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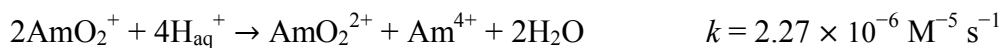
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ABSTRACT

The recent development of facile methods to oxidize trivalent americium to its higher valence states holds promise for the discovery of new chemistries and critical insight into the behavior of the $5f$ electrons. However, progress in understanding high valent americium chemistry has been hampered by americium's inherent ionizing radiation field, and its concomitant effects on americium redox chemistry. Any attempt to understand high valent americium reduction and/or disproportionation must account for the effects of these radiolytic processes. Fortunately, the effects of ionizing radiation on water and aqueous nitric acid solutions are well known. Values for the yields of the major radiolytically-produced reactive species that could conceivably react with americium, and their rate coefficients, are available for use in radiation chemical modeling. Therefore, we present a complete, quantitative, mechanistic description of the radiation-induced redox chemistry of the americium oxidation states in aerated, aqueous nitric acid, as a function of radiation quality (type and energy) and solution composition using multi-scale modeling calculations supported by experiment. The reduction of Am(VI) to Am(V) was found to be most sensitive to the effects of ionizing radiation, undergoing rapid reductions with the steady-state products of aqueous HNO₃ radiolysis, i.e., HNO₂, H₂O₂, and HO₂[•], which dictated its practical lifetime under acidic conditions. In contrast Am(V) is only

susceptible to radiolytic oxidation, mainly through its reactions with NO_3^\bullet , and is notably radiation resistant with respect to direct one-electron reduction to produce Am(IV). Our multi-scale modeling calculations predict that the lifetime of Am(V) is dictated by its rate of disproportionation,



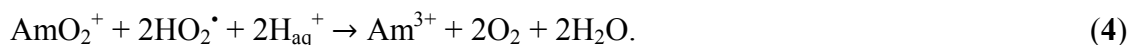
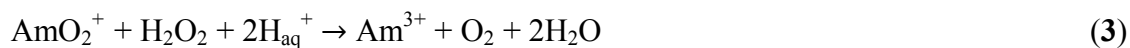
with a fourth-order dependence on $[\text{H}_{\text{aq}}^+]$ in agreement with previous experimental findings, giving an optimized rate coefficient of $k = 2.27 \times 10^{-6} \text{ M}^{-5} \text{ s}^{-1}$. This disproportionation initially produces Am(IV) and Am(VI) species, but the lack of any spectroscopic evidence in our study for Am(IV) suggests that solvent reduction of this cation occurs rapidly. The ultimate product of all the Am(VI)/Am(V) irradiations is Am(III), which shows great stability in an irradiation field.

INTRODUCTION

Americium marks the beginning of the late actinide series, the chemistry of which is characterized by prevalence of the trivalent oxidation state, a consequence of relativistic effects on electron distribution.^{1,2,3} The pervasiveness of trivalent americium (Am(III)) is due to the high Am(IV)/Am(III) redox couple ($E^0 = 2.62 \text{ V}$ vs. the saturated calomel electrode (SCE) in 1.0 M perchloric acid).^{4,5} Despite this redox constraint, Penneman and Asprey successfully oxidized Am(III) to its corresponding penta- and hexavalent americium states ($\text{AmO}_2^{+/2+}$) in the 1950s, using ammonium peroxydisulfate in nitric and perchloric acids, accessing a new frontier of americium chemistry.⁶⁻⁸ However, due to the high Am(IV)/Am(III) redox potential, only a limited number of chemical^{9,10,11} and electrochemical¹²⁻¹⁵ procedures are capable of producing these americium states.

Interest in the high oxidation states of americium has seen a resurgence due to the opportunity to explore new americium chemistries and the potential need for facilitating the separation of americium from the trivalent lanthanides, which remains a key challenge for recycling used nuclear fuel.^{9-11,15-18} The lifetimes of these americium states are beholden to a combination of chemical and radiolytic processes, the latter of which are critical to understanding these states. To date, their properties have only been empirically determined, which limits our fundamental mechanistic understanding and ability to predict their redox behavior.^{16,19-36} With respect to pentavalent americium (Am(V)/ AmO_2^+), radiolysis is believed to be responsible for its reduction in a variety of media (e.g., perchloric^{26,28,37,38}, sulfuric²⁹, and nitric acid^{35,39,40}) generally attributed to reactions involving the hydrated electron (e_{aq}^- , $E^0 = -2.9$

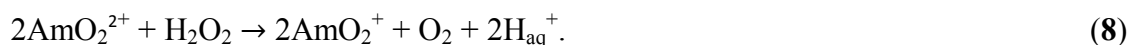
V), hydrogen atom (H^\bullet , $E^0 = -2.3 \text{ V}$), hydrogen peroxide (H_2O_2 , $E^0 = 1.8 \text{ V}$) and the hydroperoxyl radical (HO_2^\bullet , $E^0 = 1.46 \text{ V}$).^{30,32,33,41}



Am(V) is also susceptible to oxidation, for example by the hydroxyl radical (OH^\bullet , $E^0 = 2.7 \text{ V}$).⁴²



Radiolysis of hexavalent americium (Am(VI)/AmO_2^{2+}) is constrained to reductive processes:^{19,20,32,33,41,42}



Clearly, the lifetimes of Am(V) and Am(VI) , and their subsequent oxidation state distributions, are strongly dependent upon irradiation conditions. However, the water radiolysis processes, presented above are compounded by radiolytic effects/species specific to a given medium, which has led to conflicting results and mechanistic interpretations. Zaitsev *et al.* found that the rate of Am(V) reduction in nitric acid is slower than in other acids.⁴² They attributed this observation to consumption of H_2O_2 by nitric acid radiolysis products,³⁴ in particular nitrous acid (HNO_2 , $E^0 = 0.984 \text{ V}$).⁴³⁻⁵⁰



In contrast, Frolov *et al.* found that Am(V) reduction was accelerated in concentrated nitric acid, the effect being attributed to the presence of HNO_2 .⁴⁰ These conflicting observations are further exacerbated by two studies that showed nitrite³⁴ ($\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}_{\text{aq}}^+$, $\text{pK}_a = 3.2$)⁵¹ and H_2O_2 ⁵² to have little effect on Am(V) reduction in dilute nitric acid.

To quantitatively understand americium redox chemistry over a range of acidities a kinetic computer model is necessary to provide fundamental assistance in resolving these mechanistic contradictions. Therefore, here we present a comprehensive investigation into the radiation-induced chemistry of these americium states. We employ multi-scale modeling⁵³ calculations to

provide a quantitative, mechanistic description for a variety of experimental conditions (radiation quality and solution formulation) to underpin the fundamental chemical behavior of these exotic americium oxidation states.

MATERIALS AND METHODS

Experimental

Caution! The americium solutions employed in this work were highly radioactive. Handling was performed in dedicated radiological and nuclear facilities using well established radiological safety protocols.

Americium Sample Preparation. Preparation of americium solutions was performed exactly as reported in reference 16 at the Idaho National Laboratory (INL) Radiochemistry Laboratory (RCL). Oxidation was achieved by contacting on-hand americium oxide (99.9% $^{243}\text{Am}_2\text{O}_3$, 0.1% $^{241}\text{Am}_2\text{O}_3$) with concentrated nitric acid ($\geq 99.999\%$ HNO_3 trace metal basis, Sigma Aldrich), diluting to the appropriate concentration (1.0, 3.0, 6.5, and 9.0 M) with 18 M Ω deionized water, followed by addition of the solid oxidant sodium bismuthate (93% NaBiO_3 ACS Grade, Chemsavers). Solutions were vigorously shaken for up to 24 hours prior to filtration and transferred to screw-cap, semi-micro, 10 mm pathlength quartz cuvettes.

Irradiation Experiments. Alpha irradiations were achieved using self-radiolysis from the alpha decay of americium, with dose rates calculated from the respective isotopic activities of the americium solutions. Accumulation of alpha dose was by increasing residence time, with samples analyzed at regular time intervals for a minimum of 24 hours. Gamma irradiations were performed using the INL Center for Radiation Chemistry Research (CR2) Nordion Gammacell 220E ^{60}Co source unit, located in the Fuels and Applied Science Building (FASB) at the INL Materials and Fuels Complex (MFC). Samples were placed in the center of the ^{60}Co -irradiator sample chamber and lowered for exposure times corresponding to specific doses. Gamma dose rates were determined by Fricke solution dosimetry⁵⁴ corrected for ^{60}Co decay ($\tau_{1/2} = 5.27$ years, 1.17 and 1.33 MeV gamma rays) and solution density. Radiation chemical yields are reported in G -value SI units of $\mu\text{mol J}^{-1}$ ($1 \mu\text{mol J}^{-1} = 9.62 (\text{molecule } 100 \text{ eV})^{-1}$). All irradiations were performed at laboratory room temperature maintained at 20 ± 1 °C.

Analytical Procedure. Spectrophotometric techniques were used to simultaneously determine the concentrations of Am(III) ($\lambda_{\text{max}} = 503 \text{ nm}$), Am(V) ($\lambda_{\text{max}} = 718 \text{ nm}$), and Am(VI) ($\lambda_{\text{max}} = 996 \text{ nm}$) during irradiation at regular time/dose intervals, which was achieved using an Agilent Cary-6000i UV-Vis-NIR spectrophotometer. Following baseline corrections, concentrations of the respective americium oxidation states were calculated using molar extinction coefficients reported by Zalupski *et al.*⁵⁵ and Grimes *et al.*¹⁶

Calculations

Reaction Kinetics Modeling. Multi-scale modeling calculations, using a combination of stochastic⁵⁶⁻⁵⁸ and deterministic methodologies⁵³, were performed to elucidate the radiation-induced redox chemistry of americium over a range of aqueous nitric acid concentrations at 20 °C. Both gamma and alpha radiation stochastic track simulations were performed for aerated ($[\text{O}_2] = 2.5 \times 10^{-4} \text{ M}$), acidic solutions. For alpha radiation, an array of energies were simulated (0.1 to 6.0 MeV) and subsequently integrated to 5.4 MeV to derive the predicted self-radiolysis yields for americium-243. Stochastic radiation track yields, in conjunction with nitrate and nitric acid direct effect yields⁵⁹, were used as initial parameters for a deterministic model, and solved using the FACSIMILE numerical algorithm (MCPA software). The radioactive decay of americium, ingrowth and subsequent decay of daughter nuclides, and partitioning of decay energies was accounted for. For a complete description of this modeling methodology see reference 53.

Table 1. Supporting americium reactions and rate coefficients used in the multi-scale model.

chemical reaction	rate coefficient ($\text{M}^{-1} \text{s}^{-1}$)	Reference
$\text{AmO}_2^{2+} + \text{HNO}_2 \rightarrow \text{AmO}_2^+ + \cdot\text{NO}_2 + \text{H}_{\text{aq}}^+$	4.38×10^4	<i>this work</i>
$\text{AmO}_2^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{AmO}_2^+ + \text{HO}_2\cdot + \text{H}_{\text{aq}}^+$	1.69×10^7	<i>this work</i>
$\text{AmO}_2^{2+} + \text{HO}_2\cdot \rightarrow \text{AmO}_2^+ + \text{O}_2 + \text{H}_{\text{aq}}^+$	2.73×10^7	<i>this work</i>
$\text{AmO}_2^+ + \cdot\text{NO}_3 \rightarrow \text{AmO}_2^{2+} + \text{NO}_3^-$	2.50×10^8	60
$\text{AmO}_2^+ + \cdot\text{OH} \rightarrow \text{AmO}_2^{2+} + \text{OH}^-$	4.70×10^8	<i>this work</i>
$2\text{AmO}_2^+ + 4\text{H}_{\text{aq}}^+ \rightarrow \text{AmO}_2^{2+} + \text{Am}^{4+} + 2\text{H}_2\text{O}$	$2.27 \times 10^{-6} \text{M}^{-5} \text{s}^{-1}$	<i>this work</i>
$\text{Am}^{4+} + \text{H}_2\text{O} \rightarrow \text{Am}^{3+} + \cdot\text{OH} + \text{H}_{\text{aq}}^+$	$\geq 1.00 \times 10^{-4}$	<i>this work</i>

The chemical reaction set employed used compilations by Buxton *et al.*⁶¹ and Elliot and Bartels,⁶² established nitrate and nitric acid reactions outlined in reference 53, and supplementary americium reactions given in Table 1. No additional bismuthate reaction kinetics were included, as previous work showed negligible dependence on oxidant identity (bismuthate vs. copper periodate).¹⁶

RESULTS AND DISCUSSION

Trivalent Americium. Absorption spectra for the steady-state gamma irradiation of Am(III) in 9.0 M HNO_3 is given Figure 1, clearly showing negligible change in the absorption intensity (and thus concentration) of Am(III) as a function of absorbed dose.

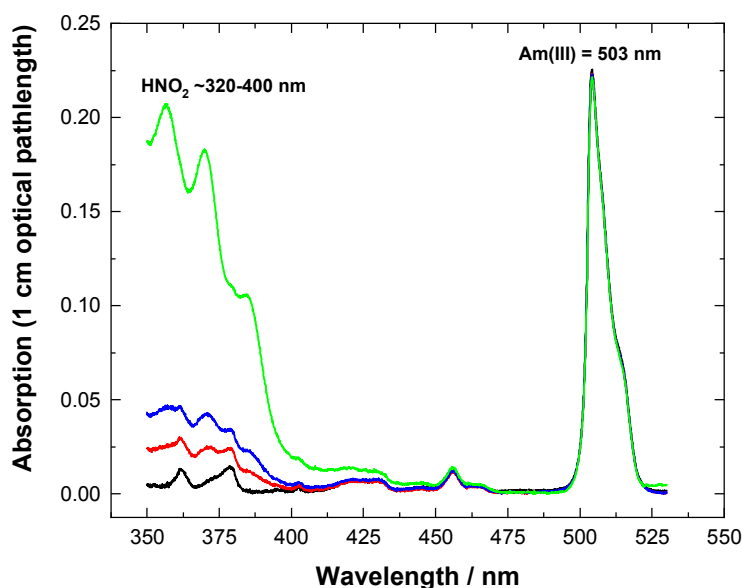


Figure 1. Absorption spectra for the gamma radiolysis (0.85 Gy s^{-1}) of 1 mM americium in 9.0 M HNO_3 : 0 (**black**), 1.5 (**red**), 3.0 (**blue**), and 15.0 kGy (**green**).

This observation is unsurprising considering the available literature for radiation-induced Am(III) chemistry concerns reactions of the electron and $\cdot\text{OH}$,^{41,63,64} both of which are completely scavenged in concentrated HNO_3 solutions, as outlined by the following reactions:
61,65



Further, the proposed one-electron transfer products would be either Am(II) or Am(IV), both of which are only stable under strongly complexing conditions, and rapidly return to Am(III) by reaction with the surrounding media.⁴ The absence of steady-state radiation-induced Am(III) redox chemistry is further suggested by the ingrowth of HNO_2 , which is the predominant steady-state product from HNO_3 radiolysis, and one of the key species responsible for driving actinide oxidation state distributions.^{16,66,67} Confirming Am(III) has little interaction with the radiolysis products of aqueous HNO_3 is crucial for interpreting the radiation-induced redox chemistries of

the americium states, because, regardless of the chemical oxidation procedure, there is always a small fraction of Am(III) present.

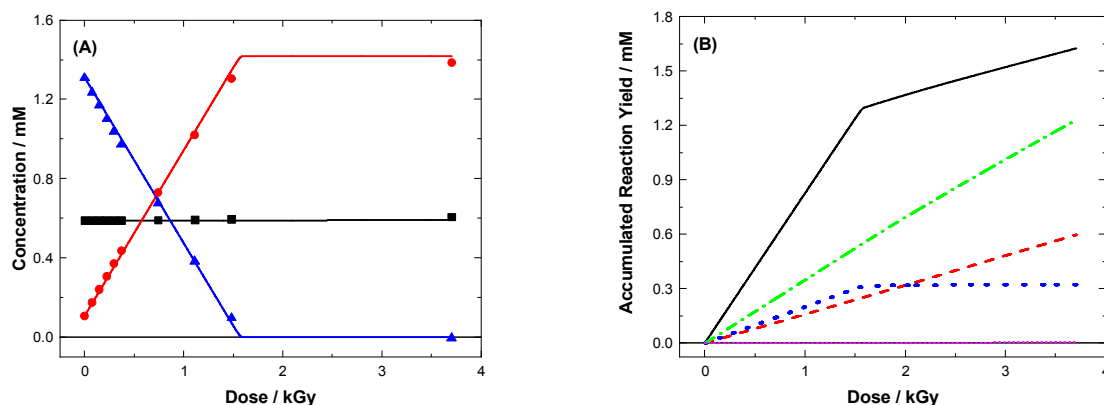


Figure 2. (A) Concentration of Am(III) (■), Am(V) (●), and Am(VI) (▲) as a function of absorbed dose for the gamma radiolysis (1.19 Gy s^{-1}) of 2 mM americium in aerated 3.0 M HNO₃. Complementary absorption spectra are shown in *Figure S1*. Solid lines are predicted values from multi-scale modelling calculations. (B) Calculated accumulated americium reaction kinetics: AmO₂²⁺ + HNO₂ (Solid Black), AmO₂²⁺ + H₂O₂ (Dashed Red), AmO₂²⁺ + HO₂[•] (Dotted Blue), AmO₂²⁺ + [•]NO₃ (Dot-Dash Green), and AmO₂²⁺ + [•]OH (Short-Dotted Magenta).

Gamma Irradiation of the Americium States. Figure 2 (A) shows changes in the measured oxidation state speciation of initially predominantly Am(VI) in 3.0 M HNO₃ solution irradiated by gamma irradiation. The Am(VI) is quantitatively converted into Am(V) as a function of absorbed dose, affording an average G -value of $0.80 \pm 0.01 \mu\text{M J}^{-1}$, until complete conversion is achieved. Within the investigated dose range, the concentration of Am(III) remains constant. Multi-scale modeling calculations, plotted alongside experimental data in Figure 2 (A), are in excellent agreement with the experimental data and provide critical mechanistic insight into the key processes responsible for the gamma radiation induced redox behavior of Am(V) and Am(VI), as given in Figure 2 (B). We found that one-electron reduction of Am(VI) to Am(V) is achieved by HNO₂ (64%)*, H₂O₂ (23%)*, and, to a lesser extent, HO₂[•] (13%)*:¹⁶



* Percentage contribution calculated from accumulated reaction kinetics, the rate coefficients for which were optimum values determined by modeling experimental data, see Table 1.

The total rate of Am(VI) reduction is slowed by re-oxidation of Am(V) by the nitrate radical ($\cdot\text{NO}_3$, $E^\circ = 2.3 - 2.6 \text{ V}$)⁶⁸ (>99%)*, and to a much lesser extent, $\cdot\text{OH}$ (<1%)*:



Once Am(VI) is completely consumed, the concentrations of all three americium oxidation states (III, V, and VI) remain constant. The steady-state reducing species (HNO_2 and H_2O_2) inhibit net re-oxidation of Am(V) to Am(VI) by $\cdot\text{NO}_3/\cdot\text{OH}$. This general trend is consistent for all investigated concentrations of americium and HNO_3 under gamma irradiation, see *Supplementary Material*. Although there is negligible difference in $G_\gamma(\text{Am(VI)})$ with respect to the concentration of americium, there is, however, a HNO_3 concentration dependence, as shown in Table 2.

Table 2. Average G -values for Am(VI) reduction in aerated, aqueous HNO_3 solutions, obtained from linear fits to data.

[HNO_3] (M)	G -Value ($\mu\text{M J}^{-1}$)	
	gamma rays (G_γ)	alpha particles (G_α)
1.0	0.87 ± 0.02	1.52 ± 0.01
3.0	0.80 ± 0.01	1.18 ± 0.01
6.5	0.70 ± 0.03	0.64 ± 0.02 ¹⁶

As the concentration of HNO_3 is increased from 1.0 to 6.5 M, the rate of Am(VI) reduction decreases. Calculations indicate that this effect is due to the acid-catalyzed reaction of HNO_2 with H_2O_2 , reaction (9), decreasing the availability of both species for Am(VI) reduction.

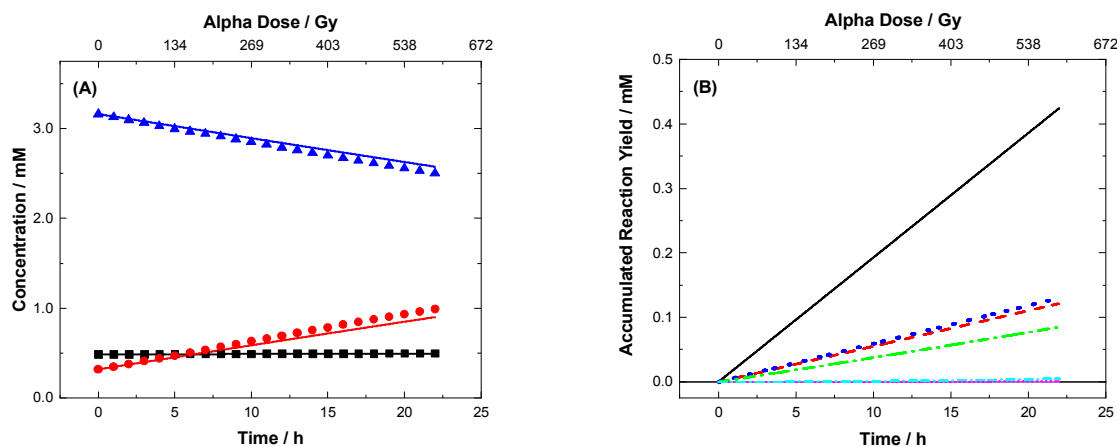


Figure 3. (A) Concentration of Am(III) (■), Am(V) (●), and Am(VI) (▲) as a function of time for the alpha self-radiolysis ($7.47 \times 10^{-3} \text{ Gy s}^{-1}$) of 4 mM americium in aerated 3.0 M HNO₃. Complementary absorption spectra are shown in *Figure S2*. Solid lines are predicted values from multi-scale modelling calculations. (B) Calculated accumulated americium reaction kinetics: AmO₂²⁺ + HNO₂ (Black Solid), AmO₂²⁺ + H₂O₂ (Dashed Red), AmO₂²⁺ + HO₂[•] (Dotted Blue), AmO₂⁺ + [•]NO₃ (Dot-Dash Green), AmO₂⁺ + [•]OH (Short-Dotted Magenta), and AmO₂⁺ disproportionation (Short-Dash-Dot Cyan).

Alpha Self-Irradiation of Americium States. The measured oxidation state speciation of pre-oxidized americium induced by alpha self-irradiation in 3.0 M HNO₃ is shown in Figure 3 (A). As the alpha dose received by the system increases with time, the concentration of Am(VI) decreases, with complimentary ingrowth of Am(V), while the residual concentration of Am(III) remains constant. These observations are consistent with those made for gamma irradiations: Am(VI) reduction by HNO₂ (63%)*, H₂O₂ (18%)*, and HO₂[•] (19%)*, and Am(V) oxidation by [•]NO₃ (>99%)* and [•]OH (<1%)*, Figure 3 (B). However, the radiolytic consumption of Am(VI) in 3.0 M HNO₃ is about 48% greater for alpha self-irradiation than for gamma, ($G_{\alpha} = 1.18 \pm 0.01 \mu\text{M J}^{-1}$). The increased rate of Am(VI) consumption here results from the higher linear energy transfer (LET) of alpha particles; i.e., in going from gamma rays to alpha particles, the rate of energy deposition along a radiation track increases, promoting second-order processes, and thereby increasing molecular yields over radical yields, e.g., H₂O₂ over [•]OH. This is demonstrated in Table 3, which shows calculated *G*-values for the products of water radiolysis at 1 μs following energy deposition in the presence of 3.0 M HNO₃.⁵⁶⁻⁵⁸

Table 3. Calculated G -values for the radiolysis of water at 1 μs in the presence of 3.0 M HNO_3 .

Species	G -Value ($\mu\text{M J}^{-1}$)	
	gamma rays (G_γ)	alpha particles (G_α)
H_2	0.01	0.02
H_2O_2	0.06	0.14 [†]
HO_2^\bullet	0.05	0.02
H_2O	0.02	0.05
$\text{NO}_3^{2-}/\text{HNO}_3^{*-}$	0.39	0.30
$^\bullet\text{NO}_3$	0.32	0.07

Firstly, $G_\alpha(\text{H}_2\text{O}_2)$ is significantly greater than $G_\gamma(\text{H}_2\text{O}_2)$, due to enhanced $^\bullet\text{OH}$ recombination.⁶¹



The effects of this are two-fold: a greater amount of H_2O_2 is available for Am(VI) reduction in alpha irradiated systems; and enhanced $^\bullet\text{OH}$ recombination reduces $G_\alpha(^\bullet\text{OH})$ and $G_\alpha(^\bullet\text{NO}_3)$, meaning there are fewer oxidizing species to slow net Am(VI) reduction. Secondly, the reduction in $G_\alpha(^\bullet\text{OH})$ and $G_\alpha(^\bullet\text{NO}_3)$ also increases the availability of HNO_2 for Am(VI) reduction, offsetting the small decrease in the yield of HNO_2 precursors, $\text{NO}_3^{2-}/\text{HNO}_3^{*-}$, a consequence of enhanced geminate and non-geminate recombination of $e_{\text{pre}}^-/e_{\text{aq}}^-$ and water cations (H_2O^{*+}).^{61,65}



Disproportionation of Am(V). For both gamma and alpha irradiation scenarios, consumption of Am(VI) ultimately leads to a steady-state concentration of Am(V) and Am(III). Prolonged irradiation of these Am(V)/Am(III) HNO_3 systems eventually leads to the reduction of Am(V) and quantitative ingrowth of Am(III), as demonstrated by the alpha self-irradiation of americium in 1.0 M HNO_3 in Figure 4 ($G_\alpha(\text{Am(V)})/G_\alpha(\text{Am(III)}) = 0.021 \mu\text{M J}^{-1}$).

[†] The calculated $G_\alpha(\text{H}_2\text{O}_2)$ for acidic nitrate solutions is slightly lower than the yield measured by Roth and LaVerne (reference 69) for aqueous solutions irradiated with 5 MeV He^{2+} ions (~ 0.169 at pH 0). This may be due to differences in LET incurred by integrating to 5.4 MeV for the ^{243}Am α -particles used in this work.

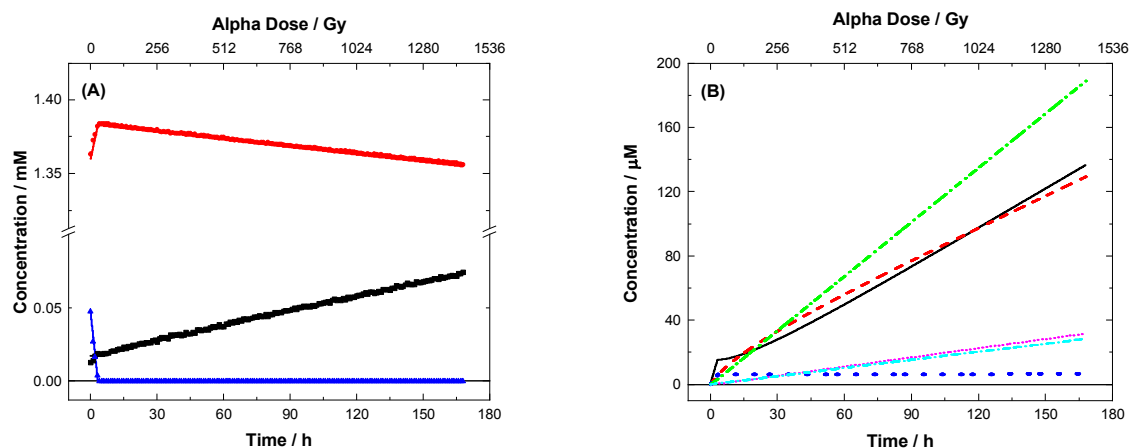
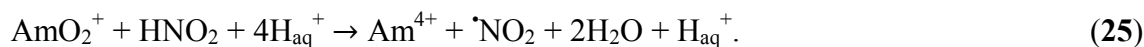
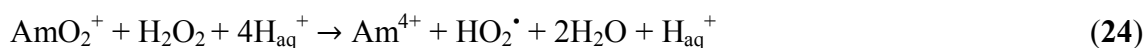
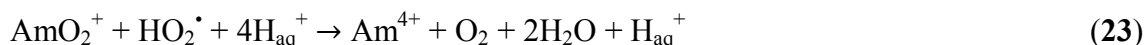
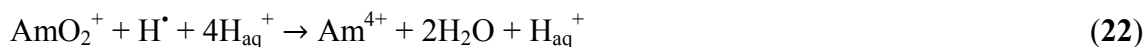


Figure 4. (A) Concentration of Am(III) (■), Am(V) (●), and Am(VI) (▲) as a function of time for the alpha self-radiolysis ($2.37 \times 10^{-3} \text{ Gy s}^{-1}$) of 1.39 mM americium in aerated 1.0 M HNO₃. Complementary absorption spectra are shown in *Figure S3*. Solid lines are predicted values from multi-scale modelling calculations. (B) Calculated accumulated americium reaction kinetics: AmO₂²⁺ + HNO₂ (Black Solid), AmO₂²⁺ + H₂O₂ (Dashed Red), AmO₂²⁺ + HO₂[•] (Dotted Blue), AmO₂⁺ + [•]NO₃ (Dot-Dash Green), AmO₂⁺ + [•]OH (Short-Dotted Magenta), and AmO₂⁺ disproportionation (Short-Dash-Dot Cyan).

A combination of radical and molecular processes have been postulated to explain the slow radiation-induced autoreduction of Am(V). In addition to reactions (1) – (4) the following reactions can also occur:^{19,20,21,26,29,31,40,43}



For aerated, aqueous HNO₃ solutions, reactions (1) and (22) are inhibited by scavenging processes, for example reactions (10), (11), (12), and the following:^{61,70,71}



This leads to additional formation of HO₂[•], H₂O₂, and HNO₂, which supports previous observations of enhanced Am(V) reduction in the presence of HO₂[•] and H₂O₂,^{27,28,30} and a reduced rate of Am(V) reduction in HNO₃ due to the intimate relationship between HNO₂ and H₂O₂, reaction (9).^{43,45} However, our multi-scale calculations disagree with this interpretation, as they show that the radiolytic reduction of Am(V) by these processes leads to significant

disagreement with experimental data, especially with respect to the changes in radiation quality. For example, even if very low rate coefficients ($<1 \text{ M}^{-1} \text{ s}^{-1}$) are employed by calculation for reactions (23), (24), and (25), significantly more Am(V) is consumed than measured, leading to ingrowth of Am(VI), which is not observed in Figure 4 (A). Agreement between experiment and calculation is attained in Figure 4 (A) and all other relevant figures in *Supplementary Information* by presuming disproportionation of Am(V) as the dominant source of reduction, instead of radiolytic reduction.

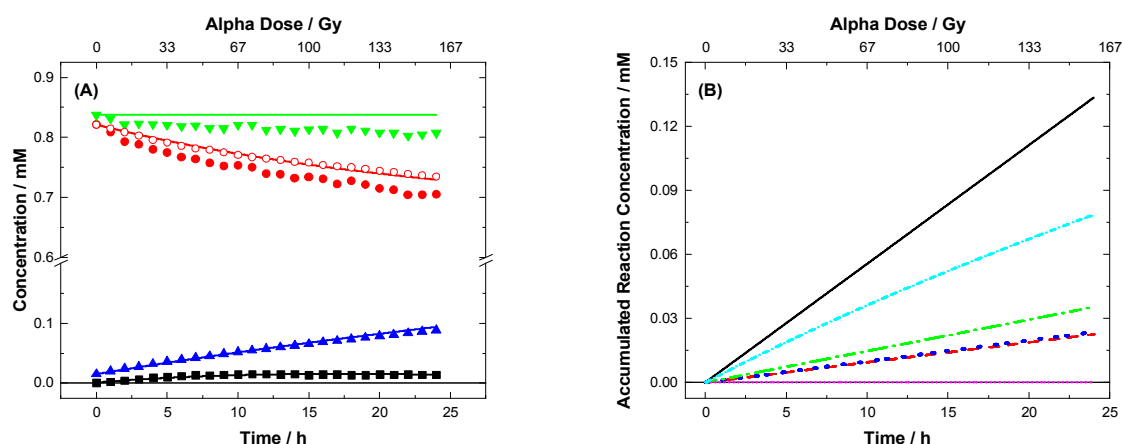
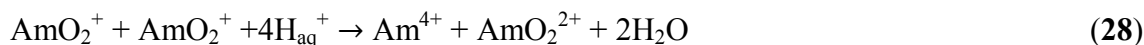
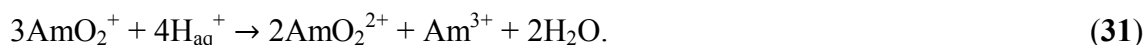


Figure 5. (A) Concentration of Am(III) (■), Am(V) (●), corrected Am(V) $\leq 5\%$ (○)[‡], Am(VI) (▲), and Am mass balance (▼) as a function of time for the alpha self-radiolysis ($1.85 \times 10^{-3} \text{ Gy s}^{-1}$) of 0.84 mM americium in aerated 6.5 M HNO₃. Complementary absorption spectra are shown in **Figure 6**. Solid lines are predicted values from multi-scale modelling calculations. (B) Calculated accumulated americium reaction kinetics: Am(VI) + HNO₂ (**Black Solid**), Am(VI) + H₂O₂ (**Dashed Red**), Am(VI) + HO₂· (**Dotted Blue**), Am(V) + ·NO₃ (**Dot-Dash Green**), Am(V) + ·OH (**Short-Dotted Magenta**), and Am(V) disproportionation (**Short-Dash-Dot Cyan**).

Disproportion of Am(V) has been postulated to proceed through the following reactions:^{26,72}



which gives the net equation:



[‡] For 6.5 M HNO₃, the initial optimized molar extinction coefficient for Am(V) ($\epsilon = 36.8 \pm 0.77 \text{ M}^{-1} \text{ cm}^{-1}$)¹⁶ afforded a reproducible progressive loss in total americium mass balance, attributed to perturbation of ϵ by radiolytic changes in solution composition and/or experimental uncertainty. Correction of ϵ by $\leq 5\%$ as a function of time gives mass balance.

Although ingrowth of Am(VI) has been observed,^{72,73,75} providing evidence for Am(V) disproportionation, we only measure this for 6.5 M HNO₃, as shown in Figure 5 and Figure 6.

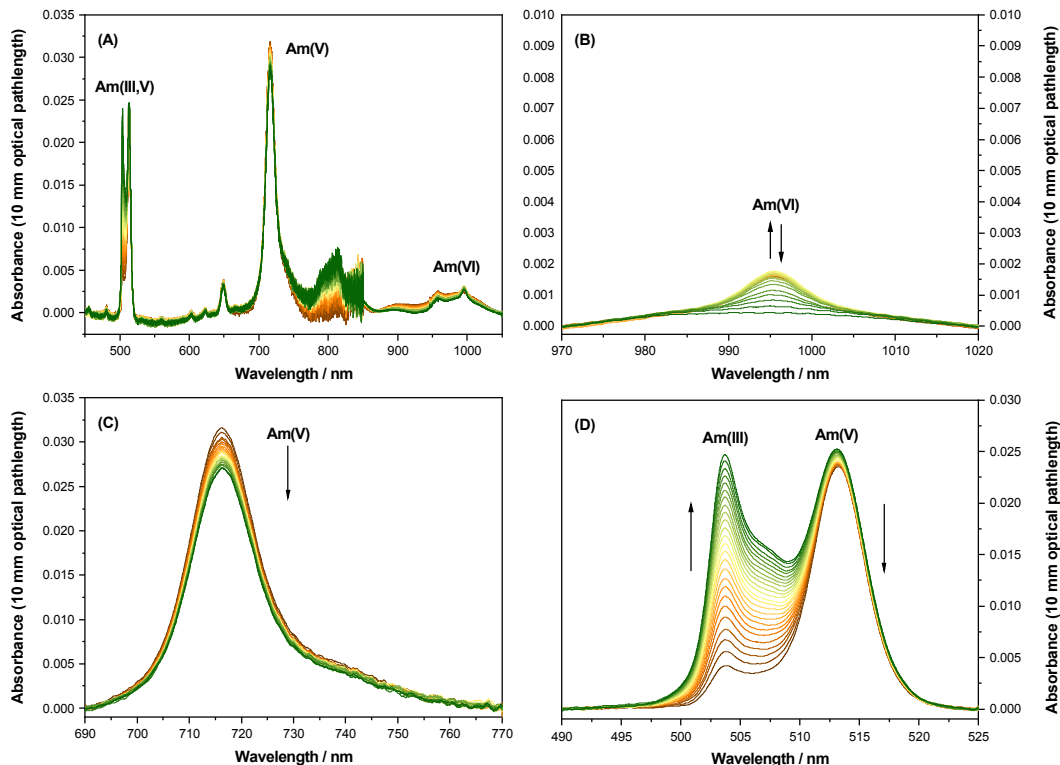


Figure 6. UV-Vis spectra for the alpha self-radiolysis ($1.85 \times 10^{-3} \text{ Gy s}^{-1}$) of 0.84 mM americium in aerated 6.5 M HNO₃: complete spectrum (A) and changes in absorption of absorption of Am(VI) at 995 nm (B), Am(V) at 718 nm (C), Am(III) and Am(V) at 503 and 513 nm (D), respectively. Arrows indicate the change in absorption peak growth or decay.

All other investigated systems showed no evidence for the steady-state ingrowth of Am(VI) from disproportionation, in agreement with Runde and Kim.²⁵ This is consistent with the accumulation of HNO₂ and H₂O₂ rapidly reducing the Am(VI) formed by disproportionation. The formation of Am(VI) in 6.5 M HNO₃ is observed because HNO₂ and H₂O₂ are consumed to a much greater extent by reaction (9). Once the concentration of Am(VI) is sufficiently high it will again compete for HNO₂ and H₂O₂, undergoing reduction and reaching a steady-state, as shown in Figure 5 (A) and Figure 6 (B).

The authors recognize the possibility of a thermodynamically favorable tri-molecular two-electron Am(V) reduction process. However, the presented calculations for Am(V)

disproportionation employ bimolecular reaction (28) only, the energetic favorability of which is kinetically driven by pseudo first-order solvent reduction of the tetravalent state (Am(IV)/Am⁴⁺). In reality, these two contrasting interpretations are likely composed of multiple elementary processes which are beyond the scope of this work. Additional efforts are currently devoted to elucidating these processes. Optimization of the individual rate coefficients for reaction (28) in 1.0, 3.0, and 6.5 M HNO₃ afforded a final, model-optimized, rate coefficient of $2.27 \times 10^{-6} \text{ M}^{-5} \text{ s}^{-1}$.

Table 4. Reported orders of H_{aq}⁺ dependency for Am(V) disproportionation.

Acid	concentration (M)	H _{aq} ⁺ order	Reference
HClO ₄	1 – 2	2.5	72
HClO ₄	3 – 8	5	72
HClO ₄	-	4	29,34,74
H ₂ SO ₄	-	4.6	29,29,72
HNO ₃	<3	1.5	40
HNO ₃	6	7	29
HNO ₃	1 – 7	4	75
HNO ₃	1.0, 3.0, and 6.5	4	<i>this work</i>

The disproportionation of Am(V) is seen to be strongly dependent upon the concentration of H_{aq}⁺, although there is some controversy over the exact dependence, as shown in Table 4. We calculate a fourth order dependency on H_{aq}⁺, which is stoichiometrically sound, and consistent with a number of findings for HClO₄ and HNO₃.^{29,34,74,75} However, it is difficult to compare the final rate coefficient calculated here with those previously reported as a consequence of differing mechanistic interpretations. This is most likely a reflection of the disparity between empirical determination and multi-scale calculation, wherein the multi-scale model prediction includes a large range of redox and radiolytic processes.

Despite the incorporation of Am(V) disproportionation, we observe no spectrophotometric evidence for the formation of Am(IV), only the ingrowth of Am(III), and, to a lesser extent, Am(VI) in 6.5 M HNO₃, as demonstrated by the UV-Vis spectra shown in Figure 6. Am(IV) has been prepared in a variety of concentrated, highly complexing media, allowing for some of its redox behavior to be discerned.^{9,76-80} These studies demonstrated that:

- In 10-15 M phosphoric acid, Am(IV) undergoes reduction without disproportionation, indicating reduction by the surrounding medium and/or radiolysis products.⁷⁶⁻⁷⁸ Lebedev *et al.* found that the rate of Am(IV) reduction is greater for lower concentrations of Am(IV), indicating that reduction by the solvent is a key process.⁷³
- Radiolytic alpha-induced reduction of Am(IV) was demonstrated by the addition of ²⁴¹Am ($\tau_{1/2}$ 432.2 years, 5.64 MeV alpha particle), which accelerated loss of Am(IV).⁸⁰
- At lower phosphoric acid concentrations Am(IV) was shown to undergo disproportionation.⁷³

With respect to this work, disproportionation of Am(V) via reaction (28) is expected to yield very small quantities of Am(IV) at any given time, making direct observation difficult under our experimental conditions. Further, considering the aforementioned redox behavior of Am(IV), these small quantities can be expected to undergo rapid pseudo first-order reduction with solvent molecules.

CONCLUSIONS

A quantitative, mechanistic, description for the effect of ionizing radiation on the americyl states in aerated, aqueous nitric acid solution has been established using a combination of experimental measurements and multi-scale computer modeling. These data were obtained for both alpha (self-radiolysis) and external gamma irradiation of americyl solutions over a range of acidity. The reduction of Am(VI) to Am(V) was found to be the most sensitive to the effects of ionizing radiation, undergoing rapid reduction with the steady-state products of HNO₃ radiolysis, i.e., HNO₂, H₂O₂, and HO₂[•], which dictated its practical lifetime under acidic conditions. In contrast, Am(V) is only susceptible to radiolytic oxidation, mainly through its reactions with NO₃[•], and is notably radiation-resistant with respect to direct one-electron reduction to produce Am(IV) in HNO₃. Our multi-scale modeling predicts that the lifetime of Am(V) is dictated by its rate of disproportionation, with a fourth-order dependence on [H_{aq}⁺] in agreement with previous experimental findings, giving an optimized rate coefficient of $k = 2.27 \times 10^{-6} \text{ M}^{-5} \text{ s}^{-1}$. This disproportionation initially produces Am(IV) and Am(VI) species, but the lack of any spectroscopic evidence in our study for Am(IV) suggests that solvent reduction of this cation occurs rapidly. The ultimate product of all the Am(VI)/Am(V) irradiations is Am(III), which shows great stability in a radiation field.

ASSOCIATED CONTENT

Supporting information available for complimentary UV-Vis spectra and additional gamma and alpha americium irradiations.

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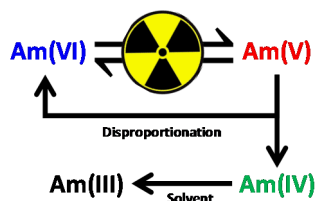
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Synopsis

A combination of experiment and multi-scaling modelling methods have been employed to elucidate the reaction mechanisms underpinning the gamma and alpha radiation-induced redox chemistry of penta- and hexavalent americium states in aqueous nitric acid solutions.