INL/MIS-21-64462-Revision-0

MRWFD Center for Radiation Chemistry Research Activities

October 2021

Changing the World's Energy Future

Gregory P Horne

Idaho National Laboratory

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Dr. Gregory P. Horne
Center for Radiation
Chemistry Research

MRWFD Center for Radiation Chemistry Research Activities

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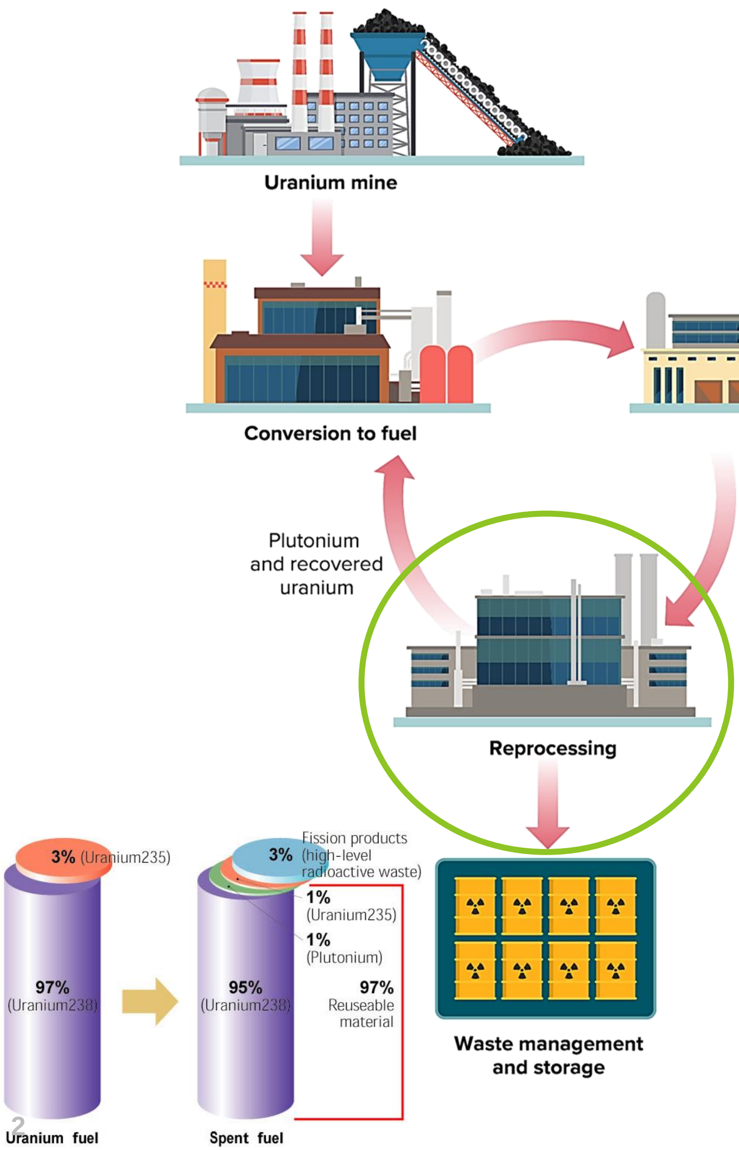
DOE-NE Aqueous Separation
2021 PIs' Meeting

NTRD Nuclear Technology Research & Development

Material Recovery & Waste Form Development

INL Idaho National Laboratory

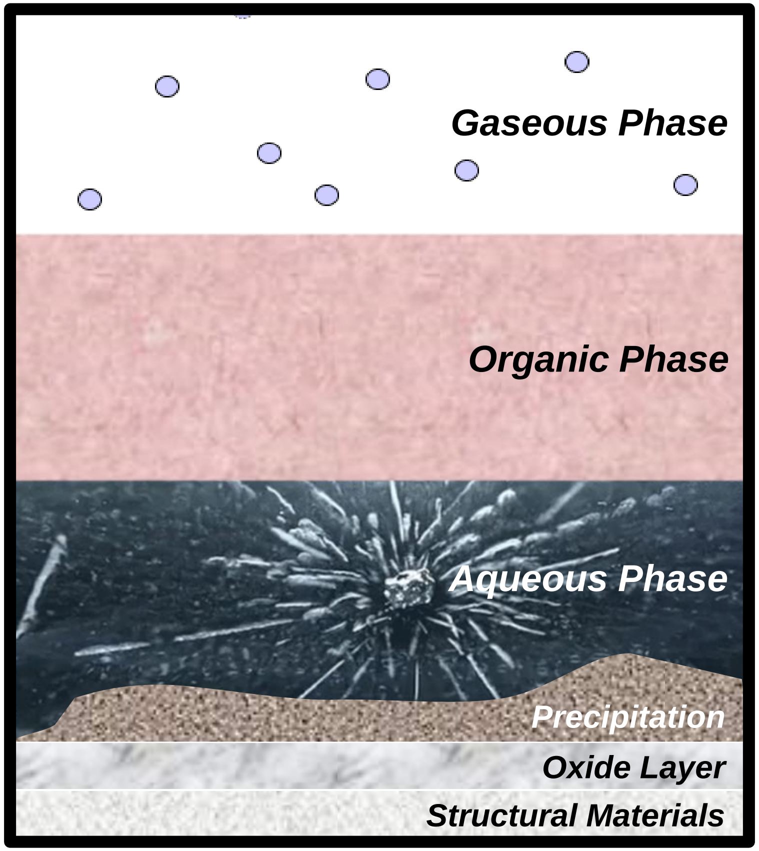
Separations R&D and Radiation Chemistry



Solvent Extraction Reprocessing

Ligands/organic diluent:HNO_3/H_2O

(± additives)



Separations R&D and Radiation Chemistry

Aim

Provide quantitative, fundamental experimental data and insight into the effects of multi-component radiation fields on aqueous separation technologies to develop and evaluate complementary predictive multi-scale modelling capabilities.

Solvent Extraction Reprocessing
Ligands/organic diluent:HNO_3/H_2O
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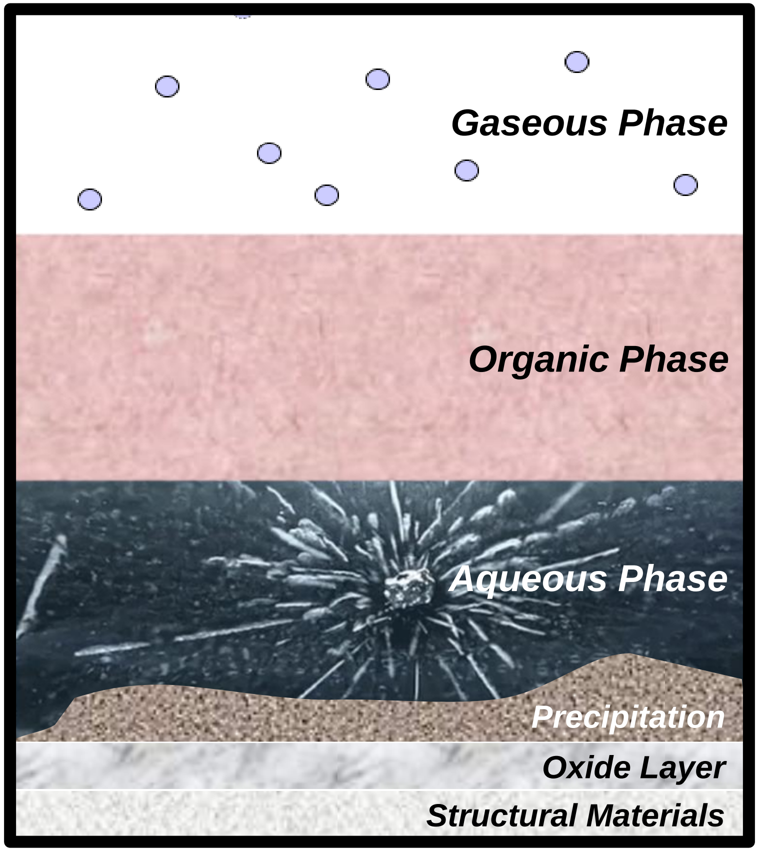
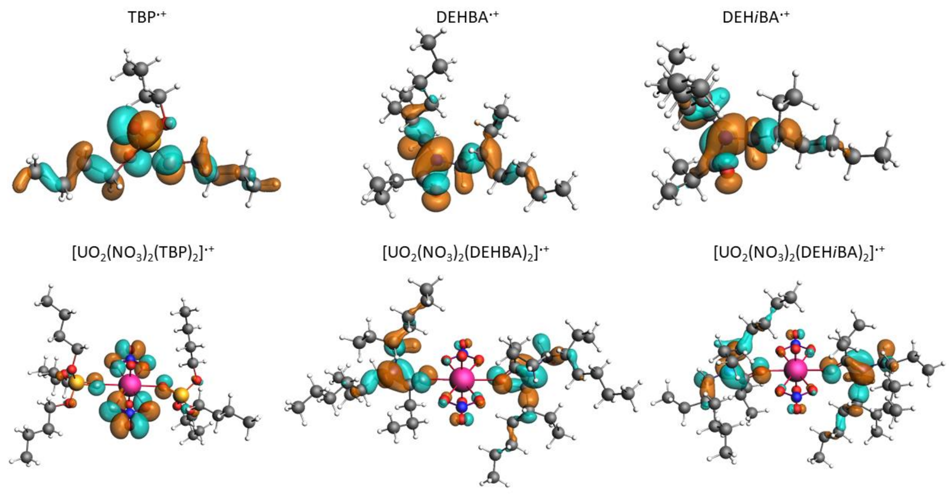


Effect of Metal Ion Complexation on the Radiolysis of TBP and Monoamide Extractants

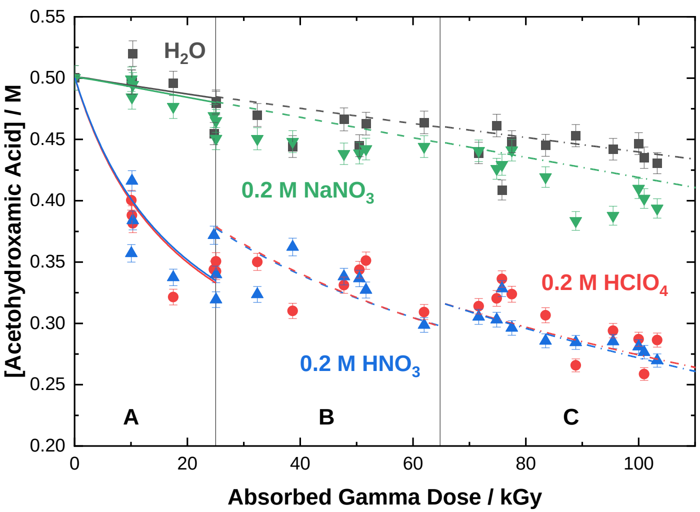
Sample	RH•+ Rate Coefficient (10^{10} M^{-1} s^{-1})
TBP	1.36 ± 0.07
$[UO_2(NO_3)_2(TBP)_2]$	-
DEHBA	0.93 ± 0.02
$[UO_2(NO_3)_2(DEHBA)_2]$	2.49 ± 0.06
DEH*i*BA	1.14 ± 0.04
$[UO_2(NO_3)_2(DEH\textit{i}BA)_2]$	1.59 ± 0.08

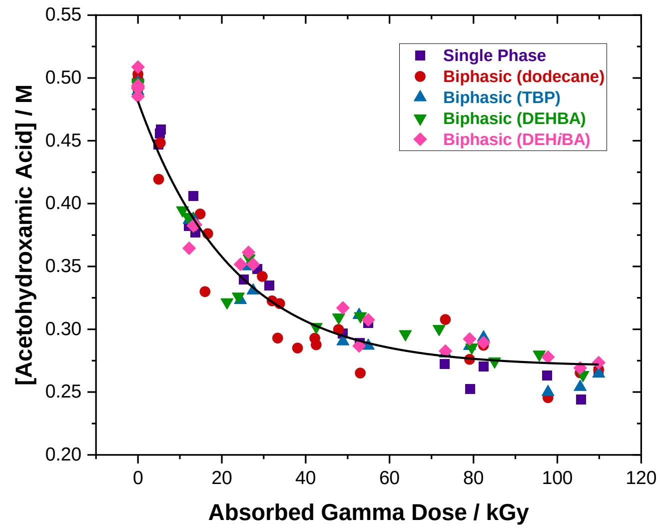


Canonical Kohn-Sham molecular orbitals of the electron holes in the geometry-optimized radical cation species for TBP, DEHBA, and DEH*i*BA.

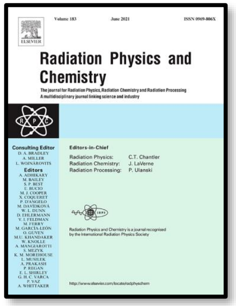
C.C. Barros, C.D. Pilgrim, A.R. Cook, S.P. Mezyk, T.S. Grimes, and G.P. Horne, Influence of Uranyl Complexation on the Reaction Kinetics of the Dodecane Radical Cation with Used Nuclear Fuel Extraction Ligands (TBP, DEHBA, and DEH*i*BA), *PCCP*, **2021**, *in review*.

Radiolytic Evaluation of AHA and CDTA Additives by Multi-Scale Modeling

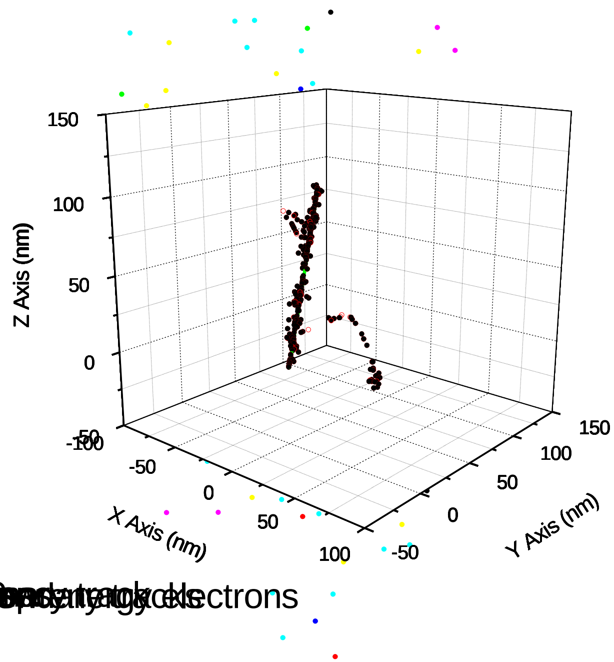


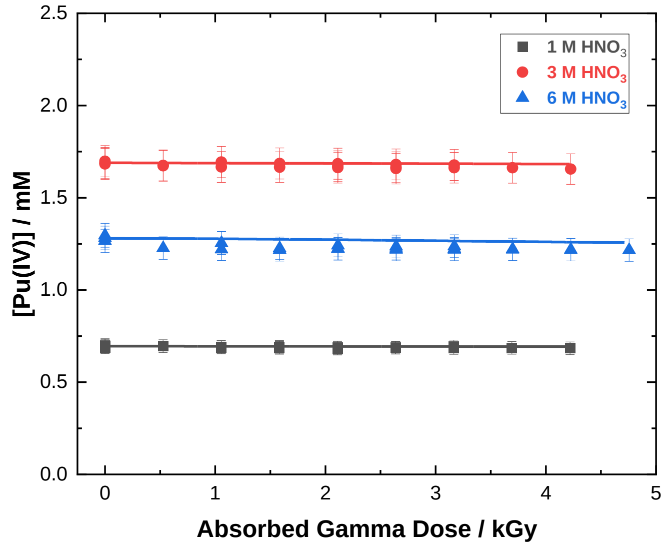


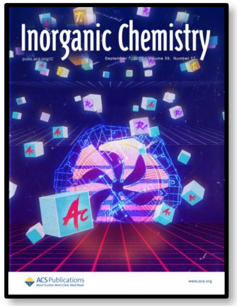
Radiolytic Species	CDTA Rate Coefficient (k, M^{-1} s^{-1})
e_{aq}^{-}	$(5.31 \pm 0.14) \times 10^7$
$H^{\bullet}$	$(2.75 \pm 0.15) \times 10^8$
$^{\bullet}OH$	$(6.41 \pm 0.11) \times 10^9$
$NO_3^{\bullet}$	$(4.06 \pm 0.10) \times 10^8$

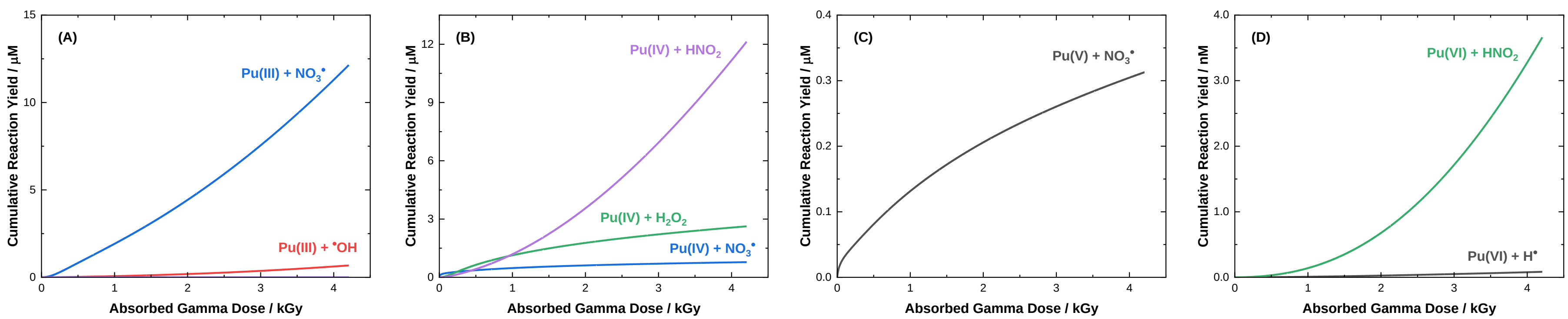


Elucidating the Radiation-Induced Redox Chemistry of Plutonium by Multi-Scale Modeling









- Clifford, P., Green, N.J.B., Oldfield, M.J., Pilling, M.,J., Pimblott, S.M., *J. Chem. Soc., Faraday Trans.*, **1986**, 82, 2673.
- Pimblott, S.M., LaVerne, J.A., Mozumder, A., *J. Phys. Chem.*, **1996**, 100, 8595.
- Horne, G.P.. Donoclift, T.A., Sims, H.E., Orr, R.M., Pimblott, S.M., *J. Phys. Chem. B.*, **2016**, *120 (45)*, 11781.

Vision for the Future (~10 Years)

Aim

- Provide quantitative, fundamental experimental data and insight into the effects of multi-component radiation fields on aqueous separation technologies to develop and evaluate complementary predictive multi-scale modelling capabilities.

Research Needs

- *Integrate* multi-scale modelling capabilities with process scale codes and phenomena.
- *Develop* multi-scale modelling capabilities for *(i)* organic and *(ii)* biphasic solution radiation chemistry.
- *Evaluate* the effect of real system formulations on previously established fundamental chemistry in ‘pristine’ systems.
- *Accelerate* molecular design through the development of advanced screening approaches

Acknowledgements

U.S. DEPARTMENT OF ENERGY








Material Recovery & Waste Form Development

cea

FLORIDA STATE UNIVERSITY

BROOKHAVEN NATIONAL LABORATORY

MANCHESTER 1824
The University of Manchester

NTRD Nuclear Technology Research & Development

AFCP

NATIONAL NUCLEAR LABORATORY

JÜLICH Forschungszentrum

Summary of FY21 Deliverables

1. **M3FT-21IN030101026:** "*Effect of Metal Ion Complexation on the Radiolysis of TBP and Monoamide Extractants*" submitted to **PCCP**, **in peer-review**.

2. **M3FT-21IN030101025:** "*Radiolytic Evaluation of CDTA and AHA Additives*" **manuscripts** in preparation for submission to ***JACS***, ***Chem. Sci.***, ***PCCP***, and ***Rad. Phys Chem***.

3. **M3FT-21IN030101027:** "*Modeling Radiation-Induced Plutonium Redox Chemistry*" model has been developed and milestone manuscript in preparation with **CEA collaborators**.