INL/MIS-20-59075-Revision-0

Radiation Chemical Kinetics of Actinide Redox Speciation

July 2020

Changing the World's Energy Future

Gregory P Horne

INL/MIS-20-59075-Revision-0

Radiation Chemical Kinetics of Actinide Redox Speciation

Gregory P Horne

July 2020

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

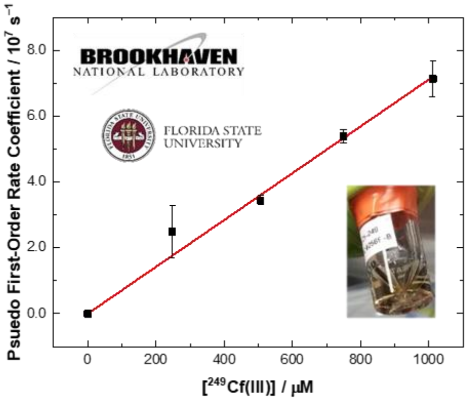
Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

LDRD: 18P38-001
PRS #: PRS/MIS-20-00387
LRS #: INL/MIS-??-?????

Radiation Chemical Kinetics of Actinide Redox Speciation

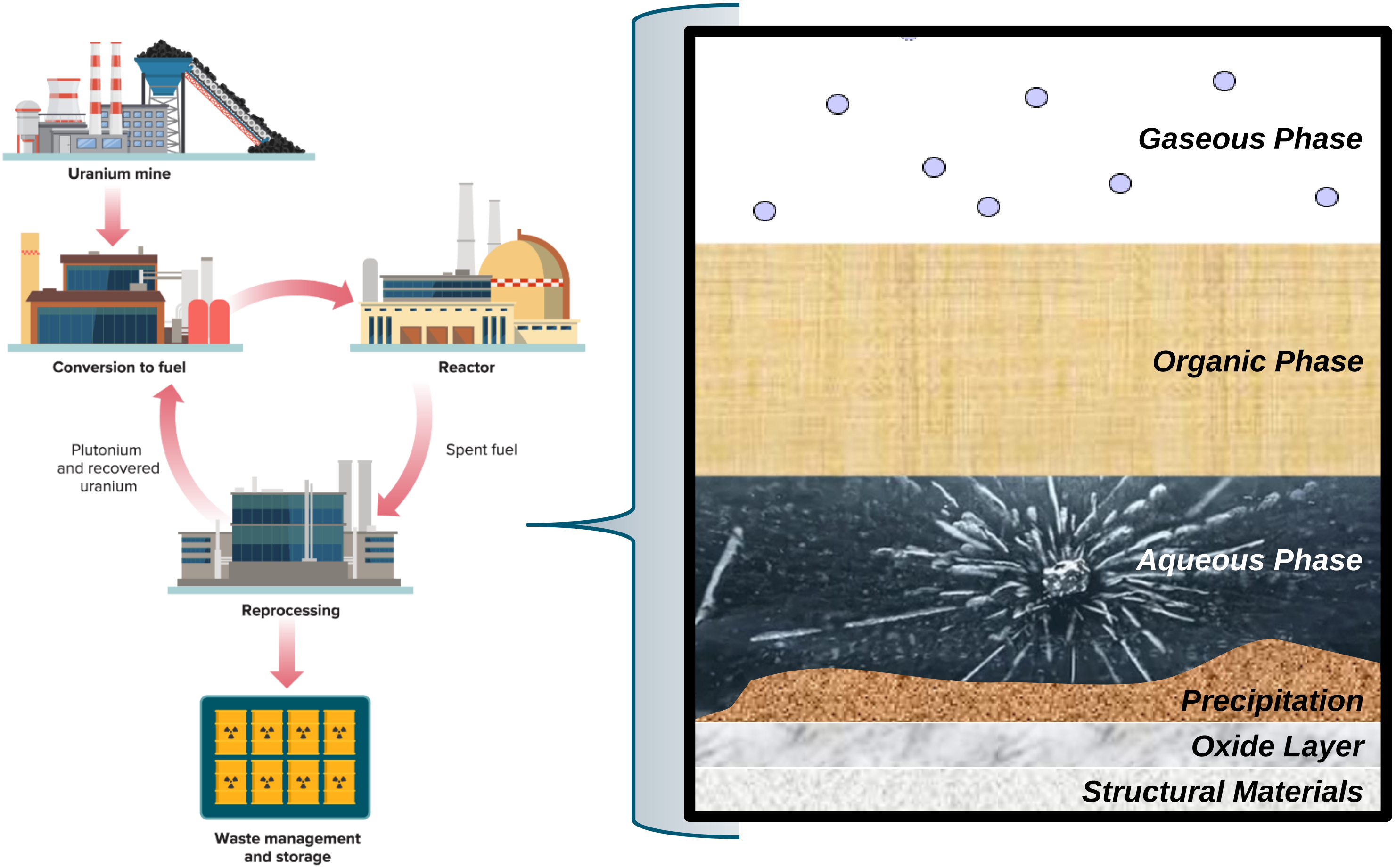
Gregory P. Horne (PI)[1], **David S. Meeker**[1,2], Travis S. Grimes[1], Peter R. Zalupski[1], Stephen P. Mezyk[3], James F. Wishart[4], and Thomas E. Albrecht-Schmidtt[2]

[1]*Center for Radiation Chemistry Research, Idaho National Laboratory, USA.*
[2]*Florida State University, Tallahassee, USA*
[3]*California State University Longbeach, USA*
[4]*Brookhaven National Laboratory, USA*



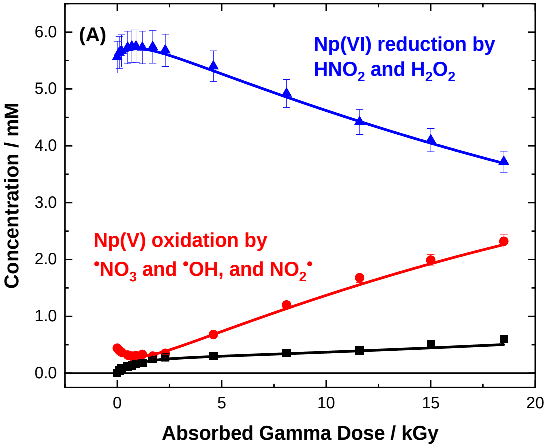
Center for Radiation Chemistry Research

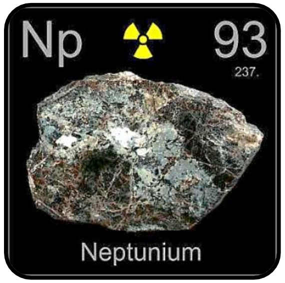
Radiation Chemistry and the Nuclear Fuel Cycle

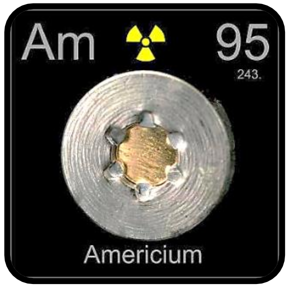


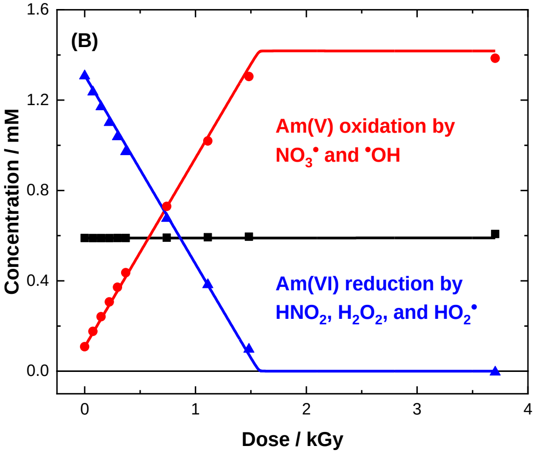
- Horne, G. P.; Grimes, T. S.; Mincher, B. J.; Mezyk, S. P., *Journal of Physical Chemistry B*, **2016**, *120 (49)*, 12643
- Grimes, T. S.; Horne, G. P.; Dares, C. J.; Pimblott, S. M.; Mezyk, S. P.; Mincher, B. J., *Inorganic Chemistry*, **2017**, *56 (14)*, 8295
- Horne, G. P.; Grimes, T. S.; Bauer, W. F.; Dares, C. J.; Pimblott, S. M.; Mezyk, S. P.; Bruce J. Mincher, B. J., *Inorganic Chemistry*, **2019**, *58*, 8551

Actinide Radiation Chemistry

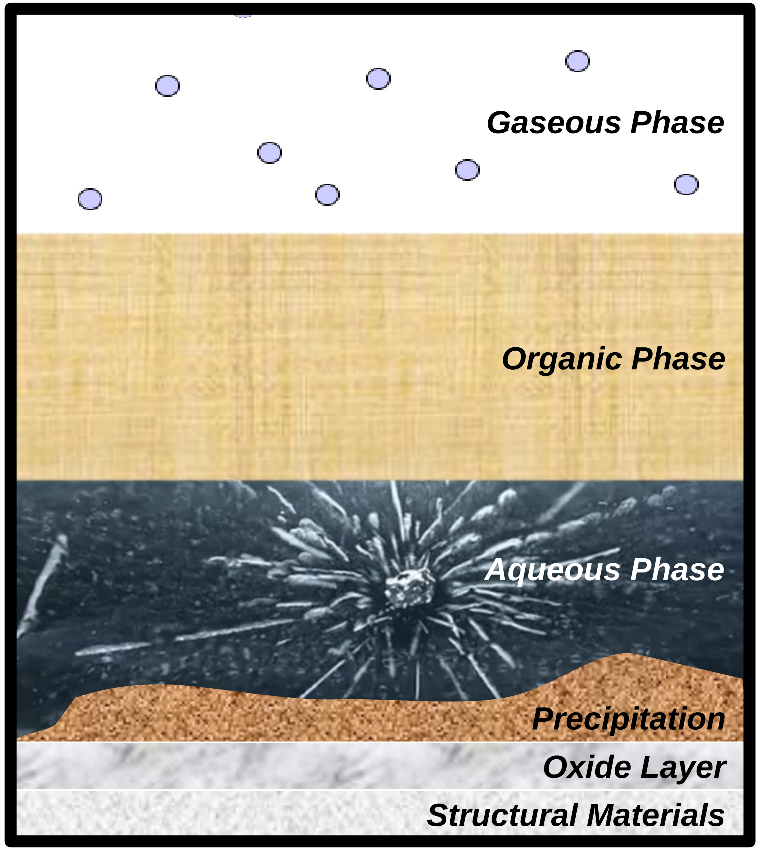








Spent Nuclear Fuel Reprocessing



- Horne, G. P.; Grimes, T. S.; Mincher, B. J.; Mezyk, S. P., *Journal of Physical Chemistry B*, **2016**, *120 (49)*, 12643
- Grimes, T. S.; Horne, G. P.; Dares, C. J.; Pimblott, S. M.; Mezyk, S. P.; Mincher, B. J., *Inorganic Chemistry*, **2017**, *56 (14)*, 8295
- Horne, G. P.; Grimes, T. S.; Bauer, W. F.; Dares, C. J.; Pimblott, S. M.; Mezyk, S. P.; Bruce J. Mincher, B. J., *Inorganic Chemistry*, **2019**, *58*, 8551

Spent Nuclear Fuel Reprocessing Radiation Chemistry

Water Radiolysis

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

Indirect HNO_3 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 HNO_3 Radiation Effects

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

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

$NO_3^{-} \rightsquigarrow {}^{\bullet}NO_3 + e_{aq}^{-}$

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

Organic Diluent Radiolysis

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

Spent Nuclear Fuel Reprocessing Radiation Chemistry

Water Radiolysis

$H_2O \rightsquigarrow e_a$

Indirect HI

$HNO_3 + {}^{\bullet}($

$NO_3^- + e_a$

$NO_3^{\bullet 2-} + |$

$NO_3^- + H$

${}^{\bullet}NO_2 + {}^{\bullet}N$

$N_2O_4 \rightarrow HNO_2 + HNO_3$

Direct HNO_3 Radiation Effects

$+ O$

$D_2 + O$

olysis

$_3, H^{\bullet}, H_2$

Radiolysis Products of Concern

e_{aq}^-, $H^{\bullet}$, ${}^{\bullet}OH$ and H_2O_2 from H_2O

${}^{\bullet}NO_3$, e_{aq}^-, and HNO_2 from HNO_3

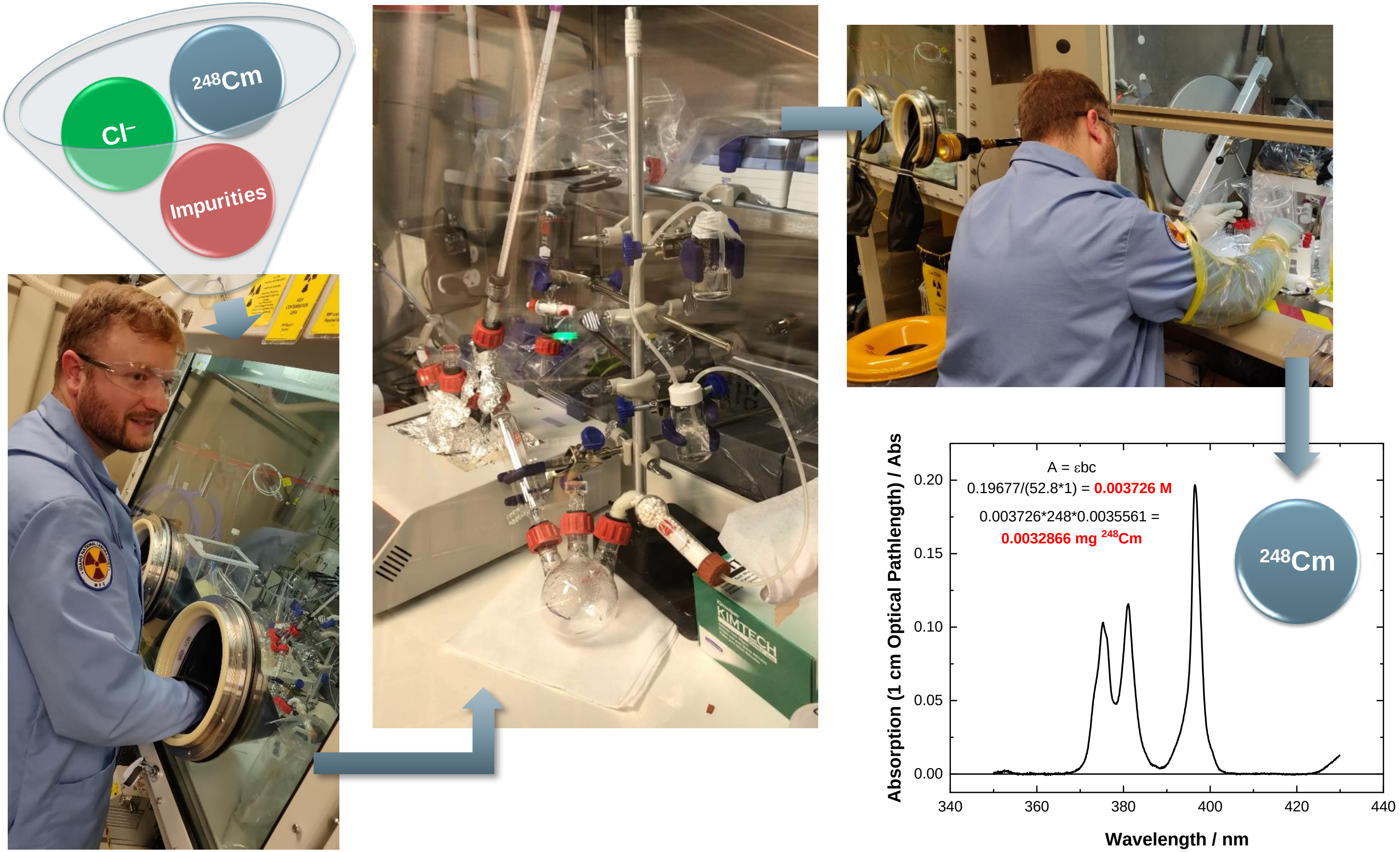
e^-, $H^{\bullet}$, $RH^{\bullet +}$, and $R^{\bullet}$ from **organic diluent**

This LDRD and the Russell L. Heath Distinguished Postdoctoral Fellowship

- Dr. Heath established a world-renowned series of γ-ray spectrum catalogs.
- This fellowship was an opportunity to conduct state-of-the-art research using unique radiation and radiochemistry facilities at INL.
- Chance to develop an actinide redox reaction kinetics database and expand INL’s *Center for Radiation Chemistry Research*.

- Heath, R.L., Scintillation Spectrometry, Gamma-Ray Spectrum Catalog, USAEC Rep. IDO-16408, 1957.
- Heath, R.L., Scintillation Spectrometry, Gamma-Ray Spectrum Catalog, USAEC Rep. IDO-16880, 1964.
- Heath, R.L., The Gamma-Ray Spectrum Catalog, CONF-730302-10.

Impact #1 – Training the Next Generation



A = εbc

0.19677/(52.8*1) = **0.003726 M**

0.003726*248*0.0035561 =

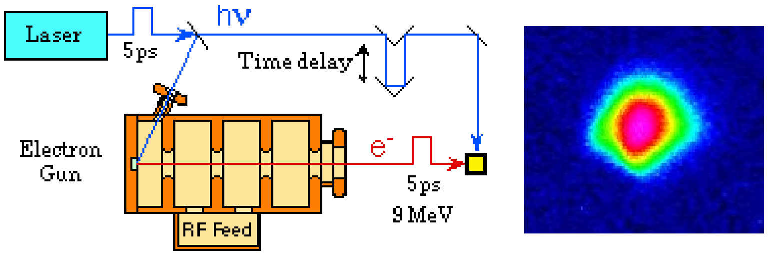
0.0032866 mg ^{248}Cm

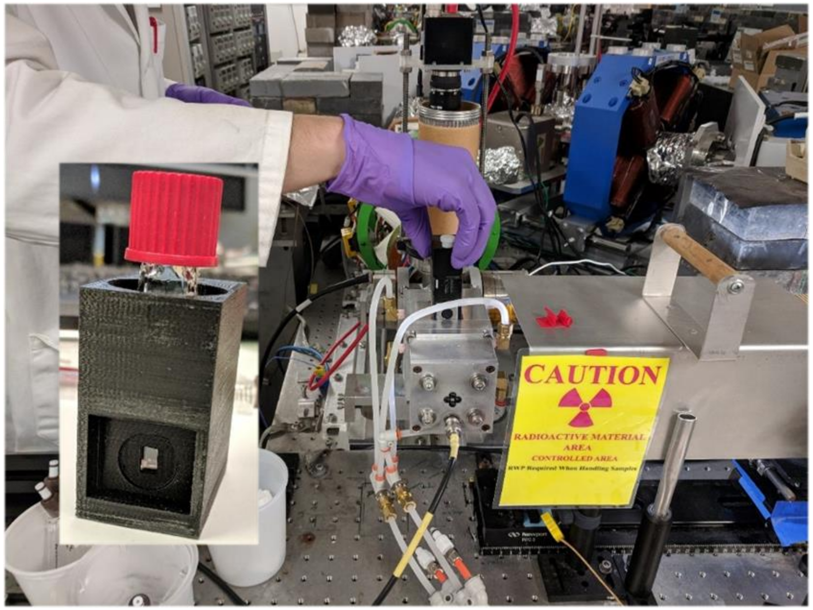
Impact #2 – Actinide Pulse Radiolysis Capability

- ***Hydrated Electron (e_{aq}^{-})***. 10 mM $HClO_4$/0.5 M *t*BuOH/N_2 saturated.
- ***Hydrogen Atom ($H^{\bullet}$)***. 100 µM PCB/0.1 M $HClO_4$/50 mM *t*BuOH/N_2 saturated.
- **Hydroxyl Radical ($^{\bullet}OH$)**. 100 µM KSCN/10 mM $HClO_4$/N_2O saturated.
- **Nitrate Radical ($^{\bullet}NO_3$)**. 6 M HNO_3/N_2O saturated.

BROOKHAVEN NATIONAL LABORATORY

FLORIDA STATE UNIVERSITY

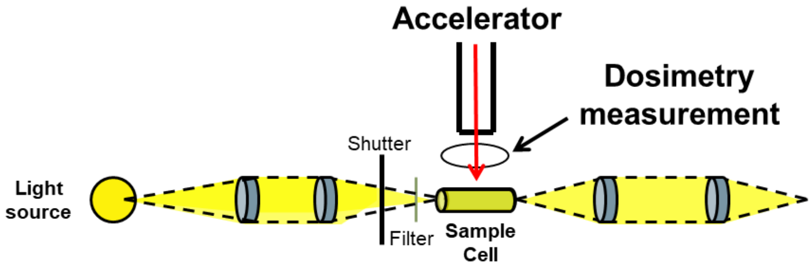




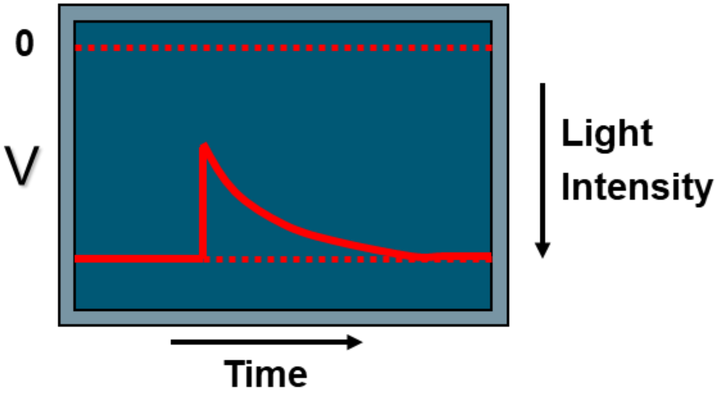
- Wishart, J.F; Cook, A.R.; Miller, J.R. *Rev. Sci. Instrum.* **2004**. 75 (11), 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

Impact #2 – Actinide Pulse Radiolysis Capability

- ***Hydrated Electron (e_{aq}^{-})***. 10 mM $HClO_4$/0.5 M *t*BuOH/N_2 saturated.
- ***Hydrogen Atom ($H^{\bullet}$)***. 100 µM PCB/0.1 M $HClO_4$/50 mM *t*BuOH/N_2 saturated.
- **Hydroxyl Radical ($^{\bullet}OH$)**. 100 µM KSCN/10 mM $HClO_4$/N_2O saturated.
- **Nitrate Radical ($^{\bullet}NO_3$)**. 6 M HNO_3/N_2O saturated.



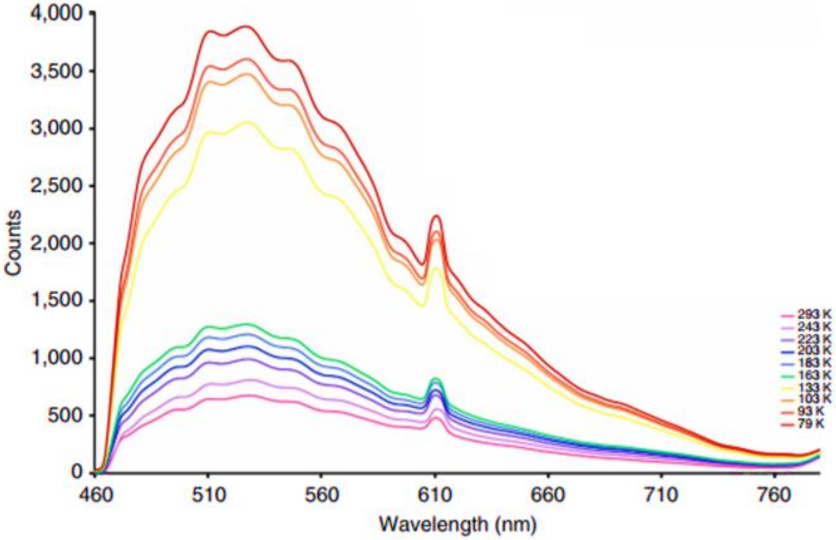
Transients are detected by optical absorption changes.

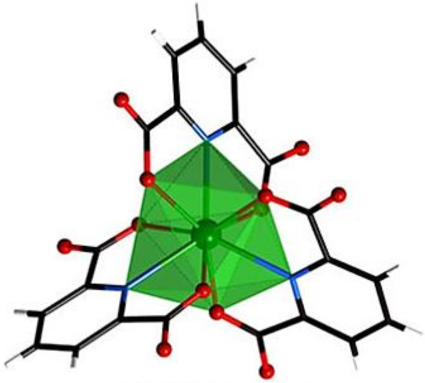


- Wishart, J.F; Cook, A.R.; Miller, J.R. *Rev. Sci. Instrum.* **2004**. 75 (11), 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

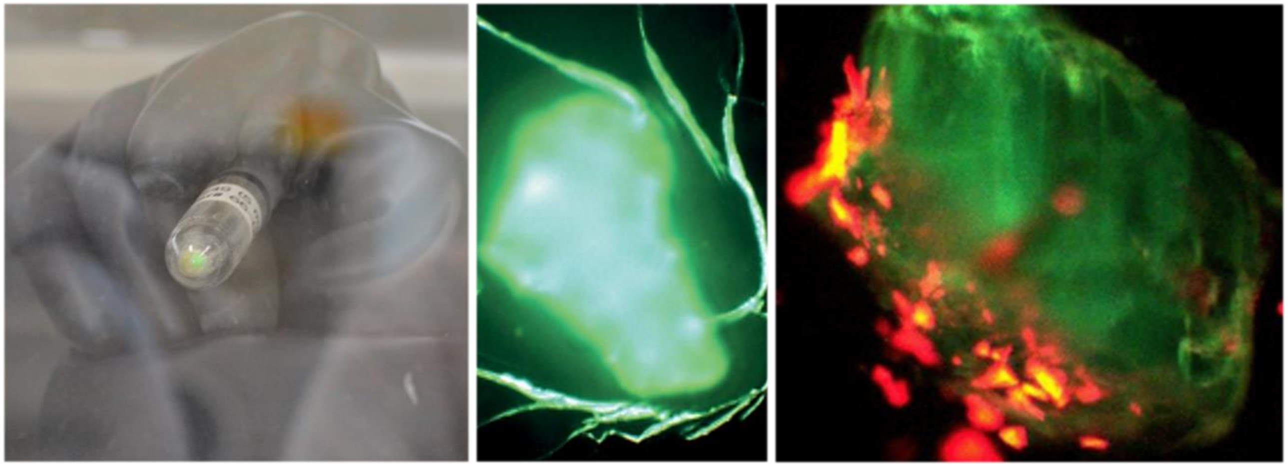
Impact #3 – Californium Radiation Chemistry

- $\tau_{1/2}$ = 351 years.
- $^{249}\mathbf{Bk} \xrightarrow{\beta^-} {}^{249}\mathbf{Cf} + \mathbf{e^-} + \overline{\boldsymbol{\nu}}$
- Many compounds exhibit a self-luminescent green glow.
- Heaviest element where macro-chemistry experiments are conducted.





$Cf(HDPA)_3 \cdot H_2O$



- Albrecht-Schmitt, T., Californium gleaming. *Nature Chemistry*, **2014**, 6, 840
- Polinski, M. *et. al. Nature Chemistry*. **2014**, 6, 387
- Cary, S. *et. al. Nat. Commun*. **2015**, 6, 6827

Impact #3 – Californium Radiation Chemistry

Hydrated Electron (e_{aq}^{-})

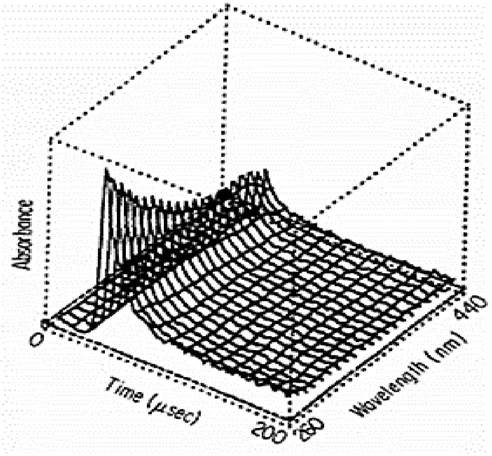
- $k(\mathbf{Cf(III)} + \mathbf{e_{aq}^{-}} \rightarrow \mathbf{Cf(II)})$

  ≥ $3 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$ and **Cf(II)**, ε ~500 $\mathrm{M^{-1}\ cm^{-1}}$ at λ = 270 nm

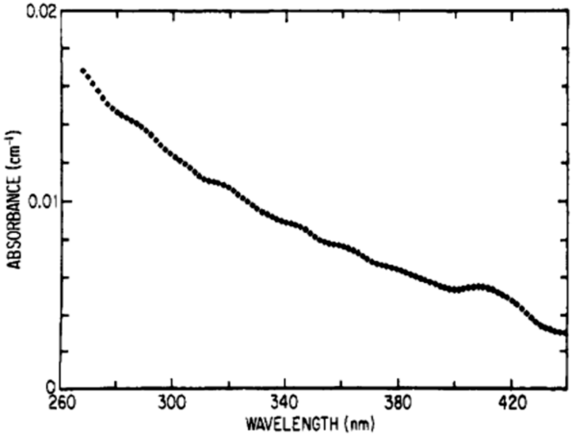
Hydroxyl Radical ($^{\bullet}OH$)

- $k(\mathbf{Cf(III)} + {}^{\bullet}\mathbf{OH} \rightarrow \mathbf{Cf(IV)} + \mathbf{OH^{-}})$

  = **?**, no transient from 240-260 nm.



Transient Absorption Signal of Cf(II)



- Sullivan, J.; Morss, L.; Schmidt, K.; Mulac, W.; Gordon, S. *Inorg. Chem.*, **1983**, *22*, 2338-2339
- Gordon, S.; Sullivan, J. C.; Ross, A. B. *J. Phys. Chem. Ref. Data*, **1986**, *15 (4)*, 1357-1367

Impact #3 – Californium Radiation Chemistry

- $k(\mathbf{Cf(III)} + e_{aq}^{-} \rightarrow \mathbf{Cf(II)})$

  $= (7.11 \pm 0.18) \times 10^{10}\ M^{-1}\ s^{-1}$

- $k(\mathbf{Cf(III)} + H^{\bullet} \rightarrow \mathbf{Cf(II)} + H_{aq}^{+})$

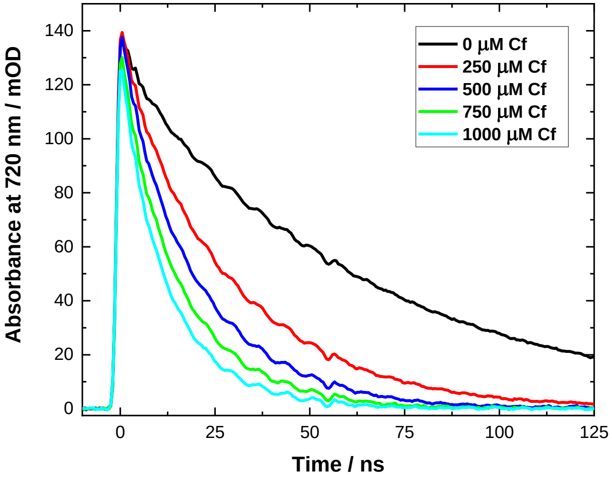
  $= (2.61 \pm 0.54) \times 10^{8}\ M^{-1}\ s^{-1}$

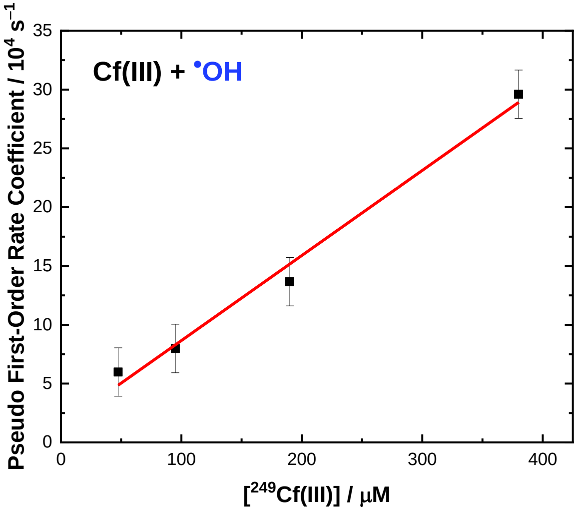
- $k(\mathbf{Cf(III)} + {}^{\bullet}OH \rightarrow \mathbf{Cf(IV)} + OH^{-})$

  $= (7.2 \pm 0.56) \times 10^{8}\ M^{-1}\ s^{-1}$

- $k(\mathbf{Cf(III)} + {}^{\bullet}NO_3 \rightarrow \mathbf{Cf(IV)} + NO_3^{-})$

  $= (2.0 \pm 0.5) \times 10^{8}\ M^{-1}\ s^{-1}$

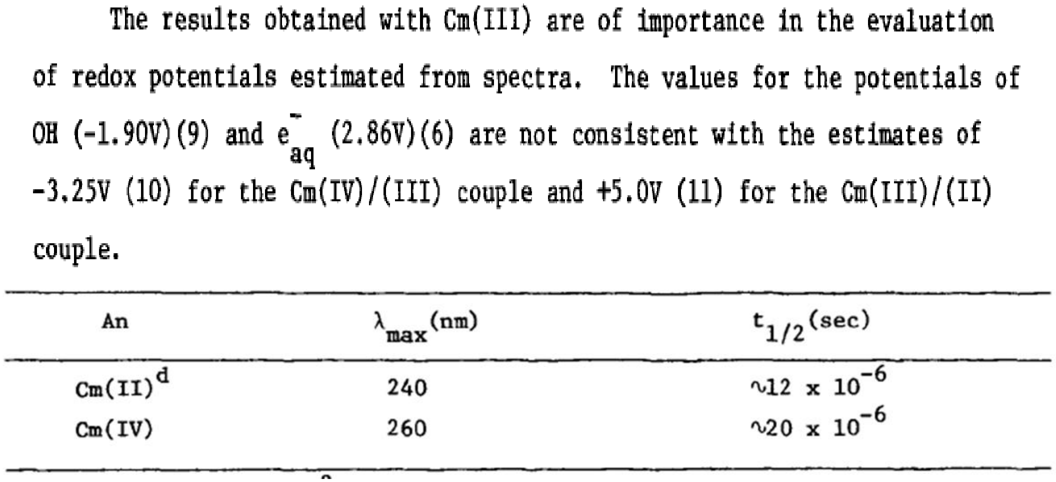




- Sullivan, J.; Morss, L.; Schmidt, K.; Mulac, W.; Gordon, S. *Inorg. Chem.*, **1983**, *22*, 2338-2339
- Gordon, S.; Sullivan, J. C.; Ross, A. B. *J. Phys. Chem. Ref. Data*, **1986**, *15 (4)*, 1357-1367

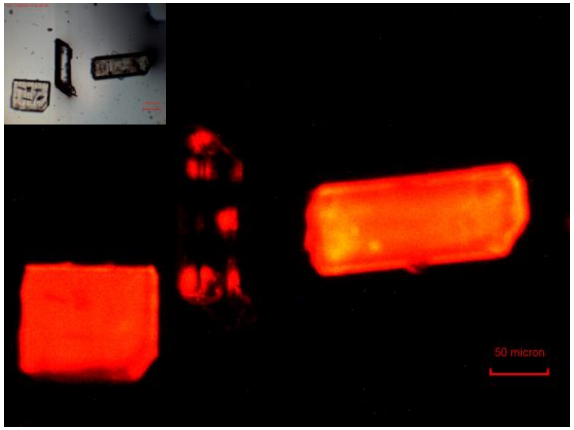
Impact #4 – Curium Radiation Chemistry

- Synthetically produced by either helium ion or neutron bombardment of Pu and/or Am isotopes.
- $\tau_{1/2}$ $(^{248}\mathbf{Cm} \rightarrow {}^{244}\mathbf{Pu} + \alpha) = 3.48 \times 10^{5}$ years.
- Only a single publication reports Cm pulse radiolysis, but no kinetics:



The results obtained with Cm(III) are of importance in the evaluation of redox potentials estimated from spectra. The values for the potentials of OH (-1.90V)(9) and e^-_{aq} (2.86V)(6) are not consistent with the estimates of -3.25V (10) for the Cm(IV)/(III) couple and +5.0V (11) for the Cm(III)/(II) couple.

An	λ_{max}(nm)	$t_{1/2}$(sec)
Cm(II)^d	240	∿12 x 10^{-6}
Cm(IV)	260	∿20 x 10^{-6}



- Sullivan, J. C.; Gordon, S.; Mulac, W. A.; Schmidt, K. H.; Cohen, D.; Sjoblom, R., *Inorg. Nucl. Chem. Let.*, **1976**, *12*, 599-601.

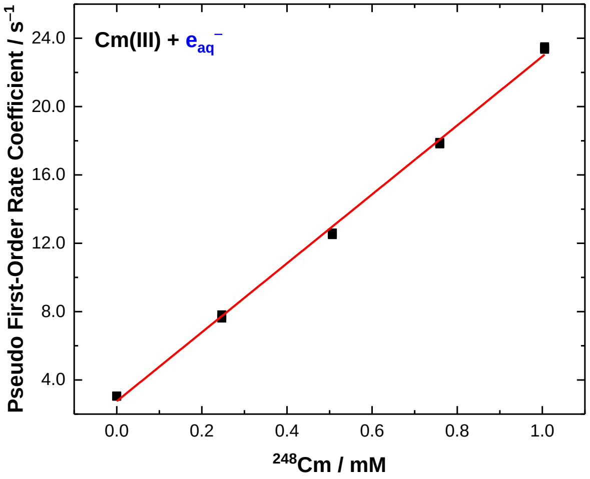
Impact #4 – Curium Radiation Chemistry

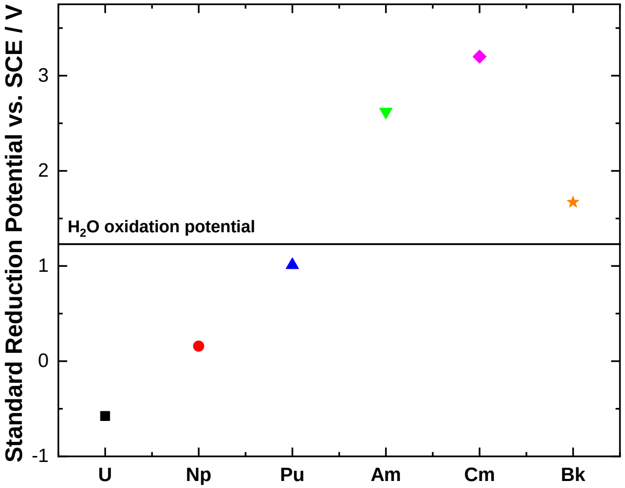
- $k(\mathbf{Cf(III)} + e_{aq}^{-} \rightarrow \mathbf{Cf(II)})$

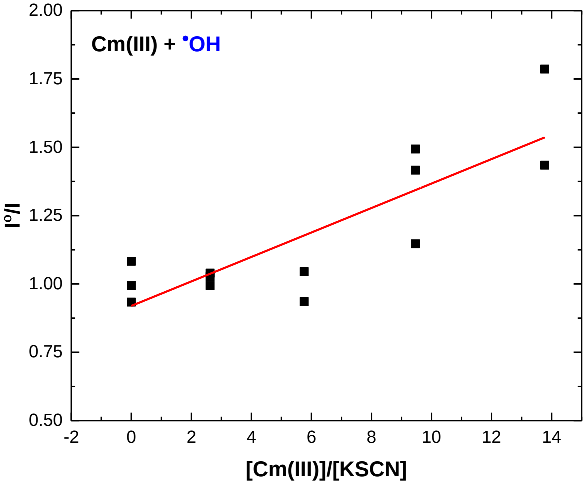
  $= (7.11 \pm 0.18) \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$

- $k(\mathbf{Cf(III)} + {}^{\bullet}\mathrm{OH} \rightarrow \mathbf{Cf(IV)} + \mathrm{OH^{-}})$

  $= (7.2 \pm 0.56) \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$







- Bard, A. J.; Parsons, R.; Jordan, J. Standard Potentials in Aqueous Solution. Marcel Dekker Inc., New York, **1985**.

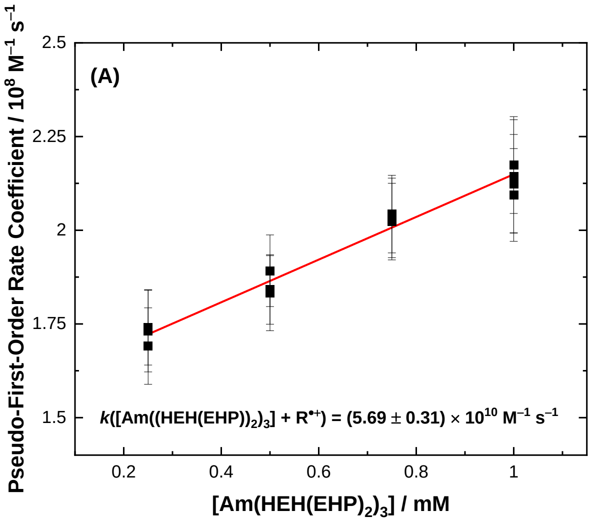
Impact #5 – Actinide Complexation Effects

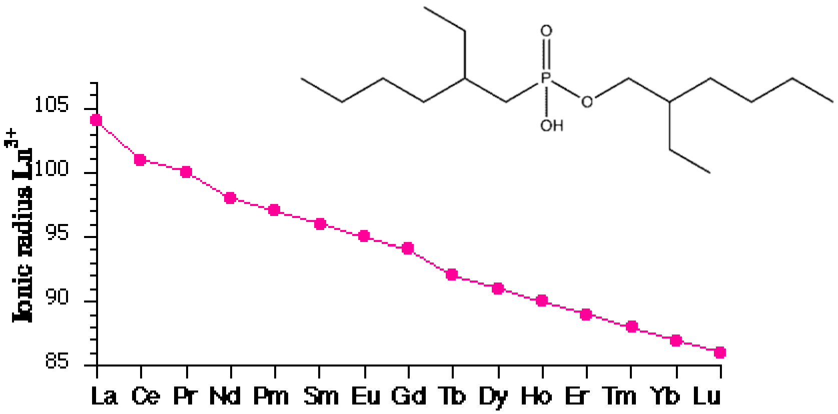
- $k(\mathbf{HEH[EHP]} + \mathbf{RH^{\bullet+}})$

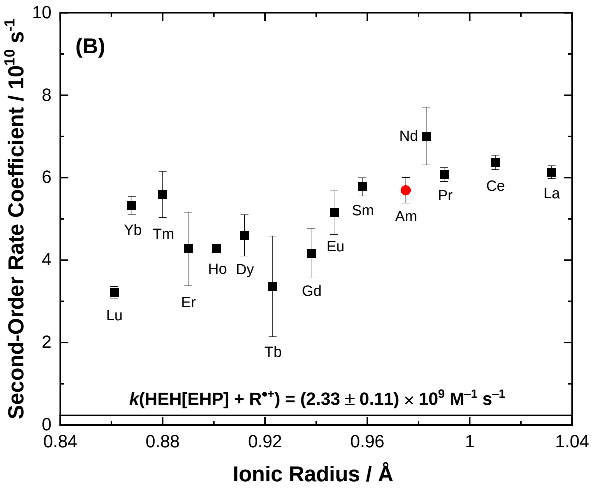
  $= (2.33 \pm 0.11) \times 10^{9}\ M^{-1}\ s^{-1}$

- $k([\mathbf{Ln/Am((HEH[EHP])_2)_3}] + \mathbf{RH^{\bullet+}})$

  $> 2 \times 10^{10}\ M^{-1}\ s^{-1}$



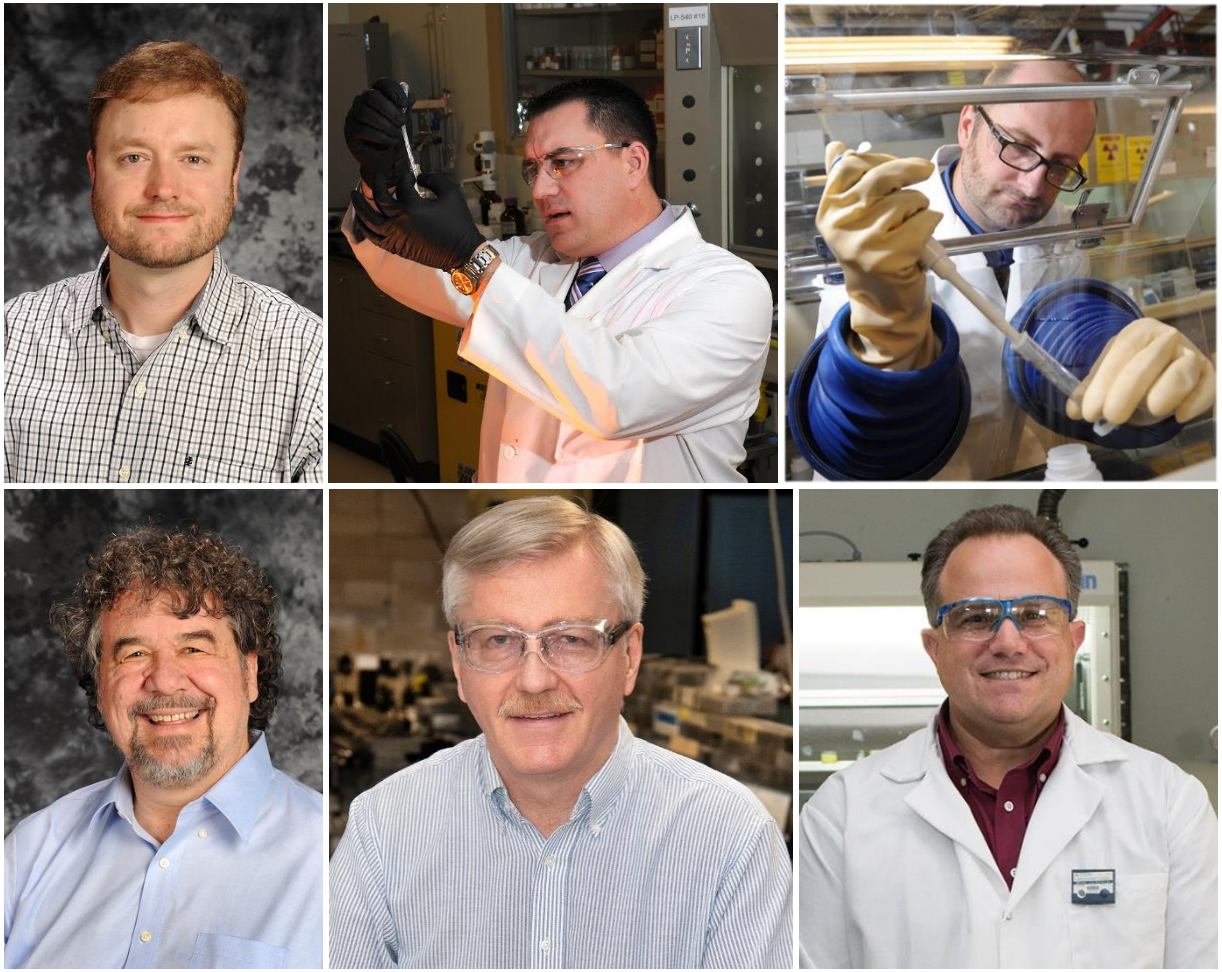




- Jensen, M. P.; Bond, A. H., *J. Am. Chem. Soc.*, **2002**, *124*, 9870
- Grimes, T. S.; Tian, G.; Rao, L.; Nash, K. L., *Inorg. Chem.*, **2012**, *51*, 6299
- Schinzel, S.; Bindl, M.; Visseaux, M.; Chermette, H., *J. Phys. Chem. A*, **2006**, *110, 11324*

Acknowledgements

U.S. DEPARTMENT OF
ENERGY



LDRD Achievements Overview

1. **Training the next generation of radiation chemists!**

2. **Established a world-leading collaborative capability!**

3. **Measured the first-ever picosecond pulse radiolysis measurements for Cf and Cm, and identified significant kinetic enhancement upon actinide complexation!**

4. **Submission and recommendation of a DOE Basic Energy Sciences proposal entitled "*Radiation-Induced Late Actinide Redox Chemistry*"!**

5. **Preparation of 3 actinide radiation chemical kinetics for submission to *Dalton Transactions* (IF = 4.174) and *Chemical Communications* (IF = 5.996)!**