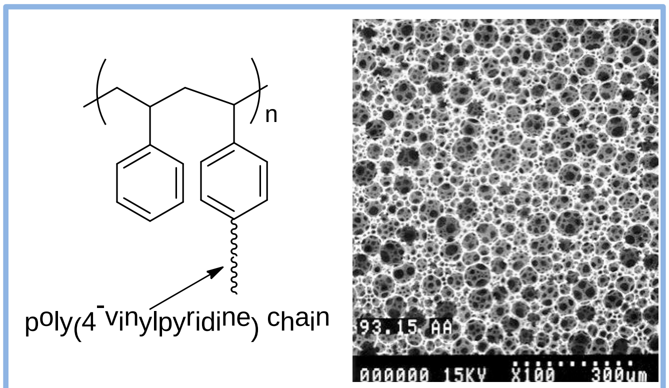
Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Pu Anion Exchange Process Intensification

This project seeks to improve the efficiency of the plutonium anion-exchange process for purifying Pu through the development of alternate ion-exchange media. The objective of the project in FY15 was to develop and test a porous foam monolith material that could serve as a replacement for the current anion-exchange resin, Reillex® HPQ, used at the Savannah River Site (SRS) for purifying Pu. The new material provides advantages in efficiency over the current resin by the elimination of diffusive mass transport through large granular resin beads. By replacing the large resin beads with a porous foam there is much more efficient contact between the Pu solution and the anion-exchange sites present on the material. Several samples of a polystyrene based foam grafted with poly(4-vinylpyridine) were prepared and the Pu sorption was tested in batch contact tests.



Schematic of polymer structure (left) and SEM image of porous foam (right).

Samples of Reillex® HPQ were tested in parallel. Results from the batch contact testing showed improved Pu sorption with the foam materials over the Reillex® HPQ resin beads.

Awards and Recognition

SRNL Laboratory Dirctor's Award for Early Career Exceptional Achievement (Taylor-Pashow)

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.

SRNL Legal Signature

Signature

Date

LDRD-2015-00072
LDRD Report

Pu Anion Exchange Process Intensification

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Collaborator: B. C. Benicewicz (University of South Carolina)

Thrust Area: ST1

Project Type: Exploratory

Project Start Date: May 1, 2015
Project End Date: September 30, 2015

The objective of this project is to develop a highly efficient Pu anion-exchange process through the development of alternate ion-exchange media. During FY15 the focus of the project was on the development of porous foam monoliths containing the poly(4-vinylpyridine) functionality to serve as the anion-exchange site. Preliminary samples of polystyrene foams grafted with poly(4-vinyl pyridine) were prepared and the Pu uptake was measured in a series of batch contact tests. The commercial standard, Reillex® HPQ, was tested in parallel. Results of the batch contact testing showed higher uptake percentages and higher Pu loadings on the porous foam monolith materials when compared to the Reillex® HPQ sample.

FY2015 Objectives

- Preparation of polymeric foam materials containing poly(4-vinylpyridine) by University of South Carolina
- Testing Pu uptake of new materials and comparison of uptake to Reillex® HPQ resin

Introduction

The Pu anion-exchange process currently performed at the Savannah River Site (SRS) 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 in the process 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. 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.

The focus during FY15 was on the preparation of porous foam monoliths for the inverse column application. SRNL collaborated with the University of South Carolina for the synthesis of these materials. The foam monoliths were grafted with poly(4-vinylpyridine) 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 hexanitrato anionic complex $[Pu(NO_3)_6]^{2-}$ 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 poly(4-vinylpyrinidine) resin, also containing quaternary amine groups.

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 76% of the emulsion by volume. A schematic of a HIPE process is shown in Figure 1. 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. Varying percentages of vinylbenzyl chloride are incorporated as a co-monomer to allow for later grafting of poly(4-vinylpyridine) chains. The poly(4-vinylpyridine) is then grafted onto the foam through reversible addition-fragmentation chain-transfer (RAFT) polymerization.

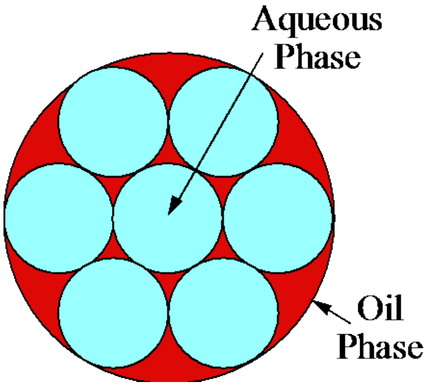

Figure 1. Schematic of HIPE process.

Batch contact testing was performed with several samples of foam materials prepared as described in the previous paragraph to determine the Pu uptake relative to the currently used Reillex® HPQ resin. Several different phase ratios were tested by adding known amounts of the foam to aliquots of a Pu solution in nitric acid. The solutions were then analyzed to determine the amount of Pu removed from solution by the foam. Samples of the Reillex® HPQ resin were tested in parallel under identical conditions.

Results/Discussion

Samples of highly uniform polystyrene monoliths were prepared with varying ratios of chloromethyl styrene co-monomer using high internal phase emulsions. The composition was optimized for greater surface functionality by increasing the volume ratio of chloromethyl styrene incorporated. After formation of the foam, poly(4-vinylpyridine) was grafted onto the surface (internal and external surfaces) using either photoinitiated polymerization or a click chemistry reaction. The grafting uniformity was improved using the click chemistry, when compared to photoinitiation. Samples of foam prepared using both photoinitiation and the click chemistry grafting were then tested for Pu uptake in batch contact experiments.

Table 1. Summary of results from batch contact testing.

Sample	Phase Ratio (mL/g)	DF	K_d (mL/g)	Pu Loading (g Pu/g IX)
Reillex HPQ	100	1.08	8.1	0.040
Foam #1	100	1.20	20.5	0.091
Foam #2	100	1.03	2.7	0.014
Reillex HPQ	50	1.14	6.8	0.032
Foam #1	50	1.21	10.6	0.094
Foam #2	50	1.10	5.2	0.025
Reillex HPQ	10	1.74	7.4	0.023
Foam #1	10	2.05	10.5	0.027
Foam #2	14.6	1.46	6.6	0.024

In the first set of batch contact testing experiments with Sample #1 (photoinitiated polymerization) of the polymeric foam material, three different phase ratios were tested with both the foam and a sample of Reillex® HPQ resin. The distribution coefficients (K_d) obtained in all tests were relatively low; however, the foam Sample #1 showed higher Pu removal and loading capacities relative to the Reillex® HPQ. These tests were repeated with an optimized Sample #2 of the polymeric foam material, prepared using the click chemistry reaction. Results from these tests actually showed lower Pu uptake than was observed with Sample #1. It is speculated that although the click polymerization allowed for more uniform grafting throughout the foam, the slower reaction may have led to shorter chains of poly(4-vinylpyridine) compared to the photoinitiated polymerization. Analysis of the foams for nitrogen content is underway to confirm this hypothesis.

FY2015 Accomplishments

- Demonstrated ability to synthesize highly uniform monoliths in moderate quantity
- Optimized foam composition for greater surface functionality (increased volume ratio of chloromethyl styrene co-monomer)
- Developed successful procedure for grafting of poly(4-vinylpyridine) using click chemistry
- Realized improved Pu uptake with a sample of the polymeric foam material. K_d values were 1.4 – 2.5 times higher than those obtained with Reillex® HPQ, depending on the phase ratio.

Future Directions

- Continue optimization of foam preparation and determine optimum degree of poly(4-vinylpyridine) grafting (i.e., number of chains and chain length).
- Fabricate small columns for flow testing using shrink wrap tubing/hose connectors
- Perform column testing with foam monoliths to determine loading parameters and achievable loading capacities.
- Scale up the column size
- Fabricate microchannel arrays containing the poly(4-vinylpyridine) functionality and evaluate these material for Pu anion exchange.

FY 2015 Publications/Presentations

None

References

None

Acronyms

DF	decontamination factor
FY	fiscal year
HIPE	high internal phase emulsion
K_d	distribution coefficient
RAFT	reversible addition-fragmentation chain-transfer
SRNL	Savannah River National Lab
SRS	Savannah River Site

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None