

Reduction Rates for Higher Americium Oxidation States in Nitric Acid

Fuel Cycle Research & Development

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SUMMARY

The stability of hexavalent americium was measured using multiple americium concentrations and nitric acid concentrations after contact with the strong oxidant sodium bismuthate. Contrary to our hypotheses Am(VI) was not reduced faster at higher americium concentrations, and the reduction was only zero-order at short time scales. Attempts to model the reduction kinetics using zero order kinetic models showed Am(VI) reduction in nitric acid is more complex than the autoreduction processes reported by others in perchloric acid. The classical zero-order reduction of Am(VI) was found here only for short times on the order of a few hours. We did show that the rate of Am(V) production was less than the rate of Am(VI) reduction, indicating that some Am(VI) undergoes two electron-reduction to Am(IV). We also monitored the Am(VI) reduction in contact with the organic diluent dodecane. A direct comparison of these results with those in the absence of the organic diluent showed the reduction rates for Am(VI) were not statistically different for both systems. Additional americium oxidations conducted in the presence of Ce(IV)/Ce(III) ions showed that Am(VI) is reduced without the typical growth of Am(V) observed in the systems sans Ce ion. This was an interesting result which suggests a potential new reduction/oxidation pathway for Am in the presence of Ce, however these results were very preliminary and will require additional experiments to understand the mechanism by which this occurs. Overall these studies have shown that hexavalent americium is fundamentally stable enough in nitric acid to run a separations process. However, the complicated nature of the reduction pathways based on the system components is far from being rigorously understood.

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ACRONYMS

INL	Idaho National Laboratory
PTFE	Polytetrafluoroethylene (Teflon)
UV/Vis	Ultra Violet/Visible

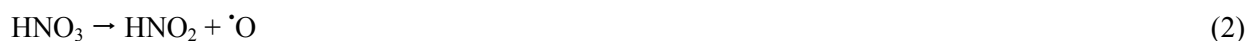
SIGMA TEAM FOR ADVANCED ACTINIDE RECYCLE: REDUCTION RATES FOR HIGHER OXIDATION STATES OF AMERICIUM

1. INTRODUCTION

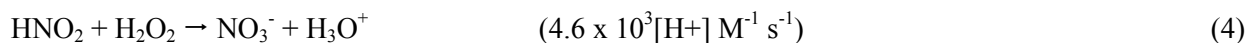
The first work describing the autoreduction of the higher oxidation states of americium was reported by Asprey and Stephanou in 1950. [1] In that report, hexavalent ^{241}Am was produced by peroxydisulfate oxidation and its reduction was observed spectrophotometrically in 1 M HClO_4 . It was reported that Am(VI) reduced to Am(V) in linear fashion. The production of Am(III) was low until all Am(VI) was reduced to Am(V) , suggesting a sequential reduction. The reduction rates were zero-order with respect to the high valent americium concentration but first-order with respect to the total americium concentration (0.9-33mM), being approximately 0.046 h^{-1} , and 0.023 h^{-1} , respectively. The effect of hydrogen ion concentration was thought to be small, while the faster rate for the Am(VI) to Am(V) reduction was attributed to only one equivalent being required for that reaction. Hall and Markin (1957) [2] reported similar kinetics for 2.6-8.0 mM total americium in 0.2 M HClO_4 , and reported 0.031 and 0.012 h^{-1} for Am(VI) and Am(V) , respectively. The authors attributed this so-called autoreduction to reaction with the H_2O_2 product of americium α -decay. The attribution is reasonable, since the main reducing agent in α -irradiated aqueous solution is expected to be H_2O_2 , which has a yield in neutral water of $0.1 \mu\text{mol J}^{-1}$. [3] The bimolecular rate constant for the reaction of Am(VI) with H_2O_2 at 25°C in perchloric acid was reported as $(4.592 \pm 0.007 - 0.12 \pm 0.01 \log[\text{H}^+])$, resulting in a value of $5.15 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in 0.1 M acid. [4] The reaction is shown in eq 1:



It should be noted that the rate constant for the reaction of Am(V) with H_2O_2 was reported by Zaitsev et al. (1960) [5] to have a similar value of $5.33 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in 0.1 M HClO_4 . However, it is known empirically that Am(V) is much more stable than Am(VI) , [1, 2, 6] possibly indicating that the reported rate constant for the $\text{Am(V)}/\text{H}_2\text{O}_2$ reaction is in error. Nitrous acid is produced from the direct radiolysis of nitrate anion and nitric acid [7]:



The yield of HNO_2 increases with the concentration of the irradiated nitric acid, although the yields reported have varied. The value probably falls in the range $(0.017) \cdot [\text{HNO}_3]$ to $0.031 \cdot [\text{HNO}_3] \mu\text{mol J}^{-1}$. [8, 9] It should also be a reducing agent for Am(VI) , based on analogy with its reduction of Np(VI) , [9] however, no rate constants have been reported. Nitrous acid and H_2O_2 effects on americium redox chemistry are partially mitigated by their reaction with each other: [7]



Based on an estimated yield of $0.02 \cdot [\text{HNO}_3]$ the concentration of HNO_2 would become competitive with H_2O_2 at HNO_3 concentrations of $> \sim 5 \text{ M}$. It can be seen that the rate of the reaction in eq. 4 should also be enhanced at higher acid concentrations. This, in combination with greater production of HNO_2 suggests that Am(VI) should be more stable at higher acidity.

Only two chemical reagents are routinely used for the preparation of Am(V) and/or Am(VI) in acidic solution. They are ammonium peroxydisulfate, $(\text{NH}_3)_2\text{S}_2\text{O}_8$ and sodium bismuthate, NaBiO_3 . Of these, only bismuthate is effective in nitric acid concentrations greater than about 0.3 M. Therefore, sodium bismuthate was used here to prepare Am(VI) over a range of nitric acid and americium concentrations, using routine procedures, [10] and the reduction of Am(VI) and subsequent appearance of Am(V) and Am(III) were monitored over time using UV/Vis spectroscopy. It was hypothesized that Am(VI) reduction would be zero-order in Am(VI) concentration, and faster at higher total americium concentrations, if radiolytically-produced H_2O_2 is the reducing agent. It was further hypothesized that Am(VI) would be more stable at high acid concentrations due to the scavenging of H_2O_2 by radiolytically produced HNO_2 . Preliminary results regarding the effect of dodecane and Ce(IV) on the reduction rate of Am(VI) are also reported.

2. EXPERIMENTAL

2.1 Materials

Sodium bismuthate (93% ACS reagent grade) was purchased from Chemsavers. Nitric acid (67-70% Omnitrace) was purchased from Fisher Scientific. The nitric acid solutions in these studies were made by dilution of the concentrated acid and standardized by titration with a standardized sodium hydroxide (50% w/w, Sigma Aldrich) solution using a phenolphthalein indicator (2% in ethanol, Sigma Aldrich). The 10 mL BD syringes (luer-lok tip) and 25 mm syringe filters (0.2 μm PTFE membrane, Pall Lifesciences) were purchased from VWR. The americium solutions were made by diluting INL stock solutions with the standardized nitric acid solutions to obtain the desired metal ion concentrations and acidities.

2.2 Oxidation Procedure

To probe the effect of americium concentrations on the reduction rates, oxidation experiments were conducted with $[\text{Am}]_{\text{total}} = 1.0, 2.0$ and 4.0 mM. The stability of Am(VI) at higher acidities was explored with oxidations at $[\text{HNO}_3] = 0.1, 1.0, 3.0$, and 6.5 M. Contact times were optimized to obtain maximum oxidation of Am(III) to Am(VI), 24 h for 1.0 and 3.0 M HNO_3 , 2 h for 6.5 M HNO_3 . The 0.1 M HNO_3 system yielded only Am(V) after a 24 h contact, and therefore no data is reported for that acid concentration.

Oxidation of Am(III) to Am(VI) was achieved by contacting 60 mg sodium bismuthate per 1 mL of Am solution. The sodium bismuthate is sparingly soluble and must be filtered away from the americium solution. After contact, the americium/sodium bismuthate solutions were loaded into the 10 mL syringe using Pasteur pipettes (the use of glass limits contact of americium solutions with the potentially reducing environment introduced by plastics) and filtered through the syringe filter. The solutions free of particulates were then loaded into quartz cuvettes and the absorption spectra were collected using a CARY 6000i.

3. RESULTS & DISCUSSION

3.1 UV/Vis Spectroscopy

The characteristic absorptions for the various oxidation states of americium are 503 and 813 nm for Am(III), 513 and 718 nm for Am(V), and 666 and 999 nm for Am(VI). These absorption intensities are converted to concentration for each americium species present in solution using the Beer-Lambert law shown in eq 5:

$$A = \epsilon bc \quad (5)$$

Where A = absorbance, ϵ = extinction coefficient or molar absorptivity, b = path length (cuvette width), c = concentration of the absorbing species. The americium concentrations are plotted as a function of time to determine the reduction rate and kinetic order of the reactions. Figure 1 shows the unique absorption bands for each oxidation state of americium in these studies.

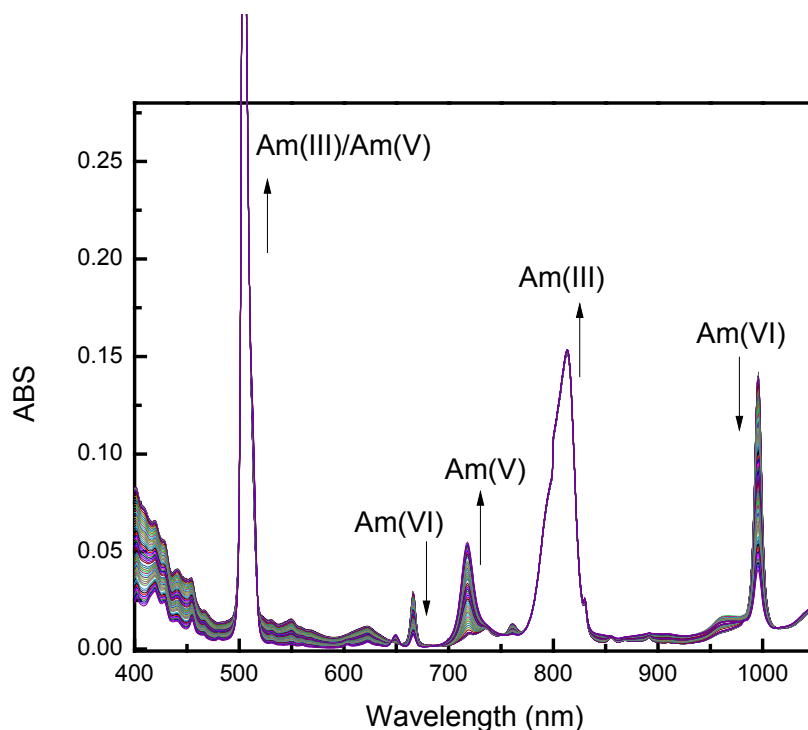


Figure 1. UV/Vis absorption spectra highlighting the multiple Am oxidation states at the corresponding wavelengths. The solution contains 4.0 mM total Am in 1.0 M HNO₃ contacted with sodium bismuthate for 24 h. The arrows indicate absorbance peak growth or reduction over a 48 h period.

The known extinction coefficients for the various oxidation states of americium are shown in table 1.

Table 1. Relevant molar extinction coefficients ϵ (M⁻¹ cm⁻¹) for various americium oxidation states used to calculate concentrations in these studies. The values reported are a combination of previously determined values by this group and gathered from the literature. [6, 11, 12]

[HNO ₃], M		Am(III)	Am(V)		Am(VI)	
		ϵ_{503}	ϵ_{513}	ϵ_{718}	ϵ_{666}	ϵ_{999}
0.1	LWCC	313.5	38.1			
0.1	1 cm	386.7		72.5	27.9	
1		320	40.3			83.3
6.5		272	36.4			

It is worth noting that due to the limited data in the literature, the extinction coefficients used in this study to calculate oxidized americium concentrations were used outside of the nitric acid concentrations they were determined in. Therefore some error is likely due to the media effects of increasing or decreasing the background electrolytes across the range of nitric acid concentrations used for these studies. However, at this time no widely accepted set of extinction coefficients for these peaks exists.

3.2 Americium Reduction Kinetics in 1.0 M HNO₃

A 24 h contact with sodium bismuthate yielded ~50% conversion of Am(III) to Am(VI), ~2% to Am(V), the remaining ~48% staying Am(III) in the 1.0 M HNO₃ system for all three americium concentrations. These data also show the Am(VI) was still detectable up to 55 h in 1.0 M HNO₃ regardless of total americium concentration. Figure 2 shows a representative sample of baseline corrected absorbance peaks used to determine concentration of the various Am species in all the nitric acid systems. The data show the disappearance of the 999 nm and 666 nm peaks (Am(VI)) as the 718 nm and 513 nm peaks grow in (Am(V)) as well as the growth of the 813 and the 503 nm peaks (Am(III)).

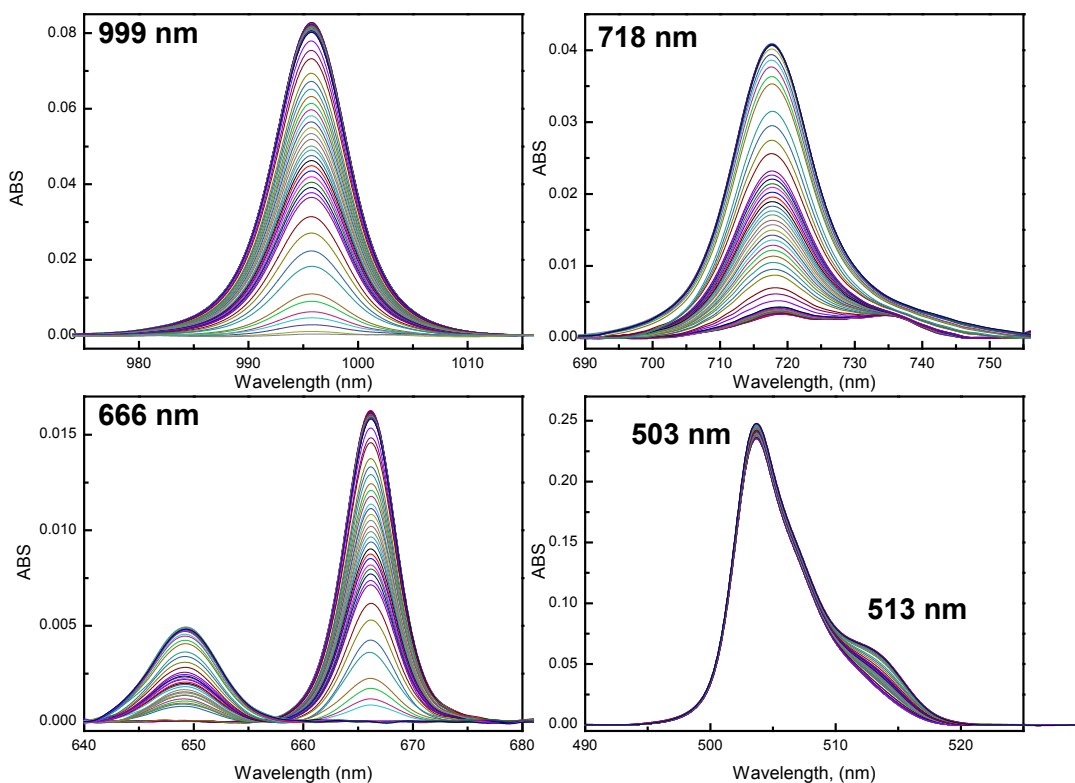


Figure 2. Absorbance peaks used to calculate the concentration of each americium oxidation state for all nitric acid systems. These data represent 2.0 mM Am in 1.0 M HNO₃, 72 h data collection.

Previous literature [1, 2] suggests that Am(VI) autoreduction occurs by reaction with its own radiolysis products, and should result in zero order kinetics with respect to the Am(VI) concentration, thus

producing linear plots of $[\text{Am(VI)}]$ vs. time. The change in absorbance peak heights illustrated in figure 2 were compared to zero order kinetic models, as shown in figure 3, for 1.0, 2.0 and 4.0 mM americium in 1.0 M HNO_3 solution.

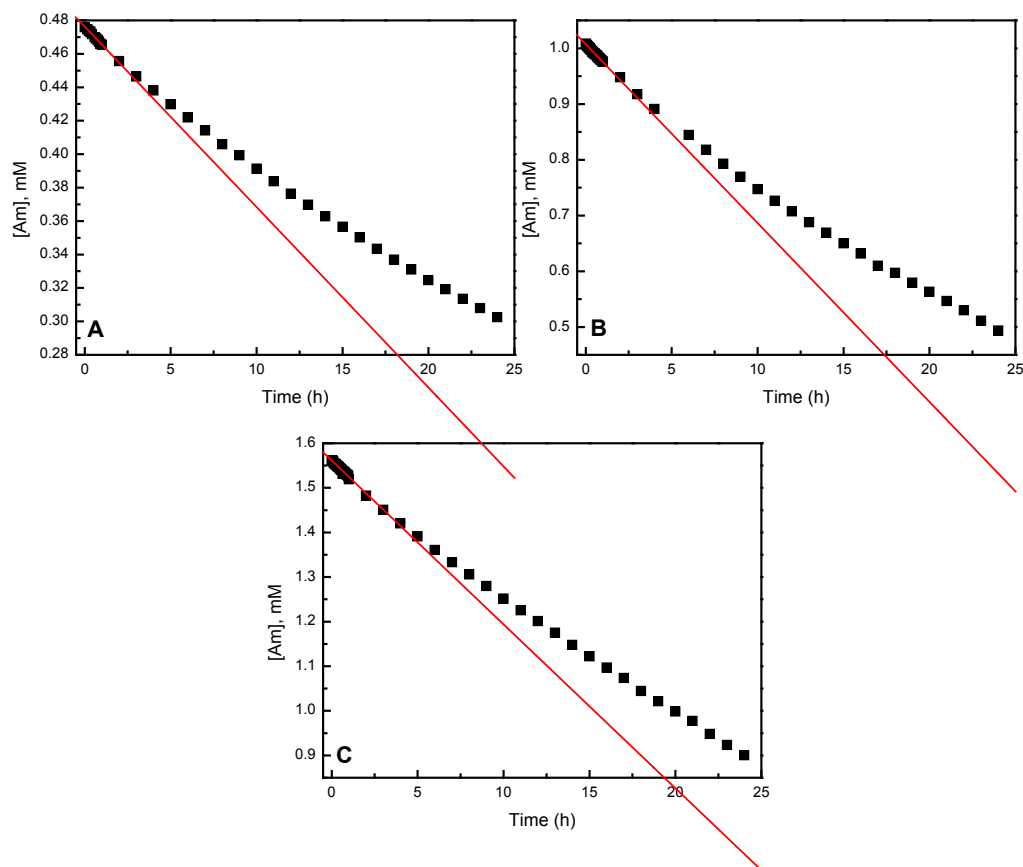


Figure 3. Concentration vs. time plots for (A) 1.0 mM Am, (B) 2.0 mM Am, and (C) 4.0 mM Am in 1.0 M HNO_3 . Squares indicate measured values and solid line indicates zero-order model.

The data in figure 3 are linear at shorter time scales up to nearly 5 h, then show significant departure from linearity for all three concentrations of americium for times up to 25 h. The initial linearity is probably the radiolytic autoreduction previously reported, while at longer time scales additional reactions become important. These data were therefore also treated using first and second order models. The results of these treatments are shown in figure 4, and did not produce linear plots consistent with first or second order kinetics. These results suggest mixed order kinetics. This would be consistent with departure from the initial zero order reduction as the radiolytically produced nitrous acid builds up to react with hydrogen peroxide, to decrease the rate of americium reduction. The disproportionation rate of Am(V) would also be expected to increase as the Am(V) concentration increases, further complicating the reduction kinetics.

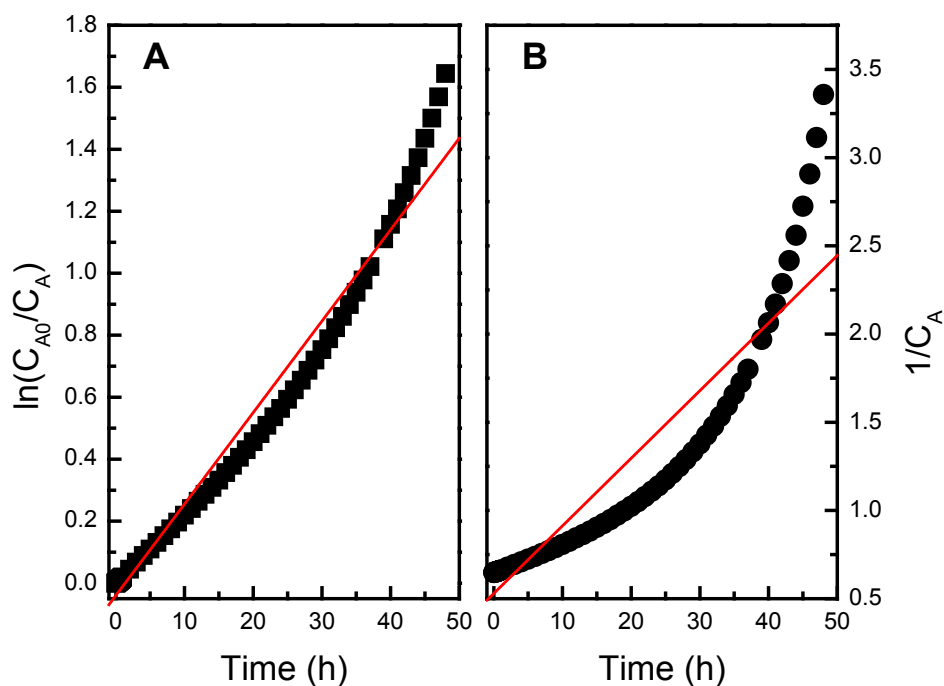


Figure 4. Analysis of the kinetic data using (A) first order (B) second order kinetic models. The plots presented are for 4.0 mM Am in 1.0 M HNO₃. Squares indicate measured data with model shown as solid line.

Although the data show complicated chemistry and the single order kinetic models are not adequate to model the Am(VI) reduction, the data in figure 3 do show linearity initially. If this linearity is considered zero order then information may be obtained by fitting the data over the 0- 2 h time scale. The obtained slopes may be divided by the total americium concentration to obtain reduction rates that are first order with respect to total americium concentration. An example of these plots and corresponding slopes are shown in figure 5.

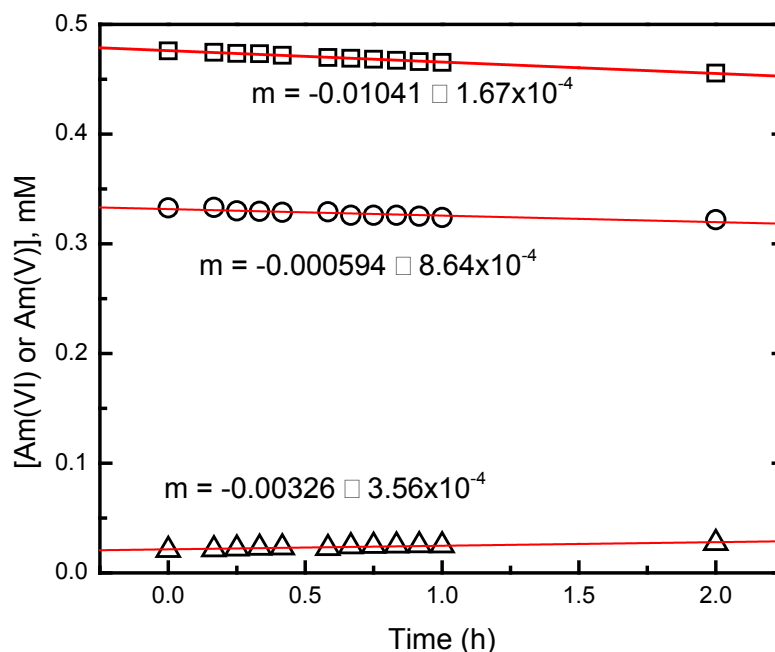


Figure 5. The autoreduction of Am(VI) and production of Am(V) in a solution containing 1.0 mM total Am and 1.0 M HNO₃. The absorptions used to calculate the Am concentration are as follows: (□) 999 nm, Am(VI), (○) 666 nm, Am(VI), (△) 718 nm, Am(V).

The results for the three americium concentrations in 1.0 M HNO₃ are reported in table 1. It can be seen that the Am(VI) rates calculated based on the 666 nm peak are not in agreement with those of the 999 nm peak. This is attributed to the large error associated with the slope determination based on this relatively weak absorbance. The data reported in table 1 show an extinction coefficient of 83.3 M⁻¹ cm⁻¹ for 999nm and 27.9 M⁻¹ cm⁻¹ for 666 nm; this represents a greater absorbance for the 999 nm peak by a factor of 3. The greater absorbance leads to more precise conversion of absorbance to concentration. However, it can be seen that increasing the americium concentration does not have any effect on the autoreduction rates of Am(VI), at least over this concentration range. It can also be seen that the rate of Am(V) production is about half the rate of Am(VI) reduction. This suggests that reduction routes for Am(VI) that bypass Am(V) may occur. This will be discussed in more detail later.

Table 2. Calculated Am(VI) reduction and Am(V) growth rates from the linear portion of the zero order kinetic plots for the 1.0 M nitric acid systems. The kinetic rates were calculated using data 0-2 h.

	999 nm		666 nm		718 nm	
[Am] _{total} , mM	Rate (h ⁻¹) ± 1 sigma		Rate (h ⁻¹) ± 1 sigma		Rate (h ⁻¹) ± 1 sigma	
4.0	0.008	0.002	0.005	0.001	0.004	0.001
2.0	0.009	0.002	0.007	0.002	0.004	0.001
1.0	0.010	0.001	0.006	0.001	0.003	0.001

3.3 Americium Reduction Kinetics in 3.0 M HNO₃

A 24 h contact with sodium bismuthate yielded ~85% conversion of Am(III) to Am(VI), ~4% to Am(V), the remaining ~10% staying Am(III) in the 3.0 M HNO₃ system for all three americium concentrations. Absorption spectra show that Am(VI) is detectable up to 72 h in 3.0 M HNO₃ for all the initial americium concentrations studied.

Attempts to model the Am(VI) reduction in the 3.0 M HNO₃ systems using the zero order kinetics proved unsuccessful since the data showed the same curvature present as in the 1.0 M HNO₃ systems. The data fitting was again not improved using first or second order kinetic models. The results of those fitting exercises resembled the results shown for 1.0 M HNO₃ in figure 4. The kinetic data did once again show linearity in the initial time periods of data collection suggesting autoreduction as found for the 1.0 M systems. The reduction rates for the 3.0 M nitric acid systems are shown in table 2.

Table 3. Calculated Am(VI) reduction and Am(V) growth rates from the linear portion of the zero order kinetic plots for the 3.0 M nitric acid systems. The kinetic rates were calculated using data 0-2 h.

	999 nm		666 nm		718 nm	
[Am] _{total} , mM	Rate (h ⁻¹)	± 1 sigma	Rate (h ⁻¹)	± 1 sigma	Rate (h ⁻¹)	± 1 sigma
4	0.010	0.002	0.007	0.001	0.004	0.001
2	0.011	0.002	0.007	0.001	0.004	0.001
1	0.008	0.001	0.010	0.002	0.005	0.001

In this case the higher Am(VI) yield allows for more confidence in the 666 nm data, and those results are in better agreement with the 999 nm results. The rates are similar to those reported for the 1.0 M HNO₃ system. Once again it can be seen that the Am(V) production is about half that of Am(VI) reduction. It appears from these two data sets that neither the americium concentration or the nitric acid concentration has any effect on the rate of autoreduction of Am(VI). These observations are made with caution for two reasons: 1) only about 8% of the kinetic data is utilized for these analyses, 2) secondary and tertiary reactions associated with radiolysis may be occurring before the 2 h limit; at this early stage of analysis, using the linear portion of the data to extract some information was a logical first approximation.

3.4 Americium Reduction Kinetics in 6.5 M HNO₃

A 2 h contact with sodium bismuthate yielded ~85% conversion of Am(III) to Am(VI), ~14% to Am(V), the remaining ~1-2% staying Am(III) in the 6.5 M HNO₃ system for all three americium concentrations. Absorption spectra show that Am(VI) is detectable after 110 h in 6.5 M HNO₃ for all the americium concentrations studied.

Consistent with the two previous nitric acid systems, attempts to model the Am(VI) reduction in the 6.5 M HNO₃ using the zero order kinetics also proved unsuccessful. Fitting iterations using first or second order kinetic models again offered no improvement. First and second order kinetic fitting exercises resembled the results shown in figure 4. A small portion of the data did show linearity in the initial time period of collection, out to 2.5 h, consistent with the assumed autoreduction for the two previous systems. Based on this linearity the same analysis was applied to the 6.5 M nitric acid systems. The Am(VI) reduction and Am(V) production rates for 6.5 M nitric acid are shown in table 3.

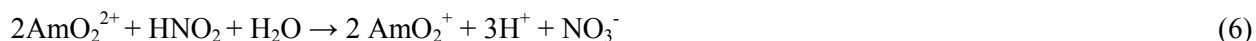
Table 4. Calculated Am(VI) reduction and Am(V) growth rates from the linear portion of the zero order kinetic plots for the 6.5 M nitric acid systems. The kinetic rates were calculated using data 0-2 h.

	999 nm		666 nm		718 nm	
[Am] _{total} , mM	Rate (h ⁻¹) ± 1 sigma		Rate (h ⁻¹) ± 1 sigma		Rate (h ⁻¹) ± 1 sigma	
4	0.012	0.003	0.005	0.001	0.003	0.001
2	0.011	0.003	0.007	0.001	0.004	0.001
1	0.009	0.002	0.006	0.002	0.004	0.001

A comparison of all the calculated Am(VI) reduction rates for 1.0 mM, 2.0 mM, and 4.0 mM americium in 1.0, 3.0, and 6.5 M HNO₃ show consistent overlap at one sigma error with an average rate for Am(VI) reduction around 0.010 ± 0.001 h⁻¹ using 999 nm, 0.007 ± 0.001 h⁻¹ using the less reliable 666 nm, and an average growth rate for Am(V) of 0.004 ± 0.0006 h⁻¹ using 718 nm. It appears that Am(V) growth rates do not correlate directly to Am(VI) reduction under any condition. This result is in agreement with those recently reported by Dares et al. [13] in 0.1 M HNO₃ using surface functionalized electrodes to electrolytically prepare Am(VI). This work suggests that there is a reduction routes bypassing Am(V) and is discussed in more detail later.

3.5 Effect of Increased Nitric Acid

The total kinetic data were collected over long time scales, e.g., up to 110 h. Collecting the kinetic data for this long has shown that Am(VI) stability increases with increasing nitric acid concentration, as was predicted, likely due to H₂O₂ and HNO₂ interactions illustrated in equation 4. Figure 6 shows normalized Am(VI) kinetic curves in 1.0, 3.0, and 6.5 M HNO₃. The data in figure 6 clearly show a decrease in the Am(VI) reduction rate over the long time periods observed for each system. This is also a clear indication that the Am(VI) reduction kinetics are slower with increasing nitric acid concentration. In addition to eq 1, other potential reduction pathways become important with increasing nitric acid concentration. These reactions involve radiolytically produced nitrous acid and disproportionation reactions of Am(V).



Thus, at least at least four pathways contribute to Am(VI), so-called, autoreduction. These are: 1) reduction by reactions with radiolytically-produced free radicals, which happen on a time scale to fast to measure here and which rate should be directly proportionally to the radiation dose rate (in this case directly proportional to the total [Am]); 2) reduction by radiolytically-produced H₂O₂; 3) reduction by radiolytically-produced HNO₂, with these mitigating each other as they grow into solution, and more-so at higher nitric acid concentration; 4) Am(V) disproportionation which increases with increasing [Am(V)] over time. Further there appear to be 1-, and 2-electron reduction pathways for Am(VI). The combined effects of all these reactions almost certainly rules out single order kinetics to describe these systems. Analyzing these types of data will require a more sophisticated approach such as stepwise model building using reactions with known reaction rate constants.

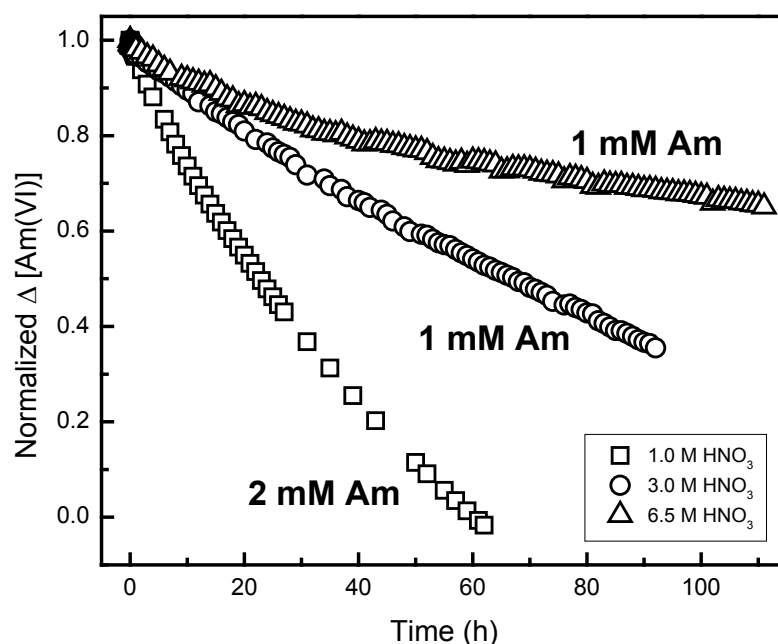


Figure 6. Normalized Am(VI) kinetic curves in 1.0, 3.0, and 6.5 M nitric acid to highlight the stability of the Am(VI) oxidation state as nitric acid is increased.

3.6 Electrolytically Determined Americium(VI) Reduction Rates

A comparison of all the calculated Am(VI) reduction rates over the linear range for 1.0 mM, 2.0 mM, and 4.0 mM americium in 1.0, 3.0, and 6.5 M HNO₃ show consistent overlap at one sigma error with an average rate for Am(VI) reduction around $0.010 \pm 0.001 \text{ h}^{-1}$ using 999 nm, $0.007 \pm 0.001 \text{ h}^{-1}$ using the less reliable 666 nm, and an average growth rate for Am(V) of $0.004 \pm 0.0006 \text{ h}^{-1}$ using 718 nm. It appears the Am(V) growth rates do not correlate directly to Am(VI) reduction under any condition. This result is in general agreement with that recently reported by Dares et al. [13] using surface functionalized electrodes to electrolytically prepare Am(VI). Those authors reported a reduction rate for Am(VI) of $2.3\text{E-}5 \text{ s}^{-1}$ (0.083 h^{-1}) with ingrowth of Am(V) at $1.6\text{E-}5 \text{ s}^{-1}$ (0.058 h^{-1}) for a 0.65 mM total americium solution containing initially 85 % Am(VI), in 0.1 M HNO₃. These rates, measured after the applied potential was turned off, are an order-of-magnitude faster than those reported here for the bismuthate system, at much lower americium and nitric acid concentrations. These authors suggested that Am(VI) had two reduction pathways; a one-electron reduction to Am(V), and a two-electron reduction to Am(IV). It is not clear why the reduction rate measured here is slower, although the presence of residual oxidant may have a role.

3.7 Effect of Organic Diluent

The stability of Am(VI) was further tested by contact with the common organic diluent, dodecane. A 1 mL aliquot of dodecane was placed on top of the americium solution in the cuvette and introduced to the spectrometer. The two phases were not agitated to create an emulsion, so any effect on the reduction kinetics introduced by dodecane would be diffusion controlled. The kinetic data were collected for 20 h and are shown in table 5.

Table 5. Reduction/Growth rates for Am(VI)/Am(V) in contact with a 1 mL aliquot of dodecane using a 2 h time increment. The americium solution contained 4.0 mM Am in 6.5 M HNO₃.

[Am] _{total} mM	999 nm		666 nm		718 nm	
	Reduction Rate (h ⁻¹)	± 1 sigma	Reduction Rate (h ⁻¹)	± 1 sigma	Growth Rate (h ⁻¹)	± 1 sigma
4.0	0.009	0.002	0.006	0.001	0.003	0.001

The results show no change in the reduction rate of Am(VI) when in contact with dodecane. A comparison of the reduction rates calculated for the same concentration of 4.0 mM Am from tables 3 & 4 show that the Am(VI) reduction rates in the absence of dodecane overlap with the observed reduction rate for the system in contact with dodecane. Comparison of the growth rates for Am(V) from data in tables 3 & 4 also show that the production of Am(V) was not influenced by contact with dodecane. This is an important result since the ultimate goal is to separate Am using solvent extraction, and dodecane is the common diluent in extraction formulations. Qualitative observations have previously shown that organophosphorous ligands such as TBP [11] and DAAP [10] are reducing toward Am(VI), but our unpublished work has suggested that monoamides such as DEHBA may be less so. Future work will measure quantitative americium reduction rates in the presence of these solvent extraction ligands. These results will provide an understanding the reduction pathways for Am(VI) in contact with organic diluents and extractants, of obvious importance in systems where the Am(VI)-containing aqueous phase may undergo multiple stages of organic phase contact.

3.8 Effect of Cerium on Am(VI) Reduction

Another factor that may influence Am(VI) stability in real world application is the presence of other redox active metals in solution. Cerium is one such example. A 1.0 mM americium solution was made 5.0 mM with Ce(III) in 6.5 M HNO₃ and oxidized concomitantly by contact with sodium bismuthate for 2 h to produce a solution containing Am(VI) and Ce(IV). The resulting solution was bright yellow from the Ce(IV), however, Ce(IV) absorbance begins at around 550 nm and did not interfere with Am(VI)/Am(V) absorbances at 999 nm, 666 nm and 718 nm. An example absorption spectrum containing Ce is shown in figure 7.

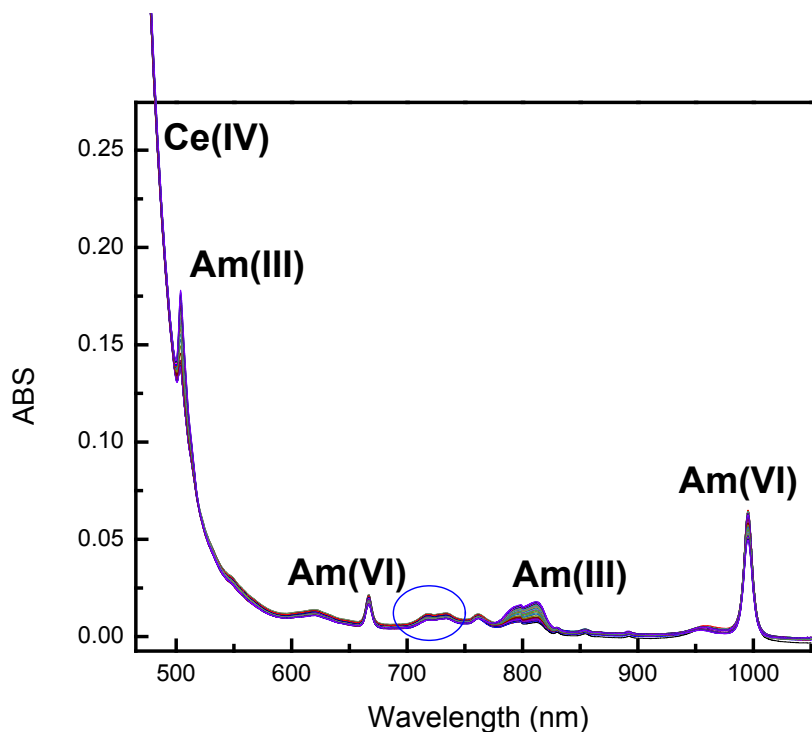


Figure 7. Characteristic absorption spectra for oxidized americium in the presence of Ce(IV). The absorbances represent 1.0 mM Am and 5.0 mM Ce in 6.5 M HNO₃.

The data show the expected absorbances at 999 nm (Am(VI)), 503 nm (Am(III)) and off scale absorbance beginning at 550 nm for Ce(IV). The Am(VI) concentration is seen to decrease with time. It can be seen in table 6 that this reduction is faster than observed in the absence of cerium as reported in tables 2-5. The absorbance peak for Am(V), 718 nm, showed no change over the 24 h period of data collection. This result is unexpected and suggests that Am(VI) reduction in the presence of cerium either bypasses Am(V), or that produced Am(V) is re-oxidized. It is probable the Am(V) is oxidized back to Am(VI) through the reduction of Ce(IV). This may be explained by taking a simplistic approach to comparing reduction potentials for Am and Ce. The reduction potential for $\text{AmO}_2^{2+} \rightarrow \text{AmO}_2^+$ is 1.6 V and the reduction potential for $\text{Ce(IV)} \rightarrow \text{Ce(III)}$ 1.76 V. Thus the reaction should be favorable. Additional experiments are currently being conducted with Am(V) and Ce(IV) to determine if this pathway is possible. However, the faster reduction of Am(VI) is unexplained, and deserves continued investigation. Additional experiments will be necessary to determine the reduction pathways for Am in the presence of not only Ce, but additional fission products found in the used fuel matrix. It should be noted that while the rate of Am(VI) reduction has increased, it still has long term stability sufficient for separations.

Table 6. Reduction rates for Am(VI) in the presence of Ce(IV) using a 2 h time increment. The americium solution contained 1.0 mM Am/5.0 mM Ce in 6.5 M HNO₃.

	999 nm		666 nm		718 nm
[Am] _{total} , mM	Reduction Rate (h ⁻¹)	± 1 sigma	Reduction Rate (h ⁻¹)	± 1 sigma	Growth Rate (h ⁻¹)
1.0	0.019	0.004	0.017	0.003	0

4. CONCLUSIONS

The stability of hexavalent americium was measured using multiple americium and nitric acid concentrations after contact with the strong oxidant sodium bismuthate. Initial studies were conducted to establish contact times to produce the greatest Am(VI) yield. It was determined that for 1.0 and 3.0 M HNO_3 , 24 h contacts produced 50% and 85% Am(VI) respectively. The 6.5 M HNO_3 systems only required a 2 h contact to achieve an 85% yield of Am(VI). Detectable Am(VI) persisted for over 48 h in 1.0 M HNO_3 , 72 h in 3.0 M HNO_3 and 110 h in 6.5 M HNO_3 . After a 24 h contact, the 0.1 M HNO_3 system produced Am(V) exclusively. The shorter necessary contact times for the higher acidities and the failure to produce Am(VI) in 0.1 M HNO_3 demonstrate that the oxidation of Am(III) to Am(VI) using sodium bismuthate has a strong proton dependence likely due to the increased solubility of BiO_3^- in more highly acidic media.

Contrary to our hypotheses Am(VI) was not reduced faster at higher americium concentrations, and the reduction was only zero-order at short time scales. Attempts to model the reduction kinetics using zero order kinetic models showed Am(VI) reduction in nitric acid is more complex than the autoreduction processes reported by others in perchloric acid. In fact, the analyses of these data over long time frames suggest that the kinetics for all the systems studied (regardless of americium or nitric acid concentration) are mixed order with complicating secondary reduction pathways introduced by secondary radiolysis products. The radiolysis products are generated by irradiation of H_2O and HNO_3 by α -decay. It appears that over time the longer-lived molecular radiolysis products such as H_2O_2 and HNO_2 build up in solution and begin to react with the Am species and/or themselves which has a large impact on the overall kinetics. Changes in the linearity of the kinetic models are indicators of additional reactions present in the systems. The data did show that our hypothesis that Am(VI) is more stable at higher nitric acid concentrations was correct.

The classical zero-order reduction of Am(VI) was found here only for short times on the order of a few hours. However, although zero-order reduction has been attributed to reduction by radiolysis products in the past, we measured no effect of changing americium concentration. We did show that the rate of Am(V) production was less than the rate of Am(VI) reduction, indicating that some Am(VI) undergoes two electron-reduction to Am(IV).

Experiments were also conducted to monitor the Am(VI) reduction in contact with the organic diluent dodecane. A direct comparison of these results with those in the absence of the organic diluent showed the reduction rates for Am(VI) were not statistically different for both systems. The result is a significant first step in understanding the potential reduction pathways for Am(VI) in solvent extraction processes since the envisioned separations using higher oxidation states will require multiple contacts with organic diluents and selected extractants.

Americium oxidations were also conducted in the presence of Ce(IV)/Ce(III) ions. These results showed that Am(VI) is reduced without the typical growth of Am(V) observed in the systems sans Ce ion. This was an interesting result which suggests a potential new reduction/oxidation pathway for Am in the presence of Ce. Currently, these results are very preliminary. Surprisingly, it also appears that the Am(VI) reduction rate was increased by a factor of 2 in the presence of Ce ion. The mechanism by which this would occur is not understood.

Overall these studies have shown that hexavalent americium is fundamentally stable enough in nitric acid to run a separations process. However, the complicated nature of the reduction pathways based on the system components is far from being rigorously understood. Additional studies will be needed before an understanding of the fundamental redox chemistry of americium is completely understood. Future work will examine the effects of extractants and other raffinate constituents on Am(VI) stability, as well as added alpha emitters to increase the alpha dose rate, but not the Am concentration.

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