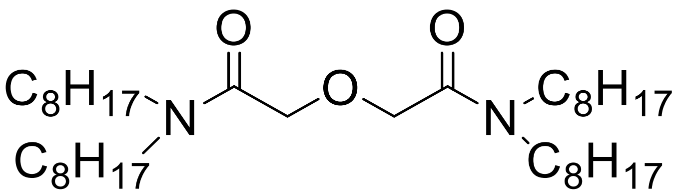


- Horne, G.P., Zarzana, C.A., Grimes, T.S., Rae, C., Ceder, J., *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, G.P., Mezyk, S.P., Mincher, B.J., Zarzana, C.A., Rae, C., *et al.*, *Rad. Phys. Chem.*, **2019**, 170, 108608.

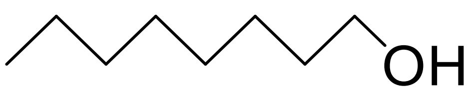
Does Addition of 1-Octanol as a Phase Modifier Provide Radical Scavenging Radioprotection for TODGA?

Gregory P. Horne, Christopher A. Zarzana, Cathy Rae, Andrew R. Cook, Stephen P. Mezyk, Peter R. Zalupski, Andreas Wilden, and Bruce J. Mincher, *Physical Chemistry Chemical Physics*, **2020**, 22, 24978-24985, https://doi.org/10.1039/D0CP04310A.

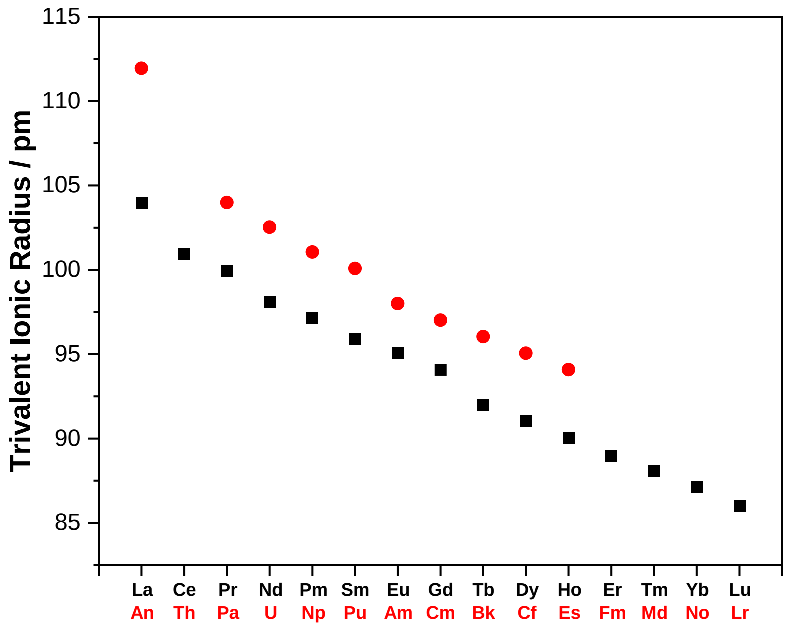
Trivalent Minor Actinide/Lanthanide Separations

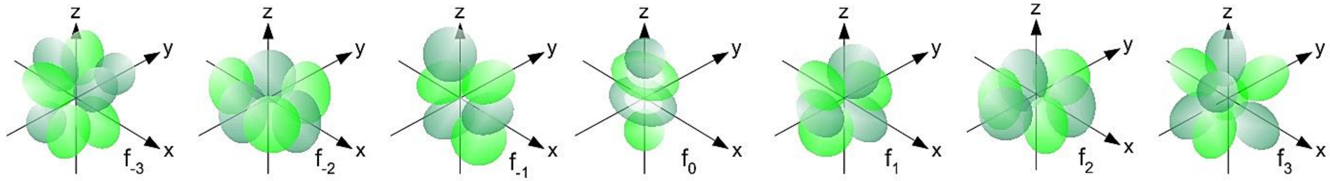


TODGA



1-octanol





- Modolo, G., Geist, A., Miguirditchian, M., Reprocessing and Recycling of Spent Nuclear Fuel, 2015, Taylor, R., Ed.; Woodhead Publishing: Cambridge, UK, 245.
- https://www.radiochemistry.org/periodictable/la_series/images/actcon.gif
- https://secureservercdn.net/45.40.146.28/23f.c5e.myftpupload.com/wp-content/uploads/2018/05/K5EcA.jpg

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

[3]

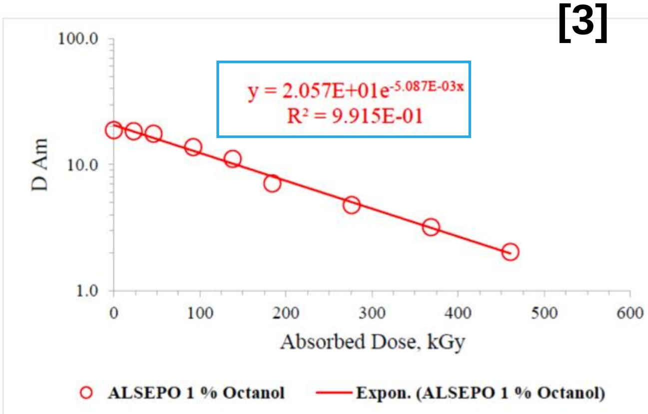


Figure 7. Plot of the americium extraction distribution ratios determined as a function of absorbed dose for the static irradiation of the ALSEPO solvent containing 1 % octanol in contact with 3 M HNO_3.

[2]

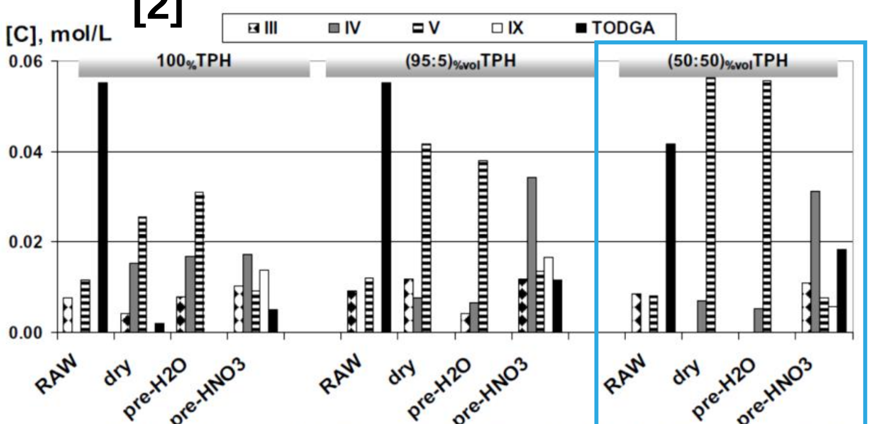


Fig. 3. Concentration of TODGA and compounds III, IV, V and IX in the different TODGA irradiated samples (up to 1000 KGy) and the corresponding D_M values. Samples 1: $100_{\%vol}$ TPH. Samples 2: $(95:5)_{\%vol}$ TPH/octanol. Samples 3: $(50:50)_{\%vol}$ TPH/octanol.

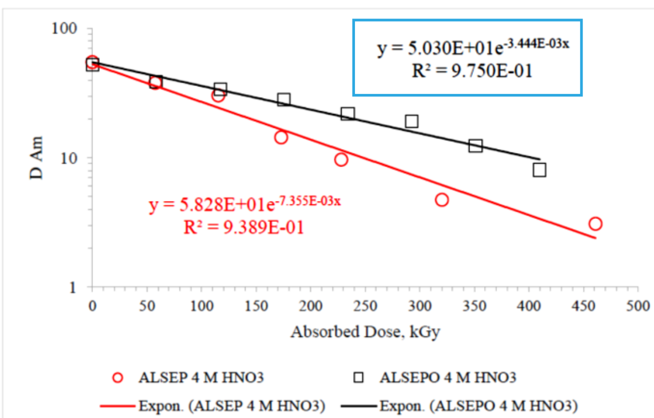


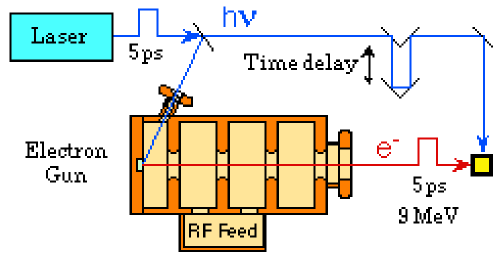
Figure 3. Plot of the americium distribution ratios determined as a function of absorbed dose for the static irradiation of the ALSEP and ALSEPO solvents in contact with 4 M HNO_3.

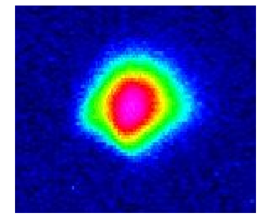
1. Sugo, Y., Izumi, Y., Yoshida, Y., Nishijima, S., Sasaki, Y., *et al.*, *Radiat. Phys. Chem.*, **2007**, *76*, 794.
2. Galán, H., Núñez, A., Espartero, A.G., Sedano, R., Durana, A., Mendoza, J.D., *Procedia Chem.*, **2012**, *7 (0)*, 195.
3. Zalupski, P.R., Peterman, D.R., INL/EXT-17-43040 Technical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

Radiation Chemistry Techniques

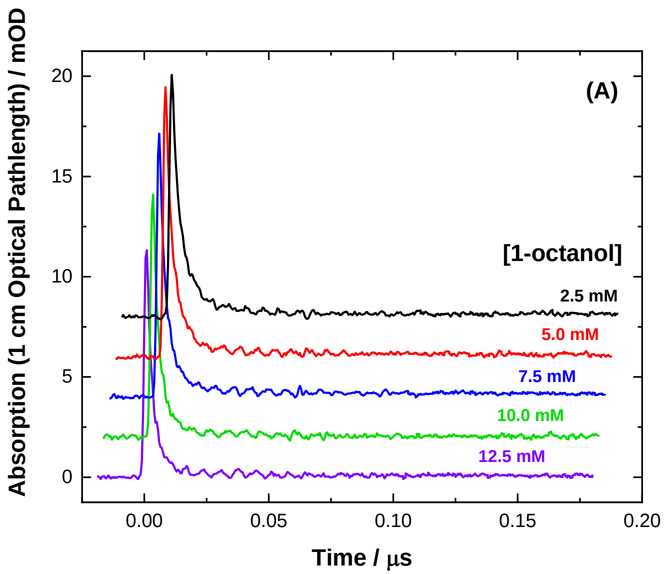
Gamma Radiolysis
(Steady-State)

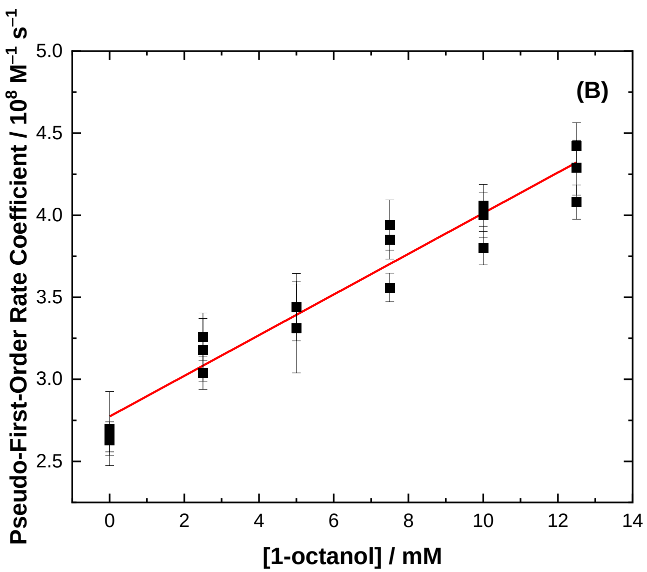
Pulsed Electron Radiolysis
(Time-Resolved)





Reaction Kinetics by Picosecond Pulsed Electron Radiolysis at Brookhaven National Laboratory

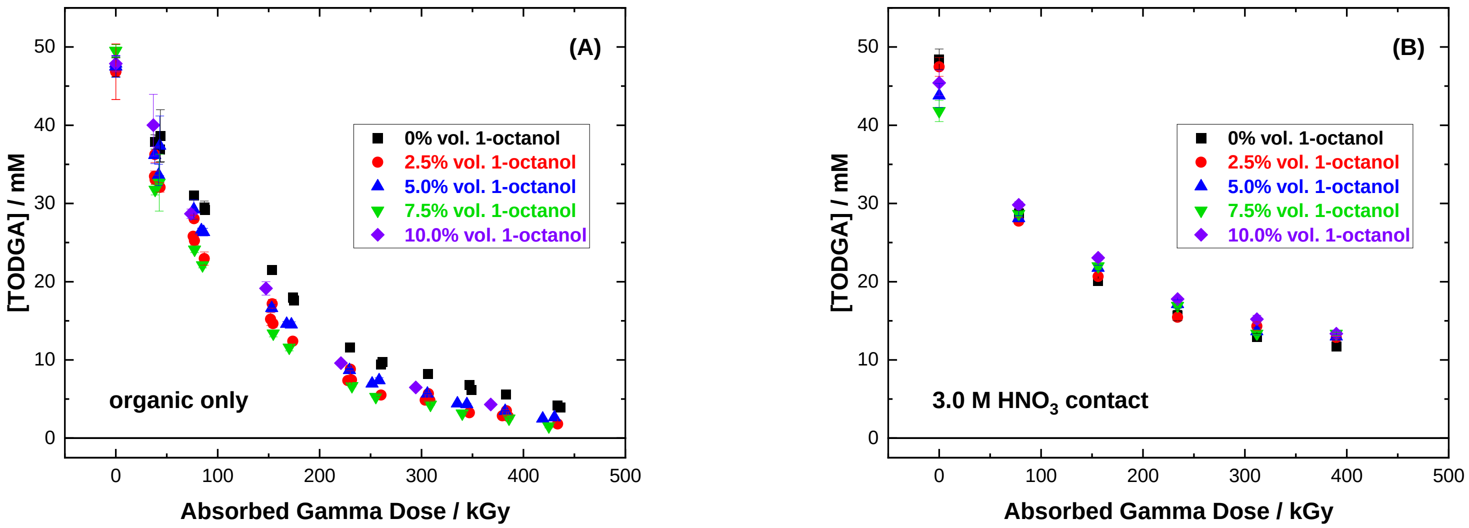




- Increasing the concentration of **1-octanol** in ***n*-dodecane**/0.5 M DCM solutions rapidly decreased the lifetime of the ***n*-dodecane radical cation** (**R-$CH_3^{\bullet+}$**)
- k(**1-octanol** + **R-$CH_3^{\bullet+}$**) = **(1.23 ± 0.07) × 10^{10} M^{-1} s^{-1}**
- k(**TODGA** + **R-$CH_3^{\bullet+}$**) = **(9.72 ± 1.10) × 10^{9} M^{-1} s^{-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.

Steady-State Gamma Radiolysis at Idaho National Laboratory



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}.

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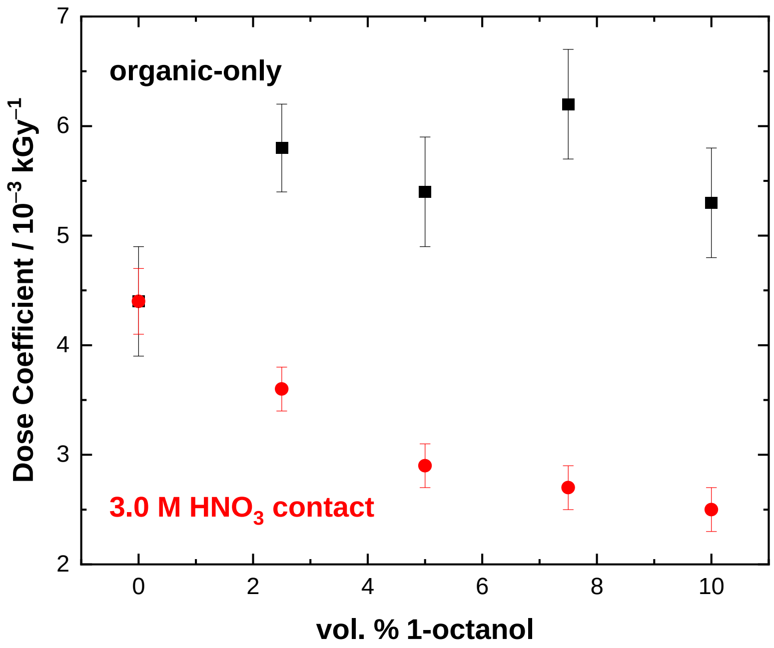

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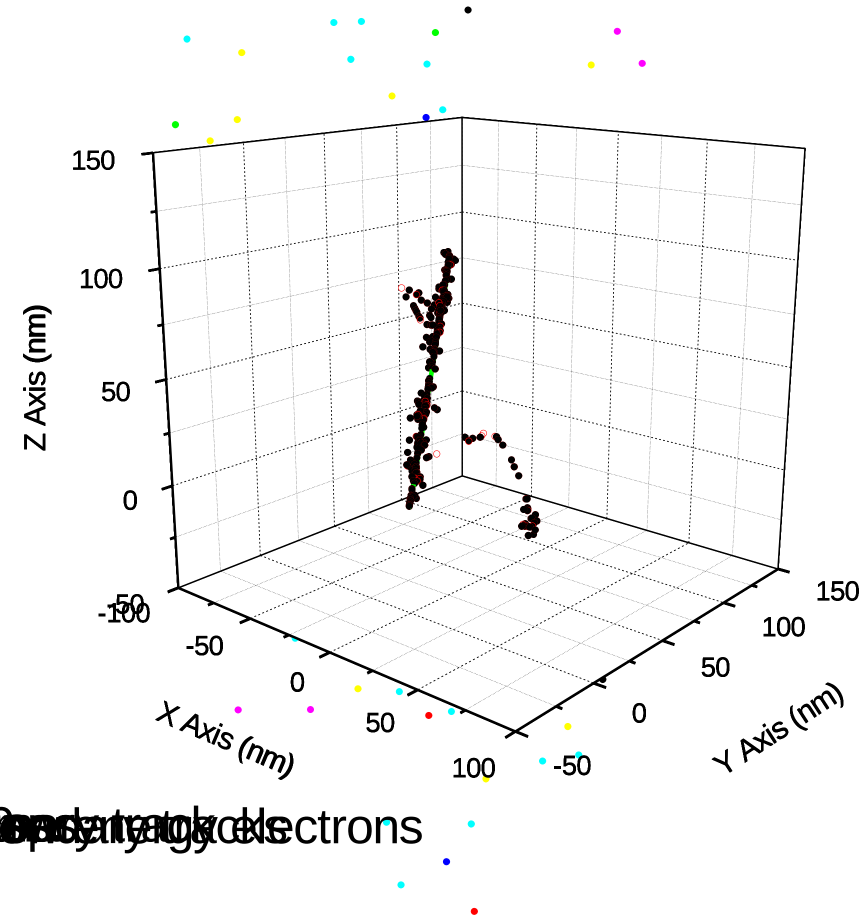
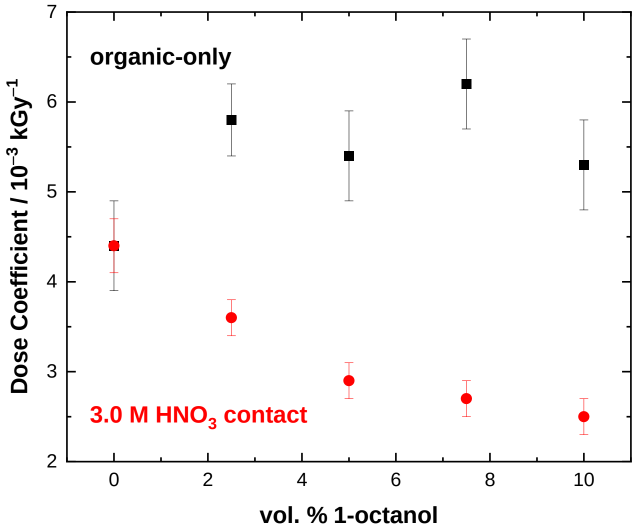
Radiation Track Chemistry



- Pimblott, S.M., LaVerne, J.A., Mozumder, A., *J. Phys. Chem.*, **1996**, 100, 8595.
- Clifford, P., Green, N.J.B., Oldfield, M.J., Pilling, M.,J., Pimblott, S.M., *J. Chem. Soc., Faraday Trans.*, **1986**, 82, 2673.

TODGA Gamma Radiolysis – Organic Only

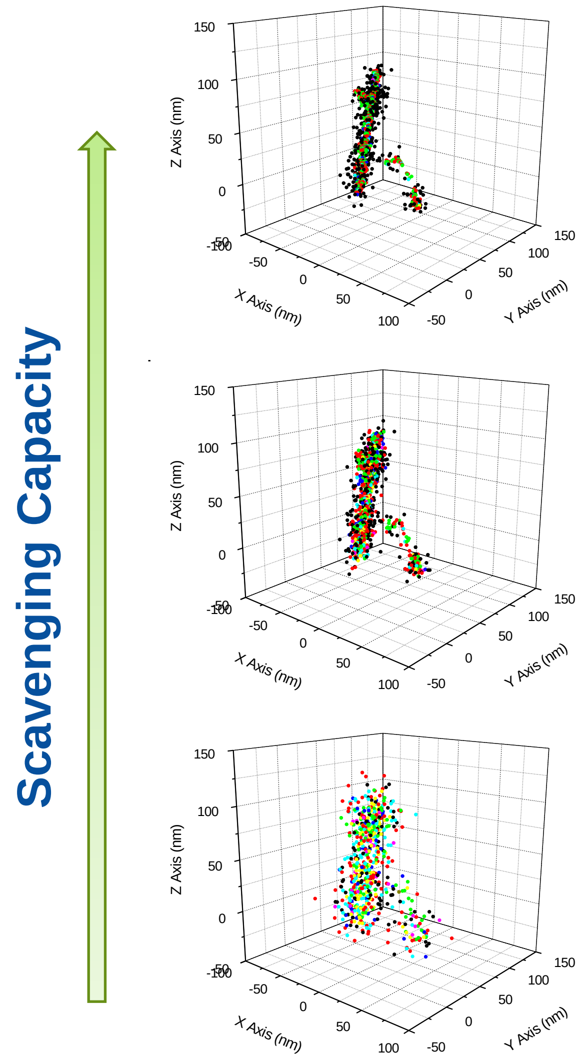


k(1-octanol + R-$CH_3^{\bullet+}$) = **(1.23 ± 0.07) × 10^{10} M^{-1} s^{-1}**

k(TODGA + R-$CH_3^{\bullet+}$) = **(9.72 ± 1.10) × 10^{9} M^{-1} s^{-1}**

k(TODGA + [1-octanol]$^{\bullet+}$) = **?**

Concentration of species	$RH^{\bullet+}$ scavenging capacity (s^{-1})
50 mM TODGA	$(4.86 \pm 0.55) \times 10^{8}$
2.5 vol. % 1-octanol (159 mM)	$(1.95 \pm 0.11) \times 10^{9}$
5.0 vol. % 1-octanol (318 mM)	$(3.91 \pm 0.22) \times 10^{9}$
7.5 vol. % 1-octanol (476 mM)	$(5.86 \pm 0.33) \times 10^{9}$
10.0 vol. % 1-octanol (635 mM)	$(7.81 \pm 0.45) \times 10^{9}$



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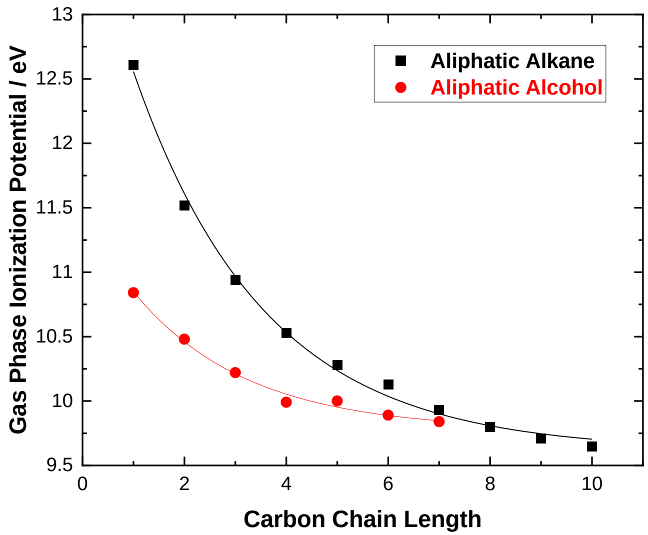

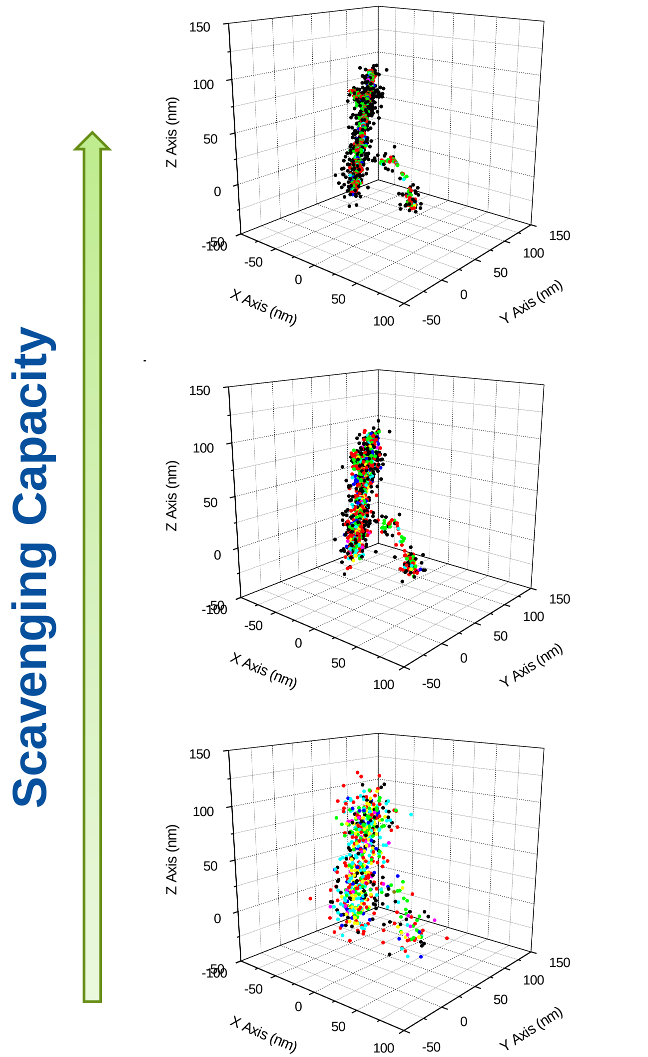

k(TODGA + $R\text{-}CH_3^{\bullet+}$) = **(9.72 ± 1.10) × 10^9 M^{-1} s^{-1}**

k(1-octanol + $R\text{-}CH_3^{\bullet+}$) = **(1.23 ± 0.07) × 10^{10} M^{-1} s^{-1}**

k(TODGA + $[\text{1-octanol}]^{\bullet+}$) = **?**

Concentration of species	$RH^{\bullet+}$ scavenging capacity (s^{-1})
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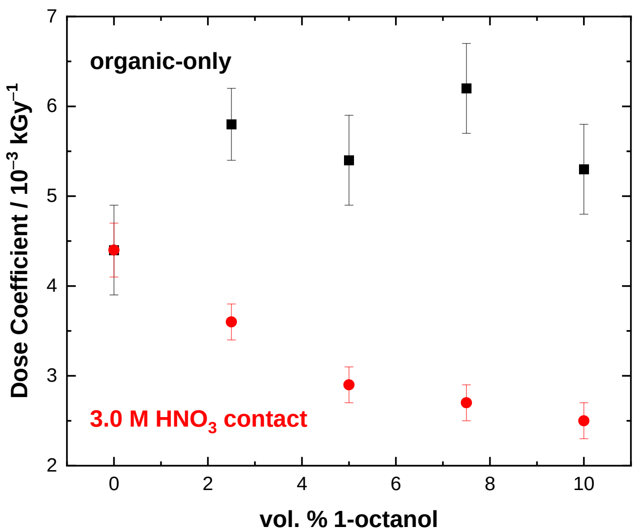
5.0 vol. % 1-octanol (318 mM)	(3.91 ± 0.22) × 10^9
7.5 vol. % 1-octanol (476 mM)	(5.86 ± 0.33) × 10^9
10.0 vol. % 1-octanol (635 mM)	(7.81 ± 0.45) × 10^9

TODGA Gamma Radiolysis – Biphasic



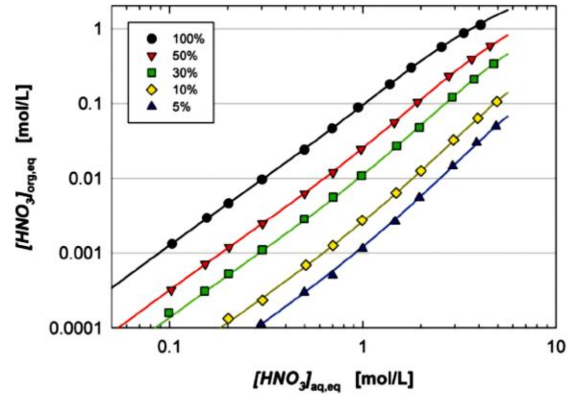


Figure 2. Extraction of nitric acid into octanol-TPH mixtures (octanol volume fraction as indicated); model predictions (lines) vs. experimental data (symbols). $A/O = 1$, $T = (20 \pm 0.5)$ °C. Experimental data from reference.[37] See Table SI 1 for experimental data.

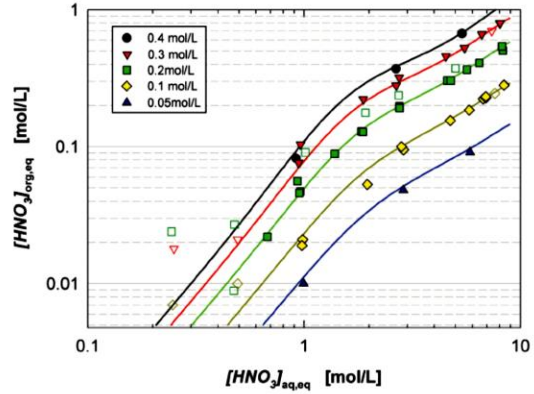
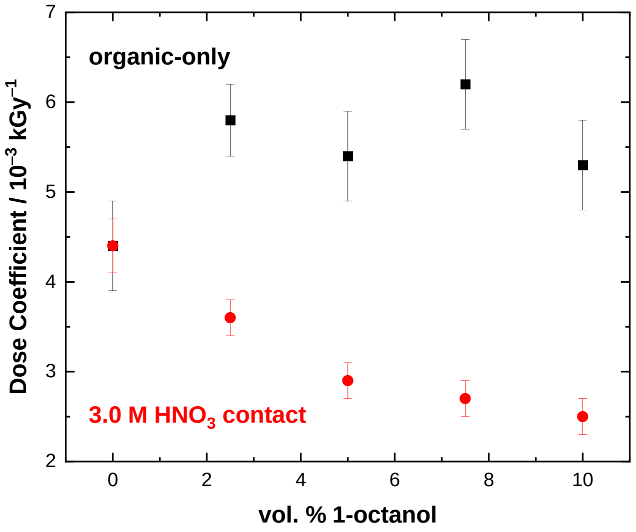


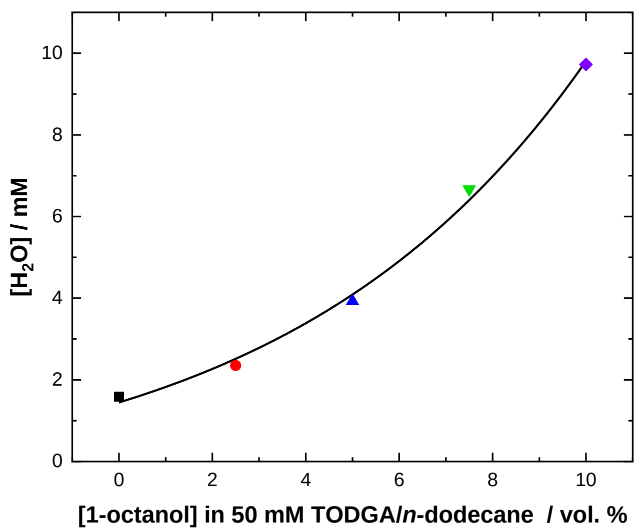
Figure 3. Nitric acid extraction into TODGA (concentration as indicated) in Exxsol D80. Model predictions (lines) vs. experimental data (symbols; open symbols excluded from fitting). $A/O = 1$. See Table SI 2 for experimental data.

- Extraction of HNO_3 into the organic phase by **TODGA** and **1-octanol**.
- Scavenging of **[1-octanol]$^{\bullet+}$** by the **HNO_3** adduct component.

- Geist, A., *Solv. Extr. Ion Exch.*, **2010**, *28(5)*, 596.
- Woodhead, D., McLachlan, F., Taylor, R., Müllich, U., Geist, A., Wilden, A., Modolo, G., *Solv. Extr. Ion Exch.*, **2019**, *37 (2)*, 173.

TODGA Gamma Radiolysis – Biphasic

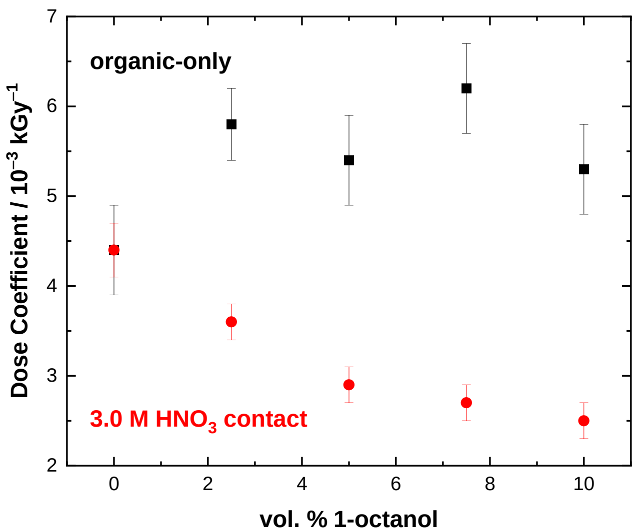




- Extraction of H_2O into the organic phase by **TODGA** and **1-octanol**.
- Scavenging of **[1-octanol]$^{\bullet+}$** by H_2O adduct component.

- 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.

TODGA Gamma Radiolysis – Biphasic

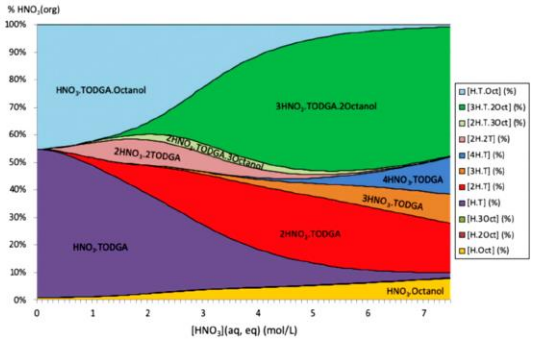


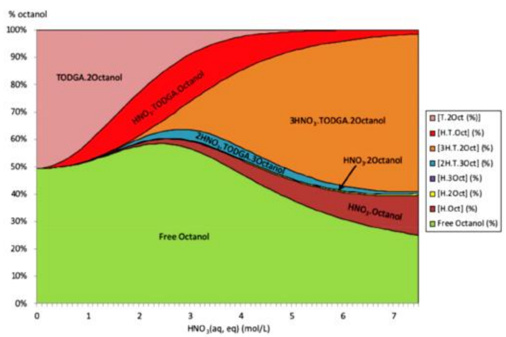
[xHNO_3/H_2O•TODGA/octanol] + [1-octanol]$^{\bullet+}$

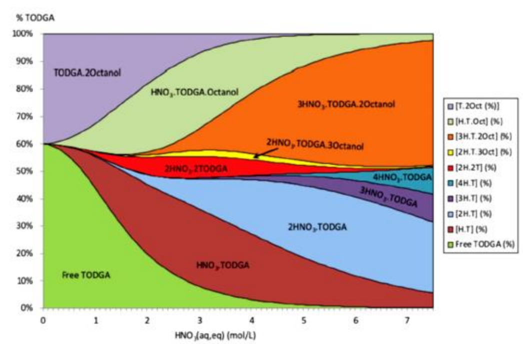
$\Downarrow$

[(x-1)HNO_3/H_2O•TODGA/octanol]

+ $^{\bullet}NO_3$/$^{\bullet}OH$ + 1-octanol + H^+







- Geist, A., *Solv. Extr. Ion Exch.*, **2010**, *28(5)*, 596.
- Woodhead, D., McLachlan, F., Taylor, R., Müllich, U., Geist, A., Wilden, A., Modolo, G., *Solv. Extr. Ion Exch.*, **2019**, *37 (2)*, 173.

Conclusions

“Observe due measure; moderation in all things”

Hesiod c. 700 BC

- **Octanol** promotes diametrically different effects on **TODGA** radiolysis in ***n*-dodecane** solutions and solvent systems.
- Differences in radiolytic behavior attributed to ***scavenging capacity*** and ***adduct competition kinetics***.
- A fundamental study resolved an applied problem by asking the question “**<u>why?</u>**”.

Acknowledgements

U.S. DEPARTMENT OF ENERGY



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