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Experimental Findings on Minor Actinide and Lanthanide Separations using Ion Exchange

Fuel Cycle Research & Development

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Reviews and Approvals

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SUMMARY

During FY14, experimental work focused in the following areas: (1) synthesis, characterization and testing of ion-exchange materials and (2) investigating methods to oxidize americium(III) in dilute nitric acid using peroxydisulfate. Ion-exchange materials tested at SRNL included antimony silicates.

Inorganic and hybrid ion-exchange materials tested previously in this project are limited to a pH of about 2. In more concentrated acid solutions, the ion-exchange material is chemically unstable or exhibits poor ion-exchange performance for metal ions. FY14 research focused on testing antimony silicates, which had been reported to exhibit good ion-exchange in 0.2 – 1.0 M nitric acid and some ion-exchange capacity in as high as 3 M nitric acid. Performance testing of archived antimony silicate samples from Prof. R. Harjula (U. Helsinki) and freshly prepared samples showed very low affinity for lanthanide ions in 0.1, 1.0 and 3.0 M nitric acid.

Tests carried out in FY14 continued work initiated the previous year to understand the effects that Pu(IV) and nitrite have on the oxidation of Am(III) by peroxydisulfate. Findings indicate that both Pu(IV) and nitrite are oxidized by peroxydisulfate. Consequently, an excess of peroxydisulfate is needed to maximize the conversion of Am(III) to Am(V).

1. INTRODUCTION

Inorganic ion exchangers have found considerable use in the purification of wastewaters, treatment of alkaline nuclear waste solutions and in the purification of actinides in concentrated and dilute nitric acid solutions. Previous work has shown that titanates, titanosilicates and hybrid-type ion exchangers based on group IV metal phosphonates do exhibit high affinities for highly charged metal cations in dilute nitric acid solution. Furthermore, the affinity for a metal cation is reduced by lowering the effective charge of the species in solution. One such approach is the oxidation of Am(III) to form the americyl species, AmO_2^+ or AmO_2^{2+}.

The inherent affinity of an ion exchanger 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.

The following concepts have emerged as the leading, but not exclusive, candidates for effective ion-exchange separations, (1) oxidation of Am(III) to Am(V) followed by ion exchange [C1], (2) ion-exchange of Am(III) and fission products (Lanthanides, Cs, Sr, Tc) followed by recovery of the Am using an oxidizing eluent [C2], (3) ion-exchange of actinyls followed by the recovery of the Am as Am(III) using a reducing eluent [C3], and (4) chromatographic separation [C4]. It is envisioned that the feed solution for ion exchange separations would be the raffinate from a PUREX, UREX or COEX™ process. To date, the ion-exchange separations are limited to an acid concentration of $\leq$0.01 M.

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 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 ^{137}Cs and ^{90}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 trivalent oxidation state is the most stable oxidation state for americium, curium, and lanthanides in aqueous solutions. The similar size of the trivalent Am, Cm and lanthanides makes their separation difficult. Inorganic ion-exchange materials generally have much more rigid frameworks and coordination sites than those of the organic-based ion-exchange materials and 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., Am^{3+}, Ln^{3+}, and Cm^{3+}) compared to the more flexible coordination environments of the organic extractants.

3. APPROACH

Our research seeks to determine if inorganic and unconventional metal-organic framework (UMOF) 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. When coupled with oxidation of Am(III), effective separation of americium from lanthanide and curium can be achieved. Our project continued investigating Am(III) oxidation with peroxydisulfate in dilute nitric acid solutions.

Since the raffinate from a PUREX, UREX or COEX™ process is at much higher acid concentration, the acid concentration in the feed solution would have to be adjusted with base. Acid adjustment can be performed, but requires the introduction of additional process chemicals and equipment. A focus of the work in FY14 was to identify ion-exchange materials that could operate at higher nitric acid concentrations (0.1 – 3.0 M).

4. SUMMARY OF RESULTS

4.1 Evaluation of Antimony Silicate Ion-Exchange Materials

Antimony silicates, $Sb_2Si_2O_7$, and metal-doped antimony silicates having a pyrochlore structure have been reported to be effective ion exchangers for cesium, strontium and cobalt in dilute nitric acid solutions.[1-3] The incorporation of more highly charged metal ions such as Ti^{4+}, Nb^{5+}, and W^{6+} was found to generally increase the distribution values particularly in the case of tungsten. As the concentration of the metal dopant increased, the crystallinity of the material decreased. Three archived antimony silicate samples were received from Prof. R. Harjula of the University of Helsinki. These samples were yellow in color and believed to be examples of tungsten-doped antimony silicates. X-ray fluorescence analysis confirmed the presence of Sb, Si and W.

Ion-exchange performance was first tested by measuring the removal of ^{154}Eu spiked into separate solutions containing ten lanthanides in 0.1, 1.0 and 3.0 M nitric acid, respectively. Table 4.2.1 provides the concentrations of each of the lanthanides in the respective three stock solutions. For the ion-exchange tests, the phase ratio of lanthanide stock solution to weight of ion-exchange sample was 100 mL/g. The ion-exchange tests were carried out at 25 ˚C with 2-mL aliquots taken from each test after 1, 2, 4 and 24 hours of contact. Each aliquot was filtered through a 0.1-micron syringe filter to remove solids. The ^{154}Eu activity in 0.5-mL of the filtrate and untreated stock solutions was measured by gamma spectroscopy using a sodium iodide detector and Packard Cobra II Auto Gamma Counter.

Table 4.2.1. Concentration of Lanthanides in Nitric Acid Stock Solutions

Element	Concentration (mM)
La	2.73
Ce	5.32
Pr	2.48
Nd	8.67
Sm	1.74
Eu	0.278
Gd	0.326
Dy	0.185
Er	0.179
Tb	0.189
Total Lanthanides	22.1

Based on the ^{154}Eu activity measured, the percentage of ^{154}Eu removed by the antimony silicate samples proved low (ca. 1.5 – 3.3%) from all three nitric acid solutions. The low removal of Eu^{3+} in the 0.1 M nitric acid solution was particularly unexpected since the literature had reported high distribution values in 0.1 M nitric acid solutions for ^{85}Sr and ^{57}Co, which would be present as the respective Sr^{2+} and Co^{2+} cations. The +3 lanthanide cations have a higher charge than the divalent Sr^{2+} and Co^{2+} ions. The ionic radii of the +3 lanthanides fall within the range spanned by that of Sr^{2+} and Co^{2+}. Thus, the antimony silicates would be expected to have an appreciable affinity for the lanthanide cations. Since these samples had been prepared about ten years earlier, the age of the samples may have contributed to the low Eu^{3+} removal. Therefore, new samples of undoped antimony silicate were prepared and tested.

Table 4.2.2. Percentage of ^{154}Eu Removed by Antimony Silicates in 0.1, 1.0 and 3.0 M Nitric Acid Solutions

Sample	% ^{154}Eu Removed in 0.1 M HNO_3	% ^{154}Eu Removed in 1.0 M HNO_3	% ^{154}Eu Removed in 3.0 M HNO_3
1-h Contact	1.70	2.06	1.55
2-h Contact	2.01	2.21	1.46
4-h Contact	2.03	3.31	2.46
24-h Contact	1.77	2.82	2.29

The fresh samples of antimony silicate were prepared using antimony pentachloride and sodium silicate as reported in reference 1. The fine white powder was analyzed by X-ray fluorescence (XRF) spectroscopy and powder X-ray diffraction (PXRD). XRF spectroscopy confirmed the presence of Sb and Si and the PXRD patter was consistent with that of the antimony silicate sample from the University of Helsinki and that published in the literature for $Sb_2Si_2O_7$ having a pyrochlore structure (see Figure 4.2.1). Consequently, tests were conducted to measure the affinity of this antimony silicate material for lanthanides using the same lanthanide composition as provided in Table 4.2.1 and with nitric acid concentrations of 0.1, 1.0 and 3.0 M, respectively.

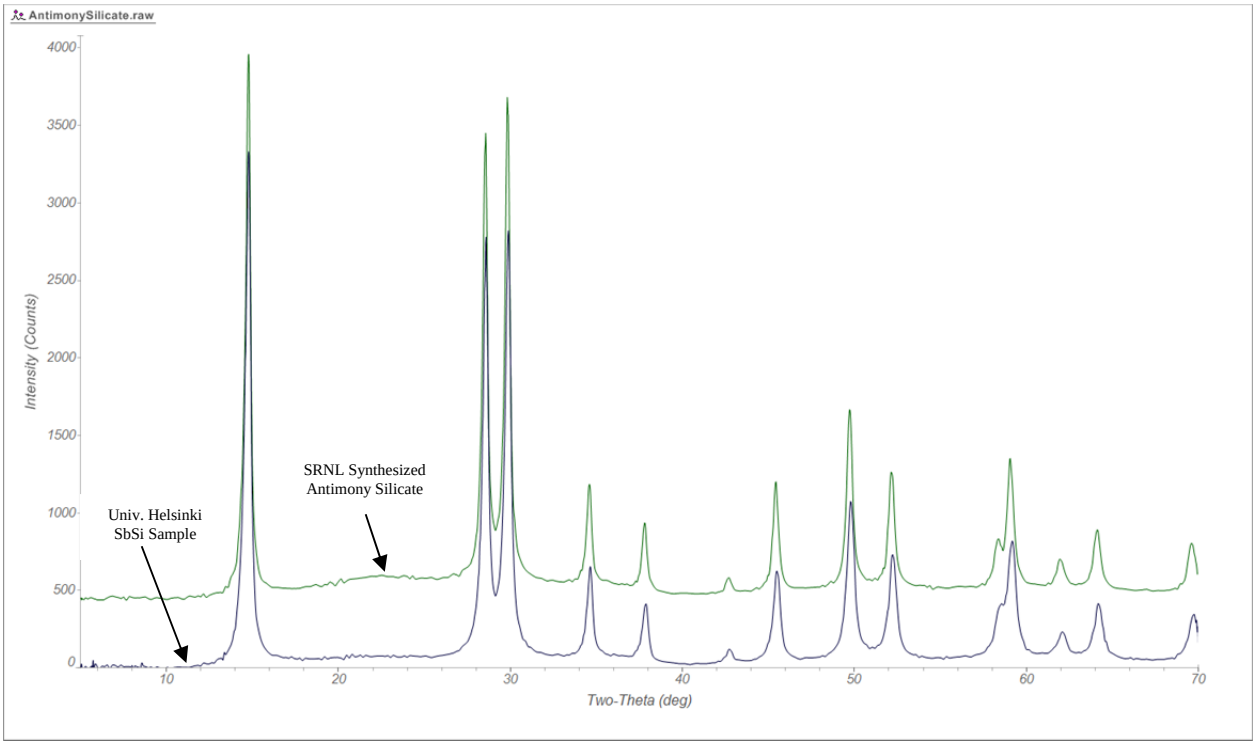

Figure 4.2.1 Powder X-Ray Diffraction Patterns of SRNL Synthesized Antimony Silicate and Antimony Silicate Sample Received from University of Helsinki

Table 4.2.3. Percentage of ^{154}Eu Removed by a Freshly Prepared Antimony Silicate in 0.1, 1.0 and 3.0 M Nitric Acid Solutions

Sample	% ^{154}Eu Removed in 0.1 M HNO_3	% ^{154}Eu Removed in 1.0 M HNO_3	% ^{154}Eu Removed in 3.0 M HNO_3
1-h Contact	1.12	0.13	0.25
2-h Contact	1.16	0.30	0
4-h Contact	1.20	0.41	0.11
24-h Contact	2.61	0	0

The measured removal of ^{154}Eu by the freshly prepared antimony silicate sample was very low and generally lower than that measured for the archived samples prepared at the University of Helsinki. The lower removal is likely due to the lower concentration of the antimony silicate used in the latter test. The lower removal may also reflect that the SRNL-synthesized sample is not doped with tungsten. Synthesis of a tungsten-doped antimony silicate sample at SRNL is in progress.

It is recommended that additional tests be carried out to measure strontium removal with the antimony silicate samples to confirm if the archived and freshly prepared samples exhibit the expected high strontium removal. If so, then we can conclude that the low lanthanide removal is due to an inherent low affinity of the material for the +3 lanthanide ions. If strontium removal is high, additional tests with actinyl ions, AnO_2^{2+}, may be warranted to determine if good separation

factors could be realized by oxidizing Am(III) to Am(VI) and then contacting the mixture of Am(VI), Ln(III) and Cm(III) with the antimony silicate.

4.2. Oxidation of Am(III) by Peroxydisulfate

During FY14 we continued development of the oxidation of Am(III) as a prelude to ion-exchange separations in dilute nitric acid solutions. 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 lanthanide(III) ions. Previous experiments have shown that the hybrid metal(IV) phosphonates and sodium titanate ion exchangers exhibit very high affinity for highly charged cations such as M^{3+} and lower affinity for mono- and di-cations. Thus, after oxidation of Am(III) to AmO_2^+, it would be expected that the ion exchangers would have a lower affinity for the AmO_2^+ allowing separation between the americium and the more highly charged lanthanide ions, Ln(III), and Cm(III) ions.

Testing sought to determine the influence that other redox active components may have on the oxidation of Am(III). Experimental findings indicated that Pu(IV) is oxidized to Pu(VI) by peroxydisulfate. However, when there is a large excess of peroxydisulfate, the presence of plutonium does not adversely affect the rate or extent of americium oxidation even if the concentration of Pu(IV) is equal to or greater than that of Am(III). Tests also explored the influence of nitrite on the oxidation of Am(III). At nitrite to Am(III) ratios up to 10:1, Am(III) was completely oxidized to Am(V) in dilute nitric acid and perchloric acid at peroxydisulfate concentrations of 0.3 M or higher.

B. Mincher and colleagues at INL have also been investigating Am(III) oxidation with peroxydisulfate. Findings from the INL and SRNL testing were combined into a joint manuscript, "Formation and Separation of Am(V) using Peroxydisulfate" for publication in a peer reviewed journal. This paper provides molar extinction coefficients for the 523 nm Am(V) absorbance peak at varying nitric acid concentrations, the influence of peroxydisulfate, Pu(IV), and nitric acid concentrations on Am(III) oxidation, and the separation of americium from lanthanides and curium by solvent extraction, column chromatography, and ion-exchange with sodium titanates.

5. REFERNCES

1. "Uptake of ^{85}Sr, ^{134}Cs and ^{57}Co by antimony silicates doped with Ti^{4+}, Nb^{5+}, Mo^{6+} and W^{6+}", Teresia Moller, Risto Harjula, Martyn Pillinger, Alan Dyer, Jon Newton, Esko Tusa, Suheel Amin, Maurice Webb and Abraham Araya, *J. Materials Chem*., **2001**, 11, 1526 – 1532.
2. Antimony Silicate Sorbent for Removal of Metal Ions, European Patent 1,080,473 B1, September 4, 2003.
3. Removal $^{of\ 85}Sr$, ^{134}Cs, and ^{57}Co Radionuclides from Acidic and Neutral Waste Solutions by Metal Doped Antimony Silicates. T. Moller, R. Harjula, and A. Paajanen, *Separation Science & Technology*, **2003**, 38(12/13), 2995 – 3007.

6. INDICATORS OF PROJECT QUALITY AND PRODUCTIVITY

Presentations

1. "Ion Exchange Based Separations of Minor Actinides", T. C. Shehee, R. Silbernagel, A. A. Alsobrook, A. Clearfield and D. T. Hobbs, presented at the 38th Actinide Separations Conference, Albuquerque, NM, May 19 – 22, 2014.
2. "Unconventional Metal-Organic Frameworks (UMOFs) for Separation of Lanthanides from Actinides and Americium from Curium", R. Silbernagel, J. D.

Burns, T. C. Shehee, D. T. Hobbs, D.T. Reed, and A. Clearfield, presented at the 38th Actinide Separations Conference, Albuquerque, NM, May 19 – 22, 2014.

Other Notable Accomplishments

D. T. Hobbs was selected as the recipient of the 2014 Glenn T. Seaborg Actinide Separations Award presented at the 38th Actinide Separations Conference in Albuquerque, NM.

7. COLLABORATORS AND PARTICIPANTS

Participants in the ion-exchange research include Dr. David Hobbs and Dr. Thomas Shehee of SRNL. Prof. Abraham Clearfield and Rita Silbernagel, graduate student, of Texas A&M University are collaborators funded by the DOE Nuclear Energy University Program. Dr. Bruce Mincher and colleagues of the Idaho National Laboratory are collaborators on Am(III) oxidation by peroxydisulfate.