Center for Hierarchical Waste Form Materials (CHWM)
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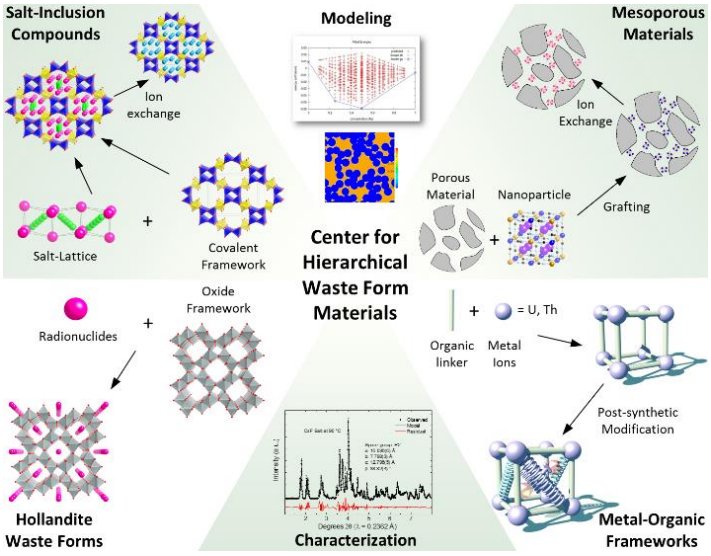
Lead Institution: University of South Carolina
Class: 2016 – 2020

Mission Statement*: To combine experiment and modeling to develop the chemistry and structure motifs needed to create hierarchical materials that effectively immobilize nuclear waste in persistent architectures.*



The Center for Hierarchical Waste Form Materials (CHWM) EFRC is organized to develop the basic science and foundational knowledge from which new waste forms can emerge. The center combines synthesis, characterization and modeling to develop and validate chemistry and structure motifs for materials that effectively immobilize nuclear waste materials into the indefinite future. Novel hierarchical structures are being developed via a bottom–up synthetic approach, where new chemical insights provide the required critical understanding of fundamental mechanisms of complexation and speciation. The outcome will be the advancement of fundamental knowledge related to hierarchical materials systems and their potential future application in waste forms.

A simple definition of a hierarchical material is that of a structural motif contained within a larger structure or framework. Conceptually, the hierarchical structures consist of porous frameworks, either repeating (crystallographically ordered) or non-repeating (disordered), whose cavities can be occupied by crystalline or non-crystalline fillers. Examples of these structures include porous crystalline salt inclusion materials (SIMs), metal-organic frameworks (MOFs), porous silica (including Prussian-blue analogues (PBA) and silver salt functionalized versions), and surface functionalized nanoparticles assembled into hierarchical constructs. Examples of fillers include crystalline salt phases, simple molecular species, silver salt nanoparticles, and Prussian-blue nanoparticles, all either freely located inside the pores or tethered/bonded to the pore walls.

The effort is supported by extensive modeling across multiple length and time scales. Ab initio modeling of alloy nanoparticle stability is utilizing derived Charge Optimized Many Body (COMB) potentials, and simulating atomic-scale processes using tools such as molecular dynamics. Thermochemical models are being developed for complex phases, such as the SIMs, that allow prediction of stability, vapor pressure, melting point, including prediction of the pore filling species, using density functional theory and by extending approaches such as topological and volume-based correlations. At the mesoscale, phase field methods are

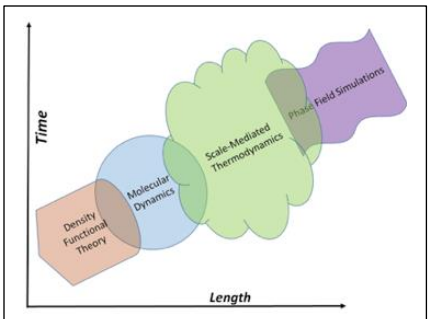


Illustration of bridging scales in modeling waste forms.

being generated for the simulation of porous solids using datasets of surface energies, thermodynamic models, and configurational thermodynamics.

Sample characterization takes advantage of in-laboratory diffraction equipment at Alfred University, state of the art calorimetry measurement systems at Clemson University, thermal analyzers at USC, and beam line facilities, including the SNS at ORNL, and the APS at ANL, for in-situ crystallization, ion-exchange, and general structural characterization. This integrated research is creating the science that will eventually lead to functional, complex material structures for efficient and effective waste sequestration. In addition, access to Savannah River National Laboratory's (SRNL's) 773-A category 2 nuclear facility will enable us to create radioactive versions of hierarchical structures, in addition to the surrogate versions, so as to better understand the unique properties of forms containing elements such as technetium.

The CHWM focuses on a number of hierarchical structures, including SIMs, MOFs, and multi-scale porous silicate structures, developing advances in synthesis, measurement of ion exchange properties, modeling of ion exchange pathways, predicting and measuring thermochemical stabilities, and applying advanced characterization tools, often in novel ways, such as synchrotron and neutron sources, to create and understand hierarchical materials that can lead to the effective immobilizing nuclear waste in persistent architectures. The cross cutting tasks effected by the use of working groups encourage information exchange between center personnel, fostering synergy between the groups, and assure that members are working toward the Center's overarching goals. Specifically, the methodology for synthesizing new uranium containing SIMs has been achieved and has allowed the Center to prepare a large number of novel frameworks, including those based on new building blocks, such as the first $[Al_2O_7(PO_3)_6]^{14-}$ secondary building unit (SBU) in uranium chemistry. The work on multi-scale porous silicate structures has resulted in the preparation of silica monoliths with multi-scale porosity, where optimization of the synthetic process has resulted in the formation of centimeter-scale silica samples with an open macro and mesoporosity. The introduction of PBA nanoparticles inside the structure was achieved by in-structure synthesis of PBAs, which enables the entire sorption capacity of the PBA particles to be used. Another class of hierarchical structures under investigation are MOFs containing U and Th that have been prepared as part of the Center work. New synthetic routes for U and Th incorporation were developed, including metal node extension, post-synthesis modifications and transmetallation. The synthesis of new linkers and capping ligands has been achieved with the goal to trap species inside the MOFs. The hollandite structure, $A_xM_8O_{16}$, is being investigated as a potential candidate for the immobilization of alkali metal radionuclides such as Rb and Cs. The chemical flexibility of the hollandite structure leads to varying degrees of structural disorder that modeling is addressing

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