Am(VI) Extraction Final Report: FY16

Fuel Cycle Technology

Prepared for
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SUMMARY

This report summarizes activities related to hexavalent Am extraction for FY16, in completion of FCR&D Milestone M3FT-16IN030103027. Activities concentrated on three areas of research: 1) centrifugal contactor hot testing, 2) Am(VI) stability studies, and 3) alternative oxidant studies. A brief summary of each task follows.

Hot Testing: A new engineering-scale oxidation and solvent extraction test bed was built at Idaho National Laboratory to allow for solvent extraction testing of minor actinide separation concepts. The test bed consists of an oxidation vessel, filtration apparatus, four, 3D printed, 2-cm diameter centrifugal contactors, feed/product vessels, and sample ports. This system replaced the previous 3 stage, 5-cm contactor test bed that was used for the initial testing in FY14. In the FY16 hot test, a feed simulant was spiked with ^{243}Am and ^{139}Ce and treated with 60 g/L sodium bismuthate for two hours to oxidize the Am(III) to Am(VI). This solution was then pumped through a filter and into the four-stage centrifugal contactor setup. The organic phase solvent formulation was 1 M diethylhexylbutyramide (DEHBA)/dodecane. The test showed that Am(VI) was produced by bismuthate oxidation and the residual oxidant was successfully filtered without back pressure buildup. Sixty-four percent of Am was extracted in the contactors using DEHBA. Both Am and Ce were quantitatively stripped by 0.1 M H_2O_2. Successful demonstration of the utility of small, printable contactors suggests that hot testing of separations concepts can now be conducted more often, since it is cheaper, generates less waste, and entails much less radcon risk than previous testing.

Am(VI) stability: A rigorous examination of reagents was conducted to determine if contaminants could interfere with Am oxidation and extraction. An series of D_{Am} measurements showed that bismuthate particle size, water source, acid quality, and DAAP batch or pre-treatment had little effect on extraction efficiency, with a mean distribution ratio of 3.74 ± 0.5, using 1 M DAAP extraction. Additionally, the purposeful addition of millimolar amounts of nitrite or H_2O_2 to bismuthate-treated Am solutions did not prevent oxidation, as long as residual solid bismuthate was present. Finally, a series of irradiation experiments using a Nordion Gammacell 220E ^{60}Co source was performed, and kinetic data for the radiolytic reduction of Am(VI) were obtained. Unsurprisingly, it was found that radiolysis reduces Am(VI), but that the presence of Ce(IV) acts as a radioprotection agent, to scavenge radiolytically-produced reducing agents, thereby enhancing the stability of the higher Am oxidation state.

Alternative oxidants: To date, sodium bismuthate is the only practical oxidant for Am with utility in solvent extraction. While successful oxidation has been demonstrated with sodium peroxydisulfate, it is impractical for solvent extraction because it is only useful in dilute acid and it introduces sulfate into the process. Oxidation has been demonstrated using silver and cobalt catalyzed ozone, however, reduction upon contact with an organic phase is instantaneous. Oxidation is successful using Cu(III) periodate, and marginally successful in initial testing using DAAP extraction. However, the distribution ratios for the oxidized Am are marginal, because Cu(III) is also rapidly reduced by the organic phase. The possibility may exist that this can be optimized.

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1. INTRODUCTION

This report is written in fulfillment of FCR&D Milestone M3FT-16IN030103027, to prepare a final report detailing the results of hot testing, Am stability studies and alternate oxidant research. This work builds upon previous work in the same areas, and the report is divided into three discreet sections detailing these disparate tasks.

1.1 Hot Testing

Previously, in FY14, it was demonstrated that Am(VI) could be prepared and maintained in the high oxidation state sufficiently long enough to enable DAAP solvent extraction in a centrifugal contactor test bed. [1, 2] Hexavalent americium distribution ratios consistent with those achieved in pre-hot test batch contacts were achieved, and the proof of principal was established that Am can be oxidized using sodium bismuthate and that the feed can be adequately filtered to remove the undissolved oxidant.

Since that time, a wide range of alternate oxidants and ligands have been investigated at several laboratories in an attempt to improve extraction efficiency and to eliminate the need for filtration that accompanies sodium bismuthate as a heterogeneous oxidant. These efforts were reviewed in an Am(VI) roadmapping effort early in FY16. [3] The conclusions of that effort were that only the sodium bismuthate oxidant was sufficiently mature to be used in an FY16 hot test. [4] That report further recommended that the FY16 hot test be conducted using bismuthate oxidation in conjunction with either DAAP or DEHBA as the ligand in the organic solvent phase. The aqueous phase was recommended to be a Ru-free raffinate simulant, as discussed in more detail later. This simulant was radio-traced with ^{243}Am and ^{139}Ce.

Toward this end, four 2-cm acrylic centrifugal contactors were purchased from Kent Wardle at ANL, where they were fabricated using 3D printer technology. The contactors were supplied as a 4-pack and upon receipt the system was configured such that Stages 1 and 2 were operated as countercurrent extraction stages, with stages 3 and 4 operated as countercurrent stripping stages. Sampling of the aqueous and organic effluents, and the strip product of the test bed was performed every two minutes during the run and these were gamma-ray counted for Am and Ce. The results of this test are given in Section 2.5 of this report.

1.2 Am Stability Studies

In the FY14 hot test campaign it was found that, although the obtained D_{Am} matched that of batch contacts using the same reagents, they were lower than often obtained in earlier batch contacts using raffinate simulant or spiked nitric acid solution. [1] Therefore, a rigorous investigation was launched to identify sources of trace reducing agents that might be inadvertently introduced during reagent preparation that could cause spuriously low D_{Am}. The results of that investigation did not identify a definitive reason for the low results obtained in FY14, and such low D_{Am} could not be reproduced. The details are given in this Section 3.1 of this report.

Also under the heading of Am stability, continued work was performed in the area of understanding the effects of the gamma-irradiation on Am(VI). A series of solutions of varying Am concentration and acidity were irradiated in the Gammacell ^{60}Co irradiator. Data collection is still in progress as of this writing. However, neither [HNO_3] or initial [Am(VI)] had an effect on the rate of Am(VI) reduction in irradiated solution. Also, the presence of Ce provided a protective effect. The results of this study are provided in Section 3.3 of this report.

1.3 Alternative oxidants

Despite the demonstrated utility of sodium bismuthate as an oxidant for the preparation of Am(VI), the fact that it is a heterogeneous oxidant has prompted a search for an alternative. The other chemical oxidants that have shown utility for Am(VI) production are Ag-catalyzed $Na_2S_2O_8$, Ag-, and Co-catalyzed ozone, and $KNa_4Cu(HIO_6)_2$ (Cu(III) periodate). As discussed in Section 4, although these oxidants are capable of oxidizing Am, they have not proven practical for use in solvent extraction. The most favorable results were found using Cu(III) periodate in conjunction with DAAP extraction. [5] However, while the D_{Am} achieved indicated extraction of some oxidized Am, they are marginal for process application. This is attributed to the rapid reduction of Cu(III) during the organic phase contact, and the absence of a holding oxidant. No Am(VI) extraction was achieved when using Cu(III) periodate as an oxidizing agent in tandem with DEHBA extraction.

Electrochemical oxidation is also being developed for use in Am oxidation, however, the latest developments in that technique will be discussed in a separate report (Milestone M3FT-16IN030103023).

2. HOT TEST

2.1 Test Bed and Methodology

An experimental setup was constructed using two fume hoods; one for the nonradioactive feed solutions and one for the oxidation/filtration/solvent extraction equipment that would handle the radio-traced simulant feed. A schematic of the test bed is shown in Fig. 1, with a photograph of the contactors in Fig. 2.

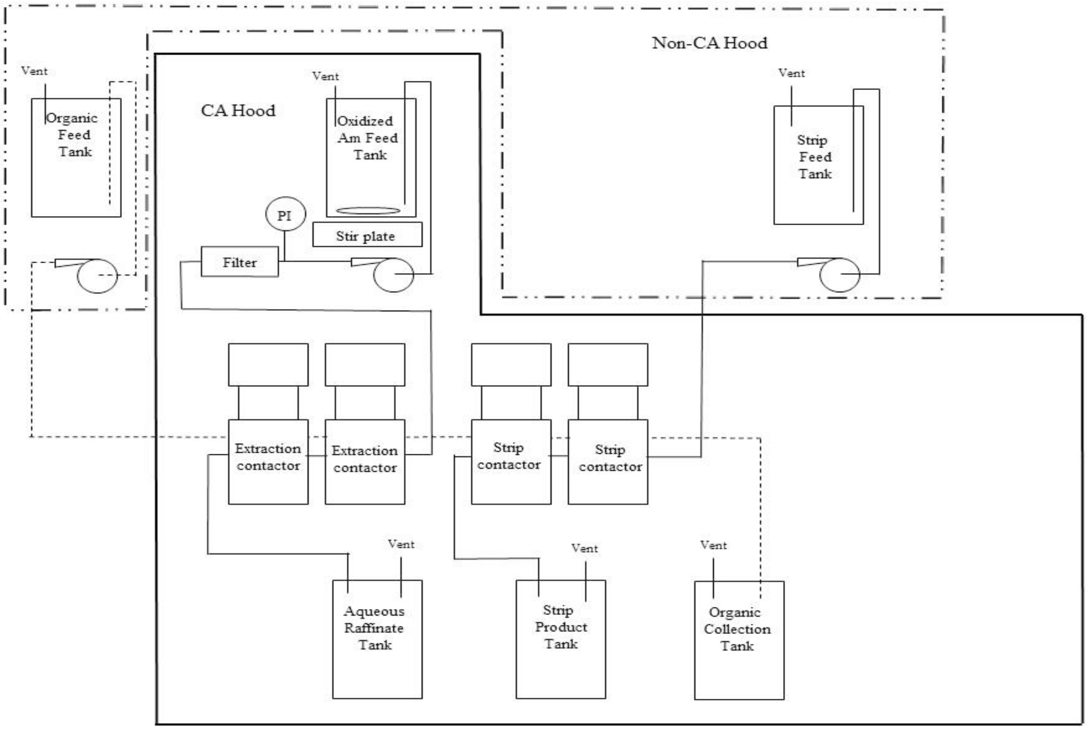

Figure 1. Schematic representation of hot test bed for centrifugal contactor extractions and stripping of Am(VI) from raffinate simulant solution.

Figure 2. Four stage centrifugal contactor test bed used in FY16 hot test.

The Ru-free simulant was spiked to the level of 868 bq/mL ^{243}Am and 258 bq/mL ^{239}Ce, as determined by post-spiking gamma-ray counting. The feed simulant's non-radiological constituents are shown in Table 1. The actual concentrations after acidity adjustment of the feed as used in the test are 50 % of those shown. The radiotracer spiked simulant was subjected to a 2 h oxidation with 60 mg/mL sodium bismuthate in a stirred, 1-L, glass beaker which served as an oxidation and feed tank. The oxidized raffinate was then pumped through PTFE tubing using an FMI (Fluid Metering Inc.) model QG150 pump drive and Q1CKC pump head (wetted parts are ceramic alumina and PVDF), through an inline, 1 μm pore size ZenPure PureFlow Capsule PTFE Teflon filter contained in a polypropylene filter housing with a PTFE back-pressure monitoring gauge. The filter and aqueous feed solution are shown in Fig. 3.

Table 1. Raffinate simulant non-radiological constituents (prior to 50 % dilution caused by acidity adjustment) as measured by ICPMS. (mM, mean of N = 4, avg % rsd = 2.75).

Element	Rb	Sr	Zr	Cs	Ba	La	Ce	Nd	Sm	Eu	Gd
Concentration	0.75	1.71	5.93	3.65	3.31	1.97	3.79	6.41	4.32	0.12	0.28

Figure 3. Aqueous feed solution undergoing bismuthate oxidation with residual bismuthate and 0.1 µm filter cartridge shown above.

Following filtration of the undissolved bismuthate, the oxidized feed solution entered the stage 1 contactor at a flow rate of 15 mL/min. There, it was contacted with 15 mL/min of 1 M DEHBA/dodecane fed from the organic feed vessel, providing an O:A = 1. This organic feed solution was previously pre-equilibrated at O:A = 1 for 1-h with bismuthate-containing 6.5 M HNO_3, following which it was decanted from the solids. Upon exiting stage 1, the raffinate entered a second stage extraction contactor, operated in counter current flow such that it contacted fresh organic phase. Stripping was also conducted in two counter current stages, at a flow rate of 15 mL/min, using a 6.5 M HNO_3 solution made 0.1 M in H_2O_2. This also provided an O:A = 1.

The operational run instructions were as follows:

- Pre-equilibrate > 300 mLs 1 M DEHBA in dodecane with an equal volume of 6.5 M HNO_3 + 18 g sodium bismuthate for 1 hour in 1 liter beaker. Let settle and separate. Pour organic into organic feed vessel.
- Oxidize 300 mL 6.5 M HNO_3-adjusted, radio-traced simulant + 18g sodium bismuthate for 2 hours in aqueous feed tank.
- Add > 350 mL 6.5 M HNO_3 to Strip feed tank. Do not add H_2O_2 at this point.
- Start contactors (3600 rpm) and visually verify they are spinning. Fill stages 1 and 2 (extraction) contactors with 6.5 M HNO_3 from Strip feed tank. Stop Strip feed pump when aqueous flow is observed exiting stage 1 contactor to the aqueous raffinate tank.
- Add 3.5 mL 30% H_2O_2 to Strip feed to bring to 0.3 % (0.1 M). Then fill stages 3 and 4 (Strip) contactors with Strip feed. Stop pump when aqueous flow is observed exiting the contactor to the Strip receiving vessel.
- After the aqueous feed has been oxidized with sodium bismuthate for 2 hours, start the contactors (if not already running).

- Start aqueous feed flow to fill filter housing and tubing up to the aqueous feed penetration on the contactor housing. Shut the aqueous feed pump off when solution gets to this point. Start organic feed pump.
- When organic feed is seen exiting Stage 2 start aqueous feed and strip feed pumps. This is T_0. Record time.
- Pull effluent aqueous and organic samples per sample schedule and record sample times.
- Sample schedule: Aqueous feed before adding sodium bismuthate, Organic, Strip, and Aqueous Raffinate effluent streams beginning at 3 minutes run time and every 2 minutes throughout test.
- After 15 minutes run time or when organic or aqueous feed is completely depleted from their feed tanks stop all feed pumps. Continue running contactors until effluent flows stop.
- Rinse contactors and pumps: Place collection bottles under contactor drains and open drain valves. Remove organic, aqueous feed and strip pump suction tubes from feed vessels and run pumps until systems are pumped dry. Place suction tubes into bottles containing 0.01 M HNO_3 rinse solution and pump through system. Start contactors and close drain valves. Fill contactors with rinse solution and let run into collection bottles at effluent tubes. Run approximately 100 mL through organic pump and 200 mL through aqueous and strip feed pumps then pull feed suction tubes and let pumps push the remainder to the contactors. Shut pumps off. Wait a minute and shut contactors off. Open drain valves and let remaining solution drain to collection bottles. Remove contactors and rinse rotors and contactor housing with hot water filled squirt bottle. Wipe out remaining rinse solution.

2.2 Materials of Construction

Samples of four acrylic plastic materials used for contactor printing were received from ANL to be evaluated for their reducing reactivity toward oxidized Am. This was examined qualitatively by performing a 2-hr sodium bismuthate Am oxidation in 6.5 M HNO_3, the presence of a 100 ± 50 mg specimen of each material, and also present during a 10-sec batch extraction with 2 mL of bismuthate pre-treated 1 M DAAP/dodecane. The contacts were performed in glass culture tubes. The results are shown in Table 2. Also shown for comparison is the mean D_{Am} for duplicate contacts with 6.5 M HNO_3 containing no plastic specimen.

Table 2. Effect of materials of construction on D_{Am} for batch contact measurements.

Specimen type	mean D_{Am}	N
Grey plastic	3.35 ± 0.35	3
Clear plastic	3.17 ± 0.55	3
Black plastic	4.54 ± 0.24	3
Clear IPA	2.93 ± 0.57	3
6.5 M HNO_3 only	5.16 ± 0.03	2

It can be seen in Table 2 that contact with the acrylics did somewhat decrease the extraction efficiency compared to specimen-free solution, probably via reduction of Am(VI). Recalling that purposeful reduction of Am(VI) was more difficult than anticipated in the FY14 test, [1, 2] and given the short contact times and limited surface areas anticipated in the centrifugal contactors it was concluded that these materials would be adequate during hot testing. This had the further benefit of enabling immediate printing of the contactors using conventional materials.

2.3 ALSEP Simulant and Ru

During November 2015, an ALSEP feed simulant solution was received from PNNL to be used for future process development. The metals concentrations in the new simulant are similar than those used in the feed for the FY14 hot test, excepting that the previous simulant did not contain Fe, Mo, Pd, Pr, Y, Ru, Sn and Te. The previous simulant did contain Ba, which is absent in the ALSEP simulant. The constituents of the FPEX FY14 test and ALSEP simulants are shown in Table 3.

Table 3. Measured simulant feed constituent concentrations (before adjustment of acid concentration, mM) for FPEX simulant used in FY14 hot test, and those of new ALSEP simulant.

Constituent	FY14 Hot Test measured	ALSEP measured
Rb	0.94	1.03
Sr	1.71	2.41
Y	--	1.38
Zr	10.9	8.17
Cs	3.69	4.99
Ba	3.66	--
La	1.98	2.31
Ce	3.83	4.12
Nd	7.4	7.51
Sm	4.59	1.42
Eu	0.12	0.29
Gd	0.20	0.19
Pr	--	1.34
Ru	--	2.79
Fe	--	0.11
Mo	--	4.54
Pd	--	0.03
Sn	--	0.18
Te	--	0.53

The extraction behavior of selected important simulant constituent metals was next evaluated by ICP-MS after using bismuthate-treatment and 1 M DAAP extraction. The results are shown in Table 4.

Table 4. ALSEP simulant DAAP solvent extraction results following adjustment to 6.5 M HNO_3 and bismuthate oxidative treatment.

Metal	Sr	Y	Zr	Mo	Ru	La	Pr	Nd	Sm	Eu	Am	Ce
D_M	<0.004	0.095	33.2	0.198	12.1	0.065	0.024	0.037	0.083	0.098	0.214	30

The distribution ratios for the lanthanides and Y are in excellent agreement with those previously measured for the FPEX simulant at this acidity. [6] As expected, Zr and Ru were well extracted, with distribution ratios slightly higher than those seen previously from the oxidized FPEX simulant (D_{Ru} = 5.4); D_{Zr} = 20 [6, 7]. However, the extraction of Am and Ce were less efficient than expected. The D_{Am} here, as measured by ICP-MS, is lower than the typical FPEX simulant value of ~ 4, and the D_{Ce} = 30 is significantly < ~300 found for FPEX raffinate. [7] This is evidence that something is limiting oxidation or extraction efficiency in the ALSEP simulant matrix.

Further Am oxidation and extraction batch contacts were performed on the ALSEP simulant, using radiometric determination of D_{Am}. Using a 10-sec contact time with 1 M DAAP and the conventional 2-h, 60 mg/mL $NaBiO_3$ oxidative treatment of the simulant adjusted to 6.5 M in HNO_3, it was again found that Am was not well extracted from this simulant formulation. These contacts resulted in $D_{Am} = 0.18 \pm 0.01$ (N = 4). As shown in Fig. 4, the D_{AmIII} at 6.5 M HNO_3 into 1 M DAAP is < 0.04, thus, this result is consistent with partial oxidation in the ALSEP simulant.

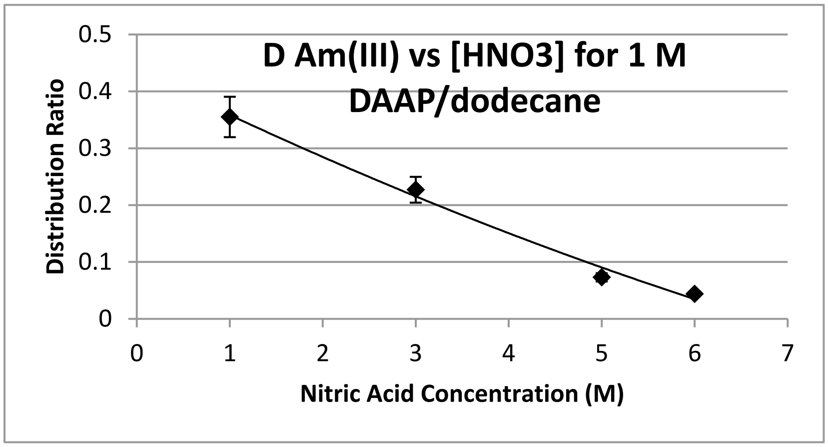

Figure 4. The extraction of Am(III) from 1 M DAAP/dodecane.

In an attempt to improve the oxidation yield, the oxidation was repeated with 120 mg/mL $NaBiO_3$; however, a similar D_{Am} of 0.21 ± 0.02 (N = 4) was found. To test whether oxidation was actually occurring but that the ligand was loaded by some constituent of the new simulant, the concentration of DAAP was doubled to 2 M. Once again, a similar D_{Am} of 0.20 ± 0.004 (N = 4) was found. The O:A was next increased to 4:1, using 1 M DAAP/dodecane. The distribution ratio was 0.26 ± 0.005 (N = 2). Further, when a 30:1 dilution was performed on the simulant, while maintaining the [HNO_3] at 6.5 M, bismuthate oxidation and extraction provided $D_{Am} = 0.702 \pm 0.069$ (N =2). These results suggest that metal loading of the organic phase is not at issue and that a constituent of the ALSEP simulant is very effective at limiting Am oxidation.

The UV/Vis spectrum of an oxidized, Am-spiked ALSEP simulant was next collected. The spectrum after the 50 % dilution caused by acidity adjustment to 6.5 M is shown in Fig. 5 (dashed line). It can be seen that the ALSEP simulant has sharp absorbance peaks at 579, 727, 788, and 878 nm, due to Nd absorbance, and broad absorbance below 560 nm that is attributed to Ru. The undiluted simulant is orange in appearance. The addition of the bismuthate oxidant did not significantly alter this spectrum (dotted line), except for a decrease in the broad absorbance at lower wavelengths, corresponding to Ru oxidation. For the Am-spiked, oxidized sample (solid line) in Fig. 5, the Am(VI) peak at 999 nm, and the Am(III) peak at 503 nm are visible, indicating only partial oxidation. Surprisingly there is no evidence of Am(V). These results demonstrate that the oxidation in the ALSEP simulant is inefficient.

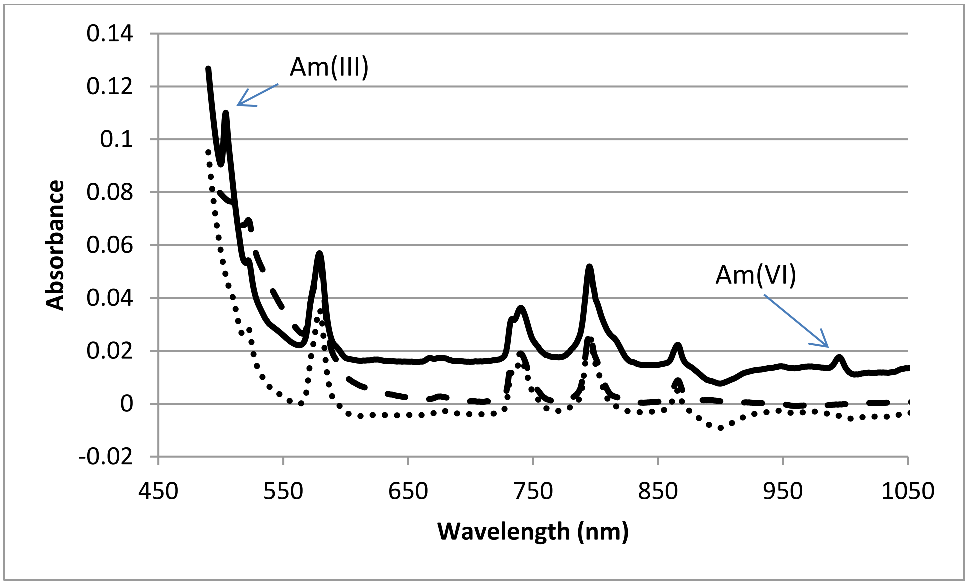

Figure 5. UV/Vis spectra of the ALSEP simulant without Am spike (dashed), without Am after BiO_3^- oxidation (dotted) and oxidized after Am spike (solid).

Tin is present in the ALSEP simulant and was added as $SnCl_2$, resulting in a [Cl^-] of 0.4 mM. Accounting for the dilution caused by acidity adjustment, the [Cl^-] in the extractions reported above was 0.2 mM. When this concentration of Cl^- was added to 6.5 M HNO_3 as NaCl, and oxidized using $NaBiO_3$, D_{Am} = 4.40 ± 0.15 (N = 4) was obtained. This low [Cl^-] is thus not responsible for hindering the oxidation.

The simulant was next pre-treated by Cu(III) oxidation, using 20 mg/mL copper periodate prior to adjusting its acidity to 6.5 M HNO_3. The solution was then oxidatively treated with bismuthate. A duplicate extraction resulted in D_{Am} = 0.385 ± 0.028. This slightly higher result suggests that some amount of the interfering agent was scavenged by the Cu(III) pre-treatment, probably by its oxidation.

A principal difference in the new simulant is its Ru concentration, at 2.8 mM. Therefore, Am-spiked 6.5 M HNO_3 solutions were made 1.5 or 3.0 mM in Ru and oxidation/extraction batch contacts were again performed. The presence of Ru suppressed Am oxidation and/or extraction, with D_{Am} = 0.36 ± 0.01 (N = 4) and 0.35 ± 0.01 (N = 4), respectively. Ruthenium-free control samples resulted in D_{Am} = 4.1 ± 0.22 (N = 2). Ruthenium is oxidized by sodium bismuthate (as well as periodates), and oxidized ruthenium is extracted by DAAP. It apparently also interferes with Am oxidation. Based on these data, it was decided that the FY16 hot test would be conducted on a Ru-free simulant.

A major goal of future work will be to investigate ways to mitigate the Ru interference. Preliminary work in this regard is currently underway at INL. UNLV Graduate Student Jason Richards visited INL as an intern this summer, and focused his summer study on characterizing Ru behavior under oxidative conditions. These data are preliminary, and will be reported elsewhere later.

2.4 Pre-Hot Test Batch Contacts

Prior to the hot test, a series of batch contacts were conducted using the same reagents to be used in the actual test. This included the oxidant, the acidity-adjusted raffinate and the organic solvent. Batch contacts were performed at an organic:aqueous ratio = 1, for contact times of 10-15 sec. The mean D_{Am} was 2.67 ± 0.10 for raffinate extraction using 1 M DAAP/dodecane (N = 3), and 2.56 ± 0.19 using 1 M

DEHBA/dodecane (N = 6). The two ligands gave identical results and since DAAP was already used in the previous test the solvent system selected for FY16 testing was 1 M DEHBA/dodecane.

Finally, an attempt was made to optimize the D_{Am} using 1 M DEHBA/dodecane by minimizing the batch contact time to 8 sec; as low as reasonably reproducible. These contacts used the exact large batches of reagents that were prepared for use as the feeds in the hot test. The oxidation was performed with new sodium bismuthate purchased for the hot test, but also another batch that had been in use for 2-3 years. The resulting D_{Am} for the old bismuthate was 3.44 (N = 2) and for the new 4.17 (N = 2). However, a D_{Am} lower than for the batch contacts was anticipated for the hot test, given lower flow rates, unknown and potentially greater contact times, and a lower stage efficiency associated with the new contactors, as well as the materials of construction.

2.5 Hot Test Results

The extraction efficiency for Am and Ce at various times during the hot test were calculated based upon gamma-ray counting of the grab samples from the organic and aqueous test bed effluents. The results are shown in Fig. 6. The results are expressed as composite distribution ratios over both countercurrent extraction stages. It can be seen that Am extraction efficiency was not as high as for the pre-hot test batch contacts. On average, the composite $D_{Am} = 1.78$ for the duration of test, corresponding to 64 % extracted. This result is lower than obtained for the batch contacts (80% extracted) and was anticipated for the reasons cited above. Finally, the countercurrent two-stage test was intended to determine whether the second stage extracted additional Am(VI), or would act as an Am strip due to the increased organic phase contact time. Given the measured extraction efficiency, the second stage may have acted as a strip, although the results are not definitive. Stripping, which was inefficient for both metals in the FY14 test, was quantitative for both metals using 0.1 M H_2O_2.

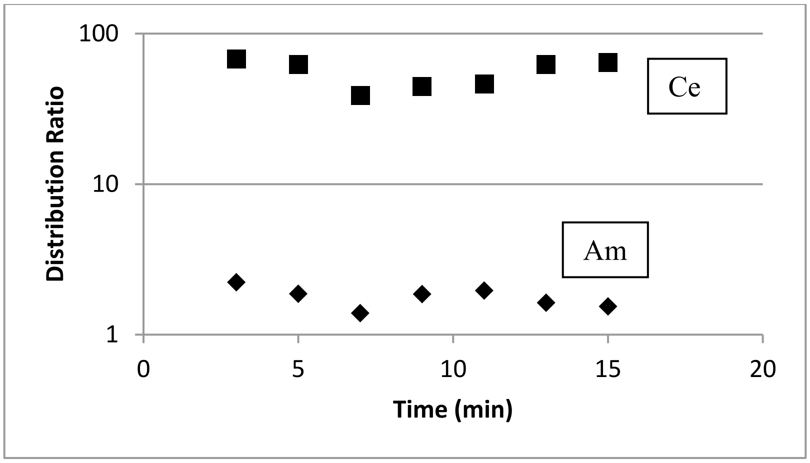

Figure 6. Composite distribution ratios for Ce and Am from Ru-free raffinate simulant using 1 M DEHBA as measured at various times during the centrifugal contactor hot test.

The results suggest several recommendations for future testing. Extraction efficiency and contact times should be measured for the new contactors, to enable a direct comparison to batch contact data. Then, a single stage extraction test will enable a determination of maximum Am extraction efficiency. A series of strip contacts should then enable the appropriate reducing agent concentrations to be selected to enable Am/Ce separation during stripping.

3. AMERICIUM STABILITY STUDIES

3.1 Parameter Evaluation Study

During the FY14 centrifugal contactor hot test, an atypically low D_{Am} ~ 1.8 was measured both during the hot test, and for the pre-hot-test batch contacts. [1, 2] An americium distribution ratio of ~ 4 was expected based upon previous batch contact work using a first cycle raffinate simulant that was diluted to adjust the nitric acid concentration of the feed to 6.5 M. [6, 7] Therefore, an investigation of the effects of reagent quality on oxidation efficiency was initiated, using oxidation and extraction from americium-spiked nitric acid solution. The parameters evaluated included: bismuthate particle size, source of deionized water for reagent preparation, source of nitric acid, and source and pre-treatment of DAAP. Except for the parameter being evaluated in each test, the standard conditions were:

- Sodium bismuthate (93%) as supplied by Chemsavers, particle size as received.
- Deionized water prepared using a nanopure system at INL facility CFA 625.
- Optima grade nitric acid supplied by Fischer.
- Dodecane (99%) supplied by Sigma Aldridge, lot # SHBD4471V.
- DAAP supplied by Eichrome, lot # ER145141.
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For each batch oxidation and extraction, the conditions were:

- 60 mg/mL sodium bismuthate oxidation of Am-spiked 6.5 M HNO_3 for 2 h.
- 60 mg/mL sodium bismuthate/6.5 M HNO_3 pre-equilibration of organic phase for 2 h.
- 10 sec, equal volume batch contact.
- Room temperature of 25 ± 1 °C.

All the individual data from these tests are summarized in Table 4. The overall mean D_{Am} = 3.74 ± 0.50 (N = 34, 25 ± 1 °C), with a range of 2.98 for one result using reagent grade acid, to two results of 4.50, using the standard conditions. Thus, none of the examined parameters excepting possibly acid quality is unambiguously identified as a problem for oxidation efficiency. No D_{Am} as low as that found during the FY14 hot test and FY14 batch extractions was measured, although it must be noted that those extractions were from the simulant, whereas these are from Am traced nitric acid. However, a value ~4 is consistent with those obtained for simulant extractions in previous work. [6, 7] The individual parameter results are discussed below.

3.1.1 Sodium Bismuthate Particle Size

The sodium bismuthate oxidant was sieved to three size fractions: 1) material that did not pass through a 0.0041 in screen (> 100 uM); 2) material that did pass through a 0.0041 but not a 0.0025 in screen (50 uM - 100 uM); and 3) material that passed through the 0.0025 in screen (< 50 uM). These size fractions were then used to perform triplicate oxidations and extractions. The individual results are shown in Table 4. The mean result for the particle size test extractions was D_{Am} = 3.49 ± 0.18 (N = 9, 24 °C). This suggests that particle size over this range had no effect on the americium oxidation yield.

3.1.2 Deionized Water Source

Americium oxidations and extractions were then performed with unsieved sodium bismuthate, using the same oxidation parameters, extraction contact time and sources of nitric acid and DAAP as above, except that the 6.5 M HNO_3 solution was prepared using either CFA625 deionized water (the same acid solution prepared and used for the particle size test above) or deionized water supplied by a different INL facility (Test Reactor Area Radioanalytical Chemistry Lab). Once again there appeared to be little difference in oxidation and extraction between the different water supplies, with the mean D_{Am} = 4.32 ± 0.17 (N = 6, 25 °C). The extractions performed in this test resulted in D_{Am} about 20 % higher than in the particle size test, although all parameters were held constant. All results for the individual extractions performed in the water test are shown in Table 4.

3.1.3 Nitric Acid Source

Using the same un-sieved sodium bismuthate, the same DAAP and dodecane as the tests above, and the CFA625 water source, the 6.5 M HNO_3 was prepared using either high purity Optima nitric acid as in the tests above, or Fischer ACS grade nitric acid. The reagent grade acid was very slightly off-color, indicating the probable presence of nitrous acid; a known reducing agent for Am(VI). The mean result was D_{Am} = 3.44 ± 0.28 (N = 6, 25 °C). The slightly higher relative standard deviation for this set of extractions was heavily influenced by one low result for the reagent grade acid, as can be seen in Table 4. The data in Table 4 suggest that there may be a slight effect due to the nitrous acid content of the nitric acid, however, the oxidative treatment must have removed much of this trace reducing agent. However, this reagent grade acid result is essentially identical to that achieved using Optima acid during the particle size tests. This is unlikely to be the cause of spuriously low D_{Am}.

3.1.4 Source or Pre-treatment of DAAP

Next, varying only the batch of DAAP used in the extraction, a mean result of D_{Am} = 3.94 ± 0.43 (N = 5, 25 °C) was obtained. As seen in Table 4, the mean value for the original batch of DAAP (lot # ER145141) provided D_{Am} about 15 % lower than did the new batch (lot # 998107), suggesting that DAAP quality may indeed have an effect. However, it should be noted that the older batch of DAAP provided distribution ratios ~ 4.3 in the water source test above. Thus, the data implicating batch quality for the ligand as a source of D_{Am} variability are not convincing.

Another set of DAAP evaluations was performed in which the extractions were repeated using the old batch, and compared to the new batch after a carbonate wash procedure on the new DAAP. That procedure was recommended by the manufacturer and consisted of four washes of the neat DAAP with 0.5 M Na_2CO_3, followed by a single wash with 0.1 M HCl, followed by three washes with water. In this case, the old batch provided a D_{Am} = 4.01 ± 0.60 (15 % rsd, N = 3, 25 °C). This is the same set of conditions which provided D_{Am} = 4.32 in the water test, and 3.69 in the DAAP batch tests (see Table 4). The washed DAAP batch resulted in a D_{Am} = 4.05 ± 0.29 (7.1 % rsd, N = 3, 25 °C). Finally, a set of extractions was performed using a DAAP solution prepared from lot # ER145141, but aged for several months, for which a small amount remained in stock. Duplicate extractions, holding all other variables constant, resulted in a mean D_{Am} = 3.67. Thus, none of the investigated parameters can definitively be identified as problematic for Am oxidation.

Table 4. Summary of batch contact D_{Am} collected for an evaluation of parameters that may affect oxidation efficiency and extraction of oxidized Am.

Parameter		D_{Am}			
		1	2	3	mean
Particle size	> 100 uM	3.45	3.15	3.64	3.41 ± 0.25

100-50	3.54	3.76	3.52	3.61 ± 0.13
< 50	3.44	3.61	3.30	3.45 ± 0.16
Water Test				
CFA625	4.48	4.18	4.48	4.38 ± 0.17
TRA RACL	4.15	4.14	4.46	4.25 ± 0.18
Acid Test				
Optima	3.65	3.59	3.69	3.64 ± 0.05
Reagent grade	3.48	2.98	3.23	3.23 ± 0.25
DAAP Test				
Batch 1 (ER145141)	4.09	3.46	3.51	3.69 ± 0.35
Batch 2 (998107)	4.26	4.38	--	4.32
Batch 1, trial 2	4.19	3.34	4.50	4.01 ± 0.60
New washed	4.13	4.29	3.73	4.05 ± 0.29
Batch 3 (ER145141)	3.45	3.90	--	3.68
Overall mean result				**3.74 ± 0.50**

3.2 Effect of Added Reducing Agents

The success of sodium bismuthate as an oxidant for Am for solvent extraction purposes has been attributed to the ability of the heterogeneous oxidant to act as its own hold oxidant. It probably does so by slow dissolution of a continuing supply of Bi(V), as the previously solubilized Bi(V) is reduced to Bi(III) in the treated solution. To investigate the effect of the residual solid oxidant on Am(VI) stability, DAAP solvent extraction D_{Am} for bismuthate-oxidized Am were measured in the presence of added reducing agents. When Am-spiked 6.5 M HNO_3 solutions were oxidized with sodium bismuthate containing 0.4 mM, or 2 mM sodium nitrite, triplicate extractions provided $D_{\mathrm{Am}} = 3.73 \pm 0.06$ and 3.58 ± 0.17, respectively. In the presence of 4 mM nitrite, duplicate extractions gave a mean of 3.81. In contrast, when an oxidized Am solution was made 1 mM in nitrite after filtration of the residual bismuthate, the mean $D_{\mathrm{Am}} = 0.01 \pm 0$ for triplicate contacts, a result consistent with the extraction efficiency expected for Am(V). In comparison, the mean for three $D_{\mathrm{Am(III)}}$ contacts under these conditions was 0.19 ± 0.03. Thus, millimolar amounts of nitrite were able to reduce Am(VI) to Am(V) in the absence of a holding oxidant. Similar results were found when H_2O_2 was added as the reducing agent.

The effects of added H_2O_2 and $NaNO_2$ were spectroscopically investigated on solutions containing initially Am(VI). Solutions of bismuthate-oxidized Am were prepared by the usual procedure with spectroscopy performed in a 100-cm waveguide liquid capillary cell. The ^{243}Am stock solution was characterized by alpha spectroscopy and found to have a concentration of 1.88 mM, and this was diluted to 7.51E-5 M in americium prior to oxidation in 6.5 M HNO_3. The initial, pre-oxidation absorbance of the Am(III) peak was 1.369, indicating an extinction coefficient of $\varepsilon_{503} = 364.6$.

Oxidation of this solution in the absence of additives provided spectra typical to that shown in Fig. 6 (dotted line, a). The Am(VI) is centered on 666 nm, and this appears to be essentially quantitative oxidation, although any absorbance for Am(III) and/or Am(V) at 503 and 513 nm, respectively, may be obscured by the broad bismuthate absorbance between 500-600 nm. If an extinction coefficient of 24 M^{-1} cm^{-1} is assumed for ε_{666}, the resulting concentration of Am(VI) is 4.5E-5 M, for a yield of 60%. However, this extinction coefficient is from a measurement in 0.1 M HNO_3, [8] and the actual value is probably lower at this acid concentration. This suggests a higher oxidation yield than calculated. A reliable set of extinction coefficients would substantially benefit high valent Am research.

When the oxidation was performed in the presence of 1.0 mM $NaNO_2$, it can be seen in Fig. 7 that the yield of Am(VI) was identical to that of the nitrite-free oxidation (solid line, b). When the solution was filtered after the oxidation to remove residual solid sodium bismuthate and then spiked with 1 mM $NaNO_2$, (dashed line, c) the Am(VI) was reduced entirely to Am(V) (513 nm) and Am(III) (503 nm), as also shown in Fig. 7. The new peak that appears at 650 nm is due to Am(V).

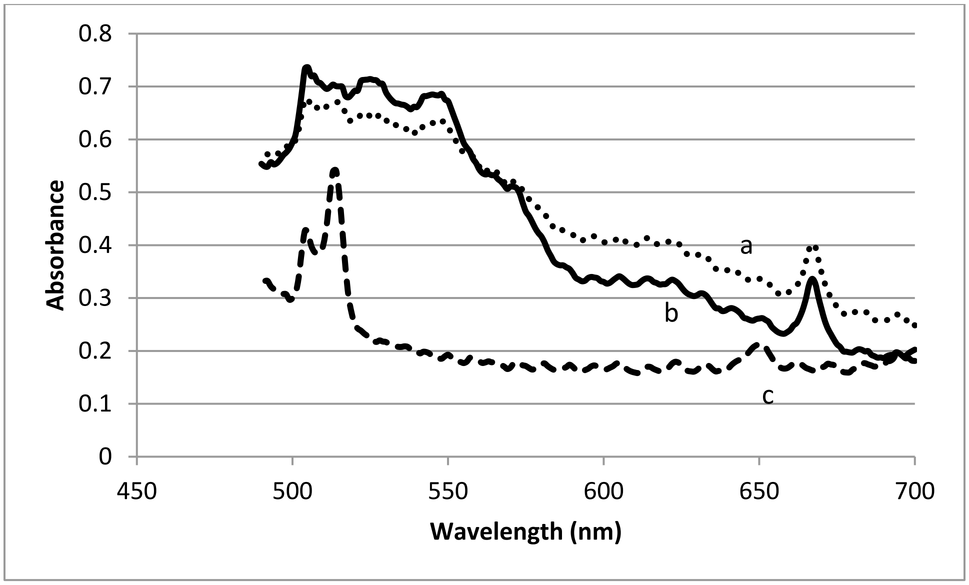

Figure 7. The yield of Am(VI) for bismuthate oxidation in the presence of added sodium nitrate: a – no added nitrite; b – 1.0 mM nitrite present during oxidation; c – 1.0 mM nitrite added after oxidation and filtration.

Identical results were obtained for oxidation in the presence of 1 mM and 10 mM H_2O_2, for which oxidation was not inhibited. This is shown for 1 mM H_2O_2 in Fig. 8, where this concentration of reducing agent had no effect on the bismuthate absorbance or Am(VI) yield. However, it is possible to overwhelm the oxidant and the addition of 100 mM H_2O_2 during the oxidation quantitatively suppressed the generation of either high valent americium species. The addition of millimolar H_2O_2 following filtration reduced Am(VI) to a mixture of Am(III) and Am(V), as was found above for nitrite additions after filtration. The results of these H_2O_2 and $NaNO_2$ addition experiments dramatically illustrate the utility of the undissolved bismuthate as a holding oxidant.

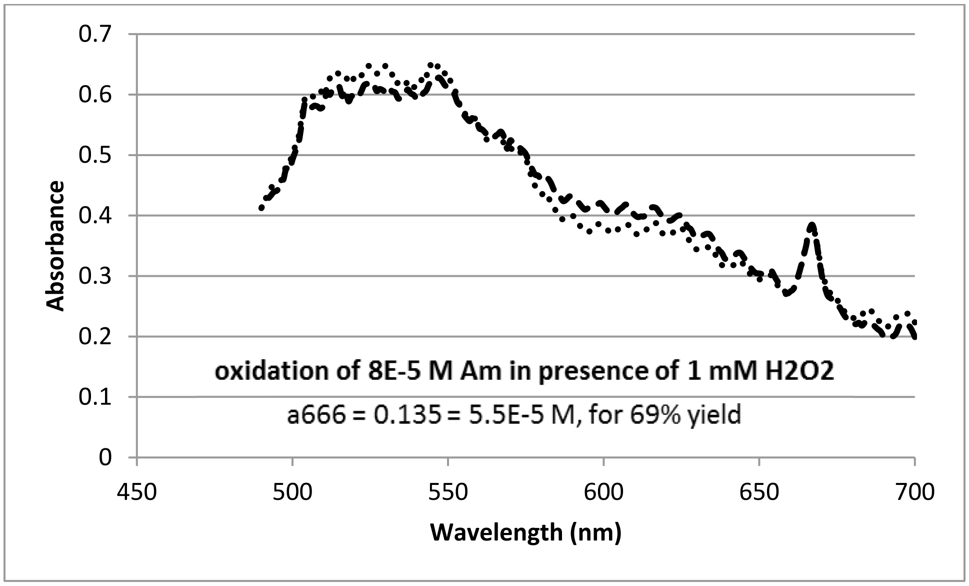

Figure 8. The yield of Am(VI) for bismuthate oxidation in the presence of added H_2O_2. Bismuthate oxidation in presence of 1 mm H_2O_2, (dashed line), oxidation in absence of 1 mM H_2O_2, (dotted line).

3.3 Radiolytic Reduction of Am(VI)

In Section 3.2 it was shown that H_2O_2 and HNO_2 are reducing agents toward Am(VI). Both are also products of the irradiation of aqueous nitric acid, produced in millimolar yields depending on the total absorbed dose. The irradiation of aqueous nitric acid produces an overall oxidizing solution through the production of transient species such as the $^{\bullet}NO_3$ and $^{\bullet}OH$ radicals. In previous LDRD-funded work at INL, it was shown that these radicals oxidized Np(V) to Np(VI) at low absorbed doses. However, as long-lived HNO_2 was produced with the accumulation of absorbed dose, the system switched to reducing chemistry with regard to Np(VI). [9] Thus, it was anticipated here that HNO_2, as well as produced H_2O_2, would act as reducing agents toward Am(VI) in irradiated aqueous nitric acid.

Americium solutions at several Am and nitric acid concentrations were irradiated using the Gammacell 220E at INL's MFC. The Nordion Gammacell 220 uses a ^{60}Co source that delivered a dose rate of 4.34 kGy h^{-1} during these experiments. The GammaCell dose rate was initially measured using standard Fricke procedures, and then subsequently corrected for ^{60}Co decay. The sample chamber temperature was approximately 30 °C. The solutions were oxidized using standard sodium bismuthate procedures, and the residual bismuthate was allowed to settle. The clear liquid was transferred to screw-capped, 1-cm pathlength UV/Vis cuvettes, and these cuvettes were irradiated for selected times to deliver known absorbed doses. After each dose increment, the UV/Vis spectrum of the irradiated solution was collected, and the appropriate peak heights (666 and 999 nm for Am(VI), 718 nm for Am(V) and 503 nm for Am(III)) were plotted versus absorbed dose to acquire dose dependent redox kinetics for Am speciation. The spectra for unirradiated control samples were also collected during the course of each experiment.

Typical spectra are shown in Fig. 9 for the decrease in Am(VI) peak height (999 nm, left), and increase in Am(V) peak height (718 nm, right) during irradiation, for 2 mM total Am in 6.5 M HNO_3. Due to the short duration of the experiments (~ 2 kGy or ~ 30 min), the unirradiated control samples showed almost no reduction in Am(VI) peak height and the reduction in Fig. 9 may be attributed to the reaction of Am(VI) with the products of aqueous HNO_3 radiolysis. The produced Am(V) is stable until much higher absorbed doses.

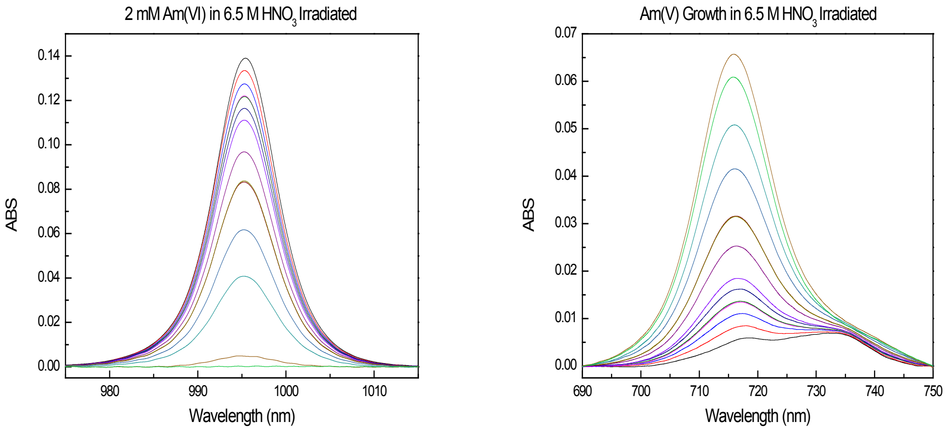

Figure 9. The decrease in absorbance at 999 nm (Am(VI)) and increase at 718 nm (Am(V)) with absorbed dose, for an irradiated aqueous nitric acid solution containing Am(VI).

The corresponding plots of Am speciation versus absorbed dose for 2 mM total Am in 6.5 M HNO_3 are shown in Fig. 10. The Am absorbance was converted to concentration assuming that the Am(III) ε_{503} = 365 M^{-1} cm^{-1}, (Section 3.2), and the Am(V) ε_{718} and Am(VI) ε_{999} were estimated as necessary to provide mass balance. The values used are shown in Fig. 10. No values for these extinction coefficients are available in the literature for this acid or acid concentration. However, for 1 M $HClO_4$ ε_{718} = 60, and ε_{999} = 83.3 M^{-1} cm^{-1} have been previously reported. [10] It can be seen that the loss in Am(VI) was accompanied by a matching increase in Am(V), with very little production of Am(III) as the irradiation progressed. Pentavalent Am is fairly stable in irradiated solution compared to Am(VI), although the final datum at 4.4 kGy absorbed dose indicates that Am(V) is starting to reduce; this is accompanied by an increase in produced Am(III).

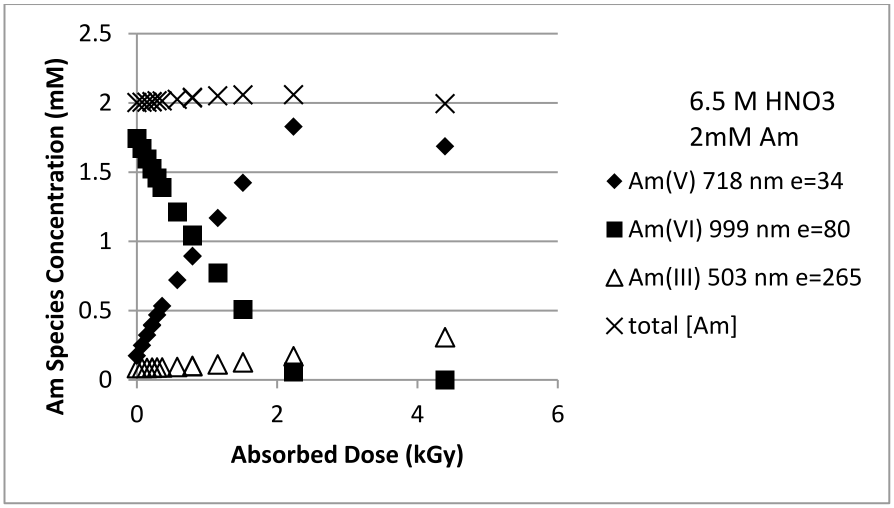

Figure 10. The decrease in concentration of Am(VI) versus absorbed dose, accompanied by the increase in Am(VI) and Am(III).

The concentration decrease of Am(VI) versus absorbed dose may be fit with a linear curve, and the slopes were constant (mean = 8.09 E-4 mmol Am(VI) kGy^{-1} ± 6.6 % rsd) across all conditions of acid and total

Am concentration. The individual values are shown in Table 5. It is not surprising that $[Am]_{tot}$ does not influence the rate of change in [Am(VI)], as the external radiation dose rates are orders of magnitude higher than those of the total Am decay. However, it was expected that Am(VI) reduction would be faster at higher $[HNO_3]$ due to higher concentrations of produced HNO_2. This was not the case.

An example is shown for the 2 mM total Am, 6.5 M HNO_3 sample, using the absorbance at 999 nm to calculate the [Am(VI)], in Fig. 11. The slope is 7.30 E-4 mmol Am(VI) kGy^{-1}. The linear concentration change with absorbed dose also implies zero order kinetics, suggesting that the rate is independent of the [Am(VI)]. Reduction by reaction with HNO_2 or H_2O_2 is expected to result in second order, or pseudo-first order kinetics. Thus, this result is difficult to mechanistically reconcile. Further work is needed in this area. It should be noted that these rates may be refined as the molar extinction coefficients for the Am species peaks become better known.

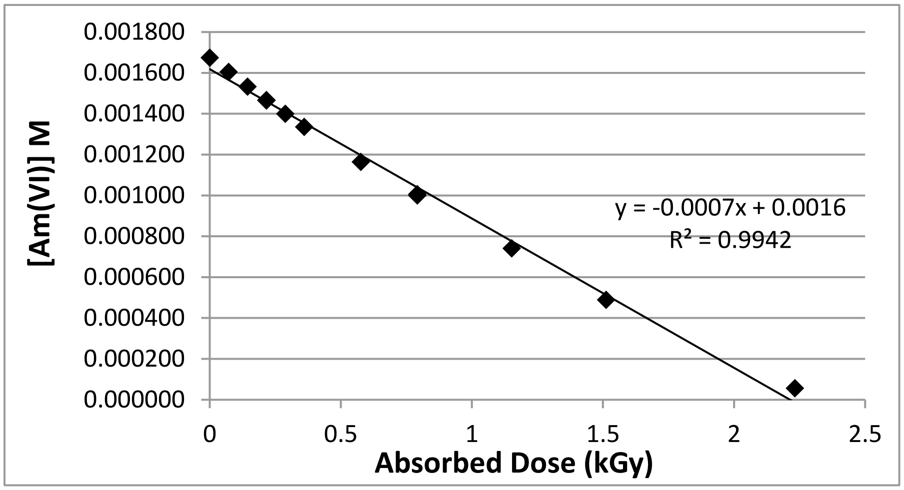

Figure 11. The decrease in Am(VI) concentration versus absorbed radiation dose for a 6.5 M HNO_3 solution containing 2 mM total Am, oxidized using sodium bismuthate. The initial Am(VI) concentration was 1.67 mM, for an 84 % oxidation yield.

Table 5. Slope, *m* (mmol Am(VI) kGy^{-1}) of the plot of the decrease in [Am(VI)] versus absorbed dose at various $[Am_{tot}]$ (mM) and $[HNO_3]$ (M). Dose rate = 4.32 kGy h^{-1}.

$[Am_{tot}]$	$[HNO_3]$	[Am(VI) yield (%)]	*m*
1	3	89.9	8.69E-4
2	1	22.6	7.76E-4
2	3	67.7	8.64E-4
2	6.5	83.7	7.31E-4
4	3	96.2	8.21E-4
4	6.5	45.8	7.95E-4

Work is currently in progress to complete the matrix of acidity and Am concentration conditions in Table 5, and to fit these data with mixed order kinetic models. Experiments at different dose rates are also planned in an effort to elucidate the mechanism of reduction. Finally, experiments were also initiated to understand the effect of other redox active metals present in the raffinate on radiolytic reduction rates for Am(VI). When irradiated in the presence of 5 mm Ce(IV), a 1 mM Am solution with initially 0.87 mM Am(VI) in 6.5 M HNO_3 exhibited a slope for the reduction rate of Am(VI) of 1.04 E-4 mmol Am(VI) kGy^{-1}. Thus, the presence of Ce(IV) increased the radiolytic stability of Am(VI) by a factor of 8, probably by scavenging produced reducing agents.

4. ALTERNATIVE OXIDANTS

A significant effort has been expended in the search for an alternative to sodium bismuthate as an oxidant. The other chemical oxidants that have shown utility for Am(VI) production are Ag-catalyzed $Na_2S_2O_8$, Ag-, and Co-catalyzed ozone, and $KNa_4Cu(HIO_6)_2$ (Cu(III) periodate). Although these oxidants are capable of oxidizing Am, they have not proven practical for use in solvent extraction. Preparation of Am(V) and Am(VI) under this program using $Na_2S_2O_8$ were summarized in ref [11]. Its utility for fuel cycle applications is limited by its inability to oxidize americium in strongly acidic solution and the generation of sulfate as a byproduct. Silver and Co catalysis using ozone was investigated at LANL and found to be ineffective when coupled with solvent extraction.

The most favorable results were found using Cu(III) periodate in conjunction with DAAP extraction. [5] However, while the D_{Am} achieved indicated extraction of some oxidized Am, they are marginal for process application. This is attributed to the rapid reduction of Cu(III) during the organic phase contact, and the absence of a holding oxidant. No Am(VI) extraction was achieved when using Cu(III) periodate as an oxidizing agent in tandem with DEHBA extraction. The use of Cu(III) as an Am oxidant is now the subject of a NEUP investigation at Colorado School of Mines and is no longer being actively pursued at INL.

Electrochemical oxidation is also being developed for use in Am oxidation, however, the latest developments in that technique will be discussed in a separate report (Milestone M3FT-16IN030103023).

5. CONCLUSION

A centrifugal contactor hot test was performed using bismuthate oxidation and using 2 cm contactors configured in a counter current fashion, employing two DEHBA extraction and two H_2O_2 stripping stages. An overall Am extraction efficiency from a Ru-free raffinate simulant of 64 % was obtained in this test. Future work will include a determination of contact time and extraction efficiency for the new contactors. The effect of trace reducing agents upon bismuthate oxidation efficiency was evaluated and it was determined that millimolar amounts of H_2O_2 or HNO_2 do not interfere as long as residual solid bismuthate is present. Am(VI) is reduced by externally applied gamma-irradiation, at rates that are independent of the initial [Am(VI)] or acid concentration. This result is inconsistent with the reduction being due to reaction with HNO_2. The presence of Ce(IV) provided radioprotection for Am(VI), increasing its lifetime by a factor of 8.

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7. INDICATORS OF PROJECT QUALITY

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