INL/CON-24-78311-Revision-0

Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis

June 2024

Amy Elizabeth Kynman, Gregory Peter Holmbeck, Brian Matthew Rotermund, Travis S Grimes, Bobby Layne, Andrew Cook, Stephen Mezyk

Changing the World's Energy Future

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

INL/CON-24-78311-Revision-0

Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis

Amy Elizabeth Kynman, Gregory Peter Holmbeck, Brian Matthew Rotermund, Travis S Grimes, Bobby Layne, Andrew Cook, Stephen Mezyk

June 2024

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, DE-AC07-05ID14517

Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis

Amy E. Kynman,[1,2*] Travis S. Grimes,[1] Stephen P. Mezyk,[3] Bobby Layne,[4] Andrew R. Cook,[4] Brian M. Rotermund[5] and Gregory P. Holmbeck[1*]

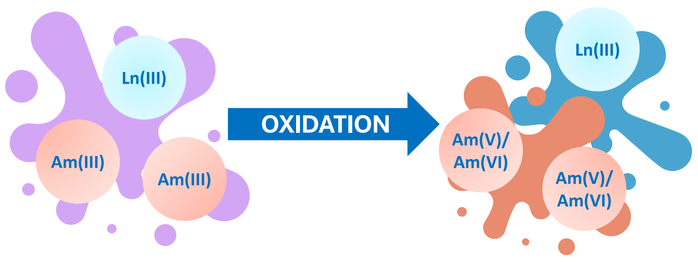
[1]Center for Radiation Chemistry Research, Idaho National Laboratory, Idaho Falls, ID, 83415, USA.
[2]Glenn T. Seaborg Institute, Idaho National Laboratory, Idaho Falls, ID, 83415, USA.
[3]Department of Chemistry and Biochemistry, California State University Long Beach, Long Beach, CA 90840, USA.
[4]Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973, USA.
[5]Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401, USA.

Download the full paper

Background

Am(III) is generated during nuclear fission and is a large contributor to the long-lived radiotoxicity of used nuclear fuel (UNF).[1]

The separation of Am(III) from other lanthanide fission products in UNF remains an enduring challenge due to the similar chemical and physical properties of these trivalent f-elements.



Selective oxidation of Am(III) to the americyl states–Am(V) or Am(VI)–has proven to be a promising separation strategy,[2] but equivalent knowledge of Am(IV) has proven more elusive.[3-5] To optimize extraction flowsheets, the role of Am(IV) in the disproportionation of Am(V) needs to be resolved.

Therefore, we have conducted the first kinetic study of the oxidation of Am(III) to produce Am(IV) under conditions relevant to UNF reprocessing, i.e. high nitric acid (HNO_3) and nitrate (NO_3^-) concentrations, non-ambient temperature.[6]

Radiation Chemistry

Under the high NO_3^-/HNO_3 concentration conditions found in UNF reprocessing, radicals and molecular products are generated by the radiolysis of aqueous solutions:[7]

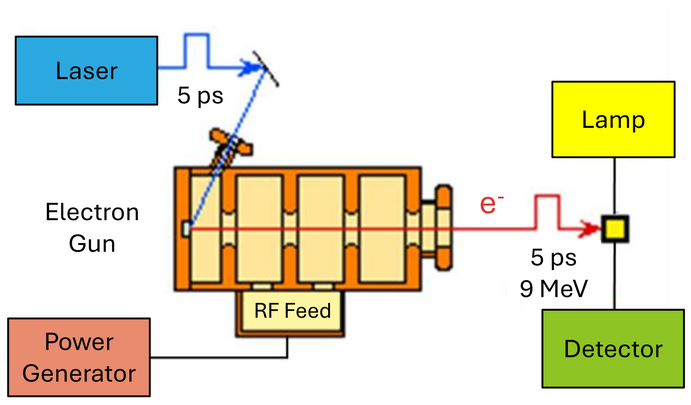
$$H_2O \rightsquigarrow e_{aq}^-, H^\bullet, {}^\bullet OH, H_2O_2, H_2, H_{aq}^+,$$

and transformed into reducing nitrous acid (HNO_2) and oxidizing nitrate ($NO_3^\bullet$) radicals.[8]

Previous work has demonstrated that $NO_3^\bullet$ can be used to transiently oxidize trivalent actinides with formally higher (III)/(IV) redox couples.[9,10]

$$Am(III) + NO_3^\bullet \rightarrow Am(IV) + NO_3^-$$

Electron Pulse Radiolysis



Transients are detected by changes in optical absorption.

Samples were prepared by purifying a solution of Am(III) in hydrochloric acid and performing an acid metathesis to yield a stock of Am(III) in 6.0 M HNO_3 that was then diluted.

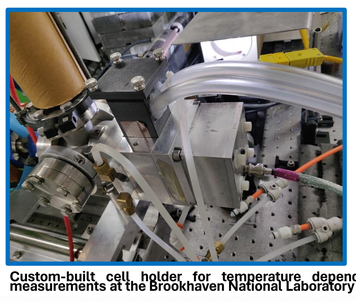
Americium stock solution prepared at the Radiochemistry Laboratory at the Idaho National Laboratory Materials and Fuels Complex.

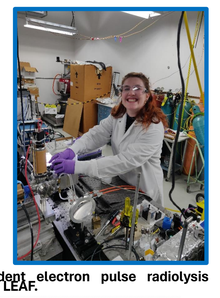
Electron pulse radiolysis measurements were conducted at the Laser Electron Accelerator Facility (LEAF) at Brookhaven National Laboratory.[11]

Temperature-Dependent Am(III) + $NO_3^\bullet$ Kinetics

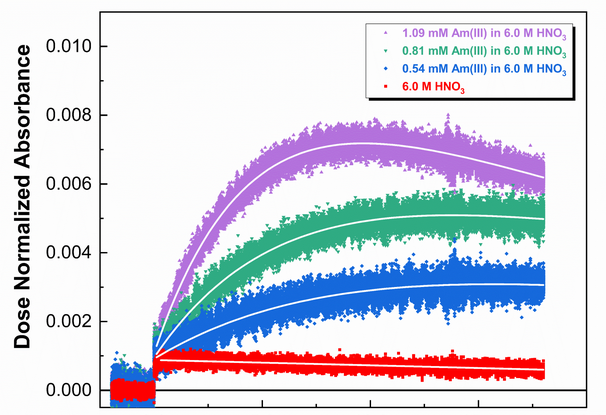
Kinetic data for the growth and decay of Am(IV) and the complementary decay of $NO_3^\bullet$ as a function of Am(III) concentration was acquired.

A custom-built cell holder allowed the first temperature-dependent radiation-induced kinetics study of an actinide element to be conducted. Derived Arrhenius and Eyring parameters give unprecedented molecular-level insight.

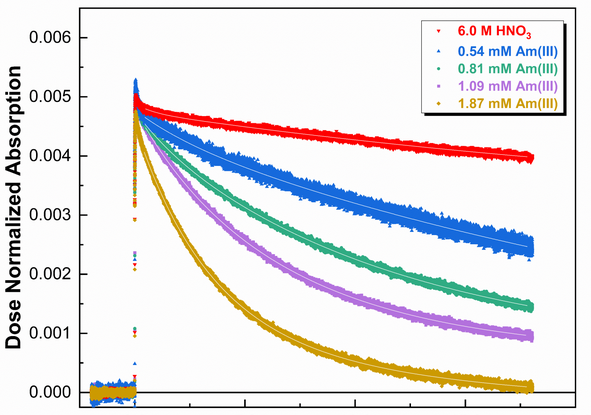




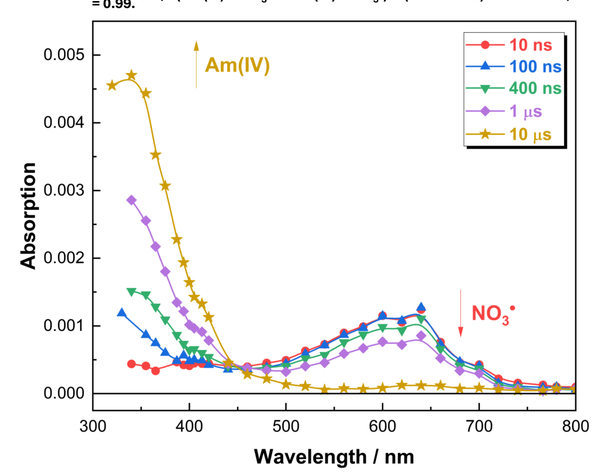
Custom-built cell holder for temperature dependent electron pulse radiolysis measurements at the Brookhaven National Laboratory LEAF.



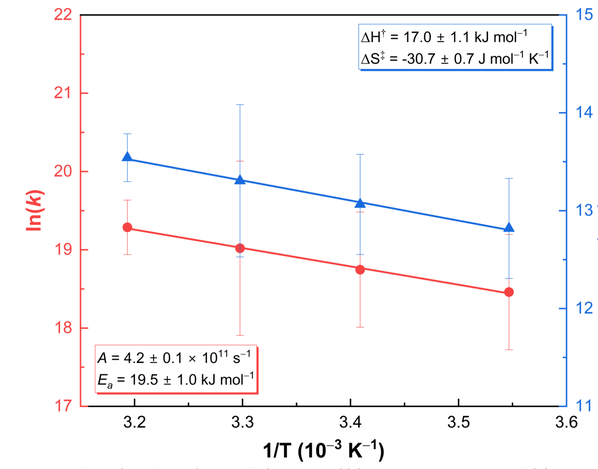
Dose normalized Am(IV) growths and decays at 365 nm from the electron pulse irradiation of Am(III) in aqueous 6.0 M HNO_3 at 22 ± 1 °C. Solid white lines are exponential growth and decay fits to data. Calculated pseudo-first-order growth rates were used to derive the corresponding second-order rate coefficient, $k(Am(III) + NO_3^\bullet \rightarrow Am(IV) + NO_3^-) = (1.32 \pm 0.06) \times 10^8\ M^{-1}\ s^{-1}$, $R^2 = 0.99$.



Complementary dose normalized $NO_3^\bullet$ decays at 632 nm from the electron pulse irradiation of Am(III) in aqueous 6.0 M HNO_3 at 22 ± 1 °C. Solid white lines are double exponential fits to data. Calculated pseudo-first-order decay rates were used to derive the corresponding second-order rate coefficient, $k(Am(III) + NO_3^\bullet \rightarrow Am(IV) + NO_3^-) = (1.38 \pm 0.03) \times 10^8\ M^{-1}\ s^{-1}$, $R^2 = 0.99$.



Dose normalized transient absorption spectra from the electron pulse irradiation of 2.32 mM Am(III) in aerated 6 M HNO_3 at 21 ± 1 °C for several time slices after the electron pulse.



Combined Arrhenius and Eyring plots utilizing second-order rate coefficient data from the reaction of Am(III) with $NO_3^\bullet$ at 8, 22, 30, and 40 ± 1 °C.

Conclusions

- Am(IV) was observed in HNO_3 for the first time.
- The average second-order rate coefficient of $k = (1.35 \pm 0.05) \times 10^8\ M^{-1}\ s^{-1}$ for the growth of Am(IV)/decay of $NO_3^\bullet$.
- The radiolytically generated Am(IV) was unstable with a lifetime of ~16 µs; sufficiently long-lived to play a critical mechanistic role under UNF reprocessing conditions.
- The first temperature-dependent kinetics study for an actinide was conducted.

References

1. Wigeland, R. A.; Bauer, T. H.; Fanning, T. H.; Morris, E. E. Separations and Transmutation Criteria to Improve Utilization of a Geologic Repository. *Nuclear Technology* **2006**, *154* (1), 95–106. https://doi.org/10.13182/nt06-3. **2.** Wang, Z.; Lu, J.-B.; Dong, X.; Yan, Q.; Feng, X.; Hu, H.-S.; Wang, S.; Chen, J.; Li, J.; Xu, C. Ultra-Efficient Americium/Lanthanide Separation through Oxidation State Control. *Journal of the American Chemical Society* **2022**, *144* (14), 6383–6389. https://doi.org/10.1021/jacs.2c00594. **3.** Runde, W. H.; Mincher, B. J. Higher Oxidation States of Americium: Preparation, Characterization and Use for Separations. *Chemical Reviews* **2011**, *111* (9), 5723–5741. https://doi.org/10.1021/cr100181f. **4.** Gordon, S.; Mulac, W. A.; Schmidt, K.; Sjoblom, R. K.; Sullivan, J. C. Pulse-Radiolysis Studies of Americium Ions in Aqueous Perchlorate Media. *Inorganic Chemistry* **1978**, *17* (2), 294–296. https://doi.org/10.1021/ic50180a021. **5.** Hobart, D. E.; K. Samhoun; Peterson, J. R. Spectroelectrochemical Studies of the Actinides: Stabilization of Americium(IV) in Aqueous Carbonate Solution. *Radiochimica Acta* **1982**, *31* (3-4), 139–146. https://doi.org/10.1524/ract.1982.31.34.139. **6.** Kynman, A. E.; Grimes, T. S.; Mezyk, S. P.; Layne, B.; Cook, A. R.; Rotermund, B. M.; Horne, G. P. Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis, Dalton Transactions, **2024**. https://doi.org/10.1039/d4dt00991f. **7.** Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals ·OH/·O− in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988**, *17* (2), 513–886. https://doi.org/10.1063/1.555805. **8.** Guillaume Garaix; Horne, G. P.; Laurent Venault; Philippe Moisy; Pimblott, S. M.; Jean-Louis Marignier; Mostafavi, M. Decay Mechanism of $NO_3^\bullet$ Radical in Highly Concentrated Nitrate and Nitric Acidic Solutions in the Absence and Presence of Hydrazine. *The journal of physical chemistry. B* **2016**, *120* (22), 5008–5014. https://doi.org/10.1021/acs.jpcb.6b02915. **9.** Horne, G. P.; Grimes, T. S.; Zalupski, P. R.; Meeker, D. S.; Albrecht-Schönzart, T. E.; Cook, A. R.; Mezyk, S. P. Curium(iii) Radiation-Induced Reaction Kinetics in Aqueous Media. *Dalton transactions* **2021**, *50* (31), 10853–10859. https://doi.org/10.1039/d1dt01268a. **10.** Rotermund, B. M.; Mezyk, S. P.; Sperling, J. M.; Beck, N. B.; Wineinger, H.; Cook, A. R.; Albrecht-Schönzart, T. E.; Horne, G. P. Chemical Kinetics for the Oxidation of Californium(III) Ions with Select Radiation-Induced Inorganic Radicals ($Cl_2^{\bullet-}$ and $SO_4^{\bullet-}$). *The journal of physical chemistry. A/The journal of physical chemistry. A.* **2024**, *128* (3), 590–598. https://doi.org/10.1021/acs.jpca.3c07404. **11.** Wishart, J. F.; Cook, A.; Miller, J. W. The LEAF Picosecond Pulse Radiolysis Facility at Brookhaven National Laboratory. **2004**, *75* (11), 4359–4366. https://doi.org/10.1063/1.1807004.

Work supported through the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517

www.inl.gov

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy

Idaho National Laboratory