Hexavalent Americium Recovery Using Copper (III) Periodate

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KEY WORDS: americium, nuclear fuel cycle, curium, solvent extraction

ABSTRACT: Separation of americium from the lanthanides is considered one of the most difficult separation steps in closing the nuclear fuel cycle. One approach to this separation could involve oxidizing americium to the hexavalent state to form a linear dioxo cation while the lanthanides remain as trivalent ions. This work considers aqueous soluble Cu^{3+} periodate as an oxidant under molar nitric acid conditions to separate hexavalent Am with diamyl amylphosphonate (DAAP) in n-dodecane. Initial studies assessed the kinetics of Cu^{3+} periodate auto-reduction in acidic media to aid in development of the solvent extraction system. Following characterization of the Cu^{3+} periodate oxidant, solvent extraction studies optimized the recovery of Am from varied nitric acid media and in the presence of other fission product, or

fission product surrogate, species. Short aqueous/organic contact times encouraged successful recovery of Am (distribution values as high as 2) from nitric acid media in the absence of redox active fission products. In the presence of a post-PUREX simulant aqueous feed, precipitation of tetravalent species (Ce, Ru, Zr) occurred and the distribution values of ^{241}Am were suppressed, suggesting some oxidizing capacity of the Cu^{3+} periodate is significantly consumed by other redox active metals in the simulant. The manuscript demonstrates Cu^{3+} periodate as a potentially viable oxidant for Am oxidation and recovery and notes the consumption of oxidizing capacity observed in the presence of the post-PUREX simulant feed will need to be addressed for any approach seeking to oxidize Am for separations relevant to the nuclear fuel cycle.

Introduction

Advanced nuclear fuel cycles aim to improve uranium fuel efficiency and decrease the amount of high-level waste (HLW), the overall radiotoxicity, and secondary waste produced during reprocessing. Only approximately five percent of the uranium in a nuclear fuel rod is consumed before fission products, particularly the lanthanides, prevent the efficient consumption of uranium in the power reactor. Lanthanides have relatively high neutron capture cross-sections and recover neutrons through (n, γ) reactions that would otherwise forward the fission process in the reactor. One way to improve uranium fuel efficiency and decrease the amount of HLW developed during nuclear power production is to selectively recover uranium, neptunium, plutonium, and americium from the fission products after their production and partial consumption in a conventional (pressurized water or boiling water) nuclear reactor. After recovery, these actinides could be either returned to a conventional reactor (plutonium or

uranium) for further power production, or transmuted in a fast neutron spectrum reactor (neptunium and americium) to decrease the decay timelines associated with these elements.[1]

The accessible redox chemistry of uranium, neptunium and plutonium allows for relatively straightforward recovery of these elements away from the fission products – especially the lanthanides. Separation of americium from the lanthanides is thought to be one of the most difficult separations in closing the nuclear fuel cycle due to their mutual stability as trivalent cations in aqueous solution and affinity for hard acid donors.[1] As a result of their comparable chemistry, the trivalent 5*f* actinides follow trivalent 4*f* lanthanides in currently operated nuclear fuel cycles.

Several options have been considered to accomplish trivalent actinides/lanthanide separations that would be compatible with advanced nuclear fuel cycle goals. Many of these approaches utilize soft donor (nitrogen, sulfur) complexants or extractants to selectively interact with the actinides over the lanthanides.[2–6] These systems can produce separation factors as high as 10,000 between americium and europium, but require the use of synthetically complex extractants, can be kinetically slow, or prohibitively sensitive to the harsh radiation environment presented from the irradiated nuclear fuel.[7–9] Additionally, these methods would require the development of at least two separation steps, since the soft donor chemistry has not been optimized for the group recovery of uranium, neptunium, plutonium and americium from the fission products. A more direct approach is to remove Am along with U, Np, and Pu after oxidation of the transuranics to the hexavalent state.[10–12] This would decrease the amount of secondary waste volumes and would function more similarly to the internationally familiar Plutonium Uranium Redox Extraction (PUREX) process.

The PUREX process utilizes tri-n-butyl phosphate (TBP) to selectively remove hexavalent, linear dioxo actinides (e.g. UO_2^{2+}) and tetravalent actinides (e.g. Pu^{4+}), from the remaining fission products, Cm^{3+}, and Am^{3+} in molar nitric acid solutions.[13] Oxidation of Am^{3+} to the hexavalent state produces the linear dioxo-cation AmO_2^{2+}, which can be separated using chemistry similar to that which removes UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}.[14,15] The significant 1.68 V oxidation potential of the AmO_2^{2+}/ Am^{3+} couple requires the process to use strong oxidizing agents.[16,17] Several approaches have been used for americium oxidation, but these approaches are only effective in dilute (< 0.1 M H^+) acid media[17], only oxidize americium to the pentavalent state or use the insoluble sodium bismuthate oxidant.[18,14,19,20] Possible separations in an advanced nuclear fuel cycle would benefit from separations compatibility with higher acid media, a soluble oxidant that would simplify solvent extraction operations and having the majority of Am in extractatable hexavalent state, as opposed to the less charge dense and poorly extracted pentavalent state.[21]

Utilizing the strong Cu^{3+} to Cu^{2+} reduction potential (2.4 V), copper (III) periodate recently demonstrated effective oxidization of Am^{3+} to AmO_2^{2+} in 0.25 to 3.5 M HNO_3 solutions.[22] The oxidation of Am^{3+} to AmO_2^{2+} was monitored using UV-Visible spectroscopy. A 10:1 molar excess ratio of Cu^{3+} periodate to Am^{3+} resulted in 99%+ conversion of Am^{3+} to AmO_2^{2+} in 0.25 – 2 M HNO_3. At 3 M HNO_3, the conversion was 98% and further decreased to 76.8% in 3.5 M HNO_3. Using the same stoichiometric ratio, $NaBiO_3$ in 3.5 M HNO_3 was found to oxidize only 19% of Am^{3+}. Increasing the molar ratio of Cu^{3+} periodate to 20:1, Am^{3+} was oxidized with 95% efficiency in 3.5 M HNO_3. Post oxidation, the resulting Cu^{2+} and periodate ions have the advantage of being soluble in nitric acid. There was an indication that periodate formed a complex with AmO_2^{2+} in 0.25 M HNO_3, but was not present at elevated nitric acid

concentrations.[22] Similarly, the periodate anion has been reported to form complexes with UO_2^{2+} at low acid conditions (pH 2.6).[23]

The effective oxidation of Am^{3+} by Cu^{3+} periodate and benign degradation products in molar nitric acid are favorable for solvent extraction processes. However, the oxidation of Am^{3+} competes with the auto-reduction of Cu^{3+} periodate in nitric acid. The auto-reduction can explain why 20:1 Cu^{3+} periodate to Am molar ratio in 3.5 M HNO_3 was necessary for quantitative oxidation to occur. This manuscript assesses the reduction kinetics of Cu^{3+} periodate in nitric acid to evaluate whether its lifetime is suitable for application in solvent extraction processes. Following the reduction studies, oxidation of ^{241}Am by Cu^{3+} periodate and extraction by diamyl amylphosphonate (DAAP) conditions were optimized, and separation of ^{241}Am from a trivalent lanthanide surrogate, ^{244}Cm, demonstrated. A final study considers the recovery of americium from an aqueous nuclear fuel simulant feed that might be anticipated after uranium, neptunium and plutonium recovery that would happen during an initial PUREX-type cleanup to focus on fission product impacts on this chemistry. This manuscript will refer to this as a 'post-PUREX' simulant.

Experimental Section

Synthesis of copper (III) periodate followed a method using potassium persulfate to oxidize copper.[24] Using a 500 mL round bottom flask, 3.12 g $CuSO_4 \bullet 5H_2O$ (Mallinckrodt), 5.34 g $NaIO_4$ (Acros organics), 16.04 g KOH (Fisher), and 2.51 g $K_2S_2O_8$ (Hach) were dissolved in 0.2 L 18 MΩ H_2O. The mixture was refluxed for 30 minutes, and then allowed to cool to room temperature. When cool, the solution was filtered through a glass fritted funnel. The filtrate was chilled in an ice bath to remove potassium sulfate. The solution was filtered once more through

the glass fritted funnel. An 8 M $NaNO_3$ solution was added to the filtrate until crystals began to form. The solution sat over night to allow the crystals to precipitate out. After crystallization, the solution was an opaque yellow color. The dark brown crystals were collected by filtration, and rinsed with 18 MΩ H_2O until they began to dissolve in order to remove any excess KOH. Lastly, the crystals were dried in a lyophilizer, Labconco freeZone 6.

The copper percent was established by dissolving a known amount of copper (III) periodate in 4 M H_2SO_4. The brown copper (III) periodate color faded to the familiar light blue Cu(II) color. The absorbance of the Cu(II) peak at 805 nm was compared to a calibration plot of $CuSO_4$ in 4 M H_2SO_4. The copper percent was found to be 9.86 ± 0.03 wt%, which is higher than other reported literature value of 7.53% using the molecular formula $Na_5[Cu\{IO_5(OH)\}_2]\bullet 12H_2O$ or 7.37% with $Na_5[Cu\{IO_5(OH)\}_2]\bullet 14H_2O$ stoichiometry.[22,24] The higher value is due to the lyophylizer's ability to remove nearly all hydrated water. As a result, the stoichiometry was calculated to be $Na_5[Cu\{IO_5(OH)\}_2]\bullet 1H_2O$ using a measured average hydration state from copper mass analysis of 9.86%. Copper (III) periodate was dissolved in water for UV-Vis spectroscopy analysis, and displayed the characteristic peaks at 420 nm, 261 nm, and 210 nm (**SI Figure 1**). An FT-IR was collected on a copper (III) periodate sample containing 7.1% Cu (close to 7.37% of $Na_5[Cu\{IO_5(OH)\}_2]\bullet 14H_2O$), and lyophilizer dried copper (III) periodate (9.86 ± 0.03 wt% Cu) (**SI Figure 2**).

Reduction of Cu^{3+} periodate was monitored via UV-Vis on an Olis RSM 1000 instrument. The stopped-flow mode was utilized to observe the reduction of Cu^{3+} peak (420 nm) at 21 scans per second for 1 second. To monitor the reduction, equal volumes of 400 μM copper (III) periodate in 18 MΩ H_2O and HNO_3 (Optima grade, Fisher) solution was injected into the stop-flow. Since equal volumes were mixed, the data is reported as the final HNO_3 concentration

whereas the initial concentration of HNO_3, prior to injection, was twice the molarity. The stopped-flow mode is limited to 235 nm collection window and cannot collect absorbance values below 250 nm, eliminating the ability to monitor periodate during the reduction. Using the normal scanning mode, excess Cu^{3+} periodate was reduced in a pH 3 HNO_3 solution. This allowed qualitative information to be collected on the periodate anion.

Prior to extraction studies, the ^{241}Am stock from Eckert and Ziegler in 1 M HCl was converted to HNO_3 media by sequential evaporations of HCl, dilutions with optima HNO_3, and final dissolution in 0.1 M HNO_3. Solvent extraction experiments were carried out by weighing 20 mg of Cu^{3+} periodate in a 2 mL glass vial. Extractant solution of 1 M DAAP (Eichrom) in n-dodecane (Fisher) was pre-equilibrated with equal volumes of the appropriate nitric acid solution for 15 minutes. The nitric acid solutions were freshly made with optima HNO_3 and 18 MΩ H_2O. The 0.1 M HNO_3 ^{241}Am stock was spiked into the nitric acid solution being studied, 0.5 – 5 M HNO_3. Carrying out one extraction at a time, 500 μL of Am spiked nitric acid was added to 20 mg Cu^{3+} periodate (62 mM) immediately followed by addition of 500 μL of pre-equilibrated 1 M DAAP. The ^{241}Am activity of each sample was 0.0010 μCi resulting in a 2.6 nM ^{241}Am concentration. For complete oxidation, the 20:1 molar excess of Cu^{3+} periodate to the tracer 2.6 nM ^{241}Am would equal an unfeasible 17 ng of Cu^{3+} periodate. The 62 mM Cu^{3+} periodate used is in significant ($\sim 10^7$) molar excess. This amount minimizes any effect from Cu^{3+} periodate auto-reduction, and ensures ^{241}Am should be thoroughly oxidized prior to contact with the extractant solution. The vial was shaken by hand for 5 seconds, and centrifuged for 30 seconds to promote phase disengagement. Both phases were sampled and counted on a Packard Cobra II auto-gamma counter, and were found to have mass recoveries of 98 ± 4%.

The ability to oxidize and extract Am from solutions encountered in nuclear fuel recycling was test on a post-PUREX simulant feed obtained from Pacific Northwest National Laboratory. This simulant contains Fe, Pr, Eu, Gd, La, Mo, Nd, Ru, Sm, Sn, Te, Zr, Sr, Pr, Y, and Ce in 2.9 M HNO_3. An analysis of the listed elements was completed on the simulant before and after contact with Cu^{3+} periodate in 1:1 mole ratio using an inductively coupled plasma – optical emission spectrometer (ICP-OES). This analysis was completed using an iCAP 6500 Duo ICP-OES in axial mode purchased from Thermo Scientific (Waltham, MA). A five point calibration curve was prepared from gravimetric dilution of 1000 ppm single element standards obtained from high Purity Standards (Charleston, SC). The calibration curve standards and dissolved samples were prepared with 2% optima nitric acid. The elements Y and Ce could not be quantified using ICP-OES due to peak interference from other lanthanide elements. Cerium was of particular interest due to its ability to form a tetravalent cation, and its interaction with Cu^{3+} periodate was therefore monitored using UV-Vis spectroscopy. Extraction experiments were completed same manner as previously described. Since the post-PUREX simulant is in 2.9 M HNO_3, the aqueous phase oxidation time was monitored from 10 to 50 second prior to mixing with pre-equilibrated 1 M DAAP for 5 seconds. The aqueous-organic contact times were adjusted from 5 to 30 seconds while maintaining a 10 second aqueous oxidation time. The ^{241}Am mass recoveries were found to be 83 ± 1%.

Curium extractions were done following the method described for Am. However, since ^{244}Cm is not a strong gamma emitter, phases were counted using Packard Tri-Carb 2500 Liquid Scintillation Counter. Triplicate extraction samples were collected, and are reported as the mean value with less than 2% standard deviation. Each sample contained an initial ^{244}Cm activity of

0.040 μCi, and mass recovery was 100 ± 2%. All extraction experiments were carried out with triplicate samples at room temperature, 24 ± 2 ºC.

Caution! *The isotopes ^{241}Am and ^{244}Cm are radioactive. All manipulation of the radioactive elements were safely handled in a radioactive designated fume hood.*

Results and Discussion

Copper (III) periodate reduction

Reduction of Cu^{3+} periodate was first monitored using UV-Vis spectroscopy with 0.001 M HNO_3 solution in excess of Cu^{3+} periodate and is presented in **Figure 1**. During reduction of Cu^{3+} periodate, the periodate absorbance decreased and shifted to lower wavelengths. The Cu^{3+} peak decreased linearly over time. The autoreduction of Cu^{3+} periodate in excess nitric acid, presented in **Figure 2A,** followed a pseudo-first order decay and the rate of this reduction was seen to have an acid dependence. **Figure 3** shows that the reduction rate increases as the concentration of acid increases from 0.05 M to 0.5 M HNO_3. **Figure 3** also demonstrates a saturation effect with respect to acid concentration on the rate of reduction. The role of periodate on Cu^{3+} periodate auto-reduction was also considered by adding sodium periodate in the presence of 0.5 M HNO_3, shown in **Figure 2B**. The observed reduction rate constant of Cu^{3+} periodate in varying amounts of excess sodium periodate are presented in **Table 1**. Rate constant values show the reduction rates decrease as the molar concentration of sodium periodate increases relative to Cu^{3+} periodate. This behavior matches what has been observed in the literature for Cu^{3+} periodate reduction under alkaline conditions.[25,26]

While reduction of higher oxidation state metal periodates under basic conditions or neutral pH conditions have been assessed in the prior literature, reports in acidic media are non-existent.[25–27] This is a reflection of the limited stability of these metal salts under acidic conditions. The information presented in **Figure 3** and **Table 1** suggests the auto-reduction mechanism for Cu^{3+} periodate under acidic conditions proceeds via a dissociative process.

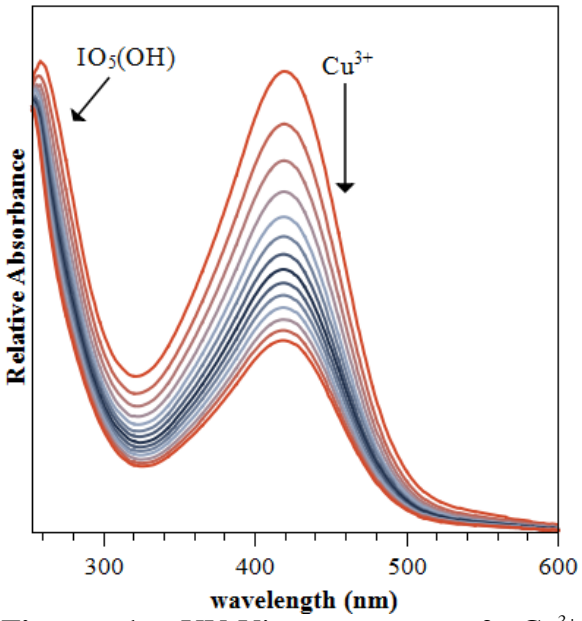

Figure 1: UV-Vis spectrum of Cu^{3+} periodate reduction in pH 3 HNO_3. The Cu^{3+} peak at 420 nm decreases overtime. The periodate peak decreases and shifts to lower wavelengths.

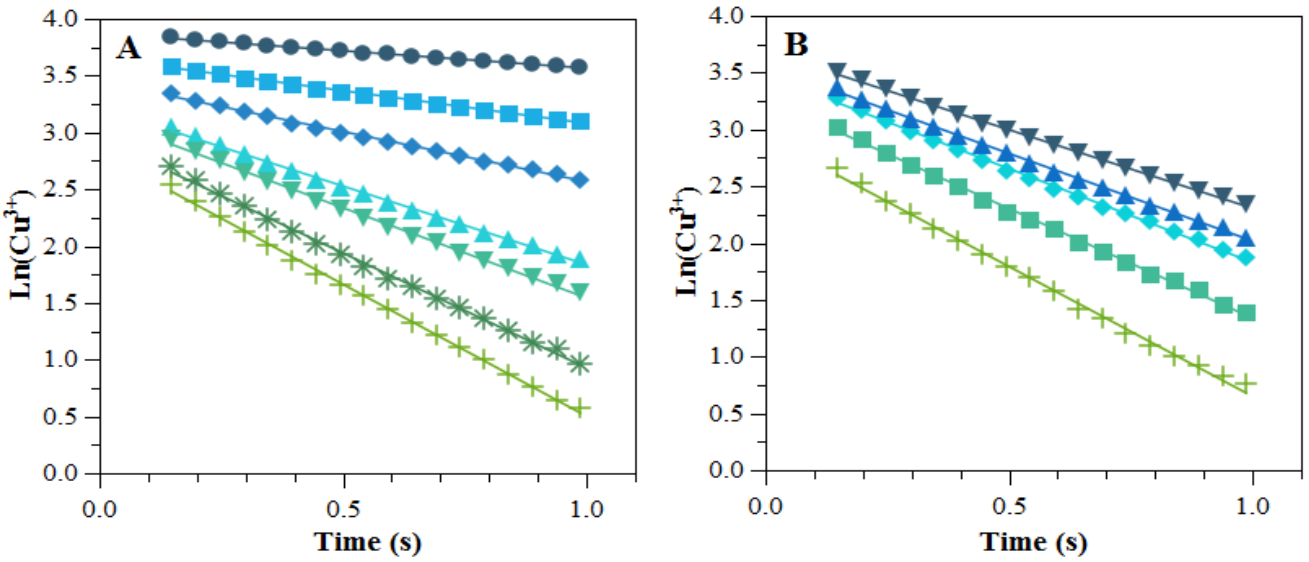

Figure 2: UV-Vis reduction of Cu^{3+} periodate set to pseudo-1st order rate law. (A) 400 μM Cu^{3+} periodate reduction in 0.05 (●), 0.10 (■), 0.15 (◆), 0.25 (□), 0.30 (□), 0.40 (✳) and 0.5 M HNO_3 (+) over 1 second. The rate of reduction increases with increased HNO_3 concentrations. (B) 400 μM Cu^{3+} periodate reduction in 0.5 M HNO_3 (cross) with molar addition of Cu^{3+} periodate:sodium periodate from 1:0 (+), 1:1 (■), 1:2 (◆), 1:3 (□), and 1:4 (□). The rate of reduction decreases as concentration of sodium periodate increases.

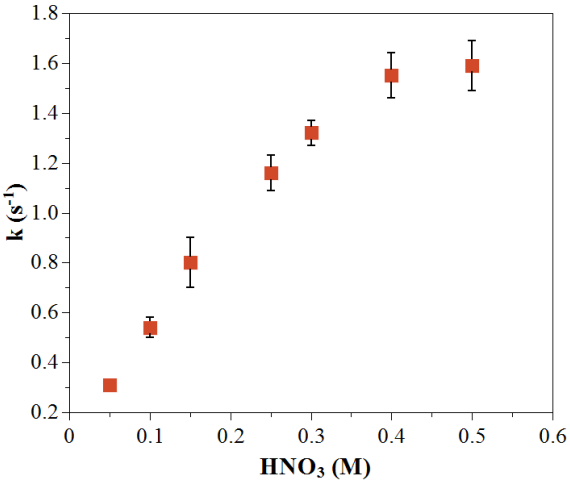

Figure 3: Acid dependency of observed rate constants for the reduction of Cu^{3+} periodate upon mixing with nitric acid.

Table 1: Pseudo-1st order rate constant for Cu^{3+} periodate reduction in 0.5 M HNO_3 with excess periodate (moles Cu^{3+} periodate:moles sodium periodate). The rate of reduction

decreases as concentration of periodate increases.

Molar ratio	k (s^{-1})
1:4	1.38 ± 0.03
1:3	1.53 ± 0.07
1:2	1.62 ± 0.10
1:1	1.87 ± 0.09
1:0	2.04 ± 0.09

Prior to mixing, the Cu^{3+} periodate solution has a pH of 10.33. Under these conditions the Cu^{3+} periodate complex predominately takes the form of $[Cu(H_2IO_6)_2]^{5-}$ with two orthoperiodate ions complexed to the Cu^{3+}. At this degree of protonation orthoperiodate allows for bidentate coordination to the metal, therefore the two ligands satisfy the coordination number of the square-planar Cu^{3+}.[27] This configuration gives the Cu^{3+} redox stability in solution. Studies in alkaline media have suggested that when one orthoperiodate ion dissociates from the complex the Cu^{3+} becomes accessible to reductants.[25,26] This dissociation process matches the observations made under acidic conditions in this study. The small protonation equilibrium constants of $H_3IO_6^{2-}$, $H_4IO_6^-$, and H_5IO_6 indicate protonation is thermodynamically favorable under acidic conditions. The equilibrium constants for these are listed in **Table 2**.[28] As one of the orthoperiodate anions leaves the Cu^{3+} complex, the periodate becomes protonated and reformation of the complex with Cu^{3+} is inhibited. This results in the coordination environment around the complex being unfilled and leaves the Cu^{3+} available to complex with reductants causing Cu^{3+} reduction to proceed more readily under higher acid concentrations.

Table 2: Equilibrium constants of various periodate species at 25°C. As pH increases, a

progressive deprotonation and dehydration of periodate species occurs.[27]

$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+$ $K = 5.1 \times 10^{-4}$

$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+$ $K = 4.9 \times 10^{-9}$

$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+$ $K = 2.5 \times 10^{-12}$

$H_4IO_6^- \rightleftharpoons IO_4^- + 2\ H_2O$ $K = 29$

The chemical species most likely being oxidized by Cu^{3+} is H_2O to O_2. The high concentration (relative to other species in solution) and oxidation potential for the H_2O to O_2 (1.22 V at pH 0) is well within the oxidative capacity of Cu^{3+} (2.4 V in water at 25 ºC).[28] Addition of excess periodate, **Table 1**, in the system momentarily shifts the protonation equilibrium of periodate anions causing Cu^{3+} to remain complexed to two orthoperiodate ligands and impedes the reduction rate. The observations made in this kinetic study appear to suggest the auto-reduction of Cu^{3+} periodate proceeds via a dissociative process, however these results alone are insufficient to fully interpret the reaction mechanism and rate law. The acid saturation effect on the rate (**Figure 3**) does however suggest the reduction rate of Cu^{3+} periodate will not be further affected by the higher acid concentrations relevant to the americium oxidation.

Actinide Solvent Extraction Studies

The impact of copper periodate on a uranium recovery by DAAP, a solvating ligand, in molar acid media (a standard solvent extraction reaction without the possibility of reduction of the metal ion) is presented in **SI Figure 3**. Metal ion extraction by DAAP from nitrate media generally proceeds as follows,

$$M^{x+} + xNO_3^- + \overline{yDAAP} \rightarrow \overline{M(NO_3^-)_x(DAAP)_y}$$

where an overbar denotes a species in the organic phase and y varies between two and three depending on how many extractants are required to saturate the extracted metal's coordination sphere. A slight decrease in uranium recovery is observed when the acid concentration is 0.5 M HNO_3. This may be related to periodate complexing of the uranyl cation at low acidities.[22,23] This study observed D = 79 ± 14 when Cu^{3+} periodate is present and 87 ± 18 without periodate at 24 ºC. Distribution ratios are within experimental error in presence and absence of Cu^{3+} periodate between 1 and 5 M HNO_3. The results show Cu^{3+} periodate did not impact extraction of uranyl cation by DAAP in molar nitric acid; therefore, it seems possible Cu^{3+} periodate would not impact other hexavalent actinide chemistries in the separation system.

Distribution values for ^{241}Am using 1 M DAAP from 0.5 M to 5 M HNO_3 oxidized by Cu^{3+} periodate and in the absence of Cu^{3+} periodate are presented in **Figure 4**. All values presented in **Figure 4** are the mean of triplicate samples with a relative standard deviation less than 13%. The results show americium has higher recovery when Cu^{3+} periodate oxidizes Am than when no oxidizer is present. Since DAAP preferentially extracts hexavalent cations over trivalent cations, this suggests oxidation of the Am to the hexavalent state is occurring in the solvent extraction system. A UV-Vis analysis, **SI Figure 4**, shows the AmO_2^{2+} peak at 666 nm in 1 M HNO_3 which matches that observed by Sinkov et al. and confirms AmO_2^{2+} is present prior to extraction by DAAP.[22] Under both extraction conditions, the distribution ratios increase between 0.5 and 1 M HNO_3. After reaching a maximum distribution ratio of 0.99 ± 0.04 at 1 M HNO_3, the distribution ratios steadily decrease as nitric acid concentration increases. The same trend is observed when the Cu^{3+} periodate oxidant is not present and trivalent americium should predominantly be in solution. This suggests the suppressed distribution ratio is due to the

increased competition of nitric acid, which is known to be extracted by solvating organophosphorus extractants, like diamyl amyl phosphonate.[29]

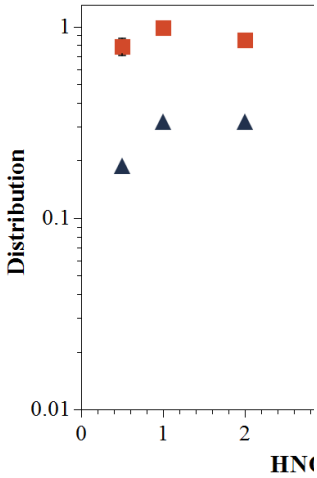

Figure 4: Distribution of ^{241}Am in presence of Cu^{3+} periodate oxidant (■) and absence of any oxidant (▲) from 0.5 to 5 M HNO_3 and 1 M DAAP in n-dodecane.

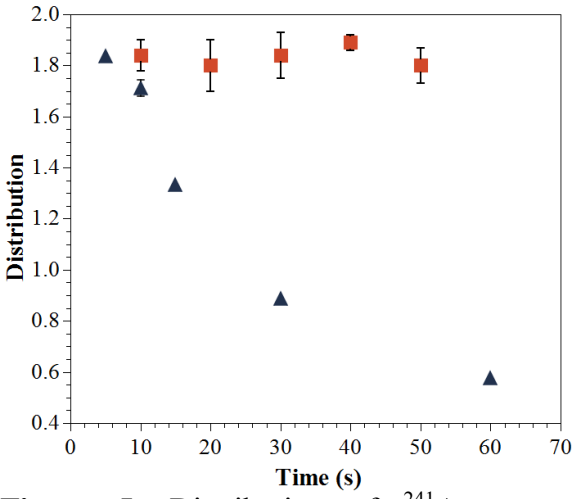

Figure 5: Distribution of ^{241}Am as a function of 1 M HNO_3 and 1 M DAAP in n-dodecane contact time (▲). Distribution of ^{241}Am as a function of Cu^{3+} periodate oxidation time in 1 M HNO_3 prior to contacting with 1 M DAAP in n-dodecane (■).

To evaluate the robustness of ^{241}Am recovery, one study considered the general presence of organic reductants by varying the aqueous/organic phase mixing times. The distribution ratios, shown in **Figure 5** as mean values with less than 8% relative standard deviation, decreased as the contact time between the two phases increased from 5 to 30 seconds. A second test considered the role of aqueous reductants by varying the americium/Cu^{3+} periodate contact time from 10 to 50 seconds prior to contacting with 1 M DAAP for 5 seconds. The americium/Cu^{3+} contact data, also presented in **Figure 5** as triplicate mean with less than 6% relative standard deviation,

shows the distribution remains constant under extended oxidation times prior to interfacing with the organic phase. While optimizing extraction conditions, a dark brown to yellow color in the aqueous phase, indicating presence of Cu^{3+} periodate, was observed to subside after mixing aqueous/organic phases for 35 – 40 seconds. In the americium/Cu^{3+} contact experiment, the aqueous solution remained dark brown even at 50 seconds prior to contacting with the organic phase. The presence of oxidant continues to re-oxidize any reduced species of americium, and makes it available for extraction by DAAP. Absence of Cu^{3+} periodate in the aqueous phase after contact with 1 M DAAP for 40 seconds versus its persistence after 50 seconds without organic contact suggests 1 M DAAP in n-dodecane solution encourages reduction. This suggests reduction of either americium or Cu^{3+} periodate by the organic phase may be a limiting factor in a solvent extraction system designed to recover hexavalent americium under acidic conditions.

Extraction Reproducibility Using DAAP

Comparing literature uranium distribution values at 2 M HNO_3, Siddall reported D = 450 with 1.1 M DAAP in n-dodecane at 30 ºC.[29] Mincher reported D = 350 at 2 M HNO_3 for 1 M

DAAP in n-dodecane at 19 ºC.[19] Results from this study, D = 80, are slightly higher than Brahmmananda Rao who reported D = 65 for 2 M HNO_3 with 1.1 M DAAP/n-dodecane at 30 ºC.[30] The literature presents significant variability in metal distribution values between studies for even more straightforward, redox inert, systems.

The Am studies in this work present differences in Am partitioning and seemed dependent on the DAAP chemical lot used from Eichrom. Under similar conditions, Am extractions completed with DAAP lot #ER-145-135 (**Figure 4**) and lot #998082 (**Figure 5**), produced distribution ratios of 0.99 ± 0.04 and 1.8 ± 0.2, respectively, at 1 M HNO_3. A recent report from Idaho National Laboratory (INL) has observed similar variations in Am recovery based on the DAAP lot.[31] Lot numbers for INL investigations were ER-145-141 and 998107. A definitive origin for the variation in Am distribution was not identified in their report and NMR investigations by this research team did not identify the origin of these variations either. One possible source of the variations in metal ion partitioning may stem from the synthesis of the DAAP molecule. DAAP is frequently synthesized using a Michaelis-Becker or Michaelis-Arbuzov reaction.[30] Either of these reactions could allow for the formation of trace phosphinates instead of a phosphate. Trace phosphinates could impact radiotracer distribution studies and might be below the detection limit of the 400 MHz liquid NMR used for characterization. An early report from Horwitz notes distillation of DAAP at 105°C prior to completing investigations.[32] This may be a crucial step in improving the reproducibility of studies using DAAP with radiotracers.

Americium separation from a trivalent f-element

The efficacy of americium separation from a trivalent *f*-element that should be inert to oxidation under these conditions, curium, was assessed using the optimized Cu^{3+} periodate extraction by DAAP. The distribution ratios of ^{241}Am and ^{244}Cm in the presence of varying acid content are presented in **Figure 6** as mean of triplicate samples with less than 10% relative standard deviation for ^{241}Am. Distribution values of Cm in the presence and absence of Cu^{3+} periodate are presented in **Figure 6** as mean of triplicate samples with less than 2% for ^{244}Cm. As the data shows, the extraction of Cm does not substantially increase in the presence of Cu^{3+} periodate. The oxidation and increased extraction of ^{244}Cm is unlikely since the 3.0 V Cm^{4+} to Cm^{3+} electrochemical potential is well above the 2.4 V Cu^{3+} to Cu^{2+} potential. The increase could be a result of minor salting out effect by the periodate anion.

Previous efforts have compared the selectivity of oxidized Am recovery with more redox inert Cm. The overall trend and distribution ratios are comparable to Mincher *et. al.* who also shows ^{244}Cm distributions decrease with increased nitric acid concentration.[20] The separation factors (D_{Am}/D_{Cm}), presented in **Figure 6**, of ^{241}Am from ^{244}Cm are 5.4, 6.4, and 6.2 for 2, 3, and 4 M HNO_3, respectively. The oxidized $^{241}Am/^{244}Cm$ separation factor at 3 M HNO_3 of 6.4 is comparable to the dipicolinic acid-functionalized crown ether Am^{3+}/Cm^{3+} separation strategy that presents a separation factor of 6.5.[33] The Cu^{3+} periodate oxidized ^{241}Am had a higher separation factor of 5.4 at 2 M HNO_3 compared to a separation factor of approximately 2 for ^{243}Am oxidized by sodium bismuthate.[20] At 4 M HNO_3, the sodium bismuthate oxidized ^{243}Am was found to have a separation factor of approximately 9 while this study achieved a value of 6.2. The results show separation of Cu^{3+} periodate oxidized ^{241}Am from a trivalent *f*-element is plausible over a broad range of acid conditions. In fact, the best separations are observed at acid concentrations comparable to the PUREX process, between 3 – 4 M HNO_3.

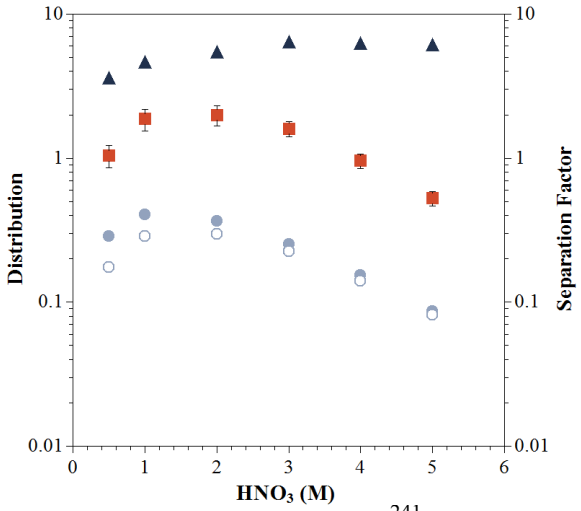

Figure 6: Distribution of ^{241}Am in the presence of Cu^{3+} periodate (■), ^{244}Cm in the presence of Cu^{3+} periodate (●), ^{244}Cm in the absence of Cu^{3+} periodate (○), and separation factors D_{Am}/D_{Cm} (▲) from 0.5 to 5 M HNO_3 with 1 M DAAP in n-dodecane.

Post-PUREX Am Recovery

The same experimental design was applied to separate ^{241}Am from the post-PUREX simulant obtained from Pacific Northwest National Laboratory. Prior to the ^{241}Am extractions, Cu^{3+} periodate was added to the simulant in a 1:1 molar ratio (Cu^{3+} periodate to total metal concentration) to observe any effects. Upon addition, a white precipitate formed. To assess which metals formed the precipitate, ICP-OES analysis was completed on the simulant before and after Cu^{3+} periodate addition (**Table 3**). Of the listed metals, the concentration of Zr, Sn, and Ru decreased substantially from 7.4, 0.111, and 2.73 mM to 0.062, 0.0049, and 0.038 mM, respectively. Precipitation of Zr^{4+} by periodate has been demonstrated previously under similar nitric acid conditions.[34] The study found the precipitate to be a 1:1 composition of Zr^{4+} to periodate with the formula $ZrHIO_6 \cdot 4H_2O$. Tetravalent Sn has also been reported to form a precipitate with periodate as $SnIO_6^-$.[27,35] A ruthenium periodate solid complex has been reported to form as $Na_6[Ru(OH_2)(IO_6)_2]$.[36,37]

Table 3: Determination of metal concentration (mM) in PNNL post-PUREX simulant by ICP-OES before and after addition of Cu^{3+} periodate to the solution.

Element	post-PUREX Stock Concentration (mM)	post-PUREX after Cu^{3+} periodate addition (mM)
Fe	0.096 ± 0.03	0.121 ± 0.004
Sr	2.26 ± 0.07	2.12 ± 0.07
Zr	7.4 ± 0.2	0.062 ± 0.002
Mo	4.4 ± 0.1	3.16 ± 0.09
Ru	2.73 ± 0.08	0.038 ± 0.001
Pd	0.090 ± 0.003	0.120 ± 0.004
Sn	0.111 ± 0.003	0.0049 ± 0.0002
Te	0.55 ± 0.02	0.53 ± 0.02
La	2.23 ± 0.07	2.15 ± 0.06
Pr	1.81 ± 0.05	1.89 ± 0.06
Nd	7.3 ± 0.2	6.8 ± 0.2
Sm	2.96 ± 0.09	1.21 ± 0.04
Eu	0.295 ± 0.009	0.286 ± 0.009
Gd	0.232 ± 0.007	0.223 ± 0.007

To a lesser extent, Mo (4.4 to 3.16 mM) and Sm (2.96 to 1.21 mM) concentrations also decreased. The Mo periodate species has been found to be dependent on pH.[27] In acidic solutions, an $IMo_6O_{24}^{5+}$ complex forms where one orthoperiodate molecule is surrounded by six MoO_6 molecules.[38] Literature on lanthanide periodate complexes is sparse, and literature on Sm periodate solid precipitate is non-existent. It is not apparent what caused the Sm concentration to decrease because as a trivalent lanthanide Sm is not expected to complex well with periodate. Cerium, on the other hand, has a 1.72 V Ce^{4+} to Ce^{3+} potential and can be oxidized by Cu^{3+} (2.4 V).[28] Cerium is present in the post-PUREX simulant, but could not be analyzed using ICP-OES due to interfering peaks. Instead, the UV-Vis of Ce^{4+} in 3 M HNO_3 was monitored before and after addition of periodate and Cu^{3+} periodate (**SI Figure 5**). After addition of periodate or Cu^{3+} periodate, a light yellow to white precipitate formed and was separated from the solution via

centrifugation. The supernatant spectra clearly show a decrease in the Ce^{4+} shoulder peak corresponding to the precipitation of Ce^{4+} with periodate. The solid Ce^{4+} complex has been reported to form in nitric acid as $CeHIO_6$.[39]

The precipitation of Ce^{4+} foreshadows the effect of periodate on actinides not discussed in this manuscript, namely Th, Np, and Pu. As a tetravalent actinide, precipitation of Th^{4+} with periodate has been demonstrated to form a $ThHIO_6$ complex. The elements Np and Pu are expected to be oxidized given their NpO_2^{2+} to NpO_2^{+} 1.24 V and PuO_2^{2+} to Pu^{4+} 1.05 V potentials. Based off the Ce^{4+} precipitation, incomplete oxidation of Pu^{4+} could cause a precipitate to form. Oxidation of Np and Pu by Cu^{3+} periodate studies are currently being assessed.

To date, the recovery of hexavalent americium in the presence of other species anticipated to be present in a used nuclear fuel aqueous processing stream hasn't been considered. This study considered how americium recovery, while in the presence of oxidizing Cu^{3+} periodate, would be affected by the presence of other metals found in the nuclear fuel recycling process. The oxidation time of the post-PUREX simulant containing ^{241}Am with Cu^{3+} periodate was increased from 10 to 50 seconds prior to contacting with DAAP for 5 seconds. During oxidation time, the precipitate formed, and was separated out from the solution via centrifugation. Shown in **Figure 7**, the distribution of ^{241}Am did not change with contact time.

The average ^{241}Am distribution ratio of 0.40 ± 0.03 is higher than the 0.19 ± 0.01 value obtained for Am^{3+} under the same acid conditions (3 M HNO_3). This indicates ^{241}Am is still being oxidized and extracted by DAAP. On the other hand, the 0.40 distribution ratio is lower than the 1.8 ± 0.2 distribution ratio obtained in the absence of other metals at 3 M HNO_3 (**Figure 6**). Holding the oxidation time constant at 10 seconds, the mixing time between aqueous and organic phases was

increased from 5 to 30 seconds. The results, **Figure 7**, show the distribution ratio begins at 0.39 ± 0.03 and decreases to 0.27 ± 0.03 as contact time increases. The decreasing distribution ratio is similar to the trend observed in the aqueous HNO_3 contacts. This further shows that while Am is being extracted, it is most likely reduced to the unfavorably extracted trivalent and pentavalent cations. The mass balance of ^{241}Am in both experiments with the used nuclear fuel simulant was 81 ± 1%.

The lower mass balance can be indicative of third phase formation, or integration of Am into a precipitate. A third phase was not observed, and can be ruled out. Sykora et al. have noted the formation of an Am^{3+} precipitate upon mixing with periodate, and several papers have discussed hydrothermal synthesis of Am crystals with iodate, the reduced form of periodate.[40–42] In addition to precipitate formation of the other metal species, it is possible that Am^{3+} precipitated out resulting in the 81% mass balance. It should be noted that periodate itself, although a strong oxidizer (1.65 V IO_4^- to IO_3^-), does not have the capacity to oxidize Am^{3+} to AmO_2^{2+} and AmO_2^{2+} periodate precipitates have not been observed.[22,41,42] Although the ^{241}Am distribution ratio was suppressed, any separation process developed to streamline advanced fuel cycle separations by americium oxidation will need to address the possibility of distribution ratio suppression in the presence of other metal species that will be oxidized by the strong oxidizers being studied (Cu^{3+} periodate, sodium bismuthate, electrochemical or silver ozone).

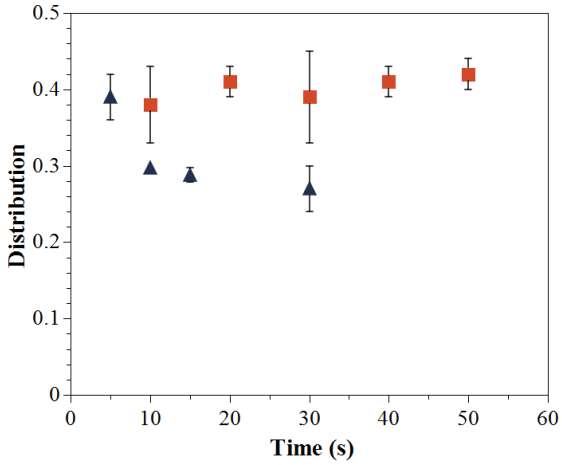

Figure 7: Distribution of ^{241}Am as a function of Cu^{3+} periodate oxidation time in 2.9 M HNO_3 post-PUREX simulant prior to contacting with 1 M DAAP in n-dodecane (■). Distribution of ^{241}Am from a 2.9 M HNO_3 post-PUREX simulant with 1 M DAAP with varying contact time (▲).

Conclusion

The oxidant Cu^{3+} periodate was found to auto-reduce in nitric acid via an inner sphere mechanism. Addition of excess sodium periodate decreased the rate of Cu^{3+} reduction, and indicates dissociation of the periodate anion from the metal cation complex as the rate limiting step. Although oxidation of Am^{3+} is competing with the auto-reduction of Cu^{3+} periodate, extraction of oxidized ^{241}Am by DAAP was achieved. Extending the ^{241}Am oxidation time in nitric acid did not impact the distribution values, but decreased with increased aqueous/organic contact times. The inability of Cu^{3+} periodate to oxidize and affect the extraction of Cm resulted in practical separation of oxidized ^{241}Am from a trivalent *f*-element under molar acid conditions analogous to the currently employed PUREX used in the nuclear fuel cycle process. The post-PUREX simulant investigations suggest further research in this area will need to address recovery of americium in the presence of other species that will most likely be present during

used nuclear fuel recycle. Future experiments will extend the use of Cu^{3+} as an oxidizer to other actinides, investigate the use of other extractants for oxidized Am recovery and examine the partitioning of fission products in the solvent extraction system.

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Funding Sources

The work at Colorado School of Mines funded by the US Department of Energy, Office of Nuclear Energy, through the Nuclear Energy University Program under contract DE-NE0008289. Work at Pacific Northwest National Laboratory and Oak Ridge National Laboratory was sponsored by Fuel Cycle Research and Development program, Office of Nuclear Energy, U.S. Department of Energy.

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Insert Table of Contents Graphic and Synopsis Here:

Oxidation of ^{241}Am by Cu^{3+} periodate competes with Cu^{3+} auto-reduction in nitric acid. An acid saturation effect does not impact the Cu^{3+} periodate reduction rate at higher acid concentrations used in used nuclear fuel solvent extraction processes. Extraction of hexavalent ^{241}Am by diamyl amylphosphonate is demonstrated. The extent to which ^{241}Am is extracted depends on acid concentration, phase mixing times, and is effected by fission products encountered in used nuclear fuel processing.