Contract No:

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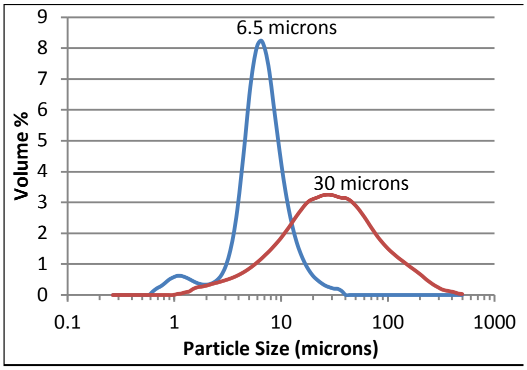
Large Particle Titanate Sorbents

This research project was aimed at developing a synthesis technique for producing large particle size monosodium titanate (MST) to benefit high level waste (HLW) processing at the Savannah River Site (SRS). Two applications were targeted, first increasing the size of the powdered MST used in batch contact processing to improve the filtration performance of the material, and second preparing a form of MST suitable for deployment in a column configuration. Increasing the particle size should lead to improvements in filtration flux, and decreased frequency of filter cleaning leading to improved throughput. Deployment of MST in a column configuration would allow for movement from a batch process to a more continuous process.

Modifications to the typical MST synthesis led to an increase in the average particle size. Filtration testing on dead-end filters showed improved filtration rates with the larger particle material; however, no improvement in filtration rate was realized on a crossflow filter.



Comparison of particle size distributions for vendor prepared baseline MST (blue) and larger particle MST (red).

In order to produce materials suitable for column deployment several approaches were examined. First, attempts were made to coat zirconium oxide microspheres (196 μm) with a layer of MST. This proved largely unsuccessful. An alternate approach was then taken synthesizing a porous monolith of MST which could be used as a column. Several parameters were tested, and conditions were found that were able to produce a continuous structure versus an agglomeration of particles. This monolith material showed Sr uptake comparable to that of previously evaluated samples of engineered MST in batch contact testing.

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-2014-00119
LDRD Report

Large Particle Titanate Sorbents

Project Team: K. M. L. Taylor-Pashow (Primary), and D. T. Hobbs

Thrust Area: ST1

Project Type: Standard

Project Start Date: March 1, 2014
Project End Date: September 30, 2015

This research project was aimed at developing a synthesis technique for producing large particle size monosodium titanate (MST). Two approaches were evaluated, increasing the particle size of the material enough to improve filtration performance in batch contact deployment, and preparing a form of the material suitable for column deployment. Filtration performance of larger particle MST was improved in dead-end filtration testing; however, filtration testing on a crossflow filter did not show improved filtration rate over the baseline material. Attempts were also made to coat zirconium oxide microspheres (196 µm) with MST to prepare a large spherical particle for column deployment. These attempts proved unsuccessful. An alternate approach was then taken to synthesize a porous MST monolith that could be deployed in a column configuration. Conditions were found to prepare an MST monolith that showed comparable Sr uptake to a previously evaluated form of engineered MST.

FY2015 Objectives

- Scale-up synthesis of large particle MST to confirm reproducibility and prepare sufficient material for crossflow filter testing
- Examine performance of material in a crossflow filter and compare to baseline MST
- Prepare MST in a form suitable for column deployment

Introduction

The high level waste (HLW) mission at SRS involves the processing of sludge and salt (supernate and saltcake). The sludge is incorporated in HLW glass during the vitrification process, while the salt is treated to remove Cs, Sr, and actinides. The separated radionuclides are incorporated into the HLW borosilicate glass along with the sludge during the vitrification process, while the decontaminated salt solution is disposed of onsite in a grout waste form referred to as Saltstone. The current salt treatment processes are performed at the pilot-scale Actinide Removal Process (ARP) and Modular Caustic-Side Solvent Extraction Unit (MCU) facilities. The larger Salt Waste Processing Facility (SWPF), currently under construction, is designed to have a throughput of about seven times that of the ARP/MCU facilities.

Filtration is the current throughput-limiting step in the ARP/MCU and SWPF. It is believed that the particle size and particle size distribution of the MST are significant contributors to low filtration fluxes that have been observed in the ARP facility. Current purchase specifications allow the vendor to supply MST powder that has as much as 10% of the material with a particle size less than 0.8 µm. The nominal pore diameter of the crossflow filter used in the ARP facility and SWPF is 0.1 µm, and a 0.5-µm filter was recently installed. Thus, the possible high fraction of fines less than 0.8 µm could be plugging the pores of the crossflow filter media resulting in reduced filtration flux. Increasing the particle size and narrowing the particle size distribution would be expected to increase the filter performance and, therefore, the throughput of both facilities that use crossflow filtration to separate MST solids from supernatants.

Possible delays in start-up of the SWPF could cause an extension of the salt processing campaign, resulting in sludge processing completing prior to completion of the salt processing. The development of processes to either speed processing of salt through the current APR/MCU facilities or to supplement this and the SWPF facility with at-tank treatment processes would help to close this possible gap and allow for completion of salt and sludge processing at the same time. One technology that has been investigated to supplement the ARP/MCU facility is the use of a small column ion-exchange (SCIX) process performed at the waste tank. The proposed technology utilizes crystalline silicotitanate (CST) in a column for removal of the Cs. MST is added directly to the tank to remove Sr and actinides in a batch-contact fashion. The process could be improved by also deploying the MST in a column, either a mixed column with the CST or a separate column; however, the relatively small size of MST currently precludes its use in a column configuration due to very high pressure drop across the column. One objective of this project was to increase the particle size of MST through modification of the synthesis to generate material suitable for column deployment. An additional benefit to column deployment is more efficient use of the sorbent, resulting in less MST (i.e., titanium) being sent to the vitrification process. The solubility of titanium in the current borosilicate glass formulation is limited. Thus, it is likely that the Defense Waste Processing Facility (DWPF) glass formulation would have to be changed to accommodate increased titanium from the use of both MST and CST.

Approach

In FY14 the sol-gel synthesis of MST was successfully modified to produce larger size particles. The typical MST synthesis results in spherical particles in the 1-10 μm size range. Through the introduction of a surfactant to the synthesis, the particle size was increased to a mean diameter of approximately 30 μm (Fig. 1). Testing in FY14 showed improved filtration performance of the larger particle material compared to the standard vendor prepared MST in dead-end filtration testing. FY15 efforts focused on scaling up the synthesis of the larger particle MST, and filtration testing using a crossflow filter, similar in design to the filter utilized in ARP for separating the MST.

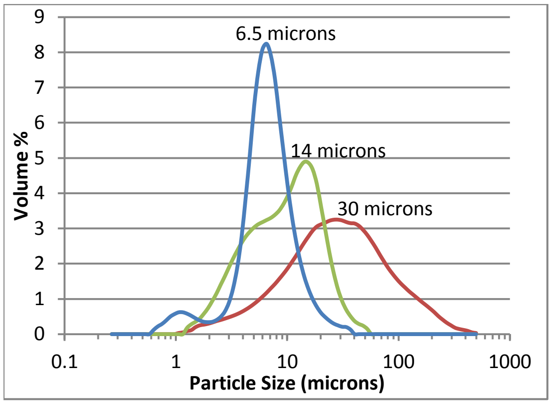


Figure 1. Comparison of particle size distributions for vendor prepared baseline MST (blue), larger particle MST (red), and larger particle MST after CUF filtration (green).

In addition, attempts to obtain particles large enough for column deployment through modifications to the sol-gel synthesis proved unsuccessful. Therefore, during FY15, several alternate approaches were explored for obtaining material suitable for column deployment. The first approach was to deposit a shell of MST onto already formed zirconium oxide microspheres. The second approach involved synthesizing a porous monolith of MST.

Results/Discussion

Previous work in FY14 had determined that the addition of Tween 20 to the sol-gel synthesis was successful at increasing the average particle size of the MST. The mean diameter of particles produced using the modified synthesis was approximately 30 µm. In FY15, this modified sol-gel synthesis was successfully increased from 1-g scale reactions to 10-g scale reactions. Several of the larger scale batches that showed improved performance in dead-end filtration testing (Fig. 2), which was performed using a 0.45-µm Nylon filter, were combined to obtain a larger sample for crossflow filtration testing. Crossflow filtration tests were performed using both 0.1 and 0.5 µm 3/8 inch ID Mott® porous metal crossflow filters, both 24 inches in length and constructed of sintered stainless steel. For the filtration tests, the MST was added to a 6.6 M Na^+ salt solution representative of the chemical composition of SRS HLW waste. Results from crossflow filtration testing did not correlate well with those obtained from the dead-end filtration testing. The larger particle MST was found to have a lower filtration flux when compared to the vendor prepared baseline MST (Fig. 3) on both the 0.1-µm and 0.5-µm filters. Particle size analysis after filtration showed that the average particle size had been reduced during the crossflow filtration (Fig. 1), perhaps indicating larger particles had been broken up during the filtration process. This, in combination with the broader distribution compared to the baseline MST, likely resulted in poorer filtration performance on the crossflow filter due to the formation of a denser filter cake.

The second objective of this project was to prepare MST in a form suitable for column deployment. During testing performed in FY14 it was evident that changes to the sol-gel synthesis would not be sufficient to produce very large (>100 µm) particles necessary for column deployment. Two alternatives were then examined. In the first, attempts were made to coat 196-µm ZrO_2 microspheres with MST. Several references were found describing the coating of titania onto zinc oxide, silica, and polystyrene spheres.[1-5] Aspects of these syntheses along with the typical MST synthesis were combined

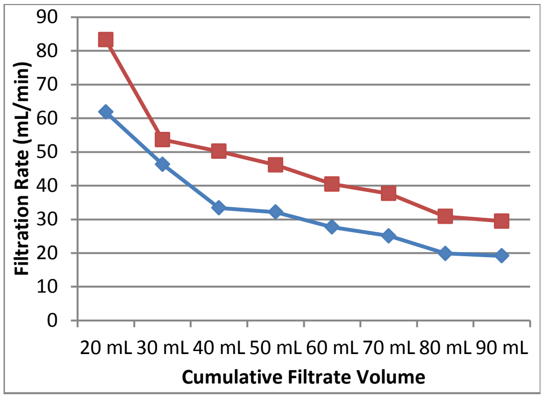


Figure 2. Results from dead-end filtration testing comparing filtration rates of vendor prepared baseline MST (blue) and larger particle MST (red).

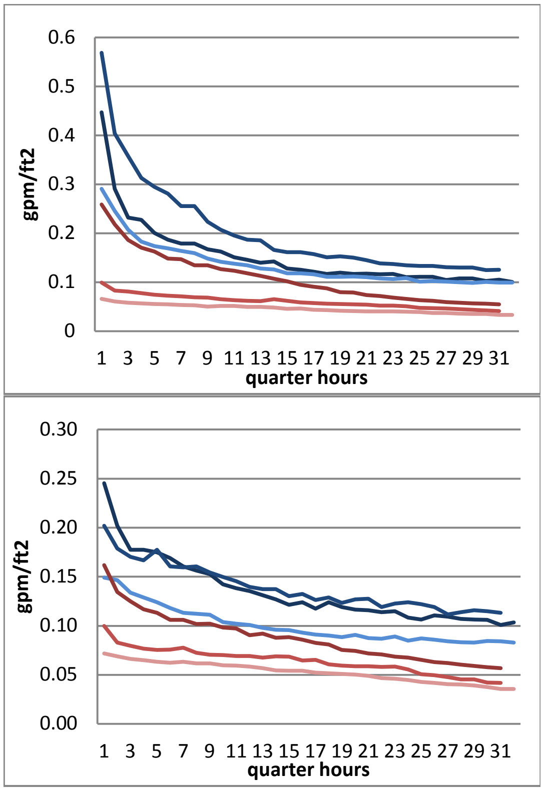


Figure 3. Filter fluxes on 0.1-µm (top) and 0.5-µm (bottom) crossflow filters of vendor prepared baseline MST (blue) and larger particle MST (red).

to generate conditions for attempting the coating of the zirconium oxide particles. Parameters such as reaction temperature, reactant concentrations, and reactant addition rates were varied. X-ray fluorescence (XRF) analysis of samples indicated the presence of Ti on some of the samples produced. These samples were then tested for Sr uptake from a HLW simulant solution spiked with ^{85}Sr. Although Ti was present, no uptake of ^{85}Sr was observed in any of the samples. This indicated the Ti that was deposited was not in the form of MST, or that insufficient MST was deposited. Attempts to increase the amount of MST on the surface through repeated coatings also proved unsuccessful.

After the coating reactions proved unsuccessful, an alternate approach for preparing material suitable for a column was evaluated. This approach involved the attempted synthesis of a porous monolith of MST which could be used as a column. Several references were found describing the preparation of porous titania monoliths starting from Ti precursors such as $Ti(O^iPr)_4$ (which is used for normal MST synthesis) and $Ti(O^nPr)_4$.[6-8] Attempts were made to reproduce these syntheses, including the addition of sodium methoxide to prepare MST monoliths. Conditions were found that appeared to produce a continuous structure versus just an agglomeration of particles. A representative scanning electron microscopy (SEM) image of this sample is shown in Figure 4. Batch contact testing was performed with a sample of this material to ensure the material retained typical MST sorption performance. Batch contact testing showed ^{85}Sr uptake comparable to a previously investigated form of engineered MST.[9] The decontamination factor (DF) obtained with samples of the MST monolith averaged 7.7 compared to 6.6 for the engineered MST in this experiment.

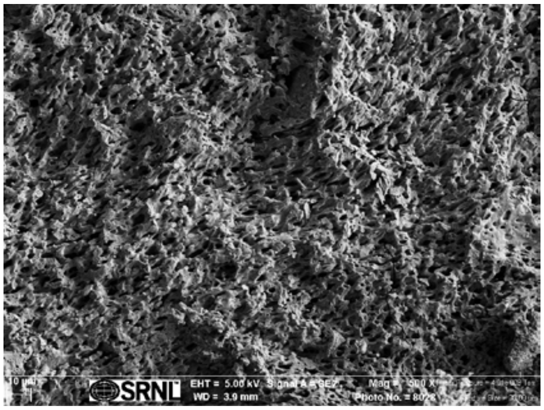


Figure 4. SEM image of MST monolith sample.

FY2015 Accomplishments

- Increased scale of reactions to produce larger particle MST from 1 g to 10 g scales.
- Performed filtration testing of larger particle MST on both dead-end and crossflow filters.
    - Results from dead-end filter testing indicated improved filtration rates over baseline MST; however, decreased filtration flux was observed in crossflow filter testing.
- Prepared porous monolith of MST that showed ^{85}Sr uptake comparable to that of previously developed engineered MST in batch contact testing.

Future Directions

- Optimize synthesis of porous MST monolith
- Perform column testing with MST monolith to determine capacity and loading characteristics

FY 2015 Publications/Presentations

None

References

1. Ocaña, M.; Hsu, W. P.; and Matijević, E. “Preparation and Properties of Uniform-Coated Colloidal Particles. 6. Titania on Zinc Oxide” *Langmuir*, **1991**, *7*, 2911-2916.
2. Hanprasopwattana, A.; Srinivasan, S.; Sault, A. G.; and Datye, A. K. “Titania Coatings on Monodisperse Silica Spheres (Characterization Using 2-Propanol Dehydration and TEM)” *Langmuir*, **1996**, *12*, 3173-3179.
3. Guo, X-C; and Dong, P. “Multistep Coating of Thick Titania Layers on Monodisperse Silica Nanospheres” *Langmuir*, **1999**, *15*, 5535-5540.
4. Imhof, A. “Preparation and Characterization of Titania-Coated Polystyrene Spheres and Hollow Titania Shells” *Langmuir*, **2001**, *17*, 3579-3585.
5. deKrafft, K. E.; Wang, C.; and Lin, W. “Metal-Organic Framework Templated Synthesis of Fe_2O_3/TiO_2 Nanocomposite for Hydrogen Production” *Adv. Mater.* **2012**, *24*, 2014-2018.
6. Chen, Y.; Yi, Y.; Brennan, J. D.; and Brook, M. A. “Development of Macroporous Titania Monoliths Using a Biocompatible Method. Part 1: Material Fabrication and Characterization” *Chem. Mater.,* **2006**, *18*, 5326-5335.
7. Konishi, J.; Fujita, K.; Nakanishi, K.; and Hirao, K. “Monolithic TiO_2 with Controlled Multiscale Porosity via a Template-Free Sol-Gel Process Accompanied by Phase Separation” *Chem. Mater.*, **2006**, *18*, 6069-6074.
8. Hasegawa, G.; Kanamori, K.; Nakanishi, K.; and Hanada, T. “Facile Preparation of Hierarchically Porous TiO_2 Monoliths” *J. Am. Ceram. Soc.*, **2010**, *93*, 3110-3115.
9. Taylor-Pashow, K. M. L.; Nash, C. A.; and Hobbs, D. T. “Testing and Characterization of Engineered Forms of Monosodium Titanate (MST)” SRNL-STI-2012-00193, Rev. 0, May 2012.

Acronyms

ARP	Actinide Removal Process
CST	crystalline silicotitanate
DF	decontamination factor
DWPF	Defense Waste Processing Facility
FY	fiscal year
HLW	high level waste
ID	internal diameter
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	monosodium titanate
SCIX	Small Column Ion Exchange
SEM	scanning electron microscopy
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
XRF	X-ray fluorescence

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None