Contract No:

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Metal-Organic Framework Glasses as Rad Contaminant Sequesters and Nuclear Waste Forms

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Abstract: *Remediation of Tc remains an unresolved problem at SRS and other DOE sites. The objective of this project was to develop novel metal organic framework (MOF) glasses for radioactive contaminant sequestration and stabilization from aqueous media. During FY20, we synthesized, characterized and evaluated additional cetyltrimethylammonium bromide (CTAB)-functionalized and F^-, Cl^-, I^-, $CF_3SO_3^-$-exchanged MIL-101-Cr samples. MIL-101-Cr-NO_3-CTAB was demonstrated to have high ReO_4^- removal capacity (139 mg/g sorbent) from artificial groundwater (AGW). Re chemical speciation and binding mechanism on MIL-101-CTAB were also studied by synchrotron X-ray absorption spectroscopy. ReO_4^- was demonstrated as being in the pore structure with slightly larger Re-O bond distances than those in $NaReO_4$ and binding with the positively charged sites of CTAB. In addition, a new Ni-TIPA MOF was demonstrated to be very stable, selective and effective for TcO_4^- removal from the SRS tank waste stream (~90% removal). The Ni-TIPA MOF sample containing ReO_4^- was prepared and shipped/planned for vitrification studies by a high-pressure technique. This research may provide a highly applicable platform for solving critical DOE and industrial problems related to nuclear environmental stewardship and nuclear power production.*

FY2020 Objectives

(1) Complete additional experiments and data analysis for CTAB-functionalized, and F^-, Cl^-, I^-, $CF_3SO_3^-$-exchanged MIL-101-Cr.
(2) Complete and submit two manuscripts.
(3) Write a user proposal to Advanced Photo Source (APS).
(4) Conduct experiments on vitrifying the crystalline Ni-TIPA containing ReO_4^-.

Introduction

^{99}Tc is a major long-lived fission product created during nuclear power generation. Over the years, Tc has been inadvertently introduced into the environment from leaks at waste storage facilities. ^{99}Tc currently is one of the key risk drivers at the Savannah River Site (SRS) and other DOE environmental management sites (most notably the Hanford Site, Paducah Gaseous Diffusion Plant, and Oak Ridge National Laboratory). The most common chemical form of Tc in liquid nuclear wastes and in the environment is anionic pertechnetate (TcO_4^-). TcO_4^- displays limited adsorption onto common sediment minerals and is highly mobile making it difficult to capture or to be immobilized [1]. As the stockpile of ^{99}Tc-bearing nuclear waste continues to increase rapidly, novel sequestration technologies are needed to reduce its potential contamination of the environmental and living organisms.

With current technologies, quaternary amine-based resins have been used to remove aqueous Tc [2]. However, these resins are expensive and have only modest TcO_4^- loading capacities from the raffinate waste streams. Chemical reductants (e.g., Fe_3S_4, soluble or structural Fe(II)) [3] and some bacteria [4] can reduce Tc(VII) to the sparingly soluble Tc(IV). However, the resulting $Tc(IV)O_2{\cdot}1.6H_2O$ has a solubility of 1.5×10^{-8} M in groundwater [5], which greatly exceeds the

EPA's maximum contaminant level of 5×10^{-10} M, and is readily re-oxidized and re-mobilized under most environmental conditions [6]. Tc reduction to form sulfides (e.g., Tc_2S_7) [7] or embedding into other sulfide phases [8] or iron oxide waste forms [9] have also been investigated. However, these methods are not practical for many applications. There are currently no demonstrated technologies that are highly efficient and cost-effective for separation of Tc-containing nuclear waste streams and remediation of aqueous Tc in the contaminated sites.

The overarching objective of this project was to develop novel metal organic framework (MOF) glasses as radioactive contaminant sequesters and nuclear waste forms. First, we need to develop novel MOF materials of high stability, high capacity and high selectivity for TcO_4^-/ReO_4- from groundwater and high pH tank waste streams. Now we have developed two new MOF materials that met these performance criteria. Second, we want to develop high pressure induced technology for vitrification of these MOF materials containing ReO_4^-, which will potentially lead to the next generation of glass waste forms for nuclear waste stabilization.

Approach

The chemical formula of MIL-101-Cr (MIL, Matérial Institut Lavoisier) is $Cr_3NO_3(H_2O)_2O(BDC)_3\cdot nH_2O$ (n ~ 25; BDC = 1,4-benzenedicarboxylate; NO_3^- can be substituted by F^-, Cl^-, I^-, or $CF_3SO_3^-$). The chromium terephthalate metal–organic framework or MIL-101-Cr comprises of trimeric chromium(III) octahedral clusters interconnected by 1,4-benzenedicarboxylates, resulting in a highly porous 3-dimentional structure [10]. The crystal structure of MIL-101-Cr-NO_3^- is shown in Fig. 1. This makes it an ideal MOF material for contaminant treatment studies. To develop modified MIL-101-Cr with higher capacity and selectivity for TcO_4^- removal, the F-, Cl-, I-, and CF_3SO_3-MIL-101-Cr MOF samples were synthesized, and cetyltrimethylammonium bromide ($(C_{16}H_{33})N(CH_3)_3Br$; CTAB)-functionalized MIL-101-Cr-NO_3 samples were also prepared, which were expected to have higher Tc removal capacity and improved stability. Powder X-ray diffraction (XRD), BET surface area measurement, thermogravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDS), and Fourier transform infrared (FTIR) spectroscopy were used for MOF characterization before and after ReO_4^- adsorption in which ReO_4^- was used as a non-radioactive surrogate for TcO_4^-, while synchrotron radiation X-ray absorption spectroscopy was applied to studying Re chemical speciation and molecular binding mechanisms after the sequestration by MOFs.

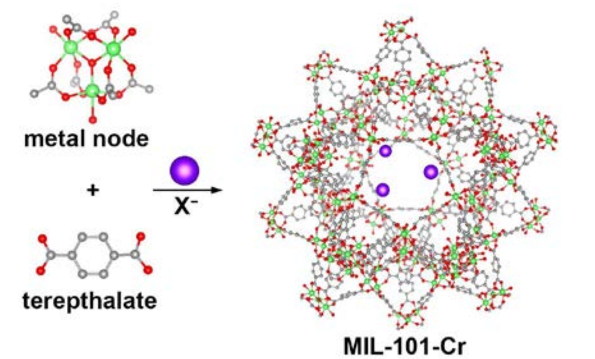

Fig. 1. The structure of MIL-101-Cr. Atom colors: Cr = green, O = red, C = gray, blue = exchangeable anions (i.e., NO_3^-, F^-, Cl^-, I^-, and $CF_3SO_3^-$).

Batch ReO_4^- adsorption experiments were conducted from AGW using the modified MIL-101-Cr MOFs. The mass of Re sorbed (q_e, mg/g) was calculated using equation 1:

$$q_e = \frac{(C_0 - C_e)\times V}{M} \quad (1)$$

where C_0 (mg/L) is the initial concentration in the control samples, C_e (mg/L) is the final concentration remaining in the solution, V is the volume of the solution (mL), and M is the mass of the sorbent (g). Adsorption isotherms of ReO_4^- onto MIL-101-Cr-NO_3 with and without CTAB functionalization were obtained at an equilibration pH ~4.0 and ~9.0. The Langmuir isotherm model (equation 2) was used to describe the data for ReO_4^- adsorption on MIL-101-Cr-NO_3-CTAB:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L \times q_{\max}} \qquad (2)$$

where q_e is the mass of ReO_4^- sorbed onto the sorbent at equilibrium, q_{max} is the saturation sorption capacity, C_e is the Re concentration in solution at equilibrium, and K_L is the Langmuir constant that is directly related to the binding site affinity. In addition, factors such as contact time (*e.g.*, 0.5–24 h), solution pH (*e.g.*, 0–10), effect of competing anions (e.g., NO_3^-, CO_3^{2-}, SO_4^{2-}, and Cl^-), and desorption and resorption behavior were evaluated for ReO_4^- removal from groundwater by the MIL-101-Cr-NO_3 without and with CTAB functionalization.

We also investigated a new Ni-TIPA MOF for Tc removal from the SRS tank waste stream, which has been demonstrated to have high stability, capacity and selectivity for TcO_4^- separation from the high pH SRS tank wastes. As a result, we further prepared and shipped a Ni-TIPA sample containing ReO_4^- for high pressure induced vitrification experiments and submitted a user proposal to the Advanced Photo Source (APS) in order to investigate vitrification behavior and transformation pressure of this crystalline MOF material and the structural states of Re in the new glass form. The ultimate goal was to develop the next generation of MOF glasses as nuclear waste forms.

Results/Discussion

1. ReO_4^- removal of MIL-101-Cr MOFs with different anions

For MIL-101-Cr with different anions, with MIL-101-Cr-NO_3 as a baseline, MIL-101-Cr-F was slightly less effective for ReO_4^- removal; while Cl-, I-, and CF_3SO_3-exchanged MIL-101-Cr materials had improved capacity for ReO_4^- sequestration. The ranking of anion-exchanged MIL-101-Cr for ReO_4^- removal was $F^- < NO_3^- < Cl^- \approx I^- \approx CF_3SO_3^-$, which was essentially in agreement with the so-called Hofmeister order for predicting anion partitioning in liquid/liquid systems [11]. These results can be explained in terms of ionic radius and standard Gibbs energies of hydration ($\Delta G_h°$) [11, 12]. I^- and $CF_3SO_3^-$ have a similar ionic radius and $\Delta G_h°$ to those of ReO_4^-/TcO_4^-, which is favorable for ReO_4^- exchange and improves the ReO_4^- removal performance. On the other hand, the ionic radius and $\Delta G_h°$ of F^- are much smaller than those of ReO_4^-/TcO_4^-, which is not favorable for ReO_4^- exchange into MIL-101-Cr-F.

2. ReO_4^- removal and characterization of CTAB-functionalized MIL-101-Cr-NO_3

ReO_4^- Removal Isotherms. The obtained saturation capacity of MIL-101-Cr-NO_3-CTAB for ReO_4^- removal from AGW was 139 mg ReO_4^-/g sorbent ($R^2 = 0.948$) at the equilibrium pH value of ~4.0 and 39 mg ReO_4^-/g sorbent ($R^2 = 0.942$) at the equilibrium pH value of ~9.0 (Fig. 2). In addition, we attempted to fit Re isotherm data for MIL-101-Cr-NO_3 (without CTAB functionalization) at pH values of ~4.0 and ~9.0 to both the Langmuir and Freundlich models, but neither model produces satisfactory results with R^2 values of < 0.90. However, the capacity of MIL-101-Cr-NO_3 for ReO_4^- removal from AGW was estimated to be ~50 mg ReO_4^-/g sorbent at pH 4.0 and ~14 mg ReO_4^-/g sorbent at pH 9.0 (Fig. 2). Therefore, CTAB functionalization on MIL-101-Cr-NO_3 significantly improved its capacity for ReO_4^- removal at pH 4.0 and 9.0 AGW.

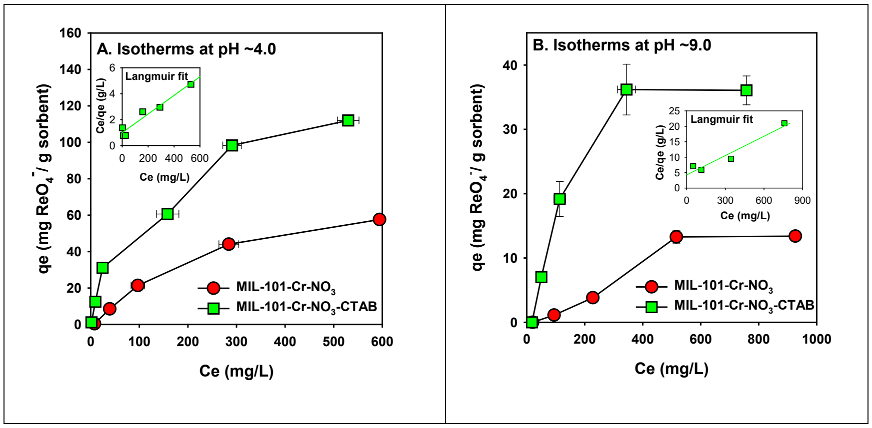

Fig. 2. Adsorption isotherms of ReO_4^- on MIL-101-Cr-NO_3 (red) and MIL-101-Cr-NO_3-CTAB (green) in artificial groundwater at pH ~4.0 (A) and ~9.0 (B) for 6 d. For MIL-101-Cr-NO_3-CTAB, Langmuir fits are shown in the insets, but the isotherm curves for MIL-101-Cr-NO_3 were not well fit by the Langmuir model.

Effect of Contact Time. The effect of contact time of ReO_4^- with these two MOF samples was further investigated to evaluate the anion exchange rate and equilibrium time. As shown in Fig. 3A, under specified experimental conditions, ~90% of ReO_4^- in AGW was removed by MIL-101-Cr-NO_3 within 30 min, while nearly 100% of ReO_4^- in AGW was removed by CTAB functionalized MIL-101-Cr-NO_3 within 10 min. These results indicate that CTAB functionalized MIL-101-Cr-NO_3 improves sorption kinetics and provides higher capacity for ReO_4^- removal compared to MIL-101-Cr-NO_3.

Effect of Solution pH. As shown in Fig. 3B, the ReO_4^- removal percentage diminished to nearly zero for MIL-101-Cr-NO_3 and to ~15% for MIL-101-Cr-NO_3-CTAB at pH ~10.0. These results may indicate that the MIL-101-Cr materials have limited applications to ReO_4^-/TcO_4^- sequestration from alkaline media such as legacy liquid nuclear waste. For both MIL-101-Cr-NO_3 samples with and without CTAB functionalization, the ReO_4^- removal capacity also diminished with a decreasing pH and its removal rate was reduced to ~13% in a 3 M nitric acid solution. These results indicate that the MIL-101-Cr-NO_3 samples become less effective for ReO_4^-/TcO_4^- removal in strongly acidic aqueous media. However, it could prove effective for ReO_4^-/TcO_4^- removal from weekly acidic to neutral aqueous media (pH 3-8) like contaminated groundwater.

Effect of Competing Anions. For MIL-101-Cr-NO_3, the presence of 5 mM NO_3^-, CO_3^{2-}, or Cl^- reduced ReO_4^- removal capacity by 32%, 34%, and 23%, respectively, while the presence of 5 mM SO_4^{2-} reduced ReO_4^- removal capacity by 89% (Fig. 3C). These results indicated that MIL-101-Cr-NO_3 had moderate affinity and selectivity for ReO_4^- over NO_3^-, CO_3^{2-}, or Cl^-, but SO_4^{2-} significantly reduced the affinity and selectivity of MIL-101-Cr-NO_3 for ReO_4^- removal. On the other hand, for MIL-101-Cr-NO_3-CTAB, the presence of 5 mM NO_3^-, CO_3^{2-}, and Cl^- reduced ReO_4^- removal capacity by 7%, 5%, and 2%, respectively, while the presence of 5 mM SO_4^{2-} reduced ReO_4^- removal capacity by only 18%. These results indicate that with CTAB functionalization, MIL-101-Cr-NO_3 substantially improves sorption affinity and selectivity for ReO_4^- over all tested competing anions.

ReO_4^- Desorption and Resorption Studies. ReO_4^- desorption and resorption behavior of MIL-101-Cr-NO_3 with and without CTAB functionalization was investigated by using 1 M KI solution as an extracting agent. Figure 5D shows ReO_4^- removal percentages of MIL-101-Cr-NO_3 and MIL-101-Cr-NO_3-CTAB during sorption/desorption cycles. For both samples, initially 92–97% of ReO_4^- was removed by the sorbent materials, then 60–62% of the anion was eluted during the first desorption step; and then ~98% of ReO_4^- was sorbed by these two MOFs during the subsequent two resorption steps. These results indicate that ReO_4^- was not completely eluted by 1 M KI solution, and after the KI desorption step, the materials remained effective for ReO_4^- removal until reaching its saturation capacity.

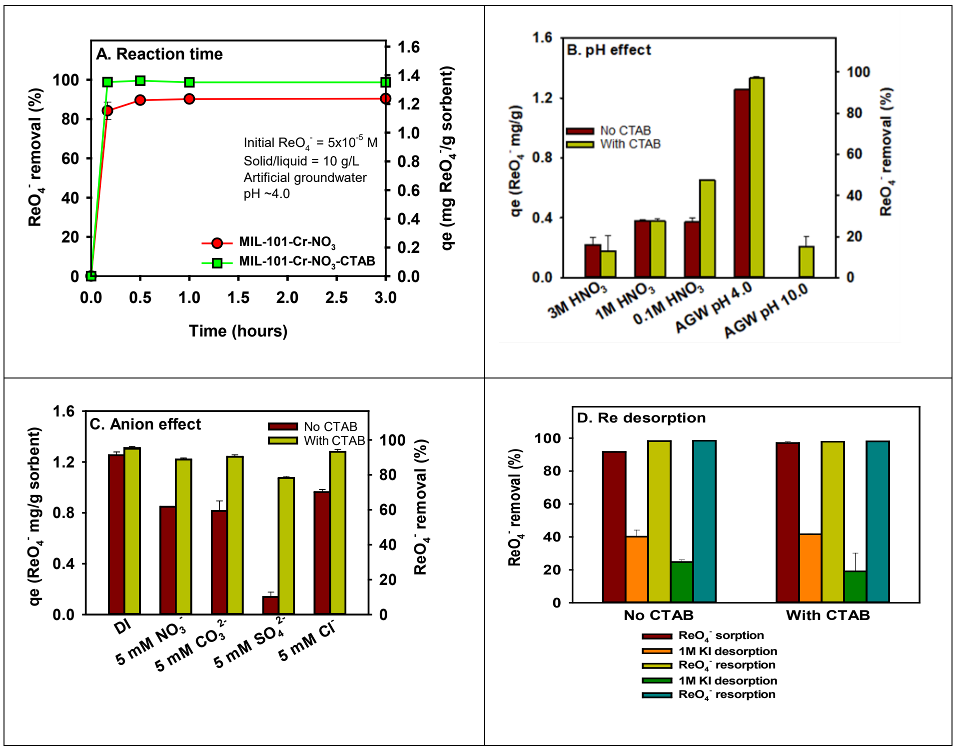

Fig. 3. ReO_4^- adsorption on MIL-101-Cr-NO_3-CTAB in AGW versus (A) reaction time, (B) pH value, (C) co-existing anions, and (D) ReO_4^- desorption/resorption cycles. The experimental conditions were: $[ReO_4^-] = 5 \times 10^{-5}$ M, solid/liquid = 10 g/L, reaction time = 1 d, pH = ~4.0.

Re L_3-edge XANES and EXAFS. The Re L_3-edge X-ray absorption near edge structure (XANES) spectra of MIL-101-Cr-NO_3-CTAB after exposure to 5×10^{-4} M ReO_4^- in pH 4.1 and 8.5 AGW are shown in Fig. 4A, in comparison with the spectrum of sodium perrhenate ($NaReO_4$). The L_3-edge absorption peaks of this MOF sample exposed to ReO_4^- were at 10535.1 eV, with another peak at about 10546.4 eV, which clearly indicated that the sequestered Re species by MIL-101-Cr-NO_3-CTAB in AGW at an equilibrium pH of 4.1-8.5 was ReO_4^-.

Re L_3-edge extended X-ray absorption fine structure (EXAFS) spectra in Fourier transform plots in R magnitude of these two samples are shown in Fig. 4B, together with the corresponding spectrum of $NaReO_4$. The experimental data are shown as dotted lines, and EXAFS fits are shown as colored lines. The Re L_3-edge EXAFS data of the MIL-101-Cr-NO_3-CTAB samples exposed to ReO_4^- were fitted with tetrahedral Re-O paths at a Re-O distance of 1.730 ± 0.004 Å with a coordination number of 3.8 ± 0.3. Thus, the Re L_3-edge EXAFS spectra of MIL-101-Cr-NO_3-

CTAB exposed to ReO_4^- in both pH 4.1 and 8.5 AGW confirmed that the Re species associated with the sorbents was ReO_4^-.

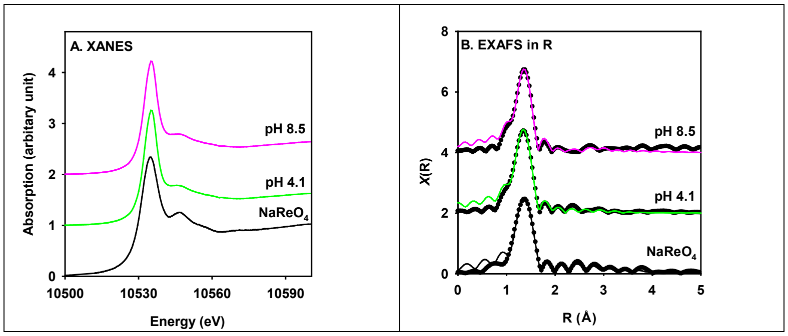

Fig. 4. Re L_3-edge X-ray absorption spectra of MIL-101-Cr-NO_3-CTAB after exposure to 5×10^{-4} M ReO_4^- in AGW at pH 4.1 (green) and 8.5 (pink), in comparison with the spectra of model compound $NaReO_4$ (black).

3. Ni-TIPA MOF for TcO_4^- removal from the SRS tank waste

A Ni-TIPA MOF was acquired from collaborators at Soochow University. The crystal structure of Ni-TIPA is shown in Fig. 5A and 5B. It has a large pore size of 10.43×16.11 Å. Ni-TIPA was demonstrated to have high stability in aqueous media across a broad pH range, up to a pH value of 14, as well as high capacity and selectivity toward ReO_4^- removal from aqueous media.

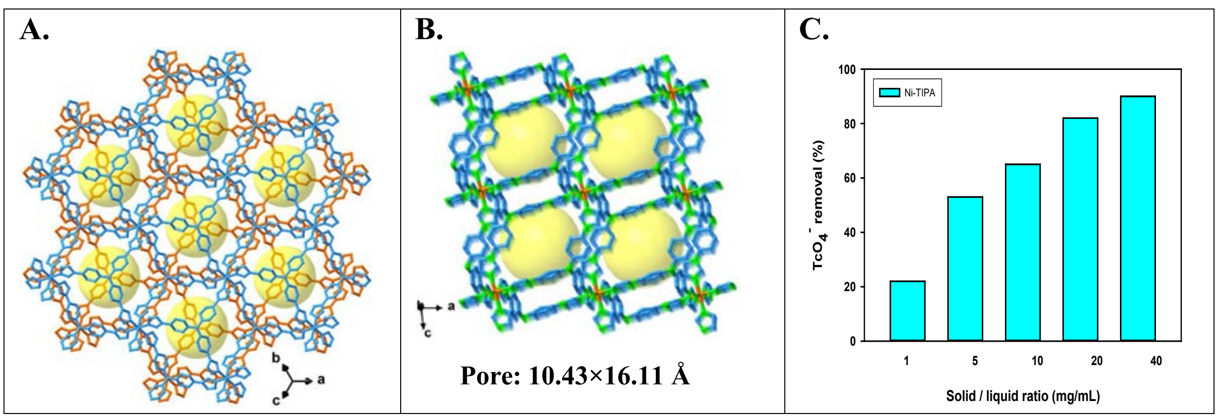

Figure 5. Crystal structure (A and B) of Ni-TIPA MOF and its performance for TcO_4^- removal from the SRS tank waste stream (C).

A series of batch contact experiments to test this Ni-TIPA MOF were performed utilizing a sample of actual SRS tank waste.[13] The batch contact test results are shown Fig. 5C. The percent removal of ^{99}Tc increased as the phase ratio increased. At the highest phase ratio tested, 90% of the ^{99}Tc was removed from the SRS tank waste solution in 3 hours, in good agreement with experimental results performed using the simulated SRS tank waste. Pressure-induced vitrification technology was attempted to be developed for this Ni-TIPA MOF with loaded ReO_4^-. The MOF glasses could be used as potential nuclear waste forms for Tc stabilization. However, these experiments were started but not completed yet due to Covid-19 lockdown.

FY2020 Accomplishments

■ Completed additional batch experiments on CTAB-functionalized MIL-101-Cr MOFs for ReO_4^- removal from AGW, including adsorption capacity, kinetics, effects of competing anions.

■ Completed additional data analysis on Re chemical speciation and molecular interaction with MIL-101-Cr through synchrotron X-ray absorption spectroscopy.
■ Completed and submitted two manuscripts to Journal of Environmental Radioactivity and Nature Communication. These manuscripts have been accepted for publication.
■ Prepared and shipped a sample for high pressure induced vitrification of Ni-TIPA MOF containing ReO_4^-. Completed and submitted a user proposal to APS for investigation of MOF vitrification behavior with pressure and Re structure in the MOF glass.

Future Directions

■ Continue developing new MOFs for higher TcO_4^- removal capacity and improved stability and selectivity, especially under alkaline conditions.
■ Develop methods for vitrifying the MOFs as nuclear waste forms so that the entrapped contaminants are stabilized without leaching out.
■ Prepare proposals to DOE EM Soil & Groundwater Remediation Program, International Program, and DOE Nuclear Energy program.

FY 2020 Peer-reviewed/Non-peer reviewed Publications

Dien Li, Natalia B. Shustova, Corey R. Martin, Kathryn Taylor-Pashow, John C. Seaman, Daniel I. Kaplan, Jake W. Amoroso, Roman Chernikov, Anion-exchanged and quaternary ammonium functionalized MIL-101-Cr metal-organic framework (MOF) for ReO_4^-/TcO_4^- sequestration from groundwater, Journal of Environmental Radioactivity, **2020**, 222, 106372.

Nannan Shen, Zaixing Yang, Shengtang Liu, Xing Dai, Chengliang Xiao, Kathryn Taylor-Pashow, **Dien Li**, Chuang Yang, Jie Li, Yugang Zhang, Mingxing Zhang, Ruhong Zhou, Zhifang Chai, Shuao Wang, $^{99}TcO_4^-$ Removal from Legacy Defense Nuclear Waste by an Alkaline-Stable 2D Cationic Metal-Organic Framework, Nature Communication, **2020**, In press.

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Acronyms

AGW	Artificial groundwater
BET	Brunauer-Emmett-Teller
CTAB	Cetyl trimethylammonium bromide
DOE	Department of Energy
EDS	Energy dispersive X-ray spectroscopy
EXAFS	Extended X-ray absorption fine structure
FTIR	Fourier transform infrared spectroscopy
MIL	Materials Institute Lavoisier
MOF	Metal organic framework
SRS	Savannah River Site
TGA	Thermogravimetric analysis
TIPA	Tris(4-(1H-imidazol-1-yl)phenyl)amine
XANES	X-ray absorption near-edge structure
XRD	X-ray diffraction

Intellectual Property

N/A

Total Number of Post-Doctoral Researchers

N/A

Total Number of Student Researchers

Corey Martin, University of South Carolina, performed research off-site.

External Collaborators (Universities, etc.)

1. Dr. Natalia Shustova, University of South Carolina
2. Dr. John Seaman, Savannah River Ecology Laboratory, University of Georgia
3. Dr. Shuao Wang, Soochow University, China
4. Dr. Tom Bennett, Cambridge University, UK