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

Project Team: Dien Li (Primary), Natalia Shustova (U of South Carolina), Kathryn Taylor-Pashow, Daniel I. Kaplan, Jake Amoroso, Tom Bennett (U of Cambridge, UK)

Subcontractor: University of South Carolina

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Abstract: *Remediation of Tc remains an unresolved challenge 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. We synthesized, characterized and evaluated ten MOFs of known crystal structure and chemistry for screening MOFs for* TcO_4^- *and* ReO_4^- *sequestration. MIL-101(Cr) was most effective for* TcO_4^- *and* ReO_4^- *sequestration from artificial groundwater at equilibration pH values with the removal capacity of 0.076 mg/g for Tc and 0.197 mg/g for Re. MIL-101(Fe), SLUG-22 and UiO-66-*NO_2 *were moderately effective under similar conditions (*$pH < 8$*). These results established a solid foundation for further development of MIL-101(Cr) and new MOFs to increase* TcO_4^- *removal capacity and improve MOF structural stability in FY19. This research may provide a highly applicable platform for solving critical DOE and industrial problems related to nuclear environmental stewardship and nuclear power production.*

FY2018 Objectives

(1) Synthesize and characterize ten MOFs of known crystal structure and chemistry.
(2) Evaluate the MOFs for TcO_4^- and ReO_4^- removal from artificial groundwater.
(3) Develop methods for vitrifying the crystalline MOFs.

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. During FY18, we synthesized and characterized ten MOFs of known crystal structure and chemistry, evaluated them for TcO_4^- and ReO_4^- sequestration from artificial groundwater, and investigated their thermal properties that would help in developing vitrification technology. Based on the selected types of MOFs, we will develop new MOFs that are expected to have higher capacity, improved selectivity and stability for TcO_4^- and other anionic contaminant sequestration from aqueous media.

Approach

A general two-step approach is adopted in the implementation of this project. First, during FY18, we synthesized, characterized and evaluated MOFs of known crystal structure and chemistry to screen out the types of MOFs that might show high capacity and high stability for TcO_4^- sequestration from groundwater. As this project has been renewed for FY19, we will focus on selected types of MOFs to develop new MOFs through ion exchange, functionalization, or scissor / insert methods. The new MOFs are expected to have higher Tc capacity and improved stability. Powder X-ray diffraction (XRD), BET surface area measurement and thermogravimetric analysis were used for MOF characterization, while synchrotron radiation X-ray absorption spectroscopy will be applied to studying Tc or Re speciation after the sequestration by MOFs.

Results/Discussion

1. Synthesis of MOFs

We set three criteria in the screening of MOFs for FY18: (i) high stability in aqueous media, including high pH solutions similar to nuclear waste streams, (ii) high capability for removing anions like TcO_4^-, I^-, IO_3^-, and organo-I^-, and (iii) potential for economical vitrification. As such, ten MOFs have been selected and prepared at the University of South Carolina (Dr. Natalia Shustova) to determine which types of MOFs are best fitted to these criteria.

1.1. ZIF-8 ($Zn(mIM)_2$; mIM = 2-methylimidazolate, ZIF = Zeolitic Imidazolate Framework)**.** Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (0.239 g, 8.03×10^{-4} mol) and 2-methylimidazole (0.060 g, 7.31×10^{-4} mol) was dissolved in 18 mL DMF in a 40 mL vial. The vial was capped and heated at a rate of 5 °C/min to 140 °C in a programmable oven, held at this temperature for 24 h, then cooled at a rate of 0.4 °C/min to room temperature. The mother liquor was then decanted and replaced with 20 mL of chloroform. Colorless crystals were collected from the upper layer (floating on the chloroform layer) and washed with DMF (10 mL x 3) and dried under high-vacuum for 1 hour [10].

1.2. ZIF-67 ($Co(mIM)_2$; mIM = 2-methylimidazolate)**.** Two separate mixtures of cobalt nitrate hexahydrate ($Co(NO_3)_2) \cdot 6H_2O$) (0.225 g, 7.73×10^{-4} mol) dissolved in 6 mL of deionized H_2O, and 2-methylimidazole (2.75 g, 3.34×10^{-2} mol) dissolved in 40 mL of H_2O were combined in a round-bottom flask equipped with a condenser and heated with stirring at 60 °C for 12 minutes. Stirring was halted after 12 minutes and the solution was left at 60 °C for 20 hours, and then cooled to room temperature. The suspension was then filtered and washed with methanol (10 mL x 3) and dried under high-vacuum for 1 hour [11].

1.3. ZIF-70 (Zn(IM)$_{1.13}$(nIM)$_{0.87}$; IM = imidazolate, nIM = 2-nitroimidazolate)**.** In a 20 mL glass vial, 5 mL from a 2-nitroimidazole stock solution (0.20 M, 1.0×10^{-3} mol) and 5 mL imidazole stock solution (0.20 M, 1.0×10^{-3} mol) were mixed together. Subsequently, 4 mL of a zinc nitrate hexahydrate stock solution (0.20 M, 8.0×10^{-4} mol) was added and stirred. The resulting solution was capped and heated at 110 ºC for 4 days, followed by natural cooling to room temperature. Upon cooling, the resulting yellow-orange crystals were filtered and washed with DMF (3 × 15 mL) [12].

1.4. UiO-66-NO$_2$ ($Zr_6O_4(OH)_4$(BDC-NO$_2$)$_6$; BDC-NO$_2^{2-}$ = 2-nitrobenzene-1,4-dicarboxylate, UiO = University of Oslo)**.** Zirconium chloride ($ZrCl_4$) (0.923 g, 3.96 x 10^{-3} mol) and 2-nitroterephthalic acid (0.845 g, 4.00 x 10^{-3} mol) were placed in a 40 mL vial and then dissolved in 10 mL of DMF, followed by the addition of 0.67 mL of concentrated hydrochloric acid. The vial was capped and heated at a rate of 1 °C/min to 120 °C in a programmable oven, held at this temperature for 16 h, then cooled at a rate of 0.4 °C/min to room temperature. The powder was then filtered, washed with DMF (10 mL x 3) then placed back in a DMF solution [13].

1.5. ZIF-71 (Zn(dcIM)$_2$; dcIM = 4,5-dichloroimidazolate)**.** A solution of zinc acetate dihydrate ($Zn(O_2CCH_3)\cdot 2H_2O$ (0.088 g, 4.0 x 10^{-4} mol) in 15 mL of methanol and a solution of 4,5-dichloroimidazole (0.219 g, 1.6 x 10^{-3} mol) in 15 mL of methanol were combined in a 40 mL vial. The vial was then sealed and let to stand at room temperature for 24 h. The methanol was then removed by pipet and 20 mL of fresh chloroform was added every day for three days. The crystalline powder was then filtered and dried under high-vacuum for 1 hour [14].

1.6. ZIF-82 (Zn(nIM)(cIM); nIM = 2-nitroimidazolate, cIM = 5-cyanoimidazolate)**.** In a 20 mL glass vial, 5 mL of a 2-nitroimidazole stock solution (0.20 M, 1.0×10^{-3} mol) and 5 mL of a 5-cyanoimidazole stock solution (0.20 M, 1.0×10^{-3} mol) were mixed together. Subsequently, 4 mL of a zinc nitrate hexahydrate stock solution (0.20 M, 8.0×10^{-4} mol) was added and stirred. The resulting solution was capped and heated at 100 ºC for 4 days, followed by natural cooling to room temperature. Upon cooling, the resulting yellow-orange crystals were filtered and washed with DMF (3 × 15 mL) [12].

1.7. MIL-101-Cr ($Cr_3F(H_2O)_2O(BDC)_3$; BDC = 1,4-benzenedicarboxylate, MIL = Materials Institute Lavoisier)**.** Chromium(III) nitrate nonahydrate (0.400 g, 1.00×10^{-3} mol) was dissolved in 4.8 mL of deionized water, then placed in a Teflon-lined autoclave. Terepthalic acid (0.164 g, 9.87×10^{-4} mol) was then added followed by the addition of 0.2 mL of HF (5.0 M, 1.0×10^{-3} mol). The autoclave was then sealed and placed in an oven at 220 ºC for 8 hours. Upon cooling, the resulting green solid was centrifuged to collect the precipitate and solvent exchanged with DMF (3 × 10 mL) with centrifugation between each exchange. The product was then heated in DMF (120 ºC, 12 h), filtered, and then boiling ethanol (80 ºC, 12 h) and filtered off [15].

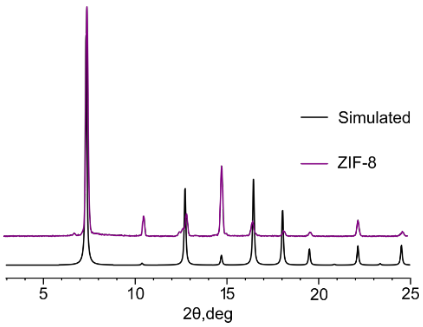
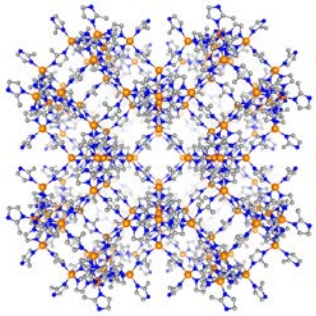
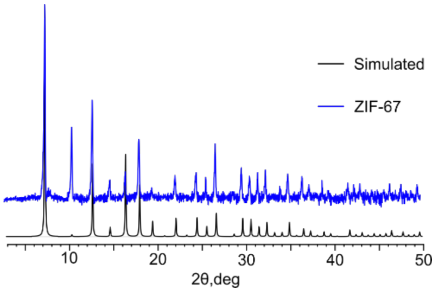
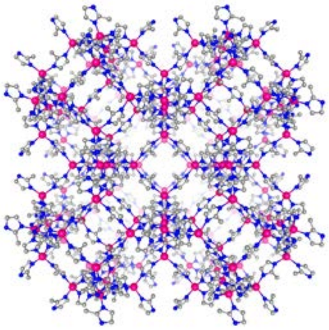
1.8. MIL-101-Fe ($Fe_3Cl(C_3H_7NO)O(BDC)_3$; BDC = 1,4-benzenedicarboxylate)**.** Iron(III) chloride hexahydrate (0.325 g, 1.20×10^{-3} mol) and terepthalic acid (0.103 g, 6.20×10^{-4} mol) were dissolved in 10 mL DMF by sonication, followed by stirring for 20 minutes. The resulting solution was then loaded into a Teflon-lined autoclave. The autoclave was then sealed and placed in an oven at 110 ºC for 24 hours. Upon cooling, the resulting brown solid was centrifuged to collect the precipitate and solvent exchanged with DMF (3 × 10 mL) with centrifugation between each exchange. The product was then heated in DMF (120 ºC, 12 h), filtered, and then boiling ethanol (80 ºC, 12 h) and filtered off [15].

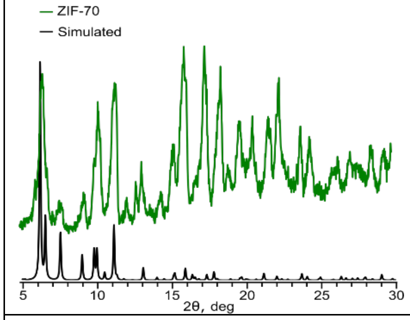
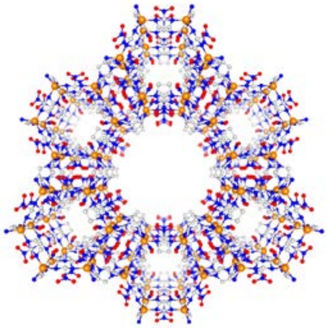
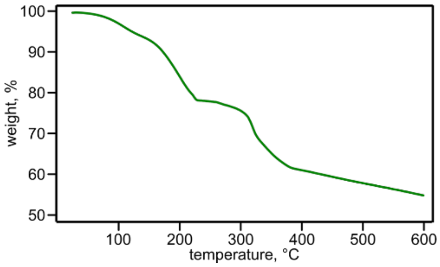
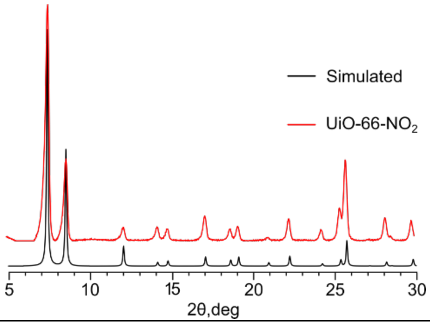
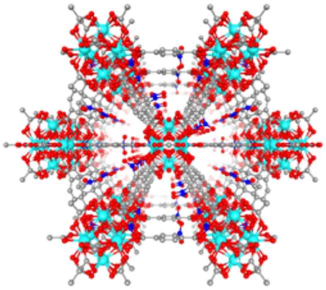
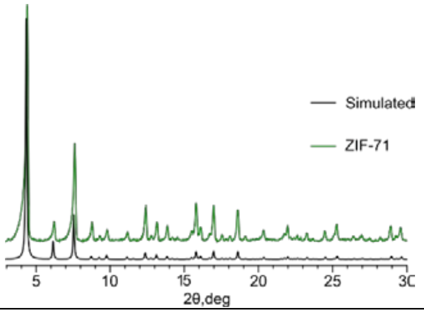
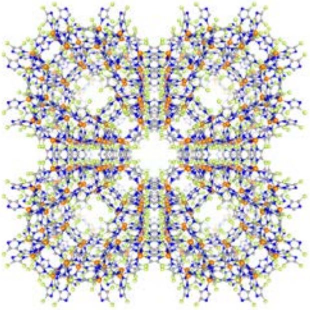
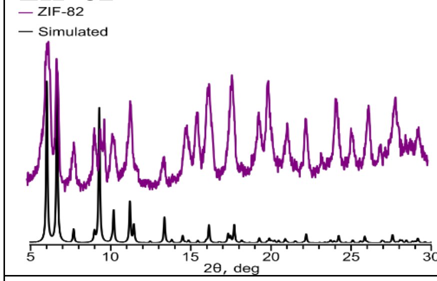
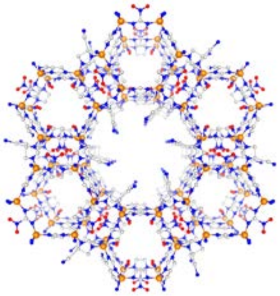
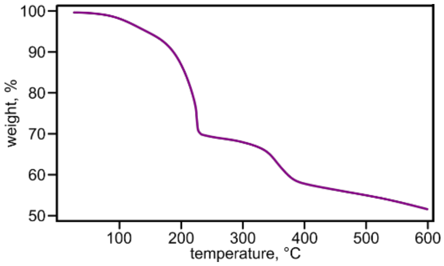
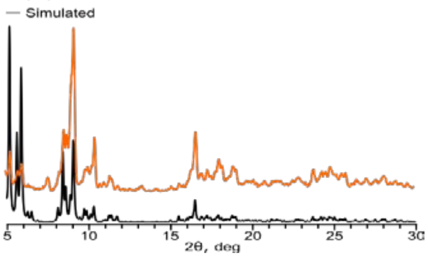
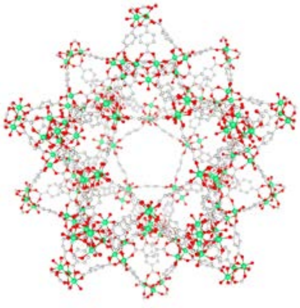
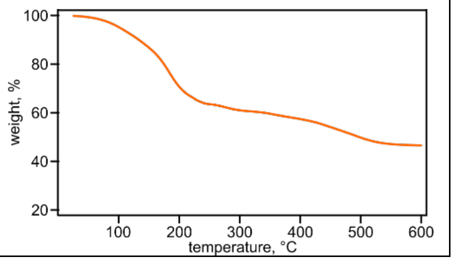
1.9. SLUG-21 ($Ag_2(bpy)_2(O_3SCH_3CH_2SO_3)$; bpy = 4,4-bipyridine, SLUG = University of California, Santa Cruz)**.** Silver nitrate ($AgNO_3$, 0.236 g, 1.40×10^{-3} mol), 1,3-ethanedisulfonic acid dehydrate (0.314 g, 1.39×10^{-3} mol) and 4,4-bipyridine (0.217 g, 1.39×10^{-3} mol) were suspended in 10 mL of deionized water and stirred for 3 minutes. The resulting mixture was loaded into a Teflon-lined autoclave, sealed, and then heated in an oven at 150 °C for 3 days, followed by natural cooling to room temperature. Upon cooling, the resulting colorless plate crystals were filtered, washed with deionized water (3 × 15 mL) and washed with acetone (3 × 15 mL) [16].

1.10. SLUG-22 ($Cu_2(bpy)_2(O_3SCH_3CH_2SO_3)$; bpy = 4,4-bipyridine)**.** Copper acetate monohydrate (0.054 g, 2.70×10^{-4} mol), 1,2-ethanedisulfonic acid dihydrate (0.073 g, 3.23×10^{-4} mol) and 4,4'-bipyridine (0.042 g, 2.70×10^{-4} mol) were suspended in 2 mL of deionized water and stirred for 30 minutes. The resulting mixture was loaded into a Teflon-lined autoclave, sealed, and then heated in an oven at 175 °C for 4 days, followed by cooling at a rate of 7 °C/hour. Upon cooling, the resulting yellow-green needle-like crystals were filtered, washed with deionized water (3 × 15 mL) and washed with acetone (3 × 15 mL) [17].

2. Characterization of MOFs

The MOFs were characterized by powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to confirm their known crystal structure (Figure 1).

A. XRD	**B. Structure**	**C. TGA**
ZIF-8 		N/A
ZIF-67 		N/A

ZIF-70  		
UiO-66-NO₂  		N/A
ZIF-71  		N/A
ZIF-82  		
MIL-101(Cr)  		

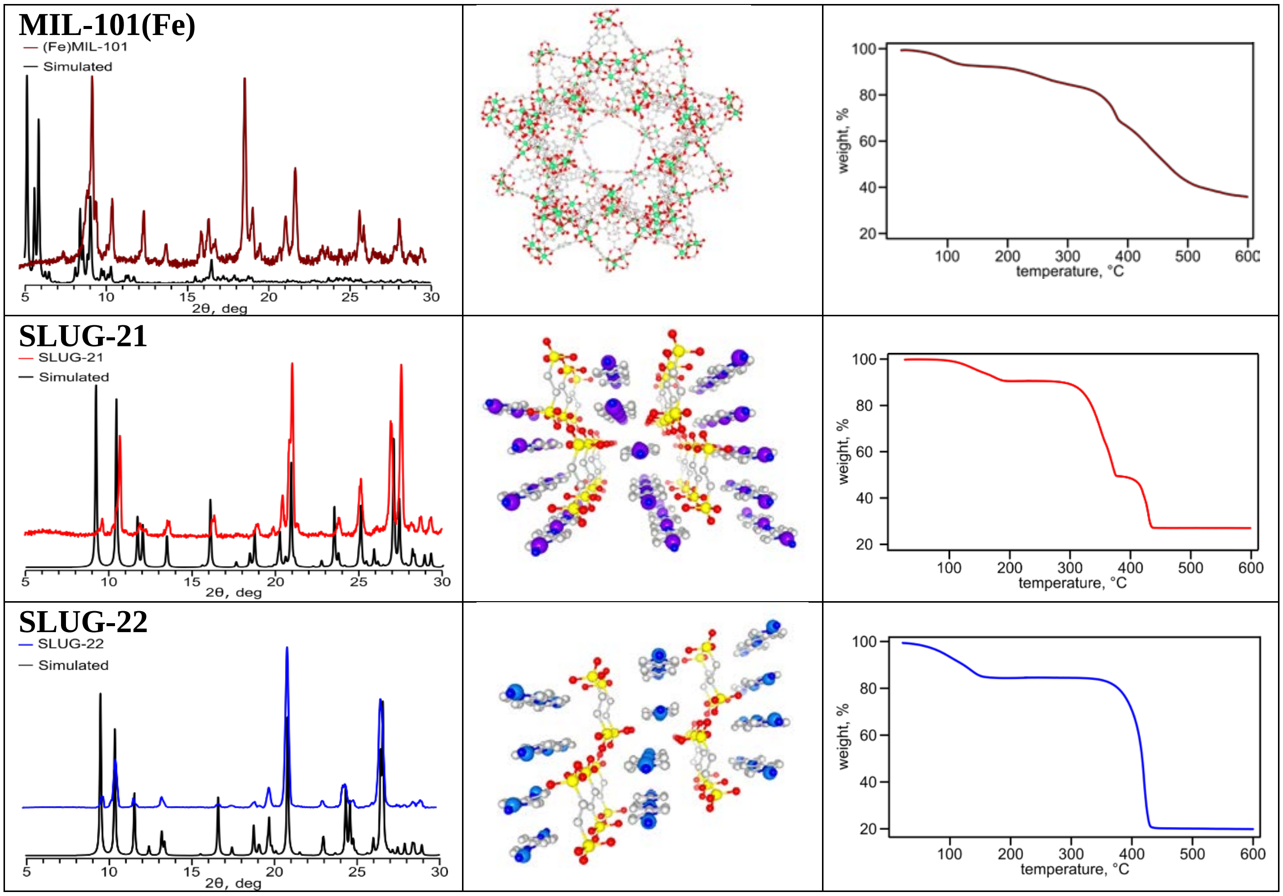


Figure 1. XRD (A), crystal structure (B) and TGA (C) of MOFs

3. Effectiveness of MOFs for TcO_4^- and ReO_4^- sequestration from artificial groundwater

The ten MOFs were evaluated for TcO_4^- and its non-radioactive surrogate, ReO_4^-, sequestration from artificial groundwater under atmospheric ($P_{CO2} = 10^{-3.5}$ atm) conditions. Sorption coefficient (K_d, mL/g) and the equilibrium sorption capacity (q_e, mg/g) were calculated using formula 1 and 2, respectively:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M} \qquad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \qquad (2)$$

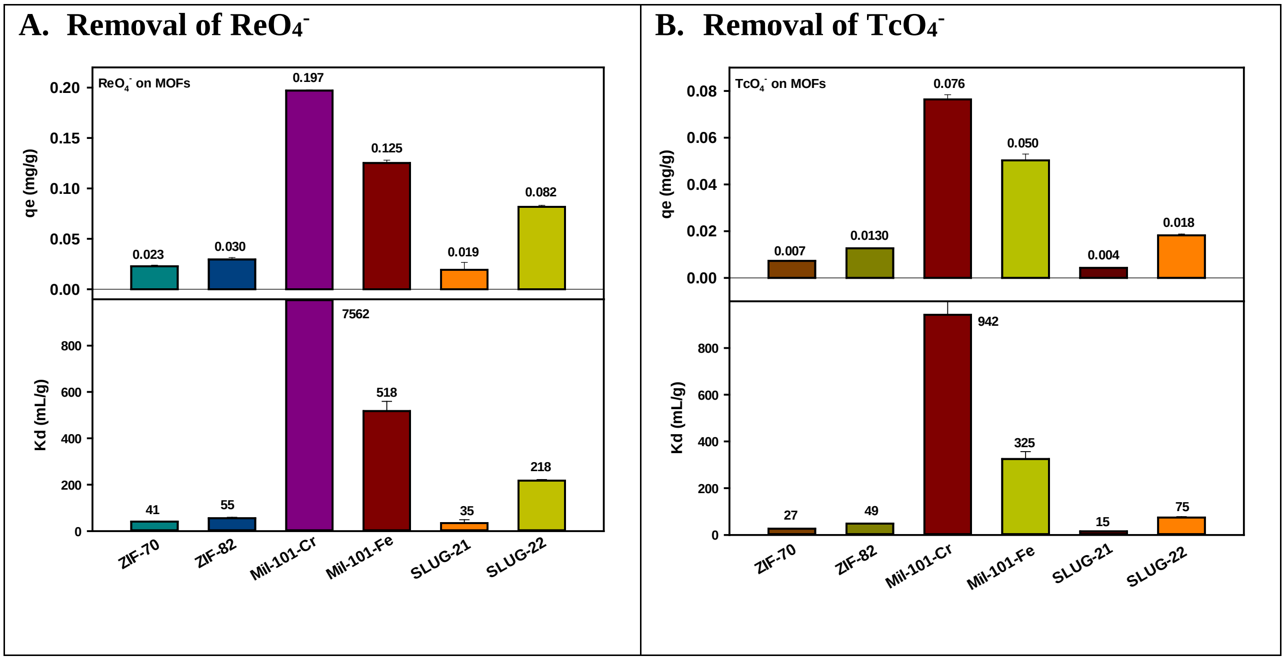
where C_0 and C_e were Tc or Re concentrations before and after adsorption, respectively, V was the total volume of liquid phase (i.e., groundwater), and M was the mass of the solid material.

The adsorption coefficients of ZIF-8, ZIF-67, ZIF-70 and UiO-66-NO_2 from the first-round sample preparation are summarized in Table 1. The results demonstrated that UiO-66-NO_2 was effective for sequestering TcO_4^- from groundwater at pH 3 and 7.5. Some MOFs were not stable under acid conditions. New MOFs need to be developed for Tc uptake under alkaline conditions.

Table 1 Adsorption coefficient (Kd, mL/g) of ZIF-8, ZIF-67, ZIF-70 and UiO-66-NO_2 for TcO_4^- removal from artificial groundwater of different pH values

MOFs	**K_d (mL/g)**		
	pH 3	**pH 7.5**	**pH 12**
ZIF-8	unstable	72	0
ZIF-67	unstable	9	0
ZIF-70	12	0	0
UiO-66-NO_2	750	156	0

The adsorption quantities of ZIF-70, ZIF-82, MIL-101(Cr), MIL-101(Fe), SLUG-21 and SLUG-22 for TcO_4^- sequestration from artificial groundwater at equilibration pH values were determined using batch experiments. The results (Figure 2) demonstrated that MIL-101(Cr) was most effective for TcO_4^- and ReO_4^- sequestration from artificial groundwater at equilibration pH values with the removal capacity of 0.076 mg/g for Tc and 0.197 mg/g for Re. MIL-101(Fe) and SLUG-22 were moderately effective for TcO_4^- and ReO_4^- sequestration under similar conditions.



A. Removal of ReO_4^-

B. Removal of TcO_4^-

Figure 2. Removal capacity of MOFs for ReO_4^- (A) and TcO_4^- (B) sequestration from artificial groundwater.

4. Potential for economical vitrification

Thermogravimetric analyses of selected MOFs were conducted (Figure 1). The results indicated that these MOFs may be vitrified using economic methods, like heating under 400 °C.

The actual vitrification technology will be developed for the eventually selected MOFs that are demonstrated to have high capacity for TcO_4^- removal and improved stability in aqueous media.

FY2018 Accomplishments

- Ten MOFs of known crystal structure and chemistry were synthesized, characterized and evaluated for TcO_4^- and ReO_4^- sequestration from artificial groundwater.
- UiO-66-NO_2 was effective for sequestering TcO_4^- from groundwater at pH 3 and 7.5.
- MIL-101(Cr) was most effective for TcO_4^- and ReO_4^- sequestration from artificial groundwater at equilibration pHs with the removal capacity of 0.076 mg/g for Tc and 0.197 mg/g for Re. MIL-101(Fe) and SLUG-22 were moderately effective for TcO_4^- and ReO_4^- sequestration under similar conditions.
- MIL-101(Cr) is targeted as a top candidate for developing new MOFs with higher TcO_4^- removal capacity and improved stability during FY19. MIL-101-Fe, UiO-66-NO_2 and SLUG-22 are potentially candidates.

Future Directions

- Develop new MOFs for higher TcO_4^- removal capacity and improved stability, especially under alkaline conditions.
- Evaluate MOFs for TcO_4^- removal under different environmental and geochemical. conditions (i.e., pH, Eh, solution chemistry) and for TcO_4^- separation from liquid nuclear wastes.
- Prepare proposals to DOE EM Soil & Groundwater Remediation Program, International Program, and DOE Nuclear Energy program.

FY 2018 Publications/Presentations

Dien Li, Natalia B. Shustova, Kathryn M. Taylor-Pashow, Daniel I. Kaplan, Jake W. Amoroso, Thomas D. Bennett, Metal-Organic-Frameworks (MOFs) for Sequestration and Stabilization of Pertechnetate (TcO_4^-) from Groundwater and Liquid Nuclear Wastes**,** *International Conference of Heavy Metals in the Environment 2018*, Athens, USA, July 21-25, **2018**.

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Acronyms

DOE	Department of Energy
MIL	Materials Institute Lavoisier
SLUG	University of California, Santa Cruz
SRS	Savannah River Site
TGA	Thermogravimetric analysis
UiO	University of Oslo
XRD	X-ray diffraction
ZIF	Zeolitic Imidazolate Framework

Intellectual Property

N/A

Total Number of Post-Doctoral Researchers

0.5 of post-doctoral researcher involved through the subcontractor with the University of South Carolina.