Investigation into the Radiolysis of PUREX Solvent Systems

Gregory P. Horne

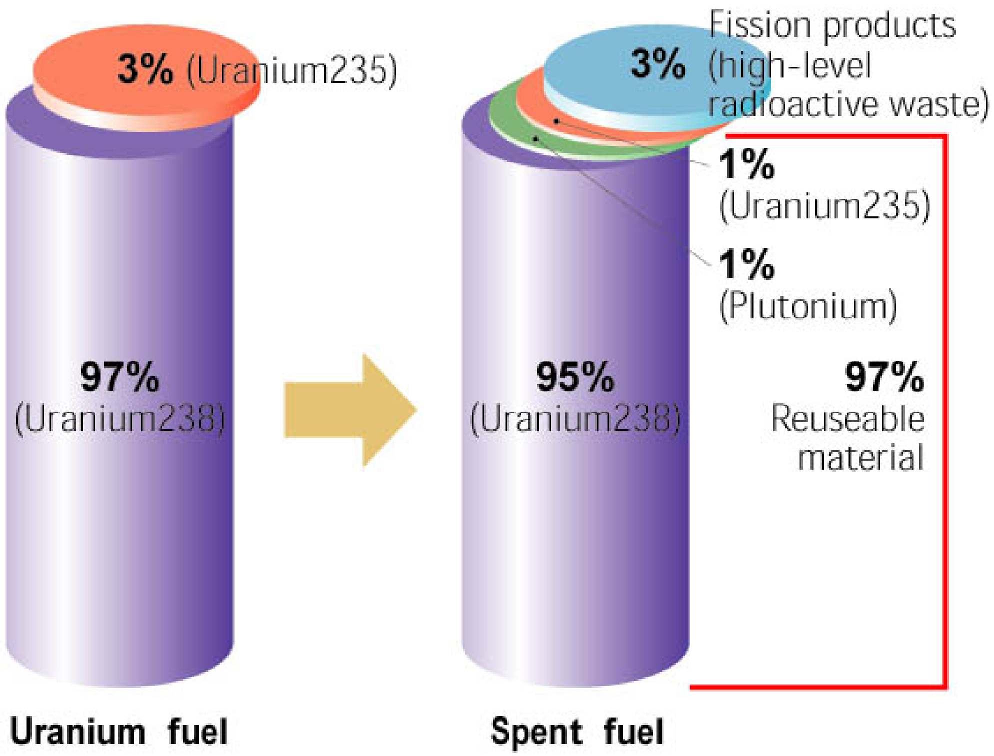
Clint A. Sharrad and Simon M. Pimblott

Colin R. Gregson, Howard E. Sims,

and Robin J. Taylor.

The PUREX Process and Radiation

- The PUREX solvent system is exposed to a multi-component radiation field; γ-rays, α-particles, β-particles, neutrons, and fission fragments.
- Nitrous acid (HNO_2) is a key degradation product as it is capable of alerting the PUREX solvent systems physical and chemical properties.



Research Aims

Provide a fundamental radiolytic foundation for the radiolysis of the PUREX solvent system, with regards to the radiolytic yield of HNO_2 as a function of:

- **Radiation Quality**
  - Gamma rays
  - Proton beams
  - Alpha particles from Pu and Am decay
- **Absorbed Dose**
  - 100 Gy to 1600 Gy
- **Solvent System Formulation**
  - $NaNO_{3(aq)}$ and $HNO_{3(aq)}$
  - $NaNO_3/HNO_3$:dodecane
  - $NaNO_3/HNO_3$:30% TBP-dodecane

Radiation Sources

^{60}Co – Gamma Radiolysis

- Foss Therapy Services Model-812 Cobalt-60 Self-Contained Irradiator Unit, delivering γ-rays with an average energy of 1.25 MeV.
- Dose rates of ~88 Gy min^{-1}.

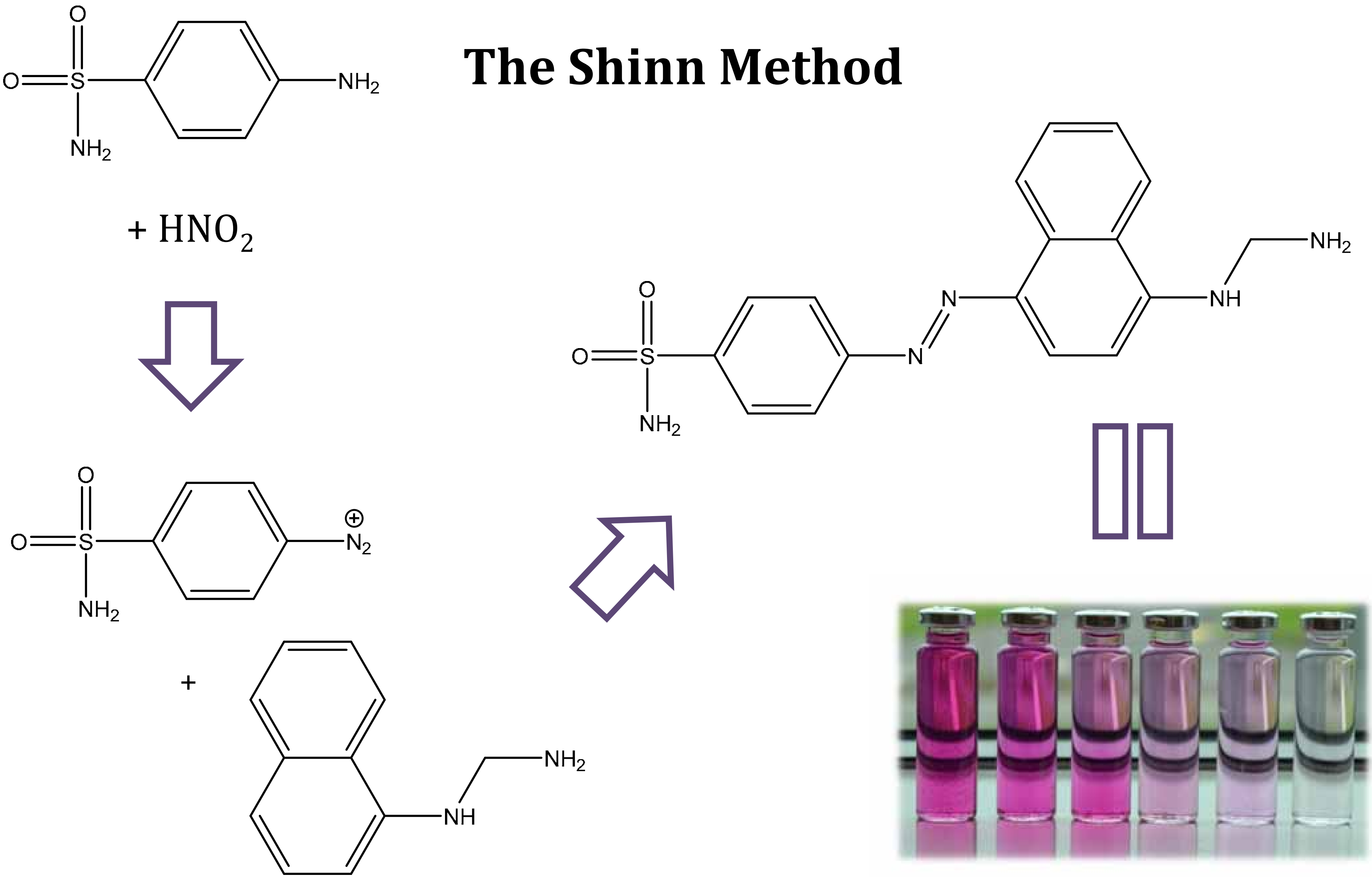
MAGNOX Pu – Alpha Radiolysis

- Legacy reprocessed Pu from MAGNOX reactor fuel.
- Mixed isotopics – ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{241}Am.
- Pu-HNO_3 solution initial activity of ~1.2×10^7 MeV s^{-1}, which equates to a dose rate of ~33.5 Gy day^{-1}.

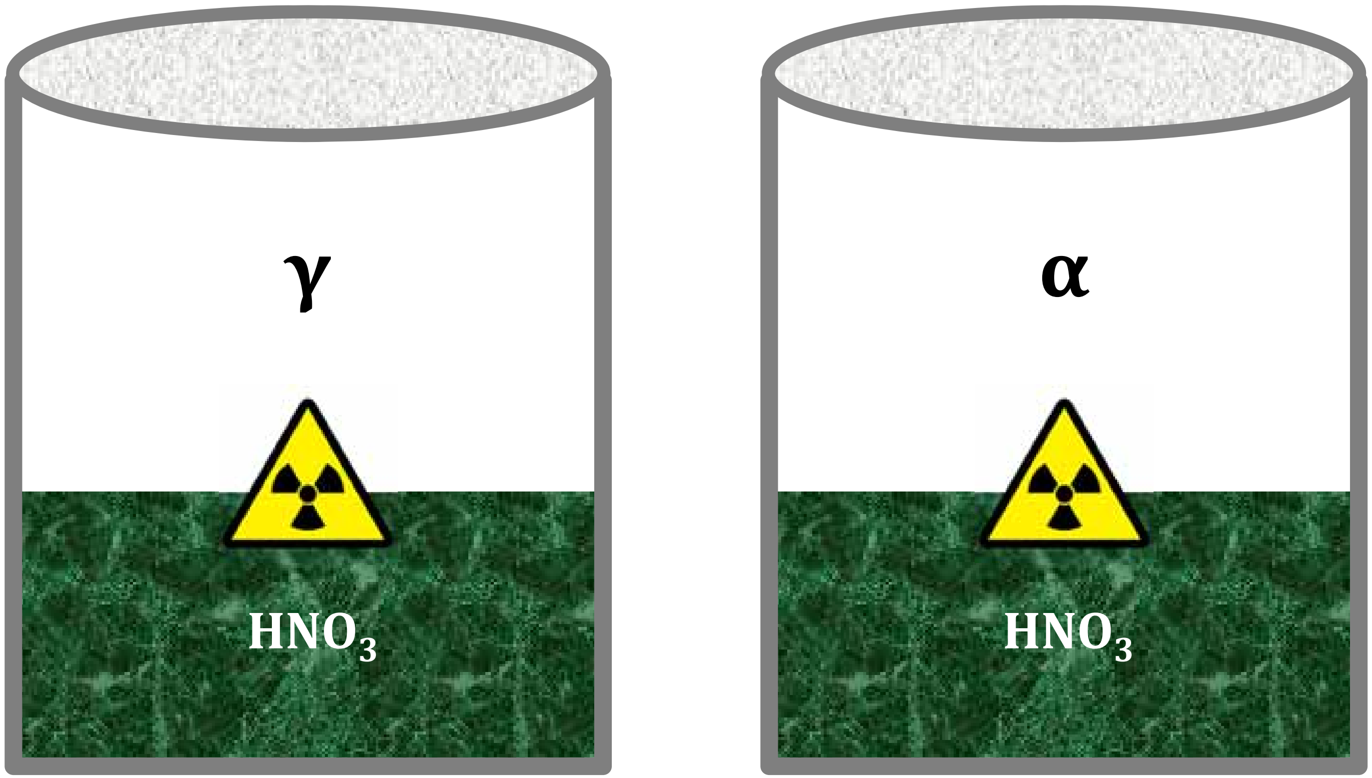
ESA Am – Alpha Radiolysis

- Freshly separated Am from 18yr old MAGNOX Pu, by the ESA project.
- Isotopic purity is ~100% ^{241}Am, chemical purity is 99.58%.
- Am-HNO_3 solution, possessing an initial activity of ~1.2×10^7 MeV s^{-1}, which equates to a dose rate of ~33.5 Gy day^{-1}.

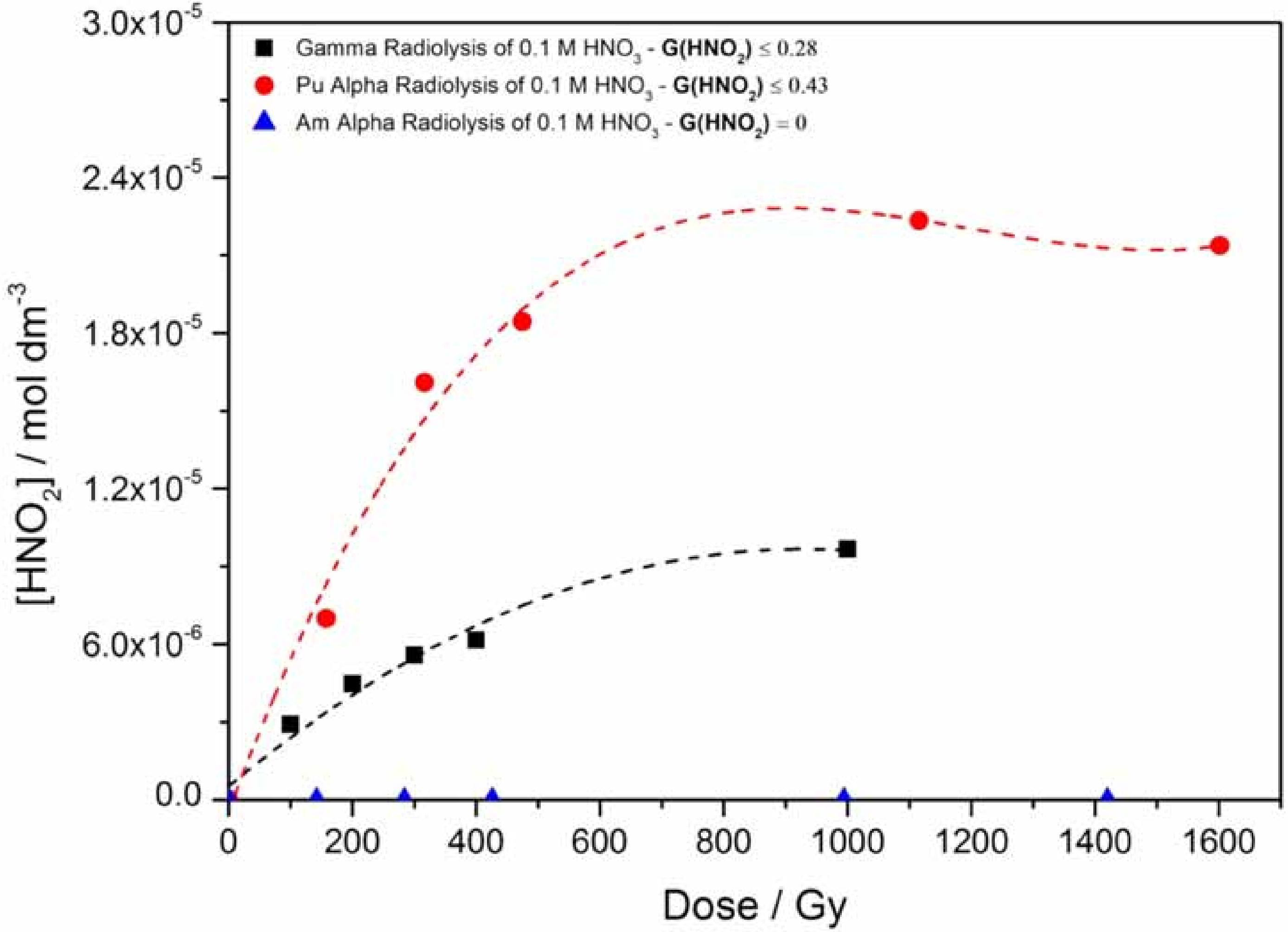
The Shinn Method



γ and α Radiolysis of Aerated HNO_3 Solutions



$[HNO_2]$ as a Function of Dose in 0.1 M HNO_3



Indirect Radiation Effects

$NO_3^- + e_{aq}^- \rightarrow \rightarrow HNO_2$

$NO_3^- + e_{pre}^- \rightarrow \rightarrow HNO_2$

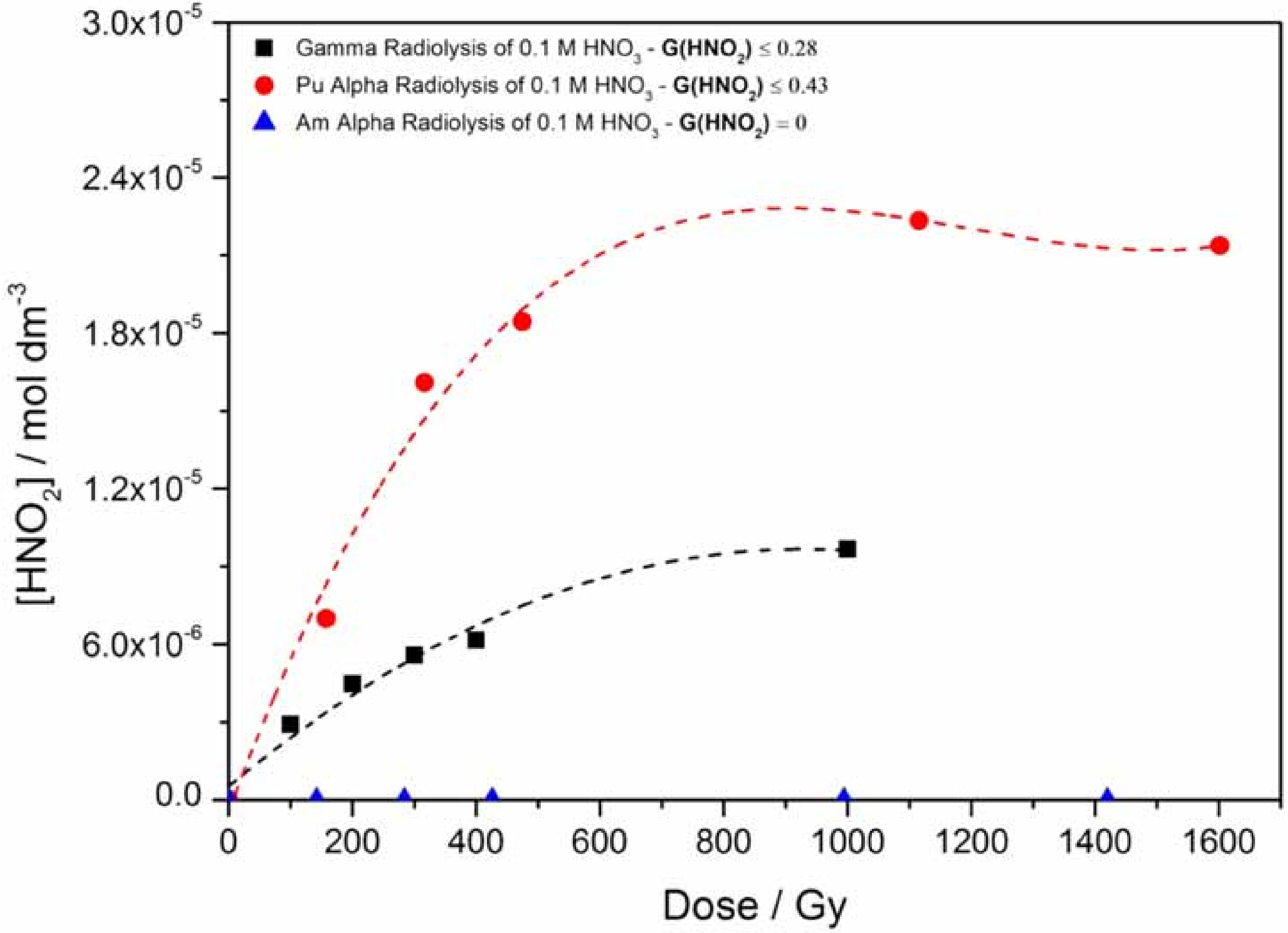
$NO_3^- + H\bullet \rightarrow \rightarrow HNO_2$

Direct Radiation Effects

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

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

$[HNO_2]$ as a Function of Dose in 0.1 M HNO_3



Secondary Radiation Induced Processes

$NO_3^{2-} + OH\bullet \rightarrow NO_3^- + OH^-$

$NO_2 + OH\bullet \rightarrow HONO_2$

$HNO_2 + OH\bullet \rightarrow NO_2 + H_2O$

$NO_2^- + OH\bullet \rightarrow NO_2 + OH^-$

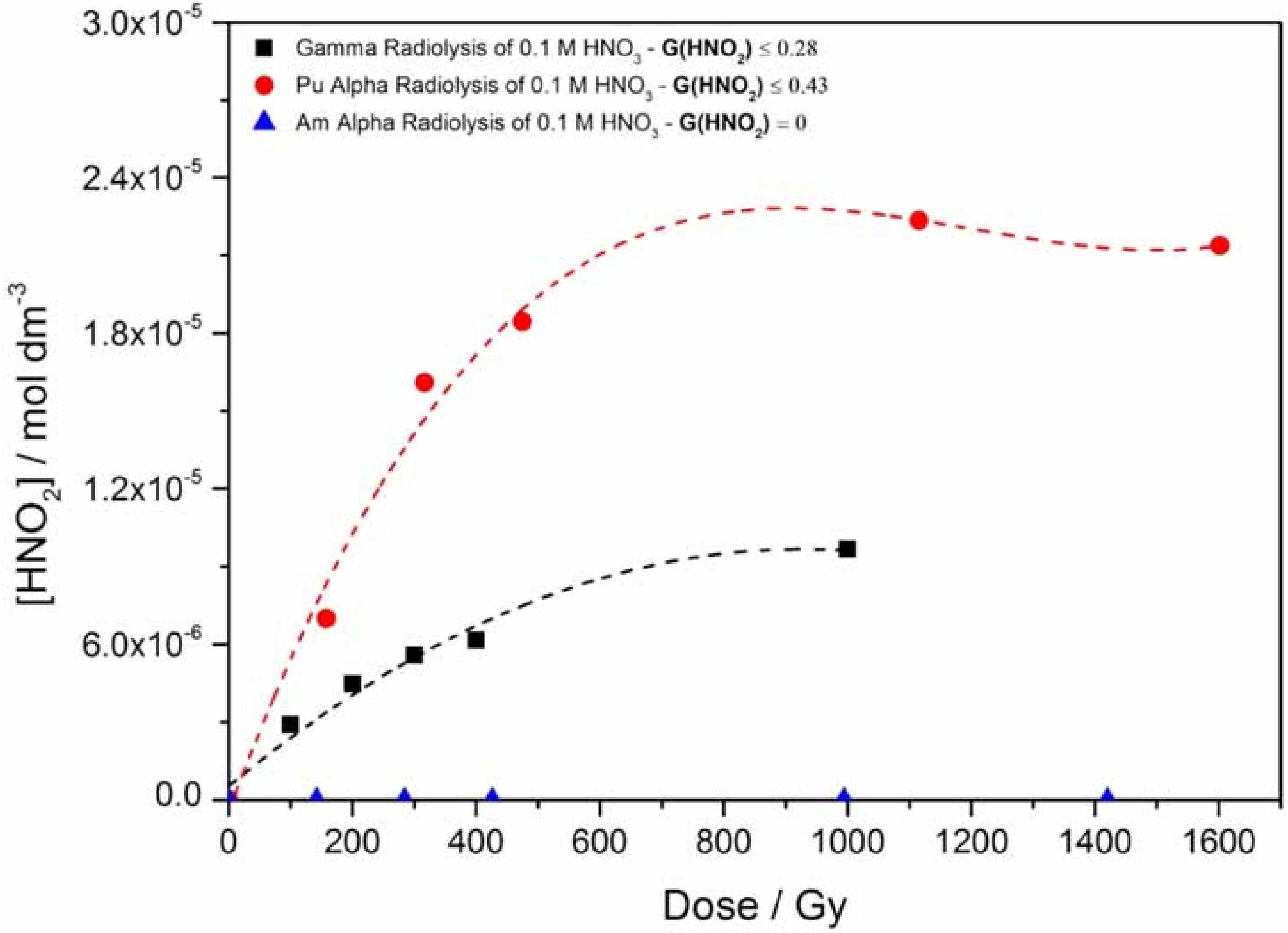
$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O$

Linear Energy Transfer Effects

- Radiolytic yields of radicals decrease with increasing LET.
- HNO_2 is essentially formed from radical precursors (e_{aq}^- and H•), and thus its radiolytic yield can be expected to be lower for high LET radiation.

Reference (Source)	$G(HNO_2)$
This work (Pu)	≤0.43
This work (Am)	0
Savel'ev *et al* (Po)	0

$[HNO_2]$ as a Function of Dose in 0.1 M HNO_3



Radiation Chemistry

Increasing LET decreases radiolytic yield of HNO_2.

Plutonium Redox Chemistry

- The Pu oxidation state equilibrium:

$$K = \frac{[\boldsymbol{Pu}(\boldsymbol{III})]\,[\boldsymbol{Pu}(\boldsymbol{VI})]}{[\boldsymbol{Pu}(\boldsymbol{IV})]\,[\boldsymbol{Pu}(\boldsymbol{V})]} = 3.2 \text{ in } 0.1 \text{ M } HNO_3$$

- Pu(IV) possesses a disproportionation:

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + PuO_2^{2+} + 4H^+$$

- Reactions with H_2O_2:

$$2Pu^{4+} + 2H_2O_2 \rightarrow 2Pu^{3+} + 2H_2O + O_2$$

$$2PuO_2^{2+} + 2H_2O_2 \rightarrow 2PuO_2^{+} + 2H_2O + O_2$$

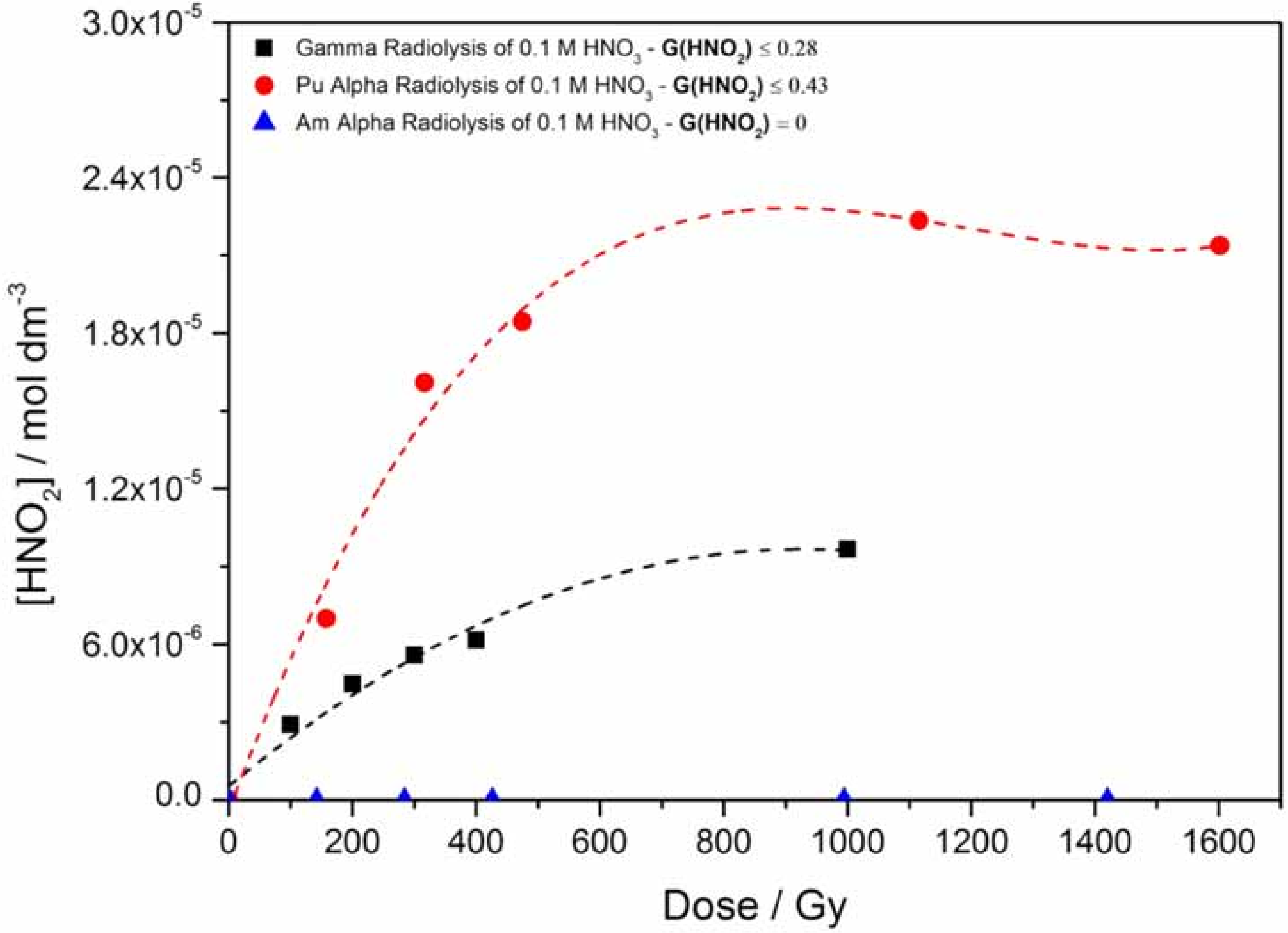
- HNO_2 oxidises Pu(III) to Pu(IV):

$$HNO_2 + H^+ + NO_3^- \rightarrow 2NO_2 + H_2O$$

$$2NO_2 \rightleftharpoons N_2O_4$$

$$Pu^{3+} + N_2O_4 \rightarrow Pu^{4+} + NO_2^- + NO_2$$

$[HNO_2]$ as a Function of Dose in 0.1 M HNO_3



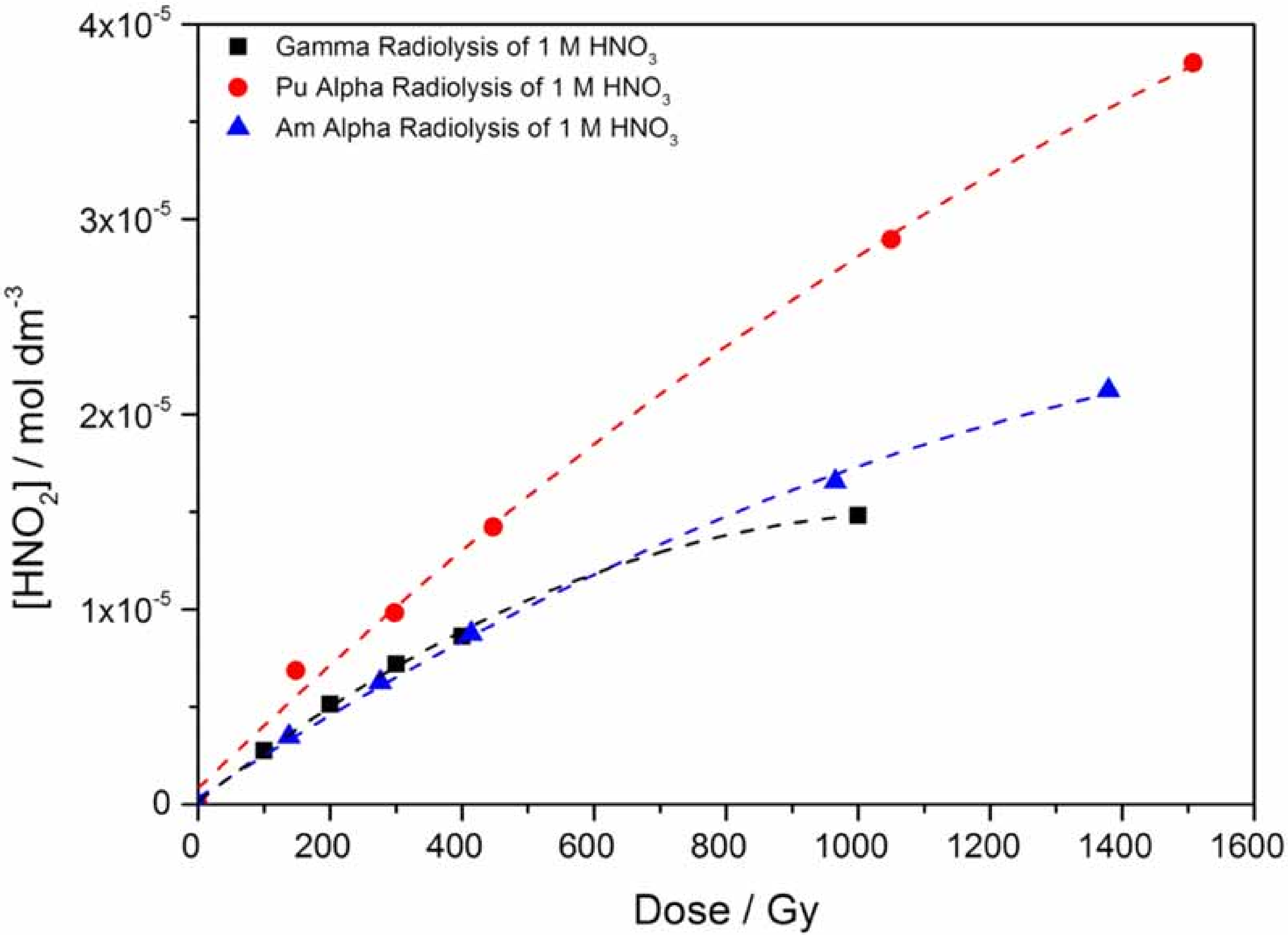
Radiation Chemistry

Increasing LET decreases radiolytic yield of HNO_2.

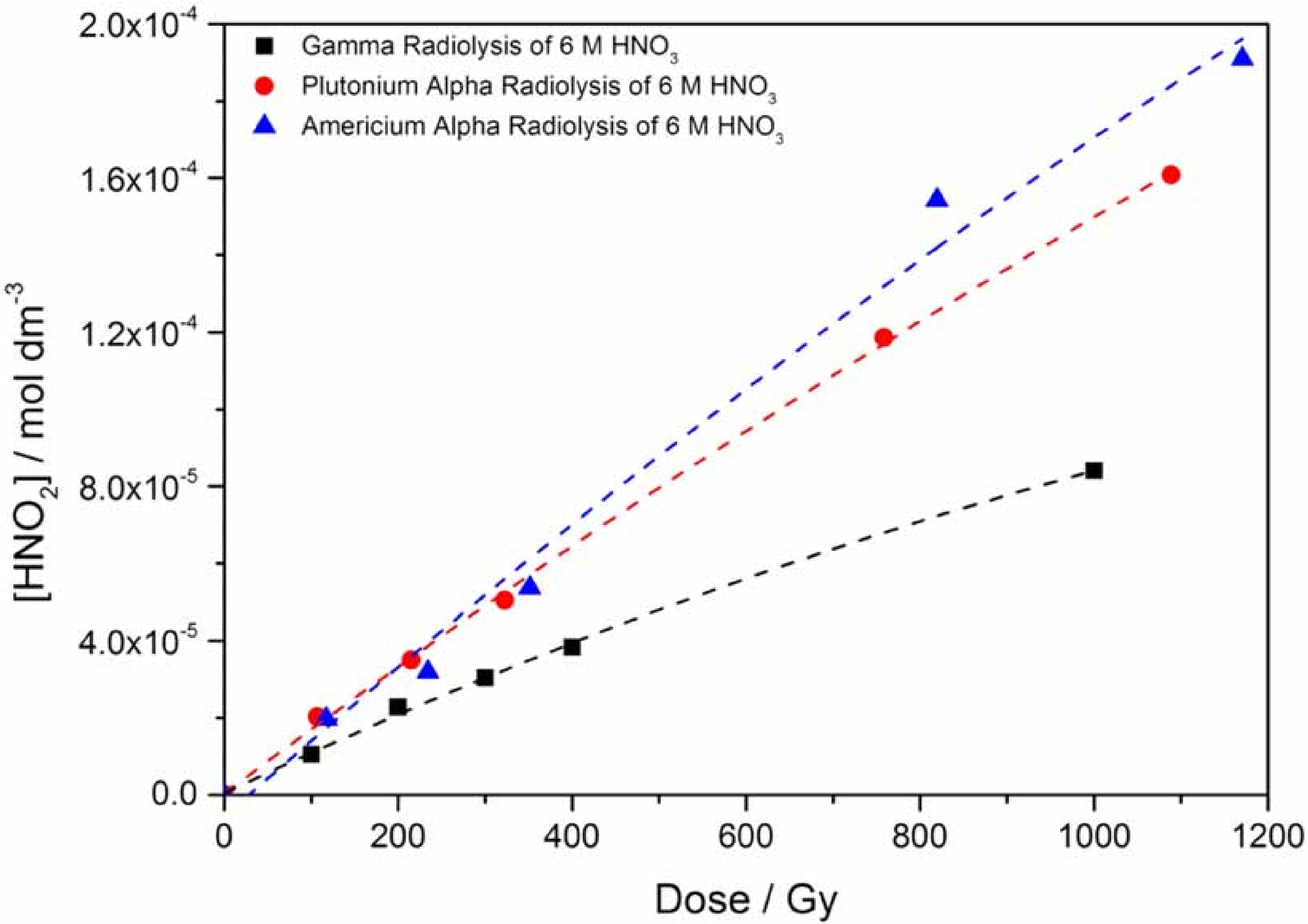
Redox Chemistry

Plutonium oxidation states compete with bulk homogeneous processes for HNO_2 and its precursors.

[HNO_2] as a Function of Dose in 1 M HNO_3



$[HNO_2]$ as a Function of Dose in 6 M HNO_3



Daughter Nuclide Recoil Energy??

- Average recoil energy for Pu and Am Average daughter nuclei is ~89 keV; a magnitude in considerable excess of that required to break chemical bonds.
- The maximum energy a heavy charge particle may transfer (Q_{max}) in a single energy transfer event is described by the following equation:

$$Q_{max} = \left[\frac{(4 \times m \times M)}{(m+M)^2}\right] + \left[\frac{1}{2}(M \times v^2)\right]$$

Q_{max} (Energy transfer to orbital e^-)~ 0.82 eV

Q_{max} (Energy transfer to H nucleus) ~ 1.49 keV

Q_{max} (Energy transfer to N nucleus) ~ 18.7 keV

Q_{max} (Energy transfer to O nucleus) ~ 21.1 keV

Preliminary Conclusions

- The radiolytic yield of HNO_2 is very much dependent upon radiation quality and the chemical properties of the radionuclides inducing radiolysis.

- Important to understand both the radiation chemistry **AND** the inherent chemical properties of the radionuclides/elements involved, and the interplay between all of the solvent system components.

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