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Experimental Findings on Actinide Recovery Utilizing Oxidation by Peroxydisulfate Followed by Ion Exchange

Fuel Cycle Research & Development

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D. T. Hobbs, T. C. Shehee

Savannah River National Laboratory
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Reviews and Approvals

D. T. Hobbs, Co-author, Separations and Actinide Science Programs, SRNL	Date
T. C. Shehee, Co-author, Separations and Actinide Science Programs, SRNL	Date
P. M. Almond, Technical Reviewer, SRNL Separations and Actinide Science Programs	Date
T. B. Brown, Manager, Separations and Actinide Science Programs, SRNL	Date
A. P. Fellinger, Manager, E&CPT Research Programs, SRNL	Date

SUMMARY

Our research seeks to determine if inorganic ion-exchange materials can be exploited to provide effective minor actinide (Am, Cm) separation from lanthanides. Previous work has established that a number of inorganic and UMOF ion-exchange materials exhibit varying affinities for actinides and lanthanides, which may be exploited for effective separations. During FY15, experimental work focused on investigating methods to oxidize americium in dilute nitric and perchloric acid with subsequent ion-exchange performance measurements of ion exchangers with the oxidized americium in dilute nitric acid. Ion-exchange materials tested included a variety of alkali titanates. Americium oxidation testing sought to determine the influence that other redox active components may have on the oxidation of Am^{III}. Experimental findings indicated that Ce^{III}, Np^{V}, and Ru^{II} are oxidized by peroxydisulfate, but there are no indications that the presence of Ce^{III}, Np^{V}, and Ru^{II} affected the rate or extent of americium oxidation at the concentrations of peroxydisulfate being used.

ACRONYMS

COEX^{TM}	Co Extraction process
K_d	distribution coefficient
PUREX	Plutonium Uranium Redox Extraction process
MST	monosodion titanate
mMST	peroxide modified monosodium titanate
SRNL	Savannah River National Laboratory
TAMU	Texas A&M University
UMOF	unconventional metal organic framework
UREX	Uranium Extraction process
UV-Vis	ultraviolet-visible

SEPARATIONS

1. INTRODUCTION

Advanced nuclear fuel cycles seek to separate actinides from each other as well as from other fission product elements in irradiated nuclear fuels for a variety of reasons including transmutation of transuranics to shorter lived nuclides beneficial to the storage of waste. Separations of minor actinides such as americium and curium from lanthanides in aqueous media are among the most difficult in radiochemistry due their similar chemical properties. Recent studies have reported successful separation of americium from lanthanides and curium by oxidation of Am^{III} to Am^{V} or Am^{VI} followed by ion exchange or solvent extraction.[1-3] Ion-exchange based separation factors are increased as the affinity of the oxidized americium, present as either AmO_2^{+} or AmO_2^{2+}, is diminished compared to that of the triply charged Ln^{3+} ions. Our research project seeks to determine if minor actinide separations can be accomplished effectively using inorganic-based materials. We postulate that by using inorganic-based materials, selectivity for minor actinides can be tailored for separations under acidic environments. Through oxidation of Am(III) to form the americyl species, AmO_2^{+}or AmO_2^{2+}, the affinity for americium is reduced by lowering the effective charge of the species in solution.

A possible insertion of the americium separation step in the nuclear fuel cycle is after the recovery of uranium through processes such as PUREX, UREX or COEX™. The raffinate from the uranium separation stage would contain varying concentrations of the transuranic elements as well as fission products in acidic aqueous solutions. A number of these elements are redox active and could oxidize upon addition of peroxydisulfate or other oxidizing agent. These elements include plutonium, neptunium, americium, cerium and ruthenium. The expected predominant oxidation states of these elements are Pu^{IV}, Np^{V}, Am^{III}, Ce^{III} and Ru^{II}.

The presence of these redox-active elements could consume the oxidizing agent and adversely impact the oxidation of Am^{III} and subsequent separation of the Am^{V} by ion exchange or solvent extraction. Uranium is also present in the raffinate at low concentrations and features multiple oxidation states in acidic aqueous solutions. However, the uranium would be expected to be present as U^{VI} and would not be oxidized further by peroxydisulfate. The literature does provide evidence that Pu^{IV}, Np^{V}, Am^{III}, and Ce^{III} can be redily oxidized in dilute acid solutions. For example, Mincher, et. al recently reported that Pu^{IV} is oxidized to Pu^{VI} in dilute nitric acid.[3] However, the oxidation of Pu^{IV} did not adversely impact the oxidation of Am^{III} when both were present in nitric acid solutions. Chistyakov, et. al investigated the oxidation of Np^{V} and Np^{IV} in 0.2 – 2.0 M perchloric acid solutions at temperatures ranging from 40 °C to 60 °C.[4-5] They reported that Np^{V} is oxidized to Np^{VI} by direct reaction of Np^{V} with the peroxydisulfate dianion, $S_2O_8^{2-}$, and the sulfate radical anion, SO_4^{-}•. Np^{IV} is also oxidized by the same reactions as well as by an intramolecular reaction of the neptunium peroxydisulfate complex, $NpS_2O_8^{2+}$. The rate of oxidation was reported to increase with an increase in neptunium concentration and temperature and a decrease in the perchloric acid concentration.[4-5]

One of the earliest studies on the oxidation of Ce^{III} with peroxydisulfate was that of Fronaeus and Ostman.[6] The authors reported that a perchloric acid solution of Ce^{III} was oxidized to Ce^{IV} by sulfate radical anion, SO_4^{-}•, produced by the thermal decomposition of peroxydisulfate at 61 °C. Furthermore, they reported that the formation of Ce^{IV} is first order with respect to peroxydisulfate, but of no simple order with respect to the Ce^{III} concentration. Matthews and Sworski investigated the quenching of Ce^{III} fluorescence upon addition of that peroxydisulfate in sulfuric acid solution.[7] They reported that the reaction is an irreversible one electron transfer reaction to produce Ce^{IV}, SO_4^{2-}, and $SO_4^{-\cdot}$.

Other studies on the oxidation of Ce^{III} with peroxydisulfate featured the addition of Ag^{I} to accelerate the oxidation reaction. For example, Prakash, et. al reported that the kinetics of the oxidation of Ce^{III} in 0.5 M sulfuric acid exhibited a zero-order dependence on Ce^{III} concentration and a first-order dependences on Ag^{I} concentration.[8] The order with respect to peroxydisulfate dianion is less than one and is decreased by both sulfuric acid and the hydrosulfate anion. The authors noted that a precipitate of potassium perchlorate formed when perchloric acid was substituted for sulfuric acid. Two papers by Milyukova, et. al reported on the oxidation of Ce^{III} with peroxydisulfate and Ag^{I} in nitric acid.[9-10] These authors reported quantitative oxidation of $10^{-4} – 10^{-6}$ M Ce^{III} to Ce^{IV} occurred at room temperature in solutions containing 0.1 – 10 M nitric acid, 0.01 M Ag^{I} and 0.1 M peroxydisulfate. In 4 M nitric acid containing 0.018 M Ag^{I}, the peroxydisulfate concentration must be $\geq$0.05 M to oxidize >90% of the Ce^{III}.

Ruthenium exhibits multiple oxidation states in acidic aqueous solutions including Ru^{II}, Ru^{III}, Ru^{IV}, Ru^{VII}, and Ru^{VIII}. Relatively long-lived isotopes of ruthenium are produced from the fission of uranium. Consequently, the chemistry of ruthenium has been studied to understand the fate of ruthenium during reprocessing of irradiated nuclear fuels. For example, Fletcher, et al reported the formation of cationic, neutral, and anionic complexes of rutheniumnitrosyl, in which ruthenium is present as Ru^{II}.[11] Wallace reported on the extraction and ion-exchange characteristics of several nitrato nitrosylruthenium^{II} complexes including the neutral trisnitratonitrosylruthenium^{II}, $(O_3N)_3Ru(NO)(H_2O)_2$.[12] The oxidation of nitrosylruthenium complexes by peroxydisulfate in dilute acid solutions has not been reported in the literature. However, based on the reported electrochemical potentials for ruthenium, nitrosylruthenium complexes would be expected to be oxidized by peroxydisulfate.[13]

Given the evidence that Np^{V}, Ce^{III} and Ru^{III} can be oxidized with peroxydisulfate, experiments were performed to confirm that these species will react with peroxydisulfate to efficiently oxidized Am^{III} to Am^{V}. Specifically, these tests sought to determine if the redox activities of these elements would adversely impact the oxidation of Am^{III} to Am^{V} in dilute acid solutions. Also of interest was the determination if the presence of these elements would produce other impacts such as the precipitation of solids. Under the oxidizing conditions presented in this work, the cerium is expected to precipitate. Precipitation of solids during the Am^{III} oxidation step would likely require a filtration step prior to ion exchange or solvent extraction. Conversely, the ruthenium can form a volatile compound and which would be expelled from the system as a gas. In an actual used fuel raffinate, the ruthenium would be radioactive thus requiring measures to be taken to collect from the offgas.

2. SIGNIFICANCE

Inorganic ion-exchange materials generally exhibit much greater radiation and chemical stability than organic-based ion-exchange materials. Consequently, these materials may be used more effectively in much higher dose radiation environments compared to organic-based materials. This advantage may be significant in developing effective separations in feed streams in which Cs and Sr have not been previously separated. Ion-exchange separations can be easily deployed in continuous and semi-continuous modes at a variety of scales. Thus, there is considerable flexibility in deploying the separation technology. Depending on the framework of the ion-exchange material, the material may also serve as a final waste form matrix for the disposal of the separated radioisotopes.

The separation of americium and curium is difficult using current liquid/liquid extraction technology. In aqueous solutions, americium and curium have relatively similar chemistry; both are stable only in the trivalent oxidation state in simple aqueous solutions without added reagents to control oxidation state, and comparable charge to size ratios limit the discriminating driving forces commonly used in liquid extraction. Inorganic ion-exchange materials generally have much more rigid frameworks and coordination sites than those of the organic-based extractants employed in solvent extraction processes. This increased rigidity may amplify the ability to discriminate based on the slight size differences between the trivalent cations (i.e., americium and curium) compared to the more flexible coordination environments of the organic extractants.

3. APPROACH

The inherent affinity of an ion exchange material for a particular metal ion can be influenced by a number of parameters including the oxidation state of the metal (i.e., effective charge density), acid concentration, and temperature. An attractive option to enhance separation of americium from curium and lanthanides is to oxidize the Am^{III} to Am^{V} or Am^{VI}. The Am^{V} and Am^{VI} oxidation states will exist in solution as the respective AmO_2^{+} and AmO_2^{2+} species which have reduced charge density compared to Am^{3+} and Ln^{3+} ions. It would be expected that the ion exchangers would exhibit reduced affinity toward the AmO_2^{+} and AmO_2^{2+} compared to that of Am^{3+} and the Ln^{3+} series of metal ions. Previous testing has shown that zirconium and tin(IV) hybrids of ideal composition $M(O_3PC_6H_6PO_3)_{0.5}(HPO_4)$, with M=Zr and Sn, and sodium titanates were effective in discriminating between ions of low charge ≤2+ and those of 3+ and 4+.[2]

3.1 Am(III) Oxidation by Peroxydisulfate

Studies continued to investigate the oxidation of americium as a prelude to ion-exchange separations. Oxidation of the Am^{III} to AmO_2^{+} reduces the effective charge density of the americium compared to Am^{III} and other +3 cations such as Cm^{III} and the trivalent lanthanide ions. For weakly acidic conditions (pH 1-3), sodium peroxydisulfate, $N_2S_2O_8$, is an effective oxidizer for Am^{III} in nitric and perchloric acid.[14-16] Oxidation conditions chosen for this work were based on those reported by Mincher et al. which provided complete oxidation of americium to $AmO_2^{+}$and/or AmO_2^{2+}.[3] Generally, all tests were performed at an acid concentration of 0.1 M in either nitric or perchloric acids, a temperature of 80 °C, and persulfate concentration varying from 0.25 – 0.70 M. The expected predominant oxidation states of the redox active species added to the tests are Np^{V}, Am^{III}, Ce^{III} and Ru^{II}. Concentrations for these species were based on a surrogate raffinate from a co extraction type process.

3.2 Ion-exchange Separations

Ion exchange tests were performed using a MST, mMST, and engineered bead form of both MST and mMST, and the commercially available sodium nonatitanate (SrTreat™). All ion-exchange tests were conducted at room temperature with a phase ratio of 100 mL/g. The pH was set to pH = 2 or 3 where the in exchanger was pre-equilibrated to the desired pH using nitric acid. The batch contacts used a rotisserie for agitation of the samples. Ion exchange separations of a surrogate raffinate were performed both with and without incorporation of an oxidation step prior to the batch contact. Adjustment of the pH was performed after the oxidation step where applicable.

4. SUMMARY OF RESULTS

4.1 Am(III) Oxidation by Peroxydisulfate

Americium was oxidized separately in nitric and perchloric acid solutions by ammonium peroxydisulfate. The competing redox active species Ce and Np were added to the solutions to test the effects on americium oxidation. Under the oxidation conditions used for americium oxidation in this work, it was previously reported to provide as much as 60% Am^{VI}. The competing redox active species of Np^{V}, Am^{III}, Ce^{III} and Ru^{II} that were added did not interfere with the oxidation though quantification using UV-Visible spectroscopy was not capable due to the large absorbance of the metals with peroxydisulfate. The interaction of Ce with the peroxydisulfate interfered with the observance of a loss of Am^{III} due the the large absorbance in the lower wavelength regions. Under the oxidizing conditions presented in this work, the cerium is expected to precipitate. Any solids formed during the course of the oxidation would have to be filtered out of the product solution. Conversely, the ruthenium forms a volatile compound and is expelled from the system as a gas. The loss of ruthenium was determined by ICP-MS analysis of the product solutions. In an actual used fuel raffinate, the ruthenium would be radioactive thus requiring measures to be taken to collect from the offgas.

4.2 Ion-exchange Separations

Under the experimental conditions chosen to oxidize americium, a precipitate forms during the course of the oxidation over a range of peroxydisulfate concentrations. The precipitate presumably is a mixture of lanthanide sulfates or double sulfate salts[14] of the lanthanides. In an evaluation of the single surrogate component, cerium, powder XRD confirmed the presence of $Ce_2(SO_4)_3$ with an unknown amorphous component. In a comparison of ammonium vs. sodium peroxydisulfate, analysis of the solution phase by ICPS shows that the precipitate was observed to decrease with an increase in the peroxydisulfate concentration. Also, there was an increase in the solubility when ammonium peroxydisulfate was used over the use of sodium peroxydisulfate.

Without the addition of peroxydisulfate, the ion-exchange materials chosen performed better as the pH increased. At pH 2, the K_d for lanthanide uptake for all of the materials chosen ranged from 1 to 14 mL/g where the worst uptake occurred for europium uptake by MST and the best uptake was for cerium by the modified MST. At pH 3, the K_d for lanthanide uptake for all of the ion-exchange materials chosen showed negligible improvement with a range from 4 to 14. Under all conditions, uptake of zirconium, molybdenum, and plutonium was better across the board than uptake of the lanthanides. Being a trivalent ion as well, americium uptake mirrored that of the lanthanides.

With the addition of the peroxydsulfate oxidizer, the ion exchange materials are expected to also perform better as the pH increases. At pH 2, K_d for lanthanide uptake for all of the materials chosen with the exception of MST was lower than was observed in non-oxidizing conditions. The uptake observed by MST showed a marginal increase when used following an oxidation step using peroxydisulfate. The average K_d for MST in this case was 10 mL/g. The best performance occurred with a batch contact occurring at pH 3 using the mMST in both the powder and engineered forms. In both cases, there was large increase in K_d for the mMST and engineered mMST over the MST. As an example, the K_d for lanthanum with MST was 5 mL/g whereas the K_d was 265 and 404 with mMST and the engineered mMST respectively.

These results indicate that the americium is not persisting in the oxidized form for the duration of the contact during ion-exchange measurements. This may be remedied through the use of a shorter contact time or by the incorporation of a holding agent into the system.

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6. PUBLICATIONS AND OTHER INDICATORS OF PROJECT QUALITY AND PRODUCTIVITY

Journal Publications

1. "Oxidation of Metal Ions by Peroxydisulfate in Dilute Nitric Acid", Shehee, T.C.; Hobbs, D. T.; *Radiochimica Acta*, **submitted**.

Presentations

1. "Studies of Peroxydisulfate Oxidation as a Prelude to Minor Actinide Separations", T. C. Shehee and D. T. Hobbs, presented at the 39th Actinide Separations Conference, Salt Lake City, UT, May 18-21, 2015.

7. COLLABORATORS AND PARTICIPANTS

Participants in the ion-exchange research include Dr. David Hobbs (SRNL), Dr. Thomas Shehee (SRNL), Prof. Abraham Clearfield, (TAMU), and Rita Silbernagel (graduate student, TAMU).