

AM(VI) PARTITIONING STUDIES: FY14 FINAL REPORT

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Am(VI) Partitioning Studies: FY14 Final Report

Fuel Cycle Technology

***Prepared for
U.S. Department of Energy
Sigma Team for Minor Actinide
Separations
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Date***

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SUMMARY

The use of higher oxidation states of americium in partitioning from the lanthanides is under continued investigation by the sigma team. This is based on the hypothesis that Am(VI) can be produced and remain stable in irradiated first cycle raffinate solution long enough to perform solvent extraction for separations. The stability of Am(VI) to autoredution was measured using millimolar americium concentrations in a 1-cm cell with a Cary 6000 UV/Vis spectrophotometer for data acquisition. At millimolar americium concentrations, Am(VI) is stable enough against its own autoredution for separations purposes. A second major accomplishment during FY14 was the hot test. Americium oxidation and extraction was performed using a centrifugal contactor-based test bed consisting of an extraction stage and two stripping stages. Sixty-three percent americium extraction was obtained in one extraction stage, in agreement with batch contacts. Promising electrochemical oxidation results have also been obtained, using terpyridine ligand derivatized electrodes for binding of Am(III). Approximately 50 % of the Am(III) was oxidized to Am(V) over the course of 1 hour. It is believed that this is the first demonstration of the electrolytic oxidation of americium in a non-complexing solution. Finally, an initial investigation of Am(VI) extraction using diethylhexylbutyramide (DEHBA) was performed.

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ACRONYMS

CFA	Central Facilities Area
CINC	Costner Industries Nevada Corporation
DAAP	Diamylamylphosphonate
DEHBA	Diethylhexylbutyramide
DEHiBA	Diethylhexylisobutryamide
FTO	Fluoride-doped tin oxide
GANEX	Group actinide extraction
INL	Idaho National Laboratory
LWCC	Liquid waveguide capillary cell
<i>n</i> -ITO	Nano-indium tin oxide
TBP	Tributylphosphate
UNC	University of North Carolina
UV/Vis	Ultraviolet/visible spectroscopy

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1. INTRODUCTION

The use of higher oxidation states of americium in partitioning from the lanthanides is under continued investigation by the Sigma Team for Minor Actinide Separation. This is based on the hypothesis that Am(VI) can be produced and remain stable in irradiated first cycle raffinate solution long enough to perform solvent extraction for separations. Our previous work has characterized the DAAP extraction of Am(VI) and the behavior of the lanthanides and other common fission products and inert constituents under the same conditions (Mincher et al. 2012). This work has allowed us to begin investigation of flowsheet concepts for such a separation (Law et al. 2014). Ideally, co-extraction of hexavalent Np, Pu, and Am could be performed simultaneously, on the raffinate from a prior uranium extraction process. The objectives of FY14 work, based on the assigned milestones were:

1. Examine the stability of produced Am(VI) under various solution conditions by examination of reduction kinetics.
2. Modify the proposed flowsheet as necessary, and run a hot test to perform americium oxidation and extraction under test bed conditions.
3. Continue collaborative research with UNC-Chapel Hill on electrolytic americium oxidation.

The most important expectation for the FY14 work was to demonstrate an understanding of Am(VI) stability well enough to support the hot test.

2. SIGNIFICANCE

The separation of americium from the lanthanides is desirable to facilitate incorporation of americium in fast reactor fuel for transmutation purposes. Development of a process to separate americium based on its oxidation state has the potential to greatly simplify current flowsheets. If americium were extracted as Am(VI) from the nitric acid concentrations typical of fuel cycle separations, selective stripping of lanthanides (III) would no longer be necessary. Further, a GANEX-type co-extraction of all the actinides from oxidized solution is readily envisioned.

3. APPROACH

In past unpublished work on this program, the stability of Am(VI) varied depending on experimental conditions. Therefore, a thorough examination of the autoreduction of Am(VI) under solution conditions of interest to fuel cycle separations was initiated in FY14. The first work describing the autoreduction of the higher oxidation states of americium was reported by Asprey and Stephanou (1950). It was shown that Am(VI) reduced to Am(V) in linear fashion with respect to time, following which Am(V) reduced in linear fashion to Am(III). The rates of reduction of the high valent species were zero order with respect to [Am(VI)] and any effect of hydrogen ion concentration was thought to be small. Hall and Markin (1957) later reported similar kinetics. The authors attributed this autoreduction to the H₂O₂ product of americium alpha decay. All this early work was performed in HClO₄ solution presumably using ²⁴¹Am, and similar investigations of americium reduction kinetics in HNO₃ have not been reported.

Since Am(VI) is now routinely prepared over a wide range of nitric acid concentrations using sodium bismuthate, that approach was used here to measure autoreduction kinetics over a range of HNO₃ concentrations. The reduction was followed by UV/Vis spectroscopy, using tracer americium in the 100-cm liquid waveguide capillary cell (LWCC), and using higher americium concentrations in a standard 1-cm cell. The higher data quality found when using the 1-cm cell in conjunction with the Cary 6000 instrument resulted in the abandonment of the LWCC for future reduction kinetics measurements. In addition, the reductive effects of contact with organic solutions and various system structural materials commonly encountered in fuel cycle separations were also investigated, using solvent extraction distribution ratios.

These findings, in conjunction with the results of the FY13 cold test, were used to design a hot test bed. This test bed was constructed in a posted contamination area-fume hood, and consisted of three stages of centrifugal contactors, with stage 1 being the extraction, stage 2 being an americium strip, and stage 3 being a cerium strip. This is the first demonstration of hexavalent americium extraction using a continuous, process-like test bed.

4. SUMMARY OF RESULTS

4.1 Hexavalent Americium Stability

The full results of the investigation into Am(VI) stability were reported in a manuscript submitted for publication, in fulfillment of program milestone number M2FT-14IN030031 requirements (Mincher et al. 2014). Only the main conclusions are summarized here. It was clearly demonstrated that a self-consistent set of extinction coefficients for the various americium species over a range of nitric acid concentrations is needed. If accurate concentrations cannot be calculated for the various americium species based on their UV/Vis absorbances, then neither can reduction rate constants be accurately calculated. However, several conclusions about Am(VI) autoreduction may be postulated. These include that the most precise measurements will be made using millimolar americium concentrations in a 1-cm cell and with the Cary 6000 UV/Vis spectrophotometer for data acquisition. The autoreduction of Am(VI) in 6.5 M HNO₃ using this equipment and data acquisition is shown in Figure 1. The most important conclusion to be drawn is that at millimolar americium concentrations, Am(VI) is stable enough against its own autoreduction for separations purposes.

The lack of dependence on nitric acid concentration suggests either that HNO₂ is not an important reducing agent toward Am(VI), or that HNO₂ is a low yield α -radiolysis product of nitric acid. Hydrogen peroxide was shown to readily reduce Am(VI) but not Am(V), in contrast to predictions based on the published rate constants for the reaction of Am(V) and Am(VI) with H₂O₂ (Zaitsev et al. 1960; Woods et al. 1974). The determination of the rate constants for the reactions of Am(V) and Am(VI) with HNO₂ and H₂O₂ would also be valuable future work. As expected, organic compounds act as reducing agents toward Am(VI), and also Am(V). This agrees with previous flowsheet development work (Law et al. 2014) that suggested that additional extraction cycles may require reoxidation. An important area of future investigation will be investigating the efficiency of the re-oxidation of previously treated americium solutions.

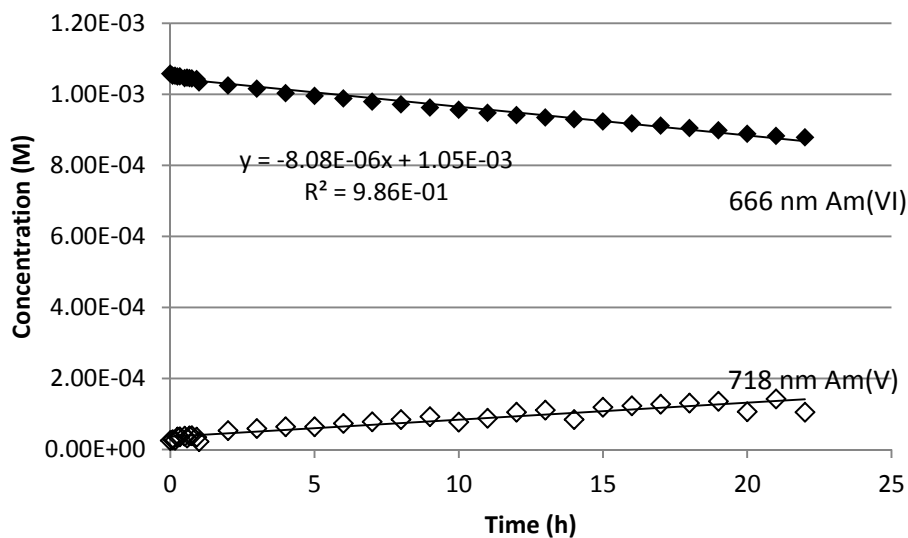


Figure 1. The autoreduction of Am(VI) in a 6.5 M HNO₃ solution containing 2×10^{-3} M total Am, based on the absorbance measured for Am(VI) at 666 nm (closed diamonds), in a 1-cm cell using the Cary 6000. Rate constant based on the mean of linear fit for the entire data set is 0.004 h^{-1} . Using the fit to only the first ten hours a rate constant of 0.005 h^{-1} was obtained.

4.2 Hot Test

A major accomplishment during FY14 was the hot test. Americium oxidation and extraction was performed using a centrifugal contactor-based test bed consisting of an extraction stage and two stripping stages. Based upon batch contact results, flowsheet design and a previous cold test, a hot test bed was successfully designed, built and operated in a radiological fume hood at CFA at INL. The work is described in detail in an FY14 FCR&D report SWF-2014-000218 (Mincher et al. 2014b), in fulfillment of milestone M3FT-14IN0303033. An $^{243}\text{Am}/^{139}\text{Ce}$ -spiked raffinate simulant feed was oxidized with sodium bismuthate, filtered through a Teflon filter, and fed into a custom built CINC 5-cm centrifugal contactor, made of materials determined to be inert toward Am(VI). Sixty-three percent americium extraction was obtained in one stage using 1 M DAAP/dodecane, in agreement with batch contacts. This demonstrates for the first time that Am(VI) can be extracted using process equipment. Although Am(VI) was also expected to be easily reduced and stripped based on batch contacts, the short residence time apparently made stripping ineffective. This finding is fortuitous in that it should now be possible to design a scrub contact into the flowsheet, which was previously thought to be impossible due to undesired americium reduction and stripping during batch contact scrubs. Cerium stripping using 0.3% H₂O₂ was also inefficient, in spite of the success of that strip during cold testing. This is again attributed to residence time of the contact. However, selective stripping should still be possible, given either longer residence times in contact with the organic phase, or more aggressive reductants in the strip solutions. The centrifugal contactor and filtration system employed in this test is shown in Figure 2.



Figure 2. Hot hood showing the three stage centrifugal contactor test bed, simulant feed reservoir and bismuthate filter. Note: The system was photographed prior to taking it hot and therefore, there are no Contamination Area postings on the hood.

4.3 Americium Electrochemistry

Promising results with a high surface-area, fluoride-doped tin oxide (FTO) electrode, coated with nano-particles of tin-doped indium oxide (*n*ITO) have been obtained. The surface was derivatized with a terpyridine ligand for binding of Am(III). At an anodic potential of 1.8 V vs. Ag/AgCl (~0.8 V below the Am (III/IV) redox couple) in a 0.1 M nitric acid/0.95 M sodium nitrate solution containing 0.4 mM total americium, approximately 50 % of the Am(III) was oxidized to Am(V) over the course of 1 hour as observed by UV/Vis spectroscopic measurements. The multi-electron oxidation of Am(III) is believed to be facilitated by coordination to the surface bound terpyridine ligand. It is believed that this is the first demonstration of the electrolytic oxidation of americium in a non-complexing solution. These results were presented in more detail in fulfillment of milestone M4FT-14IN0303032.

4.4 Butyramide Extractions

An initial investigation of Am(VI) extraction using two butyramides; diethylhexylbutyramide (DEHBA), and diethylhexylisobutyramide (DEHiBA). Of these, DEHBA had the better performance. Similarly to DAAP, the highest distribution ratios for oxidized americium extraction occurred at 6-7 M HNO₃, being slightly above 1. The mixture of 1 M DEHBA/1M TBP provided $D_{Am} \sim 4.7$. According the literature, the butyramide dihexylhexanamide may provide still higher extraction efficiency at lower concentrations, and is worthy of further investigation (Pathak et al. 2000). A benefit of this approach is that the butyramides do not seem to be as reducing toward Am(VI) as is DAAP.

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7. COLLABORATORS AND PARTICIPANTS

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- 2) Nicholas Schmitt, INL, staff collaborator, solvent extraction and UV/Vis experiments, autoreduction kinetics, hot test support.
- 3) Richard Tillotson, INL, staff collaborator, solvent extraction experiments, hot test support.
- 4) Lonnie Olson, staff collaborator, DAAP irradiation, hot test support.
- 5) Jack Law, INL, staff collaborator, flowsheet design, hot test support.
- 6) Troy Garn and Mitch Greenhaulgh, INL, staff collaborators, hot test support.
- 7) Travis Grimes, INL, staff collaborator, autoreduction kinetic measurements.
- 8) Tom Meyer, UNC-Chapel Hill, and PostDoc Chris Dare, Am electrochemistry research funded via INL participation in sigma team.
- 9) Gregg Lumetta, PNNL, Cu(III) oxidations. Funded through independent sigma team program.