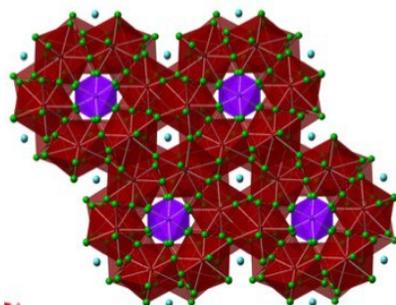


Center for Hierarchical Waste Form Materials (CHWM)
EFRC Director: Hans-Conrad zur Loye
Lead Institution: University of South Carolina
Class: 2016 – 2024

Mission Statement: *To develop the chemical understanding and hierarchical structure motifs needed to create materials for effectively immobilizing nuclear waste species in persistent architectures.*

CHWM focuses on the exploration of hierarchical structures as potential waste form materials. The Center is focused on three general areas 1) radionuclide containing hierarchical materials, 2) materials to accommodate difficult to immobilize elements, and 3) understanding transport in multi-scale porous and hierarchical materials. Specifically, we are investigating 1) complex fluorides and oxides (phosphates, borates, silicates and germanates) accommodating Pu, Np, Am, and Cm; 2) tunnel structure materials, such as hollandites, designed to contain Cs and actinides; 3) MOFs with framework nodes consisting of and/or containing U, Th, Pu, and Np, with cavities to capture Tc and I; and 4) zeolite and geopolymer composites for sequestering Cs. We have successfully synthesized, characterized, and modeled numerous actinide, Tc and I containing phases, including $\text{Na}_x\text{MPu}_6\text{F}_{30}$, $\text{Na}_x\text{MNp}_6\text{F}_{30}$, and $\text{Cs}_2\text{MNPf}_{16}$; $(\text{Ba},^{137}\text{Cs})_{1.33}(\text{Al}/\text{Cr},\text{Ti})_8\text{O}_{16}$ hollandite; Th, U, and Pu MOFs; and Cs-containing geopolymer composites.

TRU Containing Oxides and Fluorides:



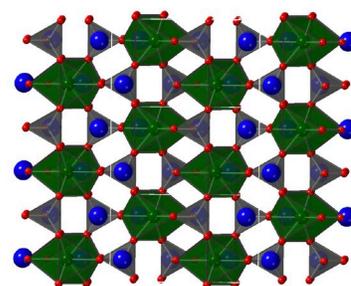
Structure of $\text{Na}_3\text{AlPu}_6\text{F}_{30}$

We are pursuing oxides and fluorides able to accommodate Pu(IV) and Np(IV) where we have synthesized and determined the structures of numerous new Np-containing fluorides of the type $\text{Na}_x\text{MNp}_6\text{F}_{30}$ (M = transition metals). In addition, we have extended this work to $\text{Cs}_2\text{MNP}_3\text{F}_{16}$ and will start to also target Pu(IV) containing analogs. New rare earth-containing double borate and phosphate phases were prepared, guided by our computing of stabilities to identify structures to readily accommodate Am(III) and Cm(III). This work resulted in the successful synthesis of single crystals of $\text{K}_3\text{Am}(\text{PO}_4)_2$, the first extended americium phosphate structure. This work is currently being extended to curium containing phosphates and borates. Single crystals of non-rad analogs belonging to the structural families discussed above were used in radiation effects studies and found to possess significant tolerance to radiation damage.

Tunnel Structure Materials:

Our research focuses on developing new hollandite compositions to sequester Cs. Using our ability to predict new tunnel structures, to determine their phase stability, as well as to develop detailed knowledge regarding their response to radiation, we prepared a series of Al- and Cr- substituted hollandites, $(\text{Ba},\text{Cs})_{1.33}(\text{Al}/\text{Cr},\text{Ti})_8\text{O}_{16}$, and determined their enthalpies of formation by high-temperature melt solution calorimetry. Interestingly, the results indicated enhanced thermodynamic stability with increased Cs content, which generally agreed with sublattice-based thermodynamic calculations. Structurally, the materials are complex and more detailed studies using neutron scattering measurements are underway. A parallel SEM/TEM study will correlate local structure features with macroscale determined stability of Cs. Atom probe tomography of these materials will be performed at the ORNL Nanophase Materials Science user facility. Irradiation studies reveal this class of materials have a high tolerance for radiation damage

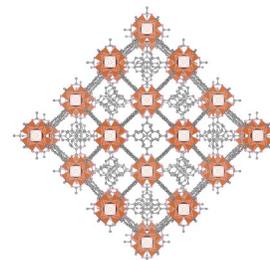
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Structure of $\text{K}_3\text{Am}(\text{PO}_4)_2$

Novel Actinide-containing MOFs:

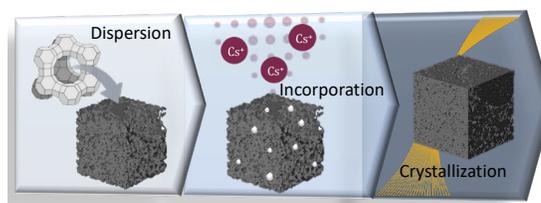
Actinide-MOFs (M = U, Th and Pu) were prepared via metal node expansion to create heterometallic nodes. Pu-MOFs have been prepared and structurally characterized. We experimentally demonstrated that the presence of capping linkers in certain Zr-MOFs significantly affects radionuclide release kinetics and to understand this process we developed a leaching model of radionuclides in Zr-MOF particles. Based on comparisons with actual experimental data, it is found that 1) the leaching of uranyl in Zr-MOF particles is a diffusion-controlled process; 2) the installation of capping linkers reduced the effective diffusion. The reduction was seen as proportional to the density of linkers, and dependent as well on the installation sequence of linkers; and 3) for Zr-MOF particles, the observed leaching kinetics can be explained by considering a thick surface layer where uranyl has an initial concentration gradient. The model correctly predicts the chemical diffusivity as a function of the installed linkers.



Single-crystal structure of Pu-MOF *Pu-Me₂BPDC-12*

Multi-Scale Porous Structures:

The Center has developed multi-scale and multi-phase materials that contain an amorphous phase (geopolymer) and crystalline particles (e.g., zeolite), and explored composites comprising geopolymers (amorphous aluminosilicates) and zeolites that are capable of entrapping and immobilizing radionuclides. We have explored different Faujasite zeolite compositions to determine the thermodynamical stability of Na-Zeolite based structures. Using this information, we prepared (Na and Cs) zeolite/geopolymer composites and studied their composition, porosity, and crystallinity to explore their retention efficiency and performance as waste form. The crystallinity conversion of the geopolymer is being performed via hydrothermal synthesis to define the role of crystallinity in Cs trapping and immobilization. To further optimize the geopolymer compositions and composite microstructures to maximize the Cs ion exchange efficiency, a generic phase field model for a system containing four phases, i.e., zeolite, geopolymer, solution within the mesopores, and the solution, was proposed and we have developed the model and simulation code to capture the effect of anisotropic thermodynamic and kinetic properties, flow-field, and electric field on ion exchange kinetics.



Geopolymer composite for Cs uptake

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