INL/CON-25-83329-Revision-0

Unravelling the radiation-induced redox chemistry of plutonium ions in aqueous solution

March 2025

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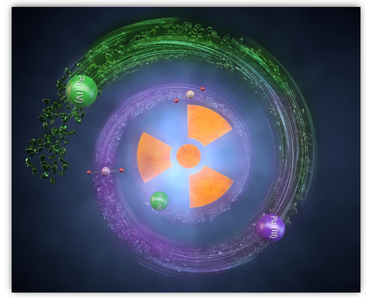
Unravelling the radiation-induced redox chemistry of plutonium ions in aqueous solution



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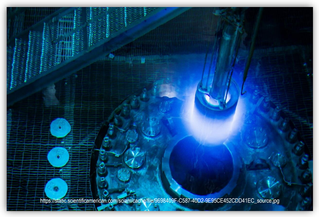
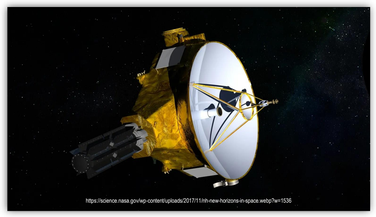
Background

- The discovery, isolation, and large-scale production of plutonium revolutionized the world by enabling the development of nuclear weapons, generating civil nuclear energy, and powering space exploration.
- Despite the importance of these technologies, our fundamental understanding of plutonium's inherent radiation chemistry is limited, hindering our ability to predict its behavior in complex environments under extreme conditions.



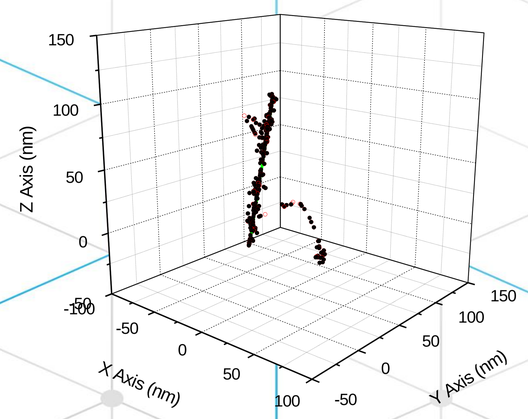


Irradiation Methods

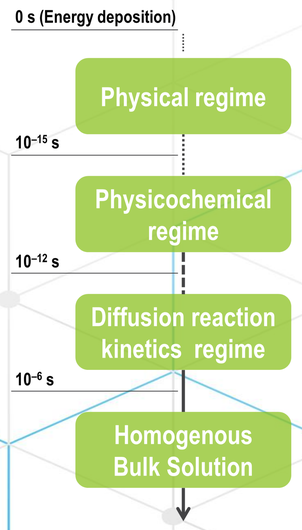
- Plutonium-239 stocks were purified via sequential TEVA and AG1-X8 column elution.
- Valence setting was performed using sodium bismuthate for Pu(VI).
- Alpha irradiations were accomplished by spiking with americium-241.
- Gamma irradiations were achieved using a Nordion Gammacell 220E cobalt-60 irradiator.
- Plutonium oxidation states were quantified through optical absorption spectroscopy, using an Agilent Cary-6000i.[1,2]

Multiscale Modeling

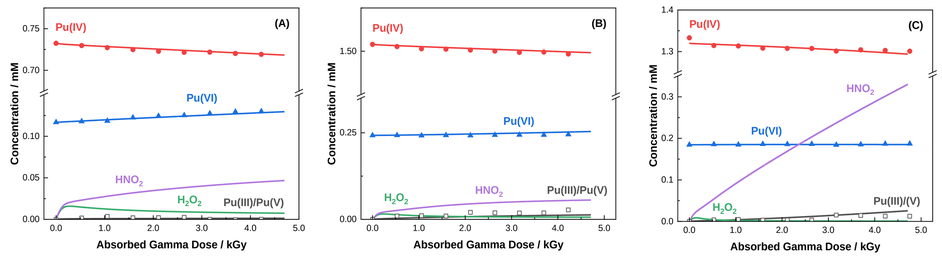
- Monte Carlo radiation track structure simulations[3,4]
- Independent reaction times calculations[5]
- Deterministic kinetic computations[6]

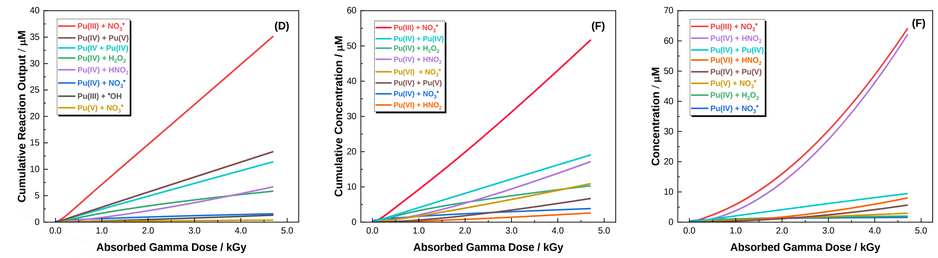


Low energy electrons



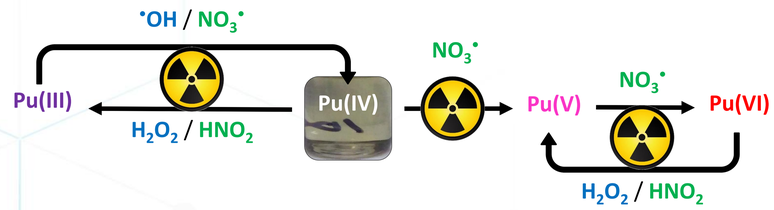
Results

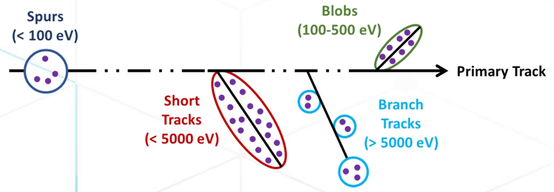




- Concentrations of Pu(III)/Pu(V), Pu(IV), Pu(VI), and significant (≥1 μM) radiolysis products as a function of absorbed gamma dose by aerated, aqueous 1 **(A)**, 3 **(B)**, and 6 **(C)** M HNO_3. Cumulative reaction output multiscale model predictions as a function of absorbed gamma dose for aerated, aqueous 1 **(D)**, 3 **(E)**, and 6 **(F)** M HNO_3, showing radiation-induced reactions with cumulative outputs ≥1 μM.[7]

Conclusions and Next Steps





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References. **(1)** Hall, Herniman, and Walter, Atomic Energy Research Establishment, AERE-C/R-712, 1951; **(2)** Myers, Hanford Atomic Products Operation, HW-44744, 1956; **(3)** Pimblott, LaVerne, and Mozumder, *J. Phys. Chem.* 1996, *100 (20)*, 8595; **(4)** Pimblott and LaVerne, *J. Phys. Chem. A* 2002, *106(41)*, 9420; **(5)** Clifford, Green, Oldfield, Pilling, and Pimblott, *J. Chem. Soc., Faraday Trans.* 1986, *82(9)*, 2673; **(6)** Horne, Donoclift, Sims, Orr, and Pimblott, *J. Phys. Chem. B* 2016, *120(45)*, 11781; **(7)** Kynman, Grimes, Conrad, Pimblott, and Horne, *Inorg. Chem.* 2024, *63(18)*, 8092.

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