INL/EXT-09-16805

Americium Separation from Nuclear Fuel Dissolution Using Higher Oxidation States

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Advanced Fuel Cycle Initiative

Prepared for
U.S. Department of Energy
Minor Actinide Separation Sigma Team
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Idaho National Laboratory
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SUMMARY

Much of the complexity in current AFCI proposals is driven by the need to separate the minor actinides from the lanthanides. Partitioning and recycling Am, but not Cm, would allow for significant simplification because Am has redox chemistry that may be exploited while Cm does not. Here, we have explored methods based on higher oxidation states of Am (Am^{V} and Am^{VI}) to partition Am from the lanthanides. In a separate but related approach we have also initiated an investigation of the utility of TRUEX Am extraction from thiocyanate solution. The stripping of loaded TRUEX by Am oxidation or SCN^{-} has not yet proved successful; however, the partitioning of inextractable Am^{V} by TRUEX shows promise.

MINOR ACTINIDE SEPARATION SIGMA TEAM
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1. INTRODUCTION

We have investigated two approaches for Am/Ln separations. The first is based on Am^{VI} which should be readily extractable by the ligands used in solvent extraction, while Am^{V} should not. The oxidation of Am and its solvent extraction will open up new opportunities for separations from the lanthanides. In the past, no reagents were available that allowed preparation of Am^{V} or Am^{VI} in highly acidic solution. Currently, the use of sodium bismuthate allows such preparation and we have previously documented Am^{VI} extraction with TBP. [1] This year we measured higher extraction efficiency with dibutylbutylphosphonate. Alternatively, the preparation of Am^{V} with bismuthate can be used to prevent Am extraction, for use with reagents such as CMPO, designed to extract the lanthanides.

The second approach is the use of thiocyanate complexation of americium to prepare an anionic complex. Anion column chromatography to separate americium from the lanthanides has been used in the past to purify gram amounts of americium in thiocyanate solution. [2] Here, we performed Am and Eu extraction experiments from thiocyanate solutions by TRUEX extraction, with the goal of extracting the lanthanides while retaining the anionic americium complex in the aqueous phase.

2. SIGNIFICANCE

A goal of the AFCI program is to simplify, and thus reduce the costs of, the separations proposed for used nuclear fuel treatment. Much of the complexity in current proposals is driven by the need to separate the minor actinides from the lanthanides. However, a scenario can be envisioned that involves partitioning and recycling Am, but not Cm, since the latter is short-lived. The approach offers new opportunities because Am has redox chemistry that may be exploited, while Cm does not. A process to selectively partition Am from the lanthanides might thus replace the complicated TALSPEAK process, or if functional early in the fuel cycle both TALSPEAK and TRUEX.

3. APPROACH

Previous LDRD-funded work at INL identified conditions under which Am may be quantitatively prepared in the pentavalent or hexavalent oxidation states, even in highly acidic solution. [1] This suggested two possibilities in separations, as discussed below.

3.1 Am^{VI} Co-extraction

Americium could be co-extracted with U, Np and Pu as the hexavalent americyl ion using a neutral organophosphorous reagent, obviating the need for the TRUEX and TALSPEAK steps. Such an approach assumes that Am can be oxidized in strongly acidic solution, and held in the hexavalent oxidation state in the presence of other metals and radiolysis products. We proposed to perform solvent extraction experiments using organophosphorous reagents to evaluate the potential of U, Np, Pu and Am co-extraction. This effort was funded under an INL LDRD. Although it is a separate effort from the Sigma Team work discussed below, it is included here as supplemental information because of its pertinence to Sigma Team.

3.2 Am^{V} Inextractability

An alternative approach would be to rely on the inextractability of Am^{V} to either leave Am in the raffinate, or to selectively strip americium from the loaded TRUEX solvent. This would obviate the need for a TALSPEAK extraction following the TRUEX separation. Therefore, we proposed to further characterize conditions for quantitative production of Am^{V} with bismuthate and to examine the kinetics and the stability of Am^{V} in acidic solution and in the presence of the organic phase. We also proposed to perform bismuthate stripping experiments on loaded TRUEX solvent. This work was funded by Sigma Team.

3.3 Thiocyanate Complexation

Americium(III) forms an anionic complex with thiocyanate (SCN^-) and is known to more strongly sorb to anion exchange resins than the corresponding light lanthanide elements. This technique has been used to separate analytical levels of Am and even small pilot plant (gram) amounts on columns. [2] This provides an opportunity to investigate both the TRUEX forward extraction of Am from thiocyanate solutions, and the stripping of americium and possibly also curium from TRUEX. Therefore, we planned to investigate Am and Eu TRUEX (CMPO/TBP/dodecane) extraction using various concentrations of the soft donor complexant NH_4SCN at different acidities. This work was funded by Sigma Team.

4. SUMMARY OF RESULTS

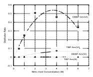
4.1 Am^{VI} Co-extraction

We have previously shown that Am^{VI} is coextracted with U^{VI}, Np^{VI}, and Pu^{VI} using the PUREX process solvent. However, trace reducing agents must be rigorously excluded, and contact times must be short. [1] The presence of 0.1 M perchloric acid is needed to increase the amount of dissolved Bi^{V}, which acts as a holding oxidant in the presence of reducing organic solvents. A maximum D_{Am} of only ~2 was achievable. We therefore investigated more basic neutral organophosphorous extractants, including dibutylbutylphosphonate. For 0.1 M solutions in dodecane, we found a factor of five increase in the D_{Am} using this ligand. [3] A comparison of Am^{VI} extraction efficiency for this phosphonate is compared to TBP in Figure 1. The data suggest that D_{Am} using this extractant would be sufficient to design a co-extraction process. Parameters in need of investigation include an examination of Am^{VI} autoreduction kinetics in this system, and the behavior of Ce and Ru, which would also oxidize under these conditions.

4.2 Oxidized Am extraction by TRUEX solvent

We have investigated Am^{VI} and Am^{V} extraction by the TRUEX solvent (0.2 M CMPO/1.4 M TBP/ Isopar L), using bismuthate oxidation in the presence of 0.1 M perchloric acid, for comparison to Eu^{III}. Elevated D_{Am} was found at ≤ 2 M HNO_3 for Am solutions prepared using conditions that should produce Am^{VI}. The initial D_{Am} of ~54 at 0.1 M HNO_3 is 50x higher than expected for Am^{III} under these conditions, and may indicate the extraction of hexavalent Am. This may be compared to U^{VI} extraction data from our lab using a TRUEX formulation with only 0.1 M CMPO, which resulted in a D_U of ~15. [4] As shown in Figure 2, a rapid decrease in extraction efficiency with increasing acidity was found. This suggests that Bi^{III}, produced from Bi^{V} reduction, may compete for CMPO. This is expected to become more severe at higher nitric acid concentrations due to additional bismuthate dissolution, and this was indeed found, as also shown in Figure 2.

The TRUEX solvent was then used to extract Am following treatment to prepare Am^{V}. These results are also shown in Figure 2. Pentavalent Am was not expected to be extracted; however D_{Am} was > 1 at nitric acid concentrations < ~ 1 M. This may indicate incomplete oxidation, or an elevation in D_{Am} due to the enhanced extractability of perchlorates.



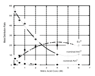
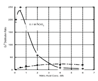


Figure 1. (left) The extraction of $\mathrm{Am^{III}}$ and $\mathrm{Am^{VI}}$ using 0.1 M TBP or dibutylbutylphosphonate. [3] Error bars shown are ± 5%.
Figure 2. (right) The TRUEX extraction of nominally $\mathrm{Am^{VI}}$ and $\mathrm{Am^{V}}$, with $\mathrm{Eu^{III}}$ shown for comparison. Error bars shown are ± 5%.

The use of 0.1 M $HClO_4$ did not elevate metal distribution ratios using the 30% TBP PUREX formulation. [1] However, for TRUEX extractions we have found a significant increase in distribution ratios due to the presence of perchlorates. This is shown for $\mathrm{Eu^{III}}$ in Figure 3. Further work is necessary to understand this phenomenon.

Since $\mathrm{Am^{V}}$ is essentially inextractable it was considered desirable to explore the option of stripping loaded TRUEX, to back-extract $\mathrm{Am^{V}}$ while leaving the lanthanides in the organic phase. Bismuthate powder in 2 M nitric acid was contacted with loaded TRUEX solvent over varying contact times. A typical plot is shown in Figure 4, where it can be seen that the presence of bismuthate decreased D_{Am}, probably due to $\mathrm{Bi^{III}}$ competition for CMPO rather than by oxidation. When the alternative oxidizing agent ammonium peroxydisulfate was used in similar experiments, D_{Am} remained high, indicating that CMPO-complexed Am was not oxidized by this reagent. These results are also shown in Figure 4, compared to a contact of loaded TRUEX solution with 2 M HNO_3. It is concluded that Am was not oxidized to $\mathrm{Am^{V}}$ in these experiments. In both cases the oxidizing species is ionic, and we considered the possibility that they do not cross the interface to oxidize CMPO-complexed Am. We therefore attempted to perform oxidative stripping using 0.1 and 0.2 % solutions of 1-pentanol or ethanol to facilitate phase transfer. No improvement in stripping was realized. It is likely that the CMPO complex protects $\mathrm{Am^{III}}$ from oxidation.

We will continue to develop a minor actinide separation based on the inextractability of $\mathrm{Am^{V}}$ by the TRUEX solvent. This will require understanding the role of perchloric acid, and establishing whether it is needed in this system. It will also require understanding the disproportionation of $\mathrm{Am^{V}}$ in nitric acid, and the necessary kinetics experiments have already been started.



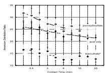


Figure 3. (left) The effect of 0.1 M $HClO_4$ on europium extraction using TRUEX solvent. Error bars shown are ± 5%.

Figure 4. (right) Americium extraction efficiency from 2 M HNO_3 using oxidative stripping versus contact time. Extractions were performed at laboratory room temperature (20 ± 2^{o}C) Fits are second-order polynomial with ± 10% error bars.

4.3 Thiocyanate complexation

Highly concentrated thiocyanate solutions have been used by others to complex Am in the anionic form. [2] In our initial experiments, loaded TRUEX was contacted with either 1 or 2 M SCN^-/0.1 M formic acid, in an attempt to strip Am as an anion. When these strip solutions were contacted with the TRUEX solvent, the emulsion instantly turned orange. This sludge thickened significantly over time and prevented organic and aqueous phase sampling. However, when the strip solution was contacted with non-pre-equilibrated, non-loaded TRUEX solvent no discoloration or third phase formation resulted. Thus, the material produced may contain precipitated formic acid originating from formate protonation after contact with extracted nitric acid in the TRUEX organic phase. The color probably originates from metal/SCN^- complexes. The iron complex, for example, is known to be red. [2]

We next attempted to scrub the loaded TRUEX solvent with acid-deficient aluminum nitrate prior to stripping. Following the 0.8 M $Al(NO_3)_3$/ 0.4 M NaOH scrub, a strip was performed without third phase formation although a light pink tint appeared. However, the distribution ratios remained high, at D_{Am} ~ 230 and D_{Eu} ~>1000. This indicates that the thiocyanate/formic acid solutions may not be capable of stripping loaded TRUEX.

We then attempted to extract Am and Eu from a SCN^-/formic acid solution. The forward extractions were very efficient, at $D_{Am} > 2000$, and D_{Eu} nearly 4000. The thiocyante/formic acid mixture appears to form extractable metal complexes. Further, attempts to strip this loaded solvent with 0.1 M HNO_3 were unsuccessful, as were attempts to strip pre-equilibrated, loaded, scrubbed, TRUEX solvent with SCN^- in the absence of formic acid. As with the bismuthate stripping attempts above, the SCN^- may not be able to complex Am across the phase boundary. Other explanations include that the CMPO-Am complex may be stronger than the SCN^--Am complex, or that SCN^- is a component of a highly extractable complex.

Future investigations along these lines will examine the TRUEX extraction of thiocyante solutions of americium, where Am is already complexed by SCN^-. However, such extractions probably can not be carried out in strongly acidic media due to protonation of SCN^-. Alternatively, quaternary ammonium salts may be employed as extractants, although also not in highly acidic media. [5] Finally, opportunities for column separations will also be explored.

4.4 Oxidized americium review

The INL PI (Mincher) has been writing a review of the chemistry of the higher oxidation states of americium in regard especially to separations. This paper is being prepared in collaboration with co-authors Gordon Jarvinen and Wolfgang Runde of LANL. The work is progressing and on schedule with a draft expected by the end of the fiscal year.

5. REFERENCES

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6. INDICATORS OF PROJECT QUALITY AND PRODUCTIVITY

1. Martin, L.R., Mincher, B.J., Schmitt, N.C. Extraction of Am(VI) with a neutral organophosphorous ligand. J. Radioanal. Nucl. Chem. accepted 26 May 09 and in press.
2. The paper above was also presented at MARC VIII, Kona, Hawaii, 7 April, 2009.
3. The INL PI (Mincher) served on the organizing committee of the symposium Nuclear Energy and the Environment, at the 238th National ACS meeting in Washington, DC in August 2009. He also chaired a session in Radiation Chemistry of Solvent Extraction Ligands in that symposium. He will be editing the resulting symposium series book.

7. COLLABORATORS AND PARTICIPANTS

1. Bruce J. Mincher, Idaho National Lab, PI
2. Leigh R. Martin, Idaho National Lab, co-researcher, especially with regard to spectroscopy of Am solutions and solvent extraction.
3. Nicholas C. Schmitt, Idaho National Lab, performs solvent extraction experiments and Am spectroscopy.
4. Richard D. Tillotson, Idaho National Lab, performs solvent extraction experiments.
5. Catherine L. Riddle, Idaho National Lab, performs solvent extraction experiments.
6. Gordon Jarvinen, LANL, co-author of review paper, funded independently.
7. Wolfgang Runde, LANL, co-author of review paper, funded independently.
8. Stephen P. Mezyk, Cal State Long Beach, kinetic analysis and modeling, expected to begin next fiscal year.