

**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).

**Disclaimer:**

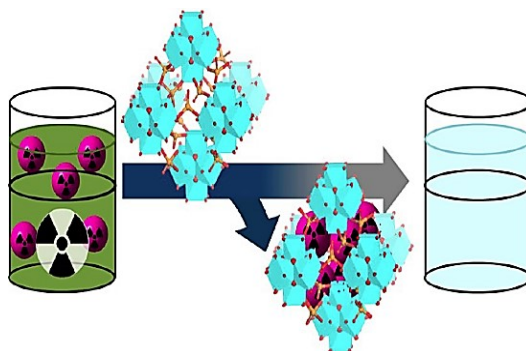
This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1 ) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2 ) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

## Quaternary Amine-Based Sodalite Sorbent for Selective Removal of Tc-99 and I-129

Technetium-99 and Iodine-129 are priority contaminants of concern, driving risk assessments at several DOE nuclear waste sites. Because these radionuclides greatly affect the catalytic redox extraction process of uranium and plutonium in the fuel cycle, their removal from spent nuclear solution is highly desirable for efficient recovery of uranium and plutonium, and mitigation of potential releases of these radionuclides to the environment. The **overarching goals** of this research project were to develop and evaluate the performance characteristics of several synthesized and commercial sequestering agents (sorbents) for dual capture of Tc-99 and I-129. Specifically, this research leveraged synthesis and modification of aluminosilicate minerals (zeolite of the faujasite type) to effectively remove radionuclides from contaminated media. Herein we developed a sorbent that: (1) binds pertechnetate ( $\text{TcO}_4^-$ ) with a sorption efficiency ( $K_d$ ) greater than any other sorbent materials previously reported in literature, 2) exhibits fast sorption kinetics and (3) uptakes  $\text{TcO}_4^-$  under acidic and oxidizing conditions where Tc-99 retention is problematic. The impact of silver modification on the capacity of these zeolites to capture both Tc-99 and I-129 was anticipated to be completed in fiscal year 2019. A **key outcome** of this research is that we made a sorbent that greatly exceeds the effectiveness of previous sorbents for binding Tc-99, a contaminant that continues to drive risk and cleanup costs for DOE. The  $K_d$  value of this sorbent is approximately  $10^9$  mL/g, whereas that for SRS soil is about 0.1 mL/g. Additional outcomes include two conference presentations, a manuscript in preparation, and a future proposal leveraging seed data from this study to solicit external funding.



### 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.

### SRNL Legal Signature

---

Signature

---

Date

## Quaternary Amine-Based Sodalite Sorbent for Selective Removal of Tc-99 and I-129

Project Team: J. O. Dickson (Primary), D. Li, and D. I. Kaplan, J. C. Seaman, and B. A. Powell

Subcontractor: SREL, Clemson University

Thrust Area: ES

Project Start Date: October 1, 2017

Project End Date: September 30, 2018

*Technetium-99 and Iodine-129 are risk-driven contaminants of high priority to DOE-EM office. Both radionuclides are prevalent at DOE nuclear waste sites. Because these radionuclides greatly affect the catalytic redox extraction process of uranium and plutonium in the fuel cycle, their removal from spent nuclear solution is highly desirable for efficient recovery of uranium and plutonium, and mitigation of potential releases of these radionuclides to the environment. The goals of this project were to develop advance sorbents for simultaneous capture of Tc-99 and I-129 from contaminated groundwater and nuclear waste*

*streams. This research examined modification of porous commercial and synthesized aluminosilicate minerals (zeolite) for enhanced retention of radionuclides. Herein we report the development of a sorbent that: (1) binds pertechnetate ( $\text{TcO}_4^-$ ) with a sorption efficiency ( $K_d$ ) greater than any other sorbent materials previously reported in literature, 2) exhibits fast sorption kinetics and (3) uptakes  $\text{TcO}_4^-$  under acidic and oxidizing conditions where Tc-99 retention is problematic. Thus, the use of quaternary-amine modified mesoporous zeolite as an amendment and/or permeable reactive barrier would be a robust strategy for Tc-99 remediation. Moreover, further modification of the evaluated zeolite materials with silver is envisioned to promote effective retention of both Tc-99 and I-129 and this study was slated for fiscal year 2019.*

### FY2018 Objectives

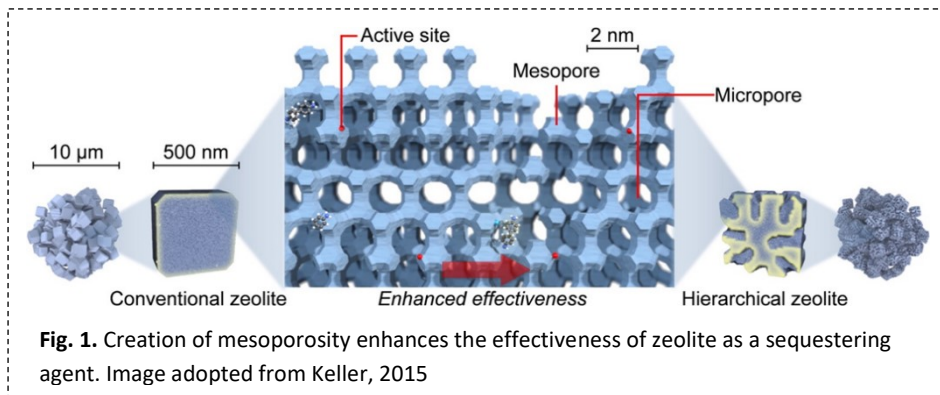
The overarching objective of the research was to develop an effective remediation technology for Tc-99 sequestration from contaminated aqueous media through syntheses, fine-tuning mineral structures and composition, and testing of the several sequestering agents. Specifically, the objectives of this projects were as follows:

- Develop quaternary ammonium-functionalized zeolite sorbents (organo-zeolite) for enhanced removal of  $\text{TcO}_4^-$  from contaminated aqueous media.
- Compare sequestration of  $\text{TcO}_4^-$  by unmodified and modified zeolite.
- Demonstrate sorbents' performance characteristics and operational conditions for beneficial use in field conditions.
- Design modified sorbents for iodine sequestration during FY2019.

### Introduction

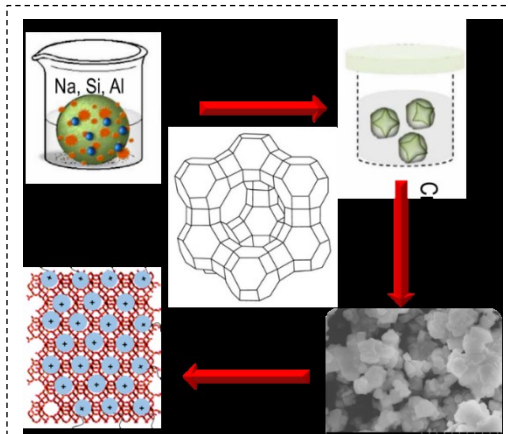
**Significance and Motivation:** As contaminants of high priority to DOE-EM mission, technetium-99 and iodine-99 are key risk drivers at several DOE sites [1]. Both are anionic radionuclides that pose potential long-term risks to public health and the environment due mainly to the burgeoning inventory, relatively long half-life, and high to extreme toxicity. Moreover, the predominant chemical speciation form of these

**Immobilization Technology:** Among proposed remedial technologies are structural immobilization and stabilization of Tc-99 and I-129 in low-temperature waste forms, such as crystalline frameworks, carbon and clay/resin-based sorbents. The application of these remediation strategies has been largely hindered by the much higher concentrations, typically by several orders of magnitude, of competing anions commonly found in groundwater and nuclear waste streams. Because there are heightened needs for cost-effective technologies for Tc-99 and I-129 remediation, a proposed alternative approach is the use of quaternary ammonium-modified silver feldspathoids, specifically zeolite of the faujasite type to sequester both anions for long-term storage.



Zeolite are porous aluminosilicate minerals comprising of alternating  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral units covalently joined by bridging O-atoms to form three-dimensional flexible frameworks with well-defined pores/cavities (Fig. 1) [6-8]. Due to the selective functionality of the 3-dimensional porous zeolite structure, removal of both Tc-99 and I-129 anions is feasible even in the presence of higher concentrations of competing ions (e.g.,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ ). Silver and quaternary ammonium-modified zeolites have been widely studied as potential hosts for I-129 and Tc-99; however, there are few published literatures on bifunctional zeolite with silver and organic group, where both ligands are distributed on and within the zeolite structure for effective immobilization of Tc-99 and I-129.

Hydrophilic zeolites with Si/Al <10 (SAFE & SOTEF samples) were hydrothermally synthesized according to published literature while hydrophobic zeolite with Si/Al >10 (SAV-15) was acquired from Zeolyst International, Malvern PA. Commercial and synthesized zeolites were modified with quaternary ammonium, specifically hexadecyltrimethylammonium bromide ( $C_{19}H_{42}NBr$ ), to enhance affinity for  $TcO_4^-$  (Figure 2). Benchtop batch studies were performed in SRS groundwater simulant and Tc-99 adsorbed to the zeolite sorbents were characterized by physicochemical techniques, such as powder X-ray diffraction, Brunauer-Emmett-Teller analysis, particle/zeta potential measurements, liquid scintillation counting, and ICP-MS. Factors such as effect of pH and counterions, and contact time were optimized for practical application of the sorbents. Rate equations and adsorption isotherms were employed to elucidate the adsorption mechanism.



**Figure 2.** A generalized synthesis and modification procedure for zeolite.

Evaluation of the performance characteristics of the zeolites by batch adsorption tests were performed by adding 100 mg of unmodified and modified sorbents to 100 mL of SRS groundwater simulant. Then  $\text{TcO}_4^-/\text{ReO}_4^-$  activity/concentration, pH and reaction time were introduced into the solid-liquid mixtures as variables. The batch mixtures were spiked either with a known Tc-99 activity or rhenium (a Tc-99 surrogate) concentration and the pH and reaction time were varied from 3.5 – 10 and 5 - 1440 minutes, respectively. Upon completion of the reaction time the mixtures were passed through 0.2- $\mu\text{m}$  polyestersulphone/polypropylene filters and the Tc-99 activity and/or rhenium concentration in each supernatant was either determined by LSC and/or ICP-MS, respectively. Sorption coefficient ( $K_d$ ), kinetic and maximum adsorptive capacity values were then calculated from the supernatant concentrations using rate equations and adsorption isotherms.

## Results/Discussion

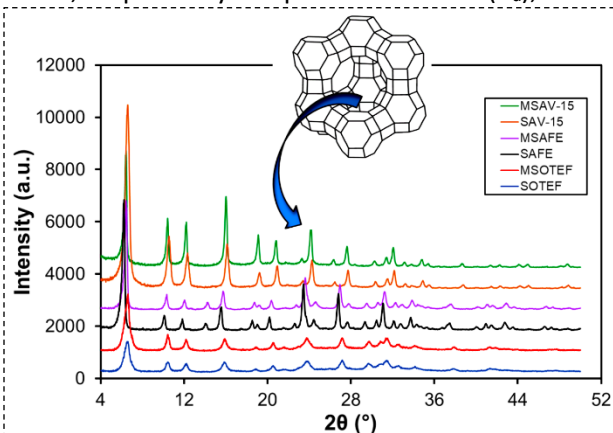
### Morphology:

The *X-ray diffraction* patterns of the unmodified and modified samples are displayed in Figure 3. The XRD indicate that the samples were predominantly zeolite of the faujasite type framework (zeolite Y). However, the SAFE and MSAFE samples contained approximately less than 10% inclusions of another zeolite phase(s). Upon modification the zeolite characteristic peaks for the MSAV-15 sample compared to the SAV-15 shifted to a lower  $2^\circ\theta$  value indicative of pore/cavity enlargement likely due to ingress of the organic ligand into the zeolite framework.

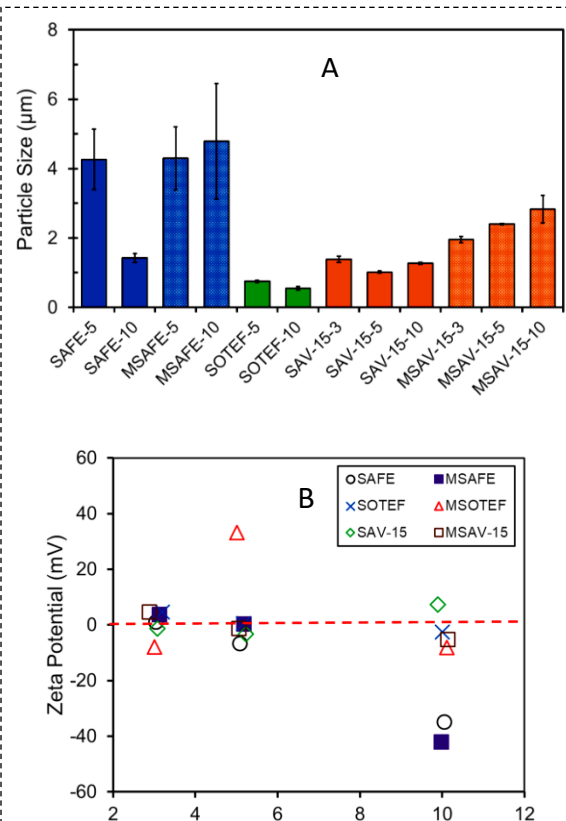
The *particle size* characterization of the unmodified and modified samples is displayed in Figure 4A. The average particle size of the zeolite materials ranged from 0.5 – 4  $\mu\text{m}$  with the SOTEF samples having the smallest particle size. The **zeta potential** measurements, indicative of point of net zero charge (PZC) on the structure is shown in Figure 4B. In general, all zeolite samples exhibited PZC at approximately pH of 5. At  $\text{pH} \leq 5$  the structure is expected to have a net positive charge whereas at  $\text{pH} \geq 5$  net negative charge.

### Batch Sorption:

*Adsorption isotherms* are important in understanding interaction of Tc-99 with the zeolites and optimizing the use of zeolites as a sorbent. Adsorption experiments at ambient pH indicate HDTMA-modified zeolites bound significant higher concentrations of Tc-



**Figure 3.** X-ray diffraction patterns of unmodified and modified zeolite Y.



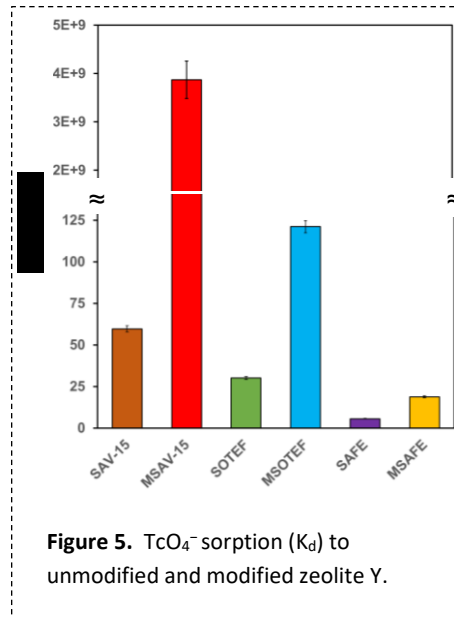
**Figure 4.** Particle size distribution (A) and PZC (B) of unmodified and modified zeolite Y.

99 compared to the unmodified zeolites. The distribution coefficient,  $K_d$ , which is the solids-to-liquid concentration ratio of the radionuclide (in units of mL/g) is used to describe the degree of sorption. High  $K_d$  values are indicative of greater extent of sorption. As shown in Figure 5, the  $K_d$  value after 24 hours of contact time at ambient pH of 5 – 8.5 for the zeolite samples were as high as approximately 5 to  $>10^9$  mL/g. For purposes of comparison, typical  $K_d$  values for SRS and Hanford soils are between 0.1 and 2 mL/g [9]. The modification of the SAV-15 zeolite with HDTMA significantly increased Tc-99 sorption to the MSAV-15 material by a factor of approximately  $10^7$ . It is worth noting that the high  $K_d$  value was calculated based on measurements near to the method detection limit. The  $K_d$  increases for MSAFE and MSOTEF samples were more moderate, approximately a factor of two and three, respectively.

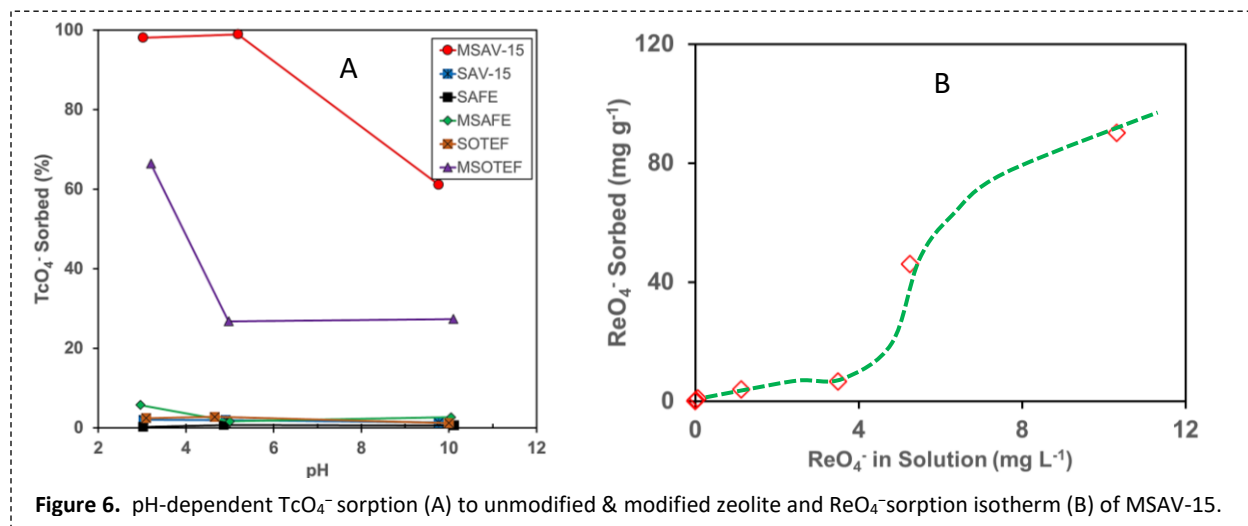
**Adsorption kinetics** of Tc-99 on unmodified and modified zeolites exhibited initial steep increase in the adsorbed Tc-99 concentration with about 90–100% of the equilibrium concentration adsorbed within 60 minutes (data not shown). Tc-99 was adsorbed quickly by MSAV-15 zeolite during the first 30 minutes of solid–liquid contact time, rapidly progressing towards equilibrium within 5 to 10 minutes. Overall Tc-99 adsorbed best to MSAV-15 zeolite.

Technetium-99 sorption to zeolite materials as a function of pH is presented in Fig. 6A. The batch experiments were conducted in a 1:1000 solid-to-SRS groundwater simulant ratio. Overall modification enhanced Tc-99 sorption to the modified sorbent materials which generally decreased with increasing pH values. Sorption of Tc-99 to MSOTEF and MSAV-15 materials varied from 27 – 66% and 61–99%, respectively. Among evaluated zeolites the MSAV-15 performed best at pH values of 3 – 5.

The maximum sorption of rhenium (Tc-99 surrogate) to MSAV-15 with increasing rhenium concentration is presented in Figure 6B.



**Figure 5.**  $\text{TcO}_4^-$  sorption ( $K_d$ ) to unmodified and modified zeolite Y.



**Figure 6.** pH-dependent  $\text{TcO}_4^-$  sorption (A) to unmodified & modified zeolite and  $\text{ReO}_4^-$  sorption isotherm (B) of MSAV-15.

The Type II adsorption isotherms (BET model identified as the Green Line in Fig. 6b) satisfactorily describe this observed adsorption on MSAV-15 zeolites. The adsorption is considered a multilayer physical adsorption of Tc-99 in the mesopores and macropores of the zeolite sorbent consistent with observed X-

ray data. It is worth noting that that a plateau of Tc-99 sorption had not been reached and it is highly likely that higher loadings of Tc-99 on the MSAV-15 sorbent could be achieved.

## FY2018 Accomplishments

- Structural and chemical modification of zeolites significantly enhanced Tc-99 binding by several orders of magnitude, resulting in  $K_d$  values as high as  $4 \times 10^9$  mL/g.
- Fast kinetic properties and high selectivity for Tc-99 were measured in the presence of competing anions.
- There was a steep increase in  $\text{ReO}_4^-$  (Tc-99 surrogate) uptake with increasing perrhenate concentration. Maximum loading capacity was over 100 mg/g and anticipated to be significantly higher with higher loading of the MSAV-15 sorbent with  $\text{ReO}_4^-$ .
- Follow-up work will focus on fine-tuning these sorbents for simultaneous capture of Tc-99 and I-129.

## Future Directions

- Seed data from this study will be leveraged to solicit external funding from the following agencies: DOE Environmental Management (EM-12 Soil and Groundwater Remediation; EM-20 Tank Waste and Nuclear Materials disposition), DOE Office of Science (SC-22.2 Materials Sciences), and DOE Office of Nuclear Energy (NE-University Programs (NEUP)).
- Additionally, study results will find application for: (1) DOE-EM Technology Development's initiative on technetium, (2) DOE-SC Basic Energy Sciences annual call in Geosciences, and (3) DOE-SC Basic Energy Sciences annual call in Separation Science.

## FY 2018 Publications/Presentations

1. Dickson J. O., Li D., Kaplan D. I., Seaman J. C., Conroy N. A., and Powell B. A., (2018). Structural Organo-Modified Feldspathoid for Selective Removal of Anionic Radionuclides. The 28<sup>th</sup> Goldschmidt conference, August 2018, Boston, Massachusetts, USA.
2. Dickson J. O., Li D., Kaplan D. I., Seaman J. C., Conroy N. A., and Powell B. A., (2018). Structural Organo-Modified Feldspathoid For Selective Removal of Technetium-99 and Iodine-129. The 19<sup>th</sup> International Conference on Heavy Metals in the Environment (ICHMET). July 2018, Athens, Georgia, USA.

## References

1. Kaplan D.I., et al., Radioiodine biogeochemistry and prevalence in groundwater Critical Reviews of Environmental Science and Technology, 2014. 44(20): p. 2287-2337
2. Jaisi D. P., Dong H., Plymale A. E. Fredrickson J. K., Zachara J. M., Heald S., and Liu C., 2009. Reduction and Long-Term Immobilization of Technetium by Fe(II) associated with Clay Mineral Nontronite, Chemical Geology, 264 (2009), pp. 127-138, doi:10.1016/j.chemgeo.2009.02.018.
3. Marshall T. A., Morris K., Law G. T. W., Mosselmans J. F., Bots P., Parry S. A., and Shaw S., 2014. Incorporation and Retention of 99-Tc(IV) in Magnetite under High pH Conditions, Environmental Science and Technology, 48 (2014), pp. 11853-11862, dx.doi.org/10.1021/es503438e.

4. Hou X., Hansen V., Aldahan A., Possnert G., Lind O. C., and Lujaniene G., 2009. A Review on Speciation of Iodine-129 in the Environmental and Biological Samples, *Analytica Chimica Acta*, 632 (2009), pp. 181-196, doi:10.1016/j.aca.2008.11.013.
5. Zhang S., Fo Y., Creeley D., Roberts K., Xu C., Li H., Schwehr K., Kaplan, D., Yeager, C., and Santschi P, 2014. Temporal Variation of Iodine Concentration and Speciation (127I and 129I) in Wetland Groundwater from the Savannah River Site, USA, *Environmental Science & Technology*, 2014, 48 (19), pp. 11218-11226, doi:10.1021/es502003q.
6. Depmeier W., The sodalite family - A simple but versatile framework structure, in: G. Ferraris, S. Merlino (Eds.) *Micro- and Mesoporous Mineral Phases* 2005, pp. 203-240.
7. Keller T., Arras J., Stefan Wershofen S., and Javier Pérez-Ramírez J., 2015. Design of Hierarchical Zeolite Catalysts for the Manufacture of Polyurethane Intermediates, *ACS catalysis*, 2015, 5, pp. 734–743, doi: 10.1021/cs5017694.
8. Smedt C., Ferrer F., Leus K., and Spanoghe P., 2015. Removal of Pesticides from Aqueous Solutions by Adsorption on Zeolites as Solid Adsorbents, *Adsorption Science & Technology*, 2015, 33, pp. 457-484.
9. Kaplan, Daniel I. *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site*. United States: N. p., 2016. Web. doi:10.2172/1281771.

## Acronyms

Al - Aluminum

DOE – Department of Energy

CO<sub>3</sub><sup>2-</sup> – Carbonate

EM – Environmental Management

HDTMA – Hexadecyltrimethylammonium

ICP-MS – Inductively coupled plasma mass spectroscopy

I<sup>-</sup> – Iodide

IO<sub>3</sub><sup>-</sup> – Iodate

NO<sub>3</sub><sup>-</sup> – Nitrate

PZC – Point of net zero charge

TcO<sub>4</sub><sup>-</sup> – Pertechnetate

ReO<sub>4</sub><sup>-</sup> – Perrhenate

Si – Silica

SRS – Savannah River Site

K<sub>d</sub> – Sorption coefficient

SAVE-15 – Commercial zeolite Y with Si/Al ≈ 80

MSAVE-15 – HDTMA-modified zeolite Y with Si/Al ≈ 80

SOTEF – Organic-template free zeolite Y synthesized according to Tang et al, 2016

MSOTEF – HDTMA-modified organic-template free zeolite Y synthesized according to Tang et al, 2016

SAFE – Zeolite Y synthesized according to Ferdov et al, 2017

MSAFE – HDTMA-modified zeolite Y synthesized according to Ferdov et al, 2017

## Intellectual Property

None

## Total Number of Post-Doctoral Researchers

Dr. Nathan Conroy, Clemson University

*LDRD-2018-00110*

*LDRD Report*

Dr. Yuyu Xie, Clemson University

Dr. Fanny Coutelot, SREL, University of Georgia