

The Radiolysis of AmVI Solutions

Bruce J. Mincher
Nicholas C. Schmitt

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Nicholas C. Schmitt**

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**Idaho National Laboratory
Fuel Cycle Research & Development
Sigma Team for Minor Actinide Separations
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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SUMMARY

The reduction of bismuthate-produced AmVI by ^{60}Co gamma-rays was measured using post-irradiation UV/Vis spectroscopy. The reduction of AmVI by radiolysis was rapid, producing AmV as the sole product. Relatively low absorbed doses in the ~ 0.3 kGy range quantitatively reduced a solution of 2.5×10^{-4} M AmVI. The addition of bismuthate to samples during irradiation did not appear to protect AmVI from radiolytic reduction during these experiments. It was also shown here that AmV is very stable toward radiation. The quantitative reduction of the AmVI concentration here corresponds to 1.4 hours of exposure to a process solution, however the actual americium concentrations will be higher and the expected contact times short when using centrifugal contactors. Thus, the reduction rate found in these initial experiments may not be excessive.

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ACRONYMS

DAAP	Diamylamylphosphonate
FCR&D	Fuel Cycle Research and Development Program
GWD	Gigawatt days
INL	Idaho National Laboratory
LDRD	Laboratory Directed Research and Development Program
UV/Vis	Ultraviolet/Visible spectroscopy

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1. INTRODUCTION

The normal oxidation state of Am is Am(III). Its chemistry is very similar to that of the trivalent lanthanides, making separation from the lanthanides a difficult problem. However, Am in its higher oxidation states (IV, V and VI) has solution chemistry sufficiently different from the lanthanides(III) to allow for a solvent extraction-based separation. For example, we have shown that Am(VI) is readily separated from the non-oxidizable lanthanides, using 1 M diamylmethylphosphonate (DAAP) in dodecane as the solvent [1]. In that work we used room temperature oxidation of Am(III) to Am(VI) with the chemical oxidant sodium bismuthate. However, AmVI is not especially stable, and reduces with a half-life of minutes due to reaction with its own radiolysis products such as hydrogen peroxide and nitrous acid, and possibly by reaction with water. This suggests that AmVI might be readily reduced in the radiation fields associated with the fuel dissolution during the solvent extraction process. However, maintenance of the hexavalent oxidation state is important to the success of the proposed separation. Therefore, a series of experiments was conducted to evaluate the rate of AmVI reduction in solutions irradiated to high absorbed doses with a ^{60}Co gamma-ray irradiator. This report was written in response to the requirements associated with FCR&D milestone M3FT-13IN0303028. The results reported here are considered preliminary, and will be used in the design of additional measurements.

2. Experimental Methods

Samples containing 2×10^{-3} M Am in 1 M HNO_3 were oxidized using NaBiO_3 by the standard procedure. [1,2] To prepare a sufficient volume for irradiation while meeting radiological work control requirements, the samples were diluted by 50% prior to use, for a final total americium concentration of 1×10^{-3} M. These were then sealed in screw-capped UV/Vis cuvettes and irradiated for pre-selected periods of time using a ^{60}Co irradiator at a dose rate of $\sim 5 \text{ kGy h}^{-1}$. Two sample sets were irradiated; one in the presence of residual bismuthate solid and one for which clear liquid had been pipetted away from the residual solid after settling. Although this second sample appeared clear initially, by the end of the irradiation experiments a small film of bismuthate was visible on the bottom of the cuvette, and it cannot be considered bismuthate-free. The absorbance of AmIII, AmV and AmVI were measured by UV/Vis spectroscopy using techniques previously developed under INL LDRD funding for observing the effects of irradiation on Np redox chemistry. [3] Briefly, samples were removed from the irradiator and the UV-vis absorbance spectra were recorded over the wavelength range 450-1050 nm using a Cary 6000 spectrophotometer. These were then returned to the irradiator to receive additional exposure to the source. The process was repeated until the desired absorbed dose was obtained. Therefore, total time elapsed does not correspond to irradiation time for these samples. Ideally, an unirradiated reference sample would also have accompanied these samples to account for any redox chemistry that occurred not associated with irradiation, however; work control requirements precluded the use of this additional Am. The absorbance spectrum of the oxidized samples was also collected immediately after bismuthate treatment, and again 38 min later, prior to the first irradiation. Therefore, some indication of the non-irradiated reduction rate was still obtained.

3. Results

3.1 Samples nominally containing only trace residual bismuthate

The spectra of the nominally non-bismuthate containing, post-oxidation sample acquired immediately after preparation, and after transport to the irradiator are shown in Fig. 1. The concentration of AmIII indicated by the peak at 503 nm ($\epsilon = 320$ [4]) may be calculated as 7.5×10^{-4} M, indicating about 25% oxidation to AmVI. Quantitative oxidation was not desired for these experiments. No trace of AmV can be seen in this solution. The elapsed time between recording these spectra was 38 minutes, however, there was no change in the magnitude of the AmVI absorbance at 997 nm, or any production of AmV. Since we have previously measured the half-life of AmVI in the absence of bismuthate at minutes depending on the nitric acid concentration the stability of this sample over 38 min seems to indicate that some traces of bismuthate remained in solution. In fact, a brown film was visible on the bottom of the cuvette at the end of the experiment.

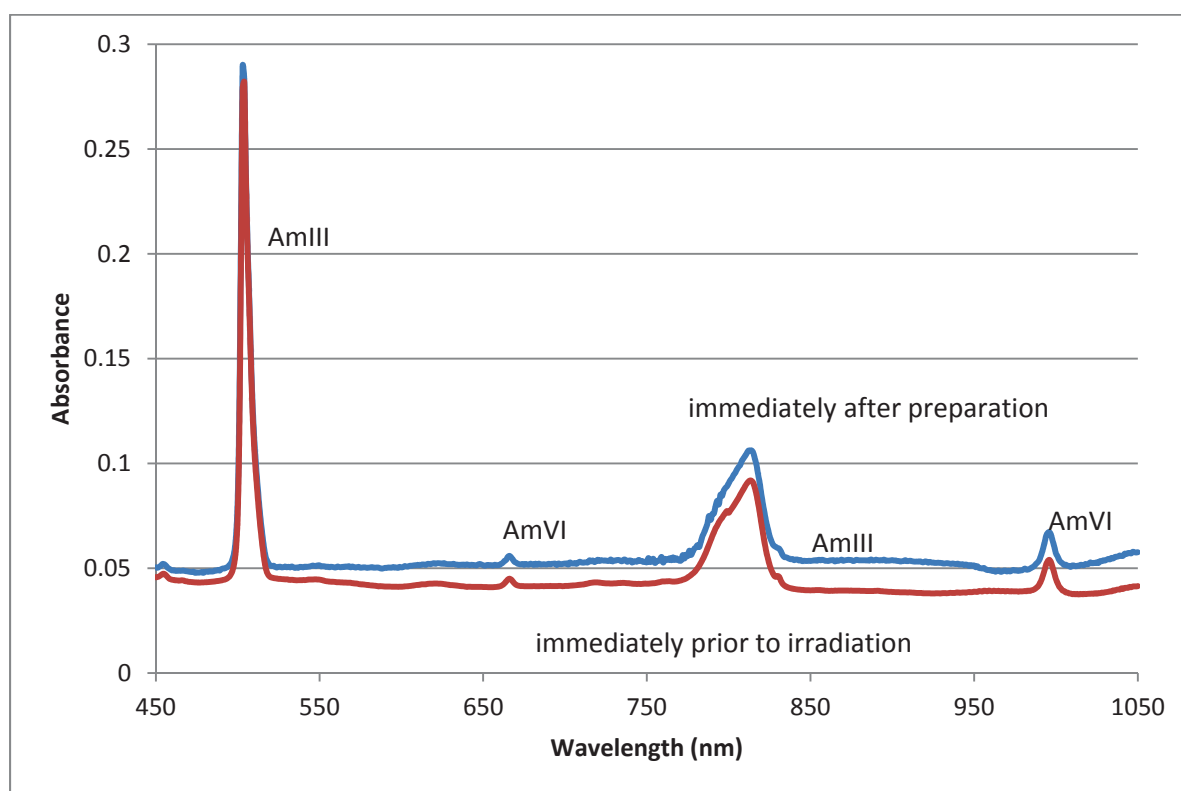


Figure 1. UV/Vis spectra of 1×10^{-3} M Am in 1 M HNO_3 oxidatively treated with sodium bismuthate. The spectra show the absorbance of AmIII and AmVI immediately after preparation, and after transport to the irradiator.

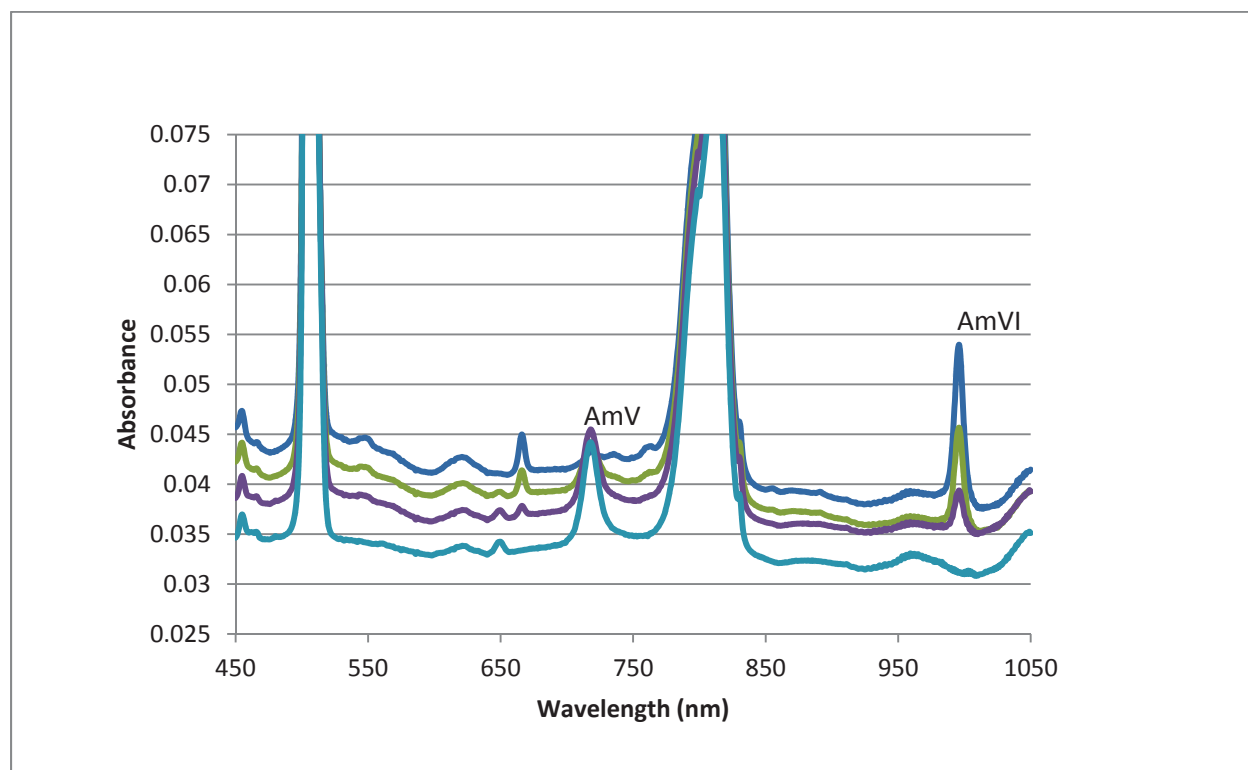


Figure 2. The radiolytic reduction of AmVI (997 nm) and ingrowth of AmV (718 nm) during irradiation by ^{60}Co gamma-rays. The maximum dose was 0.3 kGy.

Figure 2 shows the change in UV/Vis absorbance for samples initially containing 2.5×10^{-4} M AmVI (assuming an ϵ_{997} of $64 \text{ L mol}^{-1} \text{ cm}^{-1}$ [5]), irradiated in the nominal absence of residual bismuthate solid. It can be seen that the absorbance at 997 nm decreased rapidly with absorbed dose until after exposure to 0.3 kGy no AmVI was detectable. The decrease in AmVI absorbance was accompanied by the initial appearance and subsequent increase in AmV absorbance at 650 and 718 nm with absorbed dose. This indicates that radiolytic reduction of AmVI to AmV occurred, probably caused by radiolytic generation of HNO_2 , which INL LDRD work previously showed was also capable of reducing NpVI. [3]

The decrease in absorbance of AmVI at 997 nm versus absorbed dose is shown in Fig. 3. The half-dose is approximately 0.125 kGy. Since samples were removed from the irradiator and scanned in the spectrophotometer between dose increments, time passed during which the samples were not irradiated, referred to here as “real time”. If the decrease in absorbance is plotted versus real time, the half-life for AmVI was 6 minutes, similar to what has previously been measured for unirradiated AmVI in the absence of the bismuthate holding oxidant. However, given the stability of AmVI for 38 minutes in this sample prior to irradiation, its reduction here is attributed to radiolysis. However, given that the curve is not strictly linear, a dependence on the AmVI concentration may be evident, and mixed mechanisms may be causing the reduction. In contrast, the AmV produced was very stable. In Fig. 4 it can be seen that continued irradiation to a maximum absorbed dose of 12.6 kGy only slightly reduced the absorbance of AmV at 718 nm, and only a slight increase in AmIII absorbance at 503 nm was recorded. The loss in AmV and increase in AmIII are linear, suggesting independence of the reaction from AmV concentration; thus implicating reduction by radiolysis products.

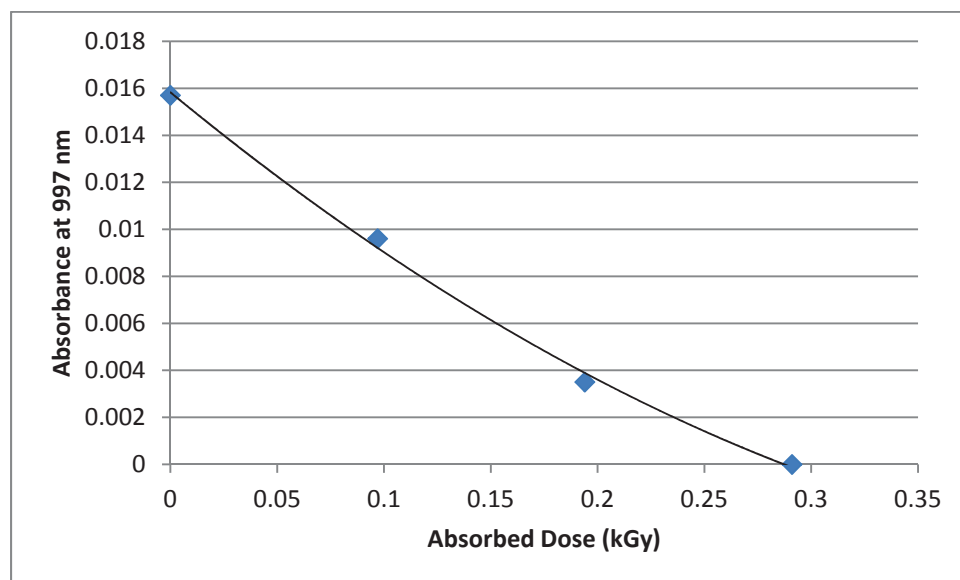


Figure 3. The decrease in absorbance at 997 nm for AmVI as it is reduced by irradiation.

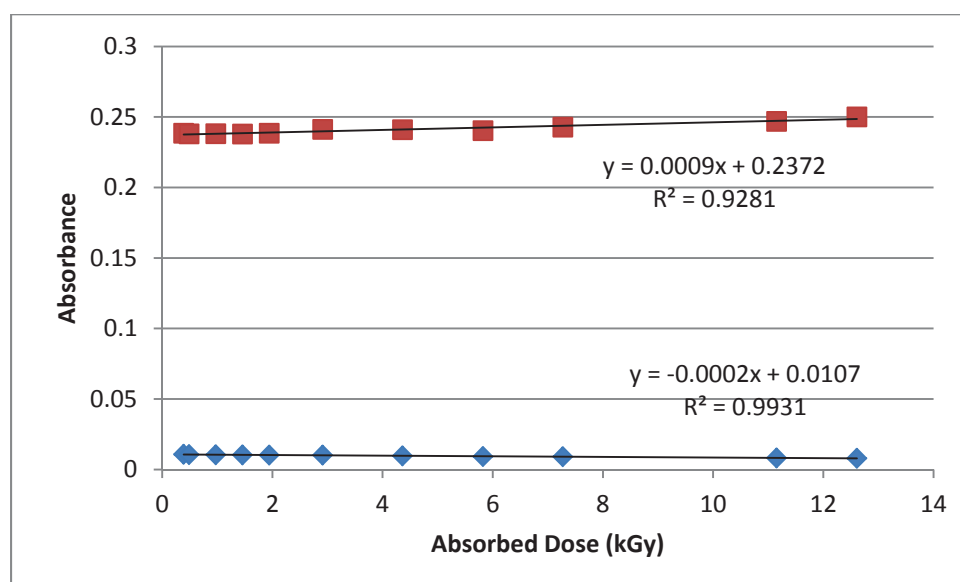


Figure 4. The radiolytic stability of AmV to absorbed doses as high as 12.6 kGy, boxes are absorbance at 503 nm for AmIII and diamonds are absorbance at 718 nm for AmV.

3.2 Samples containing macro-residual bismuthate

In the second sample set, visible, milligram amounts of residual undissolved bismuthate were left in the bottom of the UV/Vis cuvette during the irradiation. The spectra of the bismuthate-containing, post-oxidation sample acquired immediately after preparation, and after transport to the irradiator are shown in Fig. 5. The concentration of AmIII indicated by the peak at 503 nm actually decreased by about 18% during the 38 minute time delay in transferring samples to the irradiator, indicating that the oxidation of

Am to AmVI was still occurring, with the final AmVI yield being 60%. Again, no trace of AmV can be seen in the pre-irradiation solution.

Upon irradiation the very fast reduction of AmVI again occurred, with all detectable absorbance at 997 nm being gone in a few tenths of a kilogray. Also as seen with the previous sample, AmV was very stable, with only the slight positive slope for the absorbance of AmIII at 503 nm acting as an indication of AmV reduction over an absorbed dose range with 12.6 kGy max. This is shown in Fig. 6.

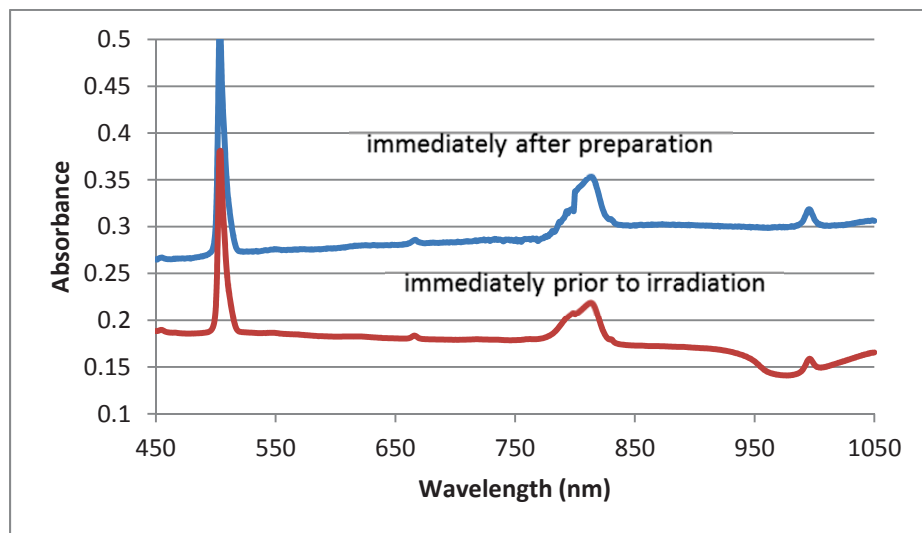


Figure 5. UV/Vis spectra of 1×10^{-3} M Am in 1 M HNO_3 oxidatively treated with sodium bismuthate. The traces show the absorbance of AmIII and AmVI immediately after preparation, and after transport to the irradiator. Milligram amounts of residual bismuthate were in contact with the sample during transport.

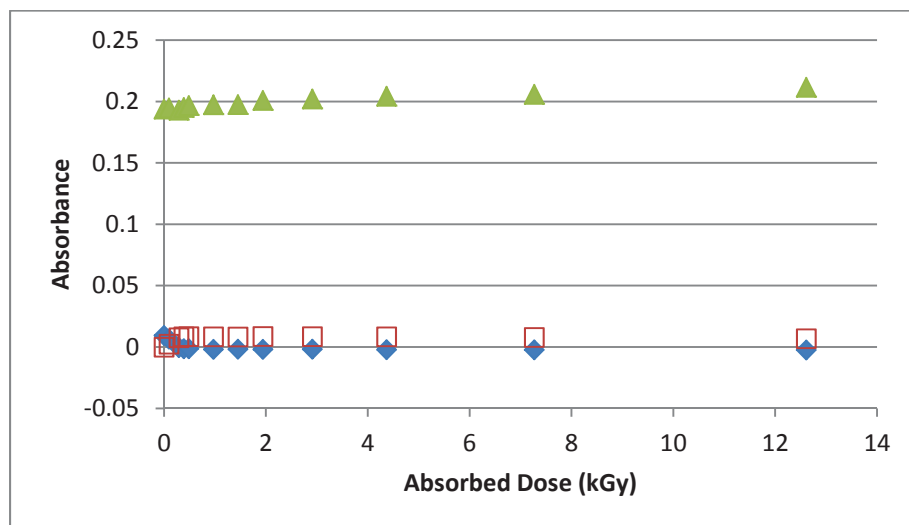


Figure 6. The reduction of AmVI (closed diamonds- 997 nm), ingrowth and stability of AmV (718 nm) and ingrowth of AmIII (503 nm) versus absorbed dose in the presence of milligram amounts of residual bismuthate.

4. Discussion, Conclusions and Future Direction

The reduction of AmVI by radiolysis was rapid, producing AmV as the sole product. Relatively low absorbed doses in the ~ 0.3 kGy range quantitatively reduced a solution of 2.5×10^{-4} M AmVI. To quantitate the G -values for reduction, higher americium concentrations should be irradiated at lower dose rates. Lower dose rates are achievable at the INL irradiator through the use of collimators in the sample chamber, and will be used in subsequent experiments. The fast reduction at relatively low absorbed doses raises a question. How much absorbed dose will the real process solution experience? If it can be assumed that the solution to be oxidized and extracted here will be similar to that in a TALSPEAK process, it has been calculated that the solution dose-rate will be on the order of 6 rad s^{-1} . [6] The referenced calculation assumed LWR reactor fuel that had received 100 GWD followed by 5 years cooling. This reported dose-rate is equivalent to 216 Gy h^{-1} . Thus, the quantitative reduction of the AmVI concentration shown here corresponds to 1.4 hours of exposure to such a process solution, while the actual americium concentrations will be higher and the expected contact times are in seconds when using centrifugal contactors. Thus, the reduction rate found in these initial experiments may not be excessive. The addition of larger amounts of residual bismuthate did not appear to protect AmVI from radiolytic reduction during these experiments. It was also shown here that AmV is very stable toward radiation. This is similar to the exceptional stability we have previously reported for AmV autoreduction in acidic solution.

These results are considered preliminary and additional experiments are planned. They will be conducted using higher Am concentrations, higher oxidation yields, and at lower dose rates. Reference samples that are not irradiated will accompany future sample irradiations.

5. REFERENCES

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