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.

H. zur Loye, T. Besmann – University of South Carolina
N. Shustova, H. Wang – University of South Carolina
S. Misture – Alfred University
K. Brinkman – Clemson University
A. Grandjean – CEA
S. Gill, L. Ecker – BNL
J. Amoroso, C. Crawford, D. DiPrete - SRNL
C. Henager, S. Hu – PNNL
S. Philpott – University of Florida

http://CHWM.sc.edu
Integration and Information flow Between Thrust Areas

Hierarchical Waste Form Materials

Synthesis Modification Optimization

Nanoparticles
Porous Frameworks
Salt Inclusion Materials

Simulation Multi-Scale Modeling

Characterization Measurement Validation

New Synthetic Strategies
New Hierarchical Architectures
Surrogate

New Modeling Solutions
Radionuclide
Synergy Via Working Groups

Working groups clustered around ideas & concepts including: new materials, modeling approaches, and characterization methods.

- An idea/concept is generated and proposed by either an individual or by a thrust.
- The assumption is that the “idea/concept” is very generic and can be any thing (e.g., an approach, specific data, a model, etc.) that supports the CHWM’s major goals.
- A working group is formed around each idea/concept and, consequently every member of each thrust will be part of at least one or more working groups;
- It is through the working groups that we achieve synergy.
A Unique Role for Modularity in Development of Actinide-Containing Metal-Organic Frameworks

5 concepts for actinide integration (e.g., metal node, metal node extension, capping linkers with anchors, ligands with actinide anchors, and guests), which were used in 8 strategies.

8 strategies for actinide integration led to bi-actinide metal-organic frameworks (MOFs) that were prepared for the first time by solid-state metathesis and metal node extension reactions.

U- and Th-containing frameworks with “unsaturated” nodes that allow capping linker installation in actinide-based frameworks.

Packing of 6 novel crystal structures
PNNL Phase Field Modeling Reveals Limiting Kinetics in Zeolite Ion Exchange

Two diffusion phenomena:
- Diffusion of ions in the boundary layer (slope 1)
- Intra-grain diffusion (slope 2)

Experimental results

Zeolite: Na-Ba exchange

Slope 1

Grain size

Slope 2
Salt-Inclusion Compounds (SICs): Covalent oxide framework with voids filled by simple salt lattices

\[ \text{UF}_4 + 4\text{SiO}_2 \xrightarrow{\text{CsF/CsCl}} \text{Ag tube crucible} \xrightarrow{800 \, ^\circ C} \text{CsF/}[\text{Cs}_3\text{F}][\text{((UO}_2\text{)(Si}_4\text{O}_{10})] \]

Non-salt-inclusion cations

[\text{AmB}_n\text{X}][\text{((UO}_2\text{)}_p\text{Si}_q\text{O}_r)_t]\]

salt-inclusion framework
Salt Inclusions can be ion exchanged
Synchrotron based X-ray diffraction methods for real time evaluation of hierarchical waste forms

**Objective**: Utilize high resolution synchrotron X-ray diffraction methods for structural characterization of uranium based Salt Inclusion Materials (SIMs)

**Approach**:
- Porous \([\text{Cs}_3\text{F}][(\text{UO}_2)(\text{Si}_4\text{O}_{10})]\) SIM ion-exchanged by soaking SIM in RbF, CsF and KBr solutions at 90°C.
- XRD data collected at XPD beamline.

**Results**:
- Rietveld refinement of the SIM before ion-exchange showed the orthorhombic crystal lattice structure.
- Transformation of orthorhombic SIM to monoclinic lattice after ion exchange.
- In situ crystal growth studies of SIMs are planned in FY18.
- Feasibility testing of containment and in situ set-up will be completed in FY17.
Reductive alloying of Au@Cu₂O core-shell nanoparticles: Adaptable coordination environment for waste storage materials.
Upcoming CHWM Posters and Talks

Talks
• Natalia Shustova “Well-Defined Actinide-Based Frameworks”
  Monday 3:40 PM, Lincoln 5
• Hui Wang “Multimetallic Nanoparticles: Alloys, Intermetallics, and Heterostructures”
  Tuesday 9:10 AM, Lincoln 5
• Theodore Besmann “Volume Based Thermodynamics Approach Applied to Salt Inclusion Materials”
  Tuesday 2:30 PM, Lincoln 5

Posters
Monday 5:00-6:30 PM
• Gregory Morrison “Molten Flux Synthesis and Ion-exchange of Uranyl Silicate Salt Inclusion Materials (PI-E-1)
• Shenyang Hu “Mesoscale Phase Field Modeling of Radioactive Species Extraction in Hierarchical Waste Form Materials: Ion Exchange in LTA Zeolite (PI-E-5)
• Simerjeet Gill “Synchrotron Based X-ray Diffraction Methods For Real Time Evaluation Of Hierarchical Waste Forms (PI-E-9)

Tuesday 3:30-5:00 PM
• Rob Koch “Reaction Pathways In Nano-scale Reduction Alloying From In-Situ X-Ray Diffraction (PII-E-5)
• Shubham Pandey “First Principles Determination of Stability Layer Adhesion in Au-Cu Nanoparticles (PII-E-12)