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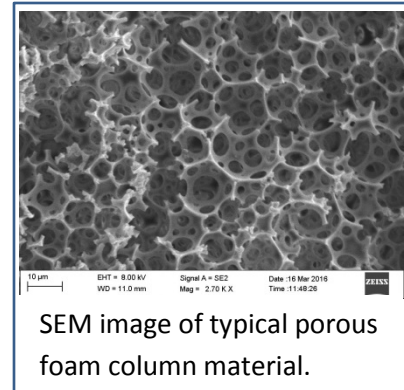
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Pu Anion Exchange Process Intensification

This research is focused on improving the efficiency of the anion exchange process for purifying plutonium. While initially focused on plutonium, the technology could also be applied to other ion-exchange processes. Work in FY17 focused on the improvement and optimization of porous foam columns that were initially developed in FY16. These foam columns were surface functionalized with poly(4-vinylpyridine) (PVP) to provide the Pu specific anion-exchange sites. Two different polymerization methods were explored for maximizing the surface functionalization with the PVP. The open-celled polymeric foams have large open pores and large surface areas available for sorption. The fluid passes through the large open pores of this material, allowing convection to be the dominant mechanism by which mass transport takes place. These materials generally have very low densities, open-celled structures with high cell interconnectivity, small cell sizes, uniform cell size distributions, and high structural integrity. These porous foam columns provide advantages over the typical porous resin beads by eliminating the slow diffusion through resin beads, making the anion-exchange sites easily accessible on the foam surfaces. The best performing samples exceeded the Pu capacity of the commercially available resin, and also offered the advantage of sharper elution profiles, resulting in a more concentrated product, with less loss of material to the dilute heads and tails cuts. An alternate approach to improving the efficiency of this process was also explored through the development of a microchannel array system for performing the anion exchange.



Awards and Recognition

None

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

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Signature

Date

Pu Anion Exchange Process Intensification

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This research is focused on improving the efficiency of the anion exchange process for purifying plutonium. While initially focused on plutonium, the technology could also be applied to other ion-exchange processes. The technology involves the use of either open-celled polymeric foams, which have large surface areas available for solute sorption, or a microchannel array device. Both of these technologies offer the advantage of convection being the dominant mechanism by which mass transport takes place, rather than diffusion. The foam materials are prepared from a high internal phase emulsion (HIPE) process and are then functionalized with poly(4-vinylpyridine) (PVP) through either a photoinitiated or thermally initiated polymerization method. The microchannel device was prepared by etching the microchannels

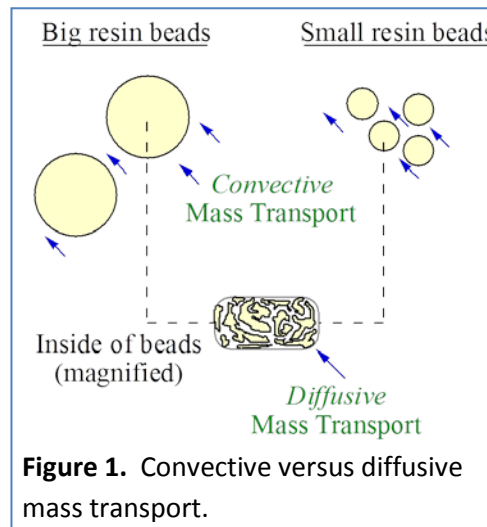
in stainless steel, and then functionalizing the surface of the microchannels with a nanospring coating, and subsequently PVP. These technologies provide an advantage over the typical porous resin beads by eliminating the slow diffusion through the beads. Eliminating the diffusive mass transport increases the ion-exchange rate, and also results in much sharper elution profiles.

FY2017 Objectives

- Optimization of poly(4-vinylpyridine) functionalization of polymeric foam materials
- Recycle testing of optimized polymeric foam materials
- Radiation stability testing of polymeric foam materials
- Fabrication and testing of microchannel array prototype device

Introduction

The Pu anion-exchange process currently performed at the Savannah River Site for purification of Pu involves the use of a commercial poly(4-vinylpyridine) resin, Reillex® HPQ, in a packed bed column. This step in the Pu purification process represents a bottleneck due to the limited volume and flow rate which can be processed. Conventional ion-exchange resins are limited by mass transfer at the solution-particle interface and diffusion through the large granular resin particles. Convective mass transport through the packed bed is much faster than diffusive mass transport inside of the resin beads (Figure 1). The diffusive mass transport can be somewhat reduced by reducing the size of the resin particles, however, this is limited by the increase in pressure drop across a column, which increases as the particle size of the



resin decreases. This project seeks to overcome these limits through the use of a novel ion-exchange configuration, either an inverse column or a microchannel array. Both of these configurations overcome the slow diffusion through conventional granular resin particles. The inverse column, which is a porous foam monolith of material, has the advantage that it can be prepared in the appropriate size and shape to be a direct replacement for the granular resin in the current facility configuration. The microchannel arrays would allow for increased throughput by simply increasing the number of arrays deployed in order to reach the desired throughput. The initial focus of the project is on the Pu anion-exchange process, but once the technology is demonstrated for this application it is envisioned that it could be modified for other ion-exchange applications by modifying the functional groups incorporated on the materials.

SRNL established collaborations with the University of South Carolina (USC) and Oregon State University (OSU) during the course of this project. USC provided the polymer synthesis expertise, and prepared foam monoliths grafted with poly(4-vinylpyridine) (PVP) chains to introduce quaternary amine functional groups as the anion-exchange sites. In high nitric acid concentrations (i.e., 7-8 M) the Pu is present as the hexanitrate anionic complex $[\text{Pu}(\text{NO}_3)_6]^{2-}$ which binds to the quaternary amine groups on the resin. This is the same chemistry utilized by the Reillex® HPQ commercial resin, which is a PVP resin, also containing quaternary amine groups. Collaborators at the OSU Advanced Technology and Manufacturing Institute (ATAMI) provided the microchannel array expertise, and developed a prototype device for testing for this application.

Approach

High internal phase emulsions (HIPE) are used as templates for the formation of the porous polymeric foam monoliths. HIPEs are water-in-oil emulsions in which the water phase comprises at least 74% of the emulsion by volume. The oil phase consists of the monomers used to prepare the polymer, crosslinking agents, and a surfactant. After polymerization and drying the resulting crosslinked polymer is an open-celled isotropic foam. The foam monoliths in this work are prepared from styrene crosslinked using divinylbenzene (DVB). Varying percentages of two different co-monomers were incorporated to allow for later grafting of poly(4-vinylpyridine) chains through either a photoinitiated polymerization or a thermally initiated polymerization. For the photoinitiated polymerizations vinylbenzyl chloride was included as the co-monomer. These foams were then subsequently treated with sodium thiosulfate to introduce free-radical initiation sites on the vinylbenzyl chloride sites.¹ The 4-vinylpyridine was then polymerized from these sites upon exposure to UV light, resulting in grafted polymer chains extending into the foam. For the thermally initiated polymerizations a new monomer was prepared that contained a TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) thermal initiating group. This new monomer (2,2,6,6-tetramethyl-1-((4-vinylbenzyl)oxy)piperidine) was then incorporated into the foam synthesis with the styrene monomer and DVB crosslinker. The TEMPO functionalized sites throughout the foam could then be used to graft the 4-vinylpyridine through thermal initiation. The final PVP content of the foams can be tuned by varying the content of the initiating co-monomer in the foam preparation (graft density) as well as by varying the reaction conditions for the PVP grafting reaction (chain length). A series of foams were prepared varying these two parameters to identify the optimal conditions for preparing the foam material with maximum Pu capacity.

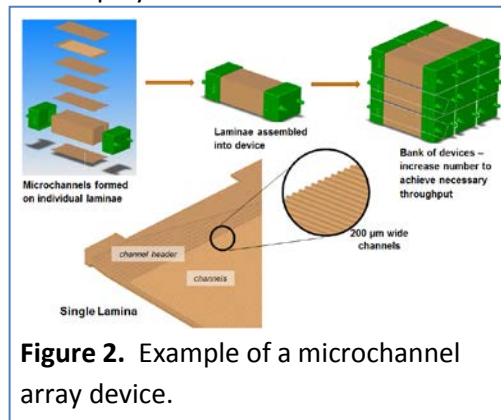


Figure 2. Example of a microchannel array device.

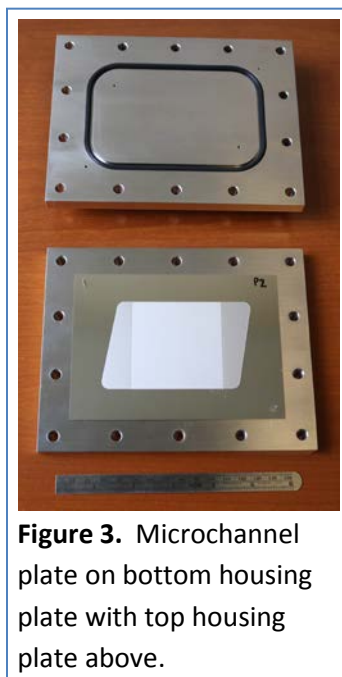


Figure 3. Microchannel plate on bottom housing plate with top housing plate above.

In addition to the porous foam columns, we also prepared a microchannel array prototype device. Figure 2 provides a schematic of a microchannel array device. In FY16 we attempted unsuccessfully to prepare the individual laminae from crosslinked PVP, which would then already contain the quaternary amine functional groups necessary for the Pu anion exchange process. In FY17, we modified our approach to decouple the material of construction for fabricating the microchannel geometries from the functional material. For this approach an array of 200 microchannels was photochemically machined into a 0.02" thick 304 stainless steel plate (Figure 3). The microchannel dimensions were 75 μm deep, 200 μm wide, and 60 mm in length. The microchannels were functionalized for ion-exchange in two steps: 1) increased specific surface area with nanosprings (NS) and 2) functionalized with PVP for adsorption. A SiO_2 NS mat with high porosity (up to 90%) was grown on the surface of the microchannels (Figure 4). The total surface area in the headers and microchannels

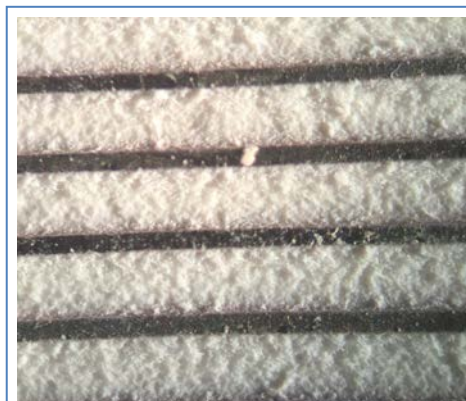


Figure 4. Nanospring mat grown and partially occupying microchannels.

was increased to approximately 15 m^2 . PVP was then coated on the surface of the NS mat based on procedures from Malynych et. al.² The plates were treated under plasma in air for 2 minutes and then submerged in a 1% solution, by mass, of 60,000 MW PVP in ethyl alcohol for 12 hours. This was followed by annealing at 120 $^\circ\text{C}$ for 3 hours.

Results/Discussion

In FY16 we demonstrated the successful preparation of porous foam columns grafted with PVP chains using both the photoinitiated and thermally initiated grafting techniques. The thermally initiated method was found to give superior results, both in terms of PVP functionalization, which translates to increased Pu loading, as well as reproducibility of the syntheses. FY17

focused on determining the optimum graft density and chain length for the thermally initiated samples to maximize the Pu capacity. The graft density can be modified by varying the amount of TEMPO functionalized co-monomer incorporated in the initial HIPE polymerization, and the chain length varies with reaction time. A series of samples with varying graft densities and chain lengths were prepared and tested. The characterization data for this set of samples is shown in Table 1. The net N content relates directly to the amount of PVP incorporated, and as can be seen, the net N content varied from ~ 9.5 wt% to ~ 11.5 wt%. For comparison, the commercial Reillex[®] HPQ has a theoretical N content of 8.75 wt%. These samples were then assembled into columns using a similar procedure used in FY16, which involves encapsulating the columns in several layers of heat shrink-tubing and fitting the ends

Table 1. Summary of Foam Column Characterization Data

Sample ID	Net N Content (%)	Weight Gain (%)	Graft Density	Chain Length
JP-2-36	9.57	366	Low	Med.
JP-2-110	11.16	599	High	Med.
JP-2-111	11.14	490	Med.	Med.
JP-2-112	10.46	450	Low	Med.
JP-2-113	11.47	722	High	High
JP-2-117	9.95	272	High	Low

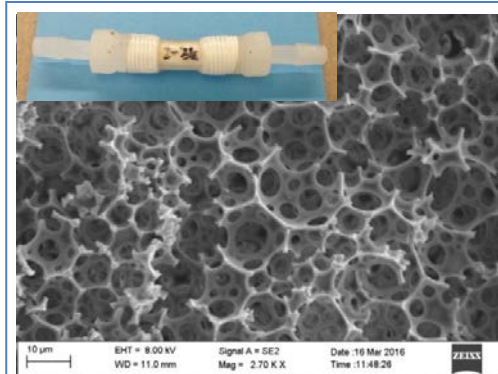


Figure 5. Photo of foam test column (inset) and SEM of foam pore structure.

columns. A sample of Reillex[®] HPQ was also tested in FY16 as a point of comparison for this work. For the Reillex[®] testing, a small glass column was packed with Reillex[®] HPQ resin. The calculated gravimetric and volumetric Pu capacities for each of the tested columns are shown in Table 2, along with the Reillex[®] HPQ data for comparison. As can be seen, these columns greatly exceed the Reillex[®] material on a gravimetric basis, partly due to the extremely low densities of the porous foams (average of 0.091 g/cm³ pre-

functionalization). However, most of the samples also outperform on a volumetric basis, with the best performing samples having volumetric capacities approximately 1.5 times that of the Reillex[®]. Sample JP-2-111, with a medium graft density and medium chain length had the highest gravimetric capacity. Increasing the graft density and/or chain length did not offer much improvement in the capacity, so it appears we've reached a level of diminishing returns at the medium graft density and chain length. This formulation was selected to move forward for additional testing including radiation stability and recycle

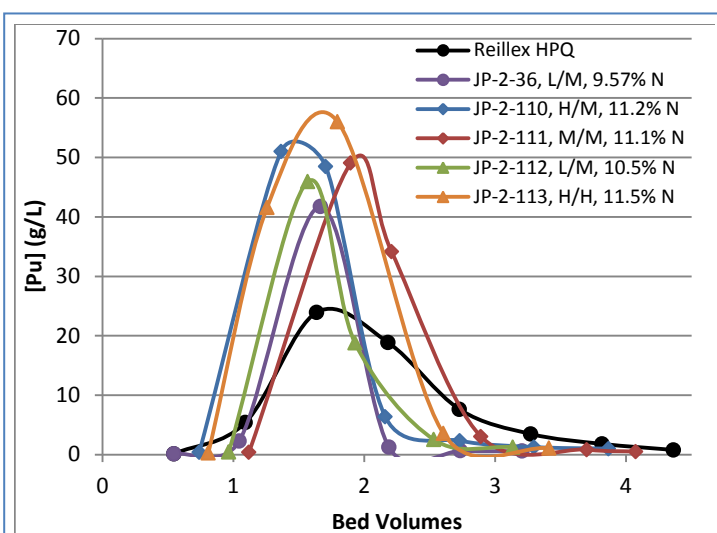


Figure 6. Elution profiles of foam column samples compared to Reillex[®] HPQ. The X/Y indicates graft density (X) and chain length (Y). L = low, M = medium, H = high

with tubing adapters. One improvement to this process made in FY17 was coating of the outside walls of the columns with a layer of epoxy, prior to the heat shrink tubing, to ensure we did not have any channeling of solution along the outside of the column. Figure 5 shows a representative SEM image of the porous foam columns, showing the open pore structure, and the insert shows an assembled column ready for Pu uptake testing.

The foam column samples were tested for Pu uptake and elution, and the Pu capacities were determined based on the amount of Pu that was eluted from the

Sample ID	Gravimetric Pu Capacity (g Pu/g)	Volumetric Pu Capacity (g Pu/mL)
JP-2-36	0.185	0.028
JP-2-110	0.260	0.054
JP-2-111	0.293	0.052
JP-2-112	0.203	0.037
JP-2-113	0.288	0.053
JP-2-117	0.102	0.017
Reillex [®] HPQ	0.038	0.034

testing. Several more samples of this composition were prepared.

In addition to the high Pu capacities of the materials, another important feature, and improvement of the foams over typical resin beads, is the elution profile, which is much sharper in the foam material due to the lack of diffusion of Pu from large resin beads during elution. The elution profiles for several of the thermally initiated samples are shown in Figure 6. As can be seen in the figure, the elution is much sharper from the foam columns, as they do not exhibit the "tail" that is seen in the Reillex[®] HPQ elution. The elution for the foam columns spans no more than 2 bed volumes in most cases; whereas the Reillex[®] HPQ elution occurs over nearly 4

bed volumes, including the dilute heads and tails cuts. Several of the foam samples reached a Pu concentration of greater than 50 g/L in the hearts cut; which represents concentration by greater than 10x from the feed solution (~4.5 g/L).

Additional testing of the foam column samples in FY17 focused on repeated use of the columns over an extended period of time. Several columns were prepared following the JP-2-111 formulation. Two of these samples were placed into 8 M nitric acid for a period of approximately 7 weeks. One of these samples was placed in a Co-60 irradiation source to irradiate the sample to a total dose of approximately 1×10^8 rads, which is the estimated maximum dose a resin column used in HB-Line would be expected to receive prior to replacement. Unfortunately, it was found that these materials were not stable to extended exposure to 8 M nitric acid. Both the irradiated and unirradiated samples were found to have decomposed at the end of the 7 week exposure; the samples were no longer solid monoliths.

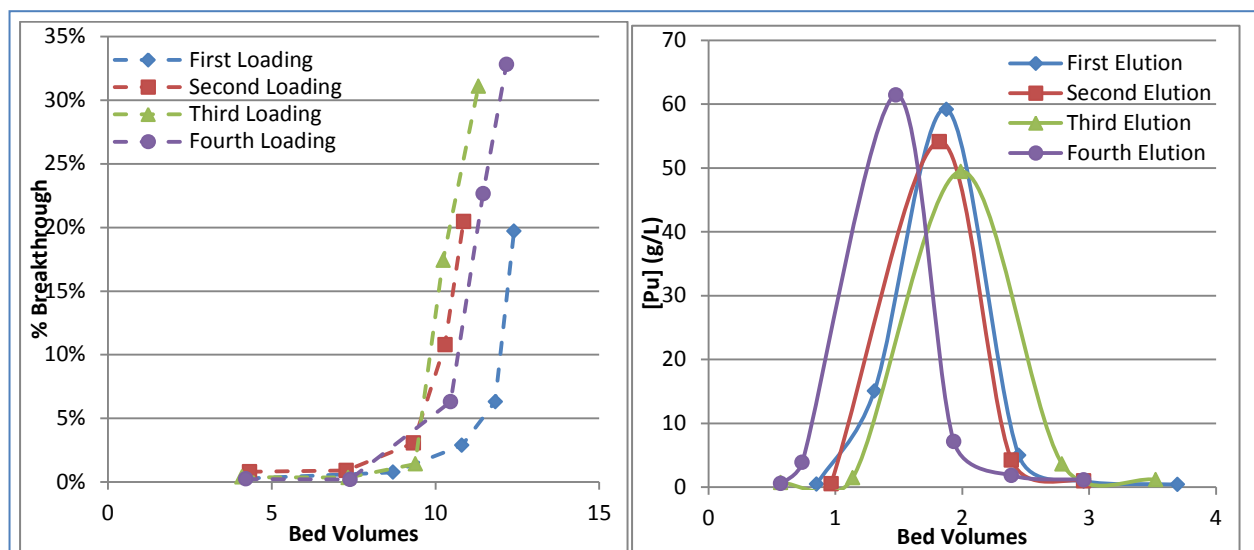


Figure 7. Loading (left) and elution (right) profiles of a single foam column sample cycled four times.

An additional sample was prepared and used for recycle testing to determine the ability to load and elute the material multiple times while retaining the initial capacity. The sample used for recycle testing was loaded and eluted for a total of four times. Cycles three and four were performed approximately 3 months after cycles one and two. The column was stored during this time having last been exposed to the elution acid (0.35 M nitric acid); which indicates the column material is stable to extended exposure

to dilute acid. The loading and elution profiles for the four cycles are shown in Figure 7. No loss of capacity was observed over the four cycles, indicating repeated loading and elution is possible. There did appear to be a slight increase in capacity after the first cycle; however, this increase is within the experimental and analytical error. Table 3 summarizes the capacities from the repeat cycles.

Cycle	Gravimetric Pu Capacity (g Pu/g)	% of Initial Capacity
1 st	0.236	100%
2 nd	0.263	111%
3 rd	0.250	106%
4 th	0.271	115%

Finally, the microchannel array prototype prepared by OSU was tested for Pu uptake. Unfortunately, the experiments indicated essentially no retention of Pu by the device. Due to limited time available after the preparation of the prototype, testing was not performed to examine the stability of the PVP

coating on the NS mat in 8 M nitric acid nor was the amount of PVP immobilized on the NS mat quantified.

FY2017 Accomplishments

- Demonstrated improved gravimetric and volumetric Pu capacities over the commercial Reillex® HPQ resin
- Demonstrated sharper elution profiles with the foam columns when compared to Reillex® HPQ
- Optimization of graft density and chain length showed highest gravimetric capacity with medium density and chain length
- Demonstrated reuse of the column for 4 cycles, with no loss of capacity

Future Directions

- Explore HIPE polymerization of PVP as foam backbone to increase long term stability in 8 M nitric acid.
- Explore other ion-exchange applications by identifying other functional groups that can be incorporated on the HIPE backbone for other applications.
- For microchannel array: Determine optimal NS material as well as develop more stable PVP functionalization, including incorporation of cross-linker or pre-functionalizing NS surface for end-chain attachment of PVP polymer

FY 2017 Publications/Presentations

1. "Porous Foam Columns for Plutonium Anion Exchange" K. M. L. Taylor-Pashow, T. C. Shehee, D. T. Hobbs, J. G. Pribyl, and B. C. Benicewicz, presented at the Nineteenth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 11, 2016.
2. "Photoinitiated Polymerization of 4-Vinylpyridine on polyHIPE Foam Surface toward Improved Pu Separations" J. Pribyl, B. Fletcher, W. Steckle, K. Taylor-Pashow, T. Shehee, and B. Benicewicz, *Anal. Chem.*, **2017**, *89*, 5174-5178.
3. "Polymeric Foams for Plutonium Anion Exchange" K. Taylor-Pashow, T. Shehee, D. Hobbs, J. Pribyl, and B. Benicewicz, presented at the 254th American Chemical Society National Meeting, Washington D.C., August 21, 2017.

References

1. B. C. Benicewicz, G. D. Jarvinen, D. J. Kathios, and B. S. Jorgensen, *J. Radioanal. Nucl. Chem.* **1998**, *235*, 31-35.
2. Malynych, S.; Luzinov, I.; Chumanov, G. *J. Phys. Chem. B* **2002**, *106* (6), 1280–1285.

Acronyms

DVB	divinylbenzene
HIPE	high internal phase emulsion
OSU	Oregon State University
PVP	poly(4-vinylpyridine)
SEM	Scanning electron microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
USC	University of South Carolina

LDRD-2016-00026

LDRD Report

Intellectual Property

Invention disclosure (SRS-17-018)

Provisional patent application filed June 12, 2017.

Total Number of Post-Doctoral Researchers

None