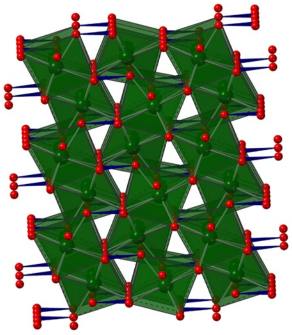
Center for Hierarchical Waste Form Materials (CHWM)
EFRC Director: Hans-Conrad zur Loye
Lead Institution: University of South Carolina
Class: 2016 – 2025

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

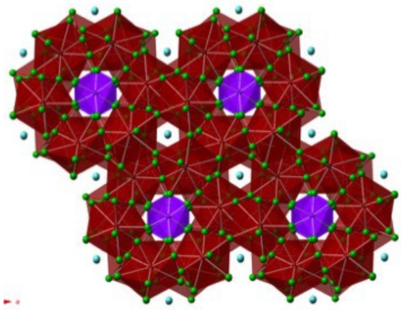
Goals:

The unique predictive and synthetic capabilities developed in the CHWM will be used to study the crystal chemistry of transuranic (TRU) containing extended crystalline structures and their response to radiation damage and radiolytic processes. The Center endeavors to understand the unique chemistry of TRU elements, their influence on the atomic environment affecting the formation of extended structures, their radiation interactions with matter, and how far-from-equilibrium processes can generate metastable phases that are yet quite robust. We hypothesize that an understanding of which types of structural elements favor radiation resiliency of TRU-containing extended structures in waste form materials requires an atomic level understanding together with detailed knowledge about structural changes caused by internal radiation damage. We furthermore hypothesize that the presence of chemically induced anti-site mixing in structures will lead to enhanced self-healing of internal radiation damage.

TRU Containing Oxides and Fluorides:


Structure of $AmBO_3$

We are pursuing oxides and fluorides able to accommodate Np, Pu, Am, and Cm, where we have synthesized and determined the structures of numerous new extended structures, including plutonium (IV) silicates - $K_2PuSi_2O_7$ and $Rb_2PuSi_6O_{15}$; Am containing silicates - $K_3Am(Si_2O_7)$ and $Cs_6Am_2Si_{21}O_{48}$; phosphates - $Na_3Am(PO_4)_2$ and $K_3Am(PO_4)_2$; borates - $Ba_3Am_2(BO_3)_4$ and $AmBO_3$; borate halides - $Ca_5Am(BO_3)_4Cl$; molybdates – $Li_{0.5}Am_{0.5}MoO_4$; and fluorides - $CsAm_2F_7$. Going forward we will pursue Cm containing analogs. Single crystals of non-rad analogs, including some belonging to the structural families discussed above, are being used in radiation damage studies to elucidate their radiation resilience and ability to self-heal.

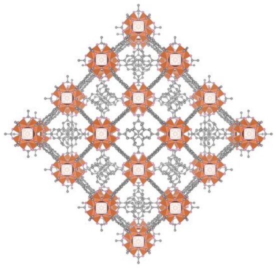

Structure of $Na_3AlPu_6F_{30}$

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-, Cr-, and Ni- substituted hollandites, $(Ba,Cs)_{1.33}(Al/Cr/Ni,Ti)_8O_{16}$, and determined 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 and synchrotron scattering measurements are underway. A parallel SEM/TEM study will correlate local structure features with macroscale determined stability of Cs. Irradiation studies reveal this class of materials has a high tolerance for radiation damage.

Novel Actinide-containing MOFs:

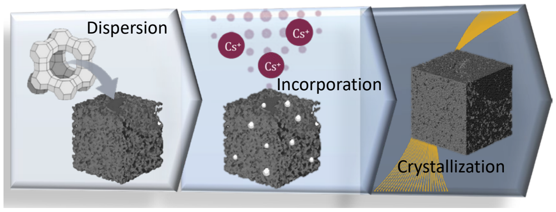
Actinide-MOFs (M = U, Th, and Pu) were prepared via metal node expansion and through the *de novo* synthesis, resulting in the preparation of materials possessing monometallic and heterometallic nodes. Pu-MOFs have been prepared and structurally characterized. We experimentally demonstrated that the 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. Furthermore, we demonstrate that 99% of captured Am cations can be retained at least for several months in the MOF matrix.



Single-crystal structure of Pu-MOF, *Pu-Me$_2$BPDC-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 alumino-silicates) and zeolites that are capable of entrapping and immobilizing radionuclides. We have explored different Faujasite zeolite compositions to determine the thermodynamic 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 forms. 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 Cs-containing 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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