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Hierarchical Materials as Tailored Nuclear Waste Forms: A Perspective

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ABSTRACT: This perspective focuses on the synthesis, characterization, and modeling of three classes of hierarchical materials with potential for sequestering radionuclides: nanoparticles, porous frameworks, and crystalline salt inclusion phases. The scientific impact of hierarchical structures and the development of the underlying crystal chemistry is discussed as laying the groundwork for the design, local structure control, and synthesis of new forms of matter with tailored properties. This requires development of the necessary scientific understanding of such complex structures through integrated synthesis, characterization, and modeling studies that can allow their purposeful creation and properties. The ultimate practical aim is to provide the means to create novel structure types that can simultaneously sequester multiple radionuclides. The result will lead to the creation of safe and efficient, long lasting waste forms for fission products and transuranic elements that are the products of nuclear materials processing waste streams. The generation of the scientific basis for working toward that goal is presented.

INTRODUCTION

The United States has spent more than half a century developing the nation's nuclear arsenal and nuclear energy infrastructure. The scale of these activities has, and will continue to result in a significant quantity of radioactive waste. These materials are generally classified and dispositioned according to their hazard level. In the United States, three main categories are recognized: low-level waste (LLW), high-level waste (HLW), and transuranic (TRU) waste. These wastes must be processed so that the radioactive and hazardous constituents become permanently stabilized and safely sequestered from the biosphere for millennia.

LLW contains short-lived radionuclides in relatively small amounts and includes materials like consumables, process chemicals, tools, etc. LLW poses relatively low risk to the biosphere and can be disposed of in shallow or above-ground vaults. HLW originates as irradiated reactor fuel, contains long-lived radionuclides, and generally has high specific activity, which may be sufficient to generate significant heat. HLW, as its name suggests, generally poses the greatest risk to the biosphere and must be sequestered through deep geologic disposal, the safest established method. TRU waste, a classification unique to the United States, is that which is not classified as HLW but contains alpha-emitting TRU radionuclide elements in greater than 100 nCi/g concentrations and with half-lives greater than 20 years. TRU waste includes primarily contaminated tools, clothing, debris, process residues, etc., used in nuclear defense and energy program activities.[1]

The United States Department of Energy (DOE) has been tasked with remediation of the nation's legacy and commercial nuclear waste.[2] Used nuclear fuel (UNF) generated from

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commercial reactors and liquid waste (or tank waste) generated from legacy programs represent the majority of the HLW inventory, with UNF amounting to a substantial majority of that total. UNF is currently stored on-site at commercial reactors throughout the United States.[1,3] The largest quantities of tank waste are stored in South Carolina (Savannah River Site), Tennessee (Oak Ridge Reservation), and Washington State (Hanford Site). Over the past two decades, the DOE Office of Environmental Management has established or is planning industrial-scale processes to remediate the approximately 300 million liters of highly radioactive waste stored in aging underground tanks at the Savannah River and Hanford Sites. Current plans are for these tank wastes to be stabilized as grout (LLW) or glass (HLW) waste forms prior to final disposal, with efforts already underway.[4]

Since the decision some decades ago to focus on glass and cementitious materials for tank wastes, a large amount of resources have been expended to design, evaluate, and establish processes to produce vitreous and cementitious waste forms. Consequently, the collective knowledge to develop alternative immobilization matrices for nuclear waste is deficient. To be sure, the decades of research and development, scientific vetting, technology demonstration, and global acceptance that have advanced current waste forms to what they are today was no simple task, nor undertaken without due reason and purpose. Indeed, these waste forms, which are almost universally accepted across nations, represent the product of technological innovation, regulatory compliance, and societal trepidation that have and will continue to surround nuclear energy. Nevertheless, there are significant quantities of material for which alternative waste forms present an opportunity to reduce the environmental and financial cost to remediate.

The materials which could benefit from new waste forms include the byproducts and secondary waste streams which are a result of inefficiencies in the process (e.g., volatile species, constituents with low solubility in glass, etc.) and limit the parent process throughput. There are also small volume wastes that do not warrant the resources to develop industrial-scalable processes, and thus for which alternative options could be considered. Finally, there are wastes that are small in volume but troublesome for known technologies (e.g., low solubilities in glass, high mobility, etc.). Fortunately, recent technological advances in materials synthesis, computational modeling, and advanced characterization now provide a foundation from which to efficiently pursue innovative waste form development that was previously not possible or prohibited by time and cost. One such strategy is to take advantage of hierarchical structures as potential waste forms. New waste forms like these are not expected to replace large scale use of glass or cementitious waste treatment technologies, which are the best compromise for performance, processability, predictability, social acceptance, and waste throughput. Alternative waste forms should be considered to augment the existing technologies (e.g., secondary and off-gas treatment) or utilized for small quantity wastes that do not warrant a national campaign to treat.

Hierarchical materials can be tailored at the molecular/crystal lattice and higher scales, which can offer opportunities to immobilize specific radionuclides in an optimized matrix. To accomplish such goals requires the generation of a fundamental understanding that allows the effective design of hierarchical materials with specific properties. Such hierarchical materials it is hoped will isolate targeted radionuclides with increased efficiencies through tolerating higher waste atom content, lower treatment cost, and more rapid processing. In this way, hierarchical materials may be a key to ultimately completing the suite of technical approaches that will speed the cost-effective sequestration of the products of the nation's processing of nuclear reactor materials.

■ CURRENT APPROACHES TO WASTE IMMOBILIZATION

Glass and cementitious waste forms have successfully been used to immobilize a variety of wastes and are currently the most widely used materials to stabilize nuclear wastes for which the U.S. DOE is responsible. However, limitations persist for these waste forms, such as, for example, glass waste loading that is constrained by crystallization and melt characteristics (e.g., viscosity, liquidus, reduction/oxidation) caused by a small proportion of the waste stream, or that is limited by volatilization and solubility of minor species generated during processing (e.g., species of ^{137}Cs, ^{99}Tc, Hg, SO_4^{2-}, Cr^{6+}, ^{129}I). Partial crystallization is known to diminish the long-term performance of glass waste forms through formation of nondurable salt phases and growth of crystals in the glass that deplete the glass matrix of network former ions (e.g., precipitation of nepheline, $(Na,K)AlSiO_4$).[5] Furthermore, the reduction/oxidation state of a glass melt is known to impact processability (e.g., foaming, noble metal segregation) and retention of volatiles during melter operation, including ^{99}Tc and Cr species.[6] Indeed, for constituents with high vapor pressures and low melt solubilities, off-gas management becomes a significant challenge to the overall vitrification process, and a secondary waste contribution.[7] The trade-off between accommodating a wide range of elements and waste loading capacity limitations causes reduced efficiencies that could be mitigated given alternative routes for handling problematic minor components.

Unlike glass, grout and cementitious waste forms do not chemically incorporate many of the waste elements, and elemental release from these materials is not well understood.[8] Cementitious waste forms encapsulate radionuclides and other highly mobile cations (e.g., ^{3}H, ^{137}Cs, ^{129}I, ^{99}Tc, etc.) in a multiphase porous matrix, and thus it follows that release of species to the environment does not involve the same chemical degradation processes as in glasses but, instead, is controlled by the transport of these mobile cation species through the porous structure.[9,10] This is a fundamental limitation for such waste forms, potentially affecting confidence in long-term stability. Again, using cementitious waste forms to accommodate those species for which they are most suited might provide substantial savings and volume reduction, with high mobility species instead sequestered in structures that ensure retention while affording reasonable loading.

■ HIERARCHICAL STRUCTURES APPROACH TO WASTE FORMS

A simple and very practical working definition of a hierarchical structure is a material with structural motifs at various length scales, together forming a larger structure or framework. Nature has abundant examples of hierarchical materials and processes, a notable case being biomineralization, which is the process responsible for the formation of biomaterials, such as

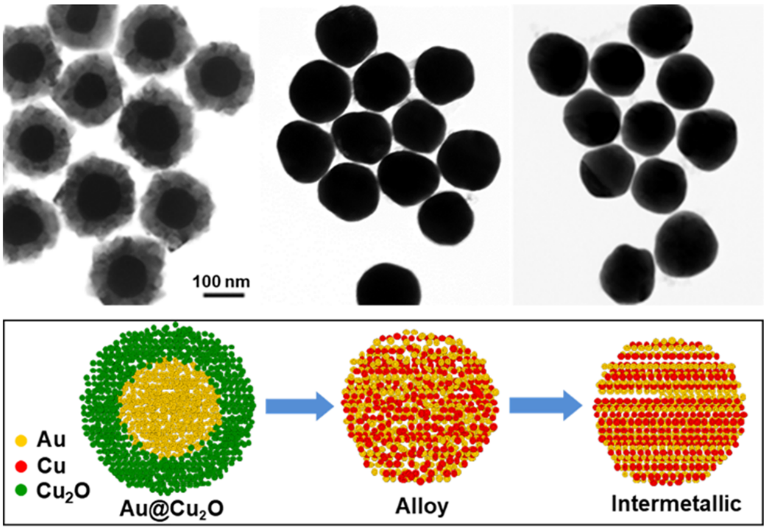

Figure 1. Model Au−Cu system illustrating initial core−shell structure that can be processed at low temperatures to form a disordered alloy and/or intermetallic phase nanoparticle depending on composition. On the top are SEM images of particles represented by the drawings below.

shells, bone, and teeth. These are formed by processes that generate hierarchically structured organic−inorganic composites. It is a bottom-up strategy starting at atomic and molecular scales with processes leading to the formation of higher scale building blocks, which in turn organize into complex hierarchical structures. Conceptually, hierarchical structures of interest for waste forms consist of porous assemblies, either repeating (crystallographically ordered) or nonrepeating (disordered), whose cavities will be occupied by crystalline or noncrystalline fillers. One approach to creating such materials relies on exploring porous structures such as crystalline salt inclusion materials (SIMs), metal−organic frameworks (MOFs), porous silica, and surface functionalized nanoparticles assembled into hierarchical constructs. Examples of fillers include salts, simple covalent molecular species, Prussian-blue analog (PBA) nanoparticles, and multimetallic nanoparticles, all either freely located inside molecular-scale framework structure pores or tethered/bonded to pore surfaces.

The multiscale motifs that assemble into the final hierarchical structure all play, individually as well as in the aggregate, important roles in potential waste sequestration materials. The multiscale structure allows us to optimize the chemical environments for different waste species and create a custom waste form that can simultaneously accommodate multiple, difficult to isolate radionuclides. This consolidation into lower volumes will help mitigate some of the issues responsible for high cost and long horizons for the ultimate remediation of our existing legacy waste. Pursuing this line of research should lead to new waste forms that permit the design of waste sequestration systems optimized such that radionuclide species are captured in the most efficient forms, whether existing or newly developed, yielding significant savings in cost and time.

In the following sections, efforts on the development and understanding of classes of hierarchichal materials are discussed with their potential to lead to new, specialized waste forms.

Nanoparticles. Nanoparticles accommodating two different metallic elements (bimetallic), or several different elements (multimetallic), can adopt a series of structurally distinct architectures, such as core−shell, alloys, and intermetallic compounds.[11,12] The nanoparticle waste form concept is to structurally, architecturally, and compositionally optimize such systems for highly mobile elements that need to be sequestered, such as ^{137}Cs and ^{99}Tc, suppressing their leachability, and processing them under conditions that avoid their volatilization. Such multimetallic nanoparticles are envisioned to function as one component in a hierarchical waste form designed specifically to contain these volatile species and to prevent their release into the environment. In addition, the larger hierarchical structure containing the multimetallic nanoparticles must, of course, ensure that the nanoparticles themselves are unable to break free and enter the environment. In order to develop such nanoparticles as stable and processable waste storage materials, the science underlying the formation and stability of multimetallic species needs to be worked out, initially by using surrogates, and ultimately to prepare these new hierarchical wastes by incorporating the mobile radionuclides of interest.

The idea of mixing multiple metallic elements together in bulk materials to achieve enhanced stability dates back to the Bronze Age, during which humans discovered that metallic Cu, when alloyed with Sn to form bronze, became mechanically more robust and chemically more inert than the monometallic Cu. Another archetypal example is stainless steel, typically made by alloying Fe with small amounts of Cr and C, which exhibits remarkably enhanced resistivity to corrosion as compared to metallic Fe. While some knowledge gained from bulk materials may still apply to nanoparticle systems, a unique set of size- and shape-dependent properties emerges when the material dimensions are reduced to the nanometer length scale. In comparison to the bulk materials, multimetallic nanoparticles represent a structurally more tunable and, thus, fundamentally more intriguing system whose chemical stability and restructuring behaviors become sensitively dependent on not only their overall composition but also on a series of nanoscale structural parameters, such as particle sizes, particle shapes, intraparticle arrangement, local lattice strain, and surface atomic coordination environments. Multimetallic

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nanoparticles may exhibit significantly enhanced stability in comparison to their monometallic counterparts,[13−15] and the thermodynamic stability of multimetallic nanoparticle-based waste forms can potentially be optimized by tailoring architectures and atomic configurations.

The nuclear waste generated from fission reactions is composed of a large library of elements spanning a vast portion of the periodic table,[16] many of which are transition metals that are prone to oxidative etching when stored in an environment accessible by water, oxygen, salts, acids, or other chemical species. Oxidation of some metal species, such as Tc and I, for example, can lead to leaching of the radionuclides from their storage matrices to the environment, which imposes a serious challenge to nuclear waste processing, storage, and management. Given the advantages of multimetallic nanoparticles as a class of structurally robust and architecturally tunable materials noted above, we are exploring accommodating multiple nuclear waste elements in the same nanoscale entity, through which enhanced stability and processability can both be achieved. The issue of miscibility will be explored, since for metals with different structures, the solid solubility will likely range from partial to full miscibility.

Of central interest is the formation of Tc-, Cs-, Mo-, or Re-bearing bimetallic or multimetallic nanoparticles. Experience exists with model systems, such as Au−Cu[15,17,18] (Figure 1) where alloying in nanoparticles can occur well below the elemental melting points and where such low temperature processing is not only more efficient but also can avoid the persistent problem of the loss of volatile radioisotopes. One caveat is the potential dealloying of these bimetallic systems, which must be avoided, for example, by choosing an appropriate compositional regime, while another is the impact of radiolysis products on these waste forms, which needs to be carefully evaluated.

Efforts with model systems is leading to the fundamental understanding needed to develop systems containing problem radionuclides such as ^{137}Cs and ^{99}Tc, which will in turn be used to validate the approach. For that reason, a “Make, Measure, Model (3M)” strategy[19] has been adopted to develop a quantitative understanding of the structure−composition−property relationships of multimetallic nanostructures through combined experimental and computational efforts integrating syntheses, characterization, and modeling.

The nanoscale nature of materials provides challenges in characterization and computational studies, further complicated should disorder occur. For example, a global challenge in the study of guest radionuclide atoms or ions in disordered nanoscale materials is differentiating between the signatures of the guest atom/ion, disorder, and size effects—an exercise which is necessary to quantitatively describe the structure and predict properties. To address these, novel approaches are being introduced which are expected to provide new insights into the atomic and mesoscale structures.

While traditional X-ray diffraction methods and some of the local structure probes such as NMR and X-ray spectroscopy are of value, the data are often inconclusive in discriminating disorder, nanoscale size features, and guest atom/ion locations and quantities. For the metallic nanoparticles of interest, as well as for other complex, hierarchical materials under consideration, the pair distribution function (PDF) approach is expected to be useful. Here, high energy X-ray or time-of-flight neutron scattering are being used to probe structural features from the atomic through the nanometer scale. Subtle material characteristics at the nanometer and smaller length scales have been characterized using the PDF method, for example, nanodomains in relaxor ferroelectrics,[20] where multication oxides show extensive clustering of cations. Similar or even greater chemical complexity is common in alloy systems, and therefore we anticipate that application of the PDF analysis tool to complex alloy nanoparticles[21,22] will allow a more complete description of the interatomic bonding and local environments that lead to, for example, improved resistance to leaching.

The reduced scale of nanoparticles makes them ideal for investigation using atomistic computational techniques, notably density functional theory[23,24] (DFT) and molecular dynamics[25] (MD) simulations. In particular, DFT is probing such effects as the influence of epitaxial strain on the stability of nanostructures, the thermodynamics of alloy formation, and the energy barriers for diffusion across bimetallic interfaces and into the metallic layers. MD simulation has examined systems of many millions of atoms and thus directly simulated bimetallic nanoparticles and characterized their short time microstructural changes and diffusion processes.

Indeed, recent work has demonstrated that integration of new, robust, statistically sound methods of fitting models to experimental PDF and XRD data, combined with iterative integration with DFT optimizations of candidate structures, yields new information describing both microstructure and the local and average atomic structures of alloy nanoparticles over length scales spanning 4 orders of magnitude. Microstructure and average structure information refined from high-resolution powder XRD measurements is used to initialize atomic scale models. Hierarchically constrained global optimization of these 640 000-atom ensembles using differential evolution allows us to quantify details of chemical short-range order, correlated disorder, and local structural distortions in alloys by fitting the experimental PDF. This quantification in turn facilitates identification of local features which are only hinted at in traditional powder XRD data. Examples of structural arrangements on the nanometer size scale arising from partial chemical correlations are shown in Figure 2.

Adding a finer level of detail, these optimized models can be used to initialize DFT calculations. DFT structure relaxation

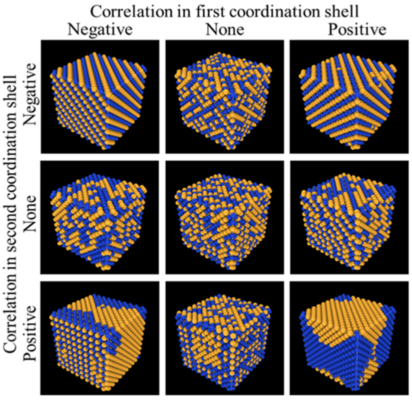


Figure 2. Examples of atomic structures that arise due to different combinations of first and second coordination shell chemical correlations in a nominal 50/50 Au/Cu solid solution. Positive correlations imply like pairs are preferred while negative correlations imply unlike pairs preferred. Gold colored spheres correspond to gold atoms, while blue ones correspond to copper atoms.

results in determination of species-dependent bond lengths that further improve model agreement, while avoiding the massive increase in model complexity that would be needed to extract this information from fits to experimental data. This manifestation of displacement disorder gives physical insight into the nature and origin of local symmetry breaking. Together, these details could be the key to understanding and engineering leaching behavior in alloys. Beyond this, these new synergistic tools will be extended to other hierarchical systems with correlated disorder.

Salt-Inclusion Materials. Another approach to the targeted development of new waste forms that simultaneously capture and store multiple radionuclides, including difficult to contain elements, such as cesium, technetium, and iodine, is salt-inclusion materials (SIMs). It is possible to create hierarchical, salt-containing framework structures that have the ability to trap numerous radionuclides through ion-exchange, where a nonradioactive salt is replaced by radionuclides that are thereby immobilized within the covalent framework for long-term storage. Using high temperature molten salts as the reaction environment,[26] we have prepared numerous examples of an intriguing class of materials, SIMs, that are inorganic framework structures containing voids occupied by an ionic salt lattice. This salt lattice can range from very simple molecular structure, a halide anion surrounded by several alkali cations,[27] to more complex dimers,[28,29] chains,[30,31] slabs,[32] and even interwoven 3D salt constructs.

As a hierarchical structure, SIMs provide a unique opportunity due to their great compositional flexibility and structural variability arising from the covalent metal oxide framework, often composed of SiO_4, PO_4, and/or transition metal oxide units. For example, $[NaK_6F][(UO_2)_3(Si_2O_7)_2]$ is a salt-inclusion material consisting of a uranyl silicate framework, $[(UO_2)_3(Si_2O_7)_2]$, a K_6F salt-inclusion, and a Na cation that is not part of the salt-inclusion.[27] More generally, a uranyl containing SIM can be described by the structural formula $[A_mB_nX][(UO_2)_p(M_qO_r)_t]$, where $[(UO_2)_p(M_qO_r)_t]$ is the framework consisting of uranyl cations, UO_2^{2+}, and M_qO_r units (M = networking forming ion such as Si or Ge), B_nX is the salt-inclusion, and A is non-salt-inclusion cations. A prototypical SIM, $[Cs_3F][(UO_2)(Si_4O_{10})]$, is shown in Figure 3.

SIMs are noteworthy because as "stuffed" porous materials, they may lead to waste forms that simultaneously capture and store multiple radionuclides. The structures can be tuned to accept sets of ions of interest via ion exchange, with an individual structure thus hosting multiple radionuclide waste elements. Furthermore, after the exchange process (performed post-synthesis in an aqueous environment), the entrances may be sealed to isolate the elements. Problematic radionuclides such as cesium and technetium can thus be transformed from volatile species to those of low chemical activity through capture in SIMs, making this potentially another extremely versatile multiradionuclide waste form.

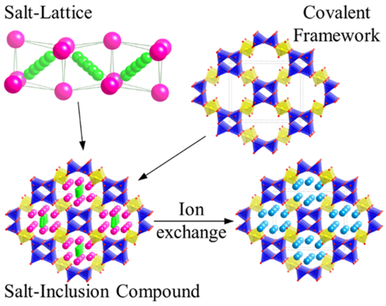


Figure 3. Hierarchical structure of a prototypical SIM, $[Cs_3F][(UO_2)(Si_4O_{10})]$, and the ion exchange process.

While SIMs were first discovered in the early 1900s,[33,34] it was not until ∼15 years ago that salt-inclusion materials were recognized as an abundant and structurally diverse set of compounds.[35,36] Historically, their synthesis has been largely serendipitous, i.e., their formation was the result of reactions that were more broadly targeting oxides,[28,37] with little effort to specifically target SIMs. Recently, a modified flux growth technique for the targeted synthesis of salt-inclusion compounds has been developed.[27,38] This technique limits the availability of oxygen within the flux melt by using a reaction vessel with a small surface area to volume ratio and by using metal halide reagents, as opposed to metal oxides. The limited oxygen availability favors the inclusion of other anions into the formed crystals, in some instances leading to the formation of SIMs. When this enhanced flux growth technique was used in our work, multiple new uranyl silicate and uranyl germanate salt-inclusion compounds were discovered. In this case, we are interested in uranium not as an element to be sequestered but rather as providing for the framework structures of interest.

For SIMs to become a viable waste form material, their crystal chemistry must be expanded to allow for the tailoring of the salt channels for specific radioisotopes. For instance, accommodating CsI will require SIMs with larger channels than that designed to accommodate NaF. One approach to expanding the crystal chemistry of SIMs is based on the concept of framework building blocks (FBBs). Different main group elements that are framework formers, e.g., Si, Ge, B, and P, provide different FBBs, such as $P_2O_7^{4-}$, $Si_4O_{10}^{4-}$, and $B_6O_{10}^{2-}$, or more complex ones, like $Al_2P_6O_{25}^{14-}$.[39] One route to alter the crystal chemistry of SIMs is to use the range of phosphates, borates, and germanates, as well as targeting mixed systems of borosilicates, borophosphates, phosphosilicates, and aluminophosphates. Inclusion of non-main-group FBBs such as vanadate, niobate, and lanthanide polyhedra can even further expand the structures.

Uranyl silicates and germanates are especially well suited to form salt-inclusion materials.[38] Thus, expanding the crystal chemistry by including other building blocks will likely present challenges. The enhanced flux growth technique developed to grow SIMs will have to be tuned to the specific building blocks that are utilized. This can be greatly aided by a more thorough understanding of how SIMs form during flux growth. As a synthetic method, the flux growth process has remained a black box until recently, when the direct observation using X-ray and neutron diffraction techniques became possible.[40−42] For example, the knowledge of how the nature of precursor species in the melt affects what intermediates form during growth and how this ultimately leads to the formation of a SIM will greatly aid the targeted synthesis for waste form applications. One experiment of particular interest is that studying the formation of $[Cs_3F][(UO_2)(Si_4O_{10})]$. Under certain conditions, the reaction of UF_4 and SiO_2 in a CsCl/CsF flux leads to the growth of $[Cs_3F][(UO_2)(Si_4O_{10})]$, while identical conditions with UO_2 as the uranium source results in β-$Cs_2(UO_2)Si_2O_6$. The technical challenges for such an experiment are substantial, including confidently containing the radioactive uranium, withstanding the corrosive fluoride flux, and providing the requisite oxygen to the reaction, all while allowing adequate penetration of the X-ray or neutron beam to pass through the sample.

Understanding how the pore size, the salt inclusion composition, and the salt inclusion structure are correlated is important for the design of a waste form. Changes that take place in the salt inclusion structure with composition remain to be fully understood, including how the framework and salt structures are potentially altered during the ion-exchange process as seen in $K_2Cs_3Cu_3(P_2O_7)_2Cl_3$, where it is possible to replace CsCl with KCl.[35]

Developing a more detailed understanding of the relationship between framework and salt inclusion structures will enable the targeted preparation of SIMs specifically tailored to certain radionuclides, currently being addressed through structural investigations and modeling. This includes direct observation of the exchange process via in situ diffraction experiments. Experiments at the Spallation Neutron Source (SNS) at ORNL enable us to follow the ion exchange process that, at times, results in a structural distortion of the SIMs' inorganic framework, to accommodate different sized salt inclusion species. In tandem, PDF analysis is allowing observation of local changes within the framework and salt that occur over the course of the exchange, providing further insight.

While complex framework materials such as SIMs can be prepared following crystal chemistry rules (atomic size, charge, etc.), thermodynamic functions such as heat and entropy to obtain Gibbs energies for these materials are nonexistent, in large measure due to their complexity. Melt solution calorimetry[43] is now uniquely providing direct measure of the formation energy of these materials. Computational techniques for predicting or analyzing potential ion exchange products using estimation/correlation techniques such as DFT and volume-based thermodynamics (VBT)[44−46] are being applied to obtain values for framework and salt constituents. Calculations utilizing such an understanding will allow determination of relative material stability and the propensity for ion exchange, with the goal of ultimately computing the efficient choice of framework and salt inclusion, and an understanding of whether a specific ion exchange is possible.

Actinide-Based Metal−Organic Frameworks. The unprecedented modularity and porosity of metal−organic frameworks (MOFs) make them cornerstone materials for a number of emergent applications, including gas storage, separation, sensing, and heterogeneous catalysis.[47−51] Yet, another unrealized potential for MOFs lies in the utilization of their unique topologies and tunable pores for development of novel architectures for effective radionuclide sequestration. The potential benefits of MOFs arise from the multiple approaches to actinide (An) integration within the framework structure. One of the main advantages is covalent bond formation, which significantly impedes leaching from the framework. Moreover, more homogeneous distribution of actinides in the structure decreases the accumulation of radiation damage. To date, there are only a few reports covering radionuclide-incorporated frameworks.[52−67]

The realization of potential applications is contingent on the fundamental understanding of the thermodynamics and kinetics of An integration inside extended structures such as MOFs. Currently, studies relative to the chemical behavior or incorporation of An species inside the MOF matrix are essentially unexplored,[66,68] necessitating additional research to harness their full potential as versatile platforms for efficient nuclear waste management. At the very least, MOFs could serve as an interim matrix for separation/removal of select radionuclides, in a system for ultimately producing robust and indefinitely stable structures that will serve as the final waste form for long-term disposition.

To illustrate the multifaceted modularity of MOFs, existing approaches for An integration are summarized in Figure 4, which demonstrates the possibility of a stepwise construction of the An-MOF hierarchical complex.[69] Actinide incorporation into the MOF extended structure can occur through several processes that can involve: (i) a metal node, (ii) an organic linker, and (iii) capture in a framework cavity. Synthetic strategies can include direct solvothermal synthesis by heating an An-containing salt in the presence of the organic ligand, metal exchange, postsynthetic metal node modification through its extension, functionalization of the organic linker with the specific anchoring group, and incorporation of actinide species inside of the MOF cavities.

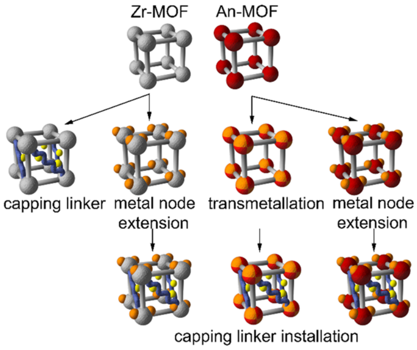


Figure 4. A schematic representation of framework modularity for actinide (An) integration on the examples of Zr- and An-based scaffolds. The integrated actinide-containing species are shown in orange and red colors: red and orange spheres represent An-based metal nodes; gray spheres, Zr-based metal nodes; gray solid sticks, organic linkers used for framework synthesis; blue sticks, capping linker; and yellow spheres, An-containing guest species.

Metal Node. The simplest way to prepare actinide containing materials is via direct synthesis, i.e., heating an An salt and an organic linker in a polar solvent such as *N*,*N*′-dimethylformamide (DMF). This solvothermal approach commonly used for MOF preparation is advantageous for working with radioactive species mainly due to the moderate temperatures used for An integration, which therefore does not typically lead to the creation of volatile radioactive species, in contrast to the ~1000 °C temperature regime required for the preparation of radionuclide-containing borosilicate glasses. In general, this synthetic method is used for An immobilization inside the metal nodes of the MOF of interest. Recently, additional synthetic strategies for An integration have been implemented, including metal node extension and postsynthetic cation exchange in which uranium and thorium were integrated into metal nodes.[69] In some cases, two An elements can be integrated through direct synthesis, via processing with two actinide salts and an organic linker.[53] The An salts are only required for the *direct* synthesis of An-MOFs. Other routes for An integration inside of a framework are available and do not rely on An salts. For instance, framework pores are accessible for any type of An-containing species, while linkers modified with specific anchors could be used for coordination of different cationic radionuclides.

Organic Linker. To utilize the organic linker for An integration, it is functionalized with an anchoring group for selective An capture.[70−73] Several examples of these anchors are shown in Figure 5. Some of them, such as diethoxyphosphorylurea, acylamide, and phosphine oxide groups, have already been successfully used for the extraction of UO_2^+ and Th^{4+} from aqueous solutions.[70−74] Chelating An-containing species inside the MOF matrix can lead to significant changes in framework photophysical properties and, therefore, open a pathway to monitor actinide capture by utilization of, for example, photoluminescence as a sensitive detection tool. Functionalization of organic linkers employed in MOF synthesis can thus not only result in good absorbents but also give rise to new "smart" sponges with tunable functionalities for real-time monitoring. And due to the high framework modularity, MOFs can be utilized as a platform for the installation of another type of organic linker—a capping ligand, which seals the pores of the MOF. The actinide species can therefore be exchanged into the MOF and then sealed to leaching via a capping ligand,[75−77] thereby creating the nascent waste form. Simultaneous capping linker installation and actinide species incorporation has resulted in a material with 52 wt % of Th.[69]

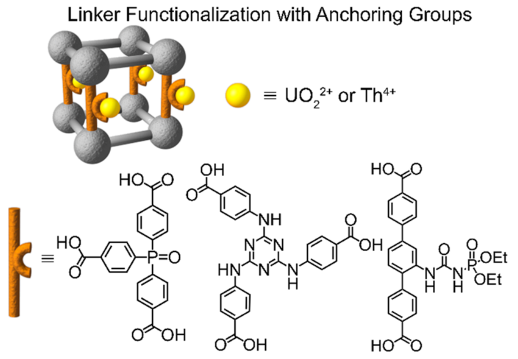


Figure 5. Actinide integration through coordination of radionuclides to the specific linker anchors.

Pores. The MOF "classical" applications including gas storage and separation are based on utilization of their main property—intrinsic porosity. This phenomenal porosity is also a key factor for efficient capture of radionuclide-containing species with further sealing of An-containing guests inside the cavity through installation of additional linkers as pore caps (described above). For instance, MOF porosity and modularity could potentially solve current concerns in nuclear waste management associated with capture and sequestration of highly volatile gases produced from nuclear fission (e.g., iodine) or pertechnetate species.[78−80]

However, efficient utilization of nanoporous materials to capture volatile radionuclide species requires mechanistic studies of adsorption/desorption kinetics, as well as development of synthetic routes for modification of pore microenvironment to enhance iodine-binding affinity.[81] The incorporation of guest species inside a porous framework can be achieved not only by a diffusion route but also through an ion-exchange process.[82] Thus, due to the high surface area and low structural density, these materials can potentially contain a significant An content.

Since the design space for actinide MOFs is virtually unlimited, the utilization of theoretical/computational methods is necessary to accelerate the development of novel, potentially stable MOF architectures. As an example, online databases of MOF structures could be used to sample representative potential host structures, and those energetically favorable to incorporate a radionuclide could be identified. Thus, we believe that synergy between experiment and theory/modeling are necessary to delineate the energetically favorable actinide-containing structural motifs, thereby allowing the identification of further MOF candidates as bases for improved nuclear waste forms. Efforts to use electronic structure calculations in identifying MOF structures for sequestering radionuclides are being pursued. Quantum chemical (QC) methods that go beyond Hartree−Fock theory are widely used to describe the energetics of small molecules with high accuracy. Density functional theory is also being investigated as a method complementary to the QC approaches in that it can be used to describe large unit-cell periodic systems such as MOFs; however, it generally does not provide the same level of accuracy. Fortunately, initial calculations on appropriately terminated molecular fragments of MOF indicate that hybrid methods, such as B3LYP, bring much of the accuracy of QC methods with the relative computational efficiency of DFT methods. They can thus provide valuable guidance as to whether specific radionuclides (e.g., Tc, Am, Cm) can be integrated into specific MOF structures through cationic exchange including, for instance, $M_3(BTC)_2$ MOFs (M = Zr and BTC^{3-} = benzene-1,3,5-tricarboxylate) and their effects on the electronic structure.[83]

Porous Silica with Multiple Scales of Porosity for Capturing Radionuclides. Nuclear waste management generally overlooks the step between the synthesis process of a specific waste form structure and the actual waste (liquid or gaseous). Indeed, an extraction step, from the liquid or gaseous waste, is needed to obtain an initial flow that can be used directly as raw material for a specific containment matrix. In this context, the concept of a porous silica or glass-based material with the dual function of entrapment and confinement was developed within a hierarchical material approach. Research is thus being conducted to assemble a robust confinement vehicle using monolithic supports with a continuous three-dimensional multiscale porous structure to house the nanoparticles. The main properties desired of these hierarchical materials include (a) the ability to extract the targeted radionuclide from diverse liquid nuclear waste (different pH, different salinity...) or from gaseous waste streams, in cases of volatile radionuclides such as iodine; (b) a high capacity and selectivity in order to minimize the volume of the final waste form; (c) long-term resistance to both radiation and chemical damage; and (d) an optimized porous structure for high capacity and efficient extraction.

A number of materials have been developed to selectively extract radionuclides from different liquid waste streams, focusing primarily on volatile and hazardous radionuclides such as Cs, Sr, and I.[84] Among these, ferrocyanide compounds were shown to be excellent candidates for Cs entrapment,[85] while zeolitic structures can readily entrap Sr and, to a lesser extent, Cs,[86,87] and silver-nitrate phases for iodine species.[88] All of these bulk materials are extremely efficient for the selective extraction of the targeted materials; however, the significant challenge for these is low loading in the final waste form. Indeed, during the extraction step, only the surface of the adsorbents is in contact with the liquid or gaseous waste stream, and the large grain size of these materials results in a large volume.[84,89]

One remedy is to utilize the entire volume of the adsorbent by using nanoparticles that effectively provide 100% exterior surface, thereby not only reducing the overall volume of the waste form but also improving the kinetics of absorption.[90] As shown in Figure 6a, the micrometer-sized PBA particles are able to entrap about 0.75 mmol of Cs per gram of PBA, whereas the nanosized particles have a capacity of 1.2 mmol of Cs per gram of PBA. Furthermore, these nanosized PBA particles greatly reduce the time it takes to extract Cs (Figure 6b).

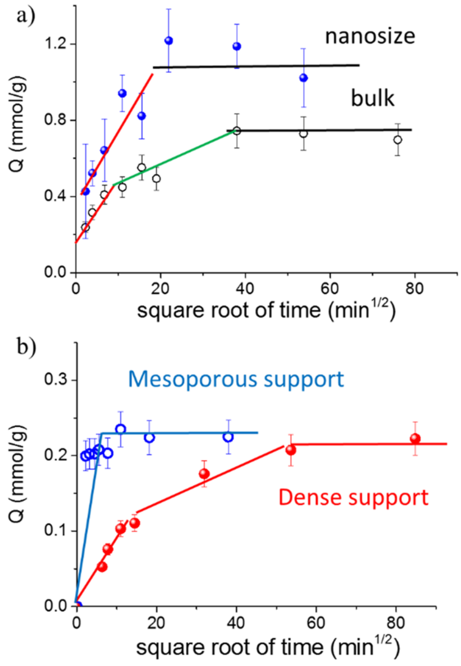


Figure 6. Cs extraction using Prussian-Blue Analogous (PBA) adsorbent inserted into a inorganic support. Effect of the size of PBA and of the porosity of the support. (a) "Nanosize" corresponds to KCu-PBA nanoparticles inserted into silica materials,[95,111] and bulk corresponds to micrometer-sized KCu-PBA.[94] (b) Mesoporous support corresponds to KCu-PBA nanoparticles inserted into silica materials and dense support to KNi-PBA loaded into a dense zirconia matrix.[112]

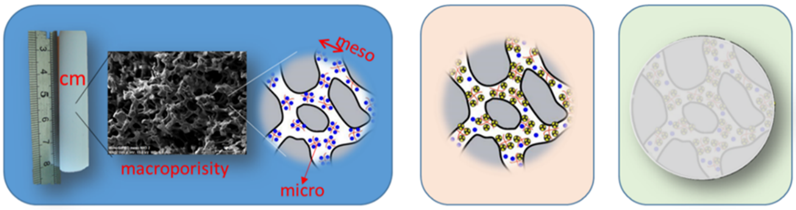
The utilization of loose nanoparticle-based materials by themselves is, for obvious safety reasons, not an acceptable approach for either extraction or confinement, and thus, the creation of a hierarchical structure consisting of a monolithic support in which the nanoparticles are bound and confined is being pursued. Specifically, research is being conducted to assemble continuous three-dimensional multiscale porous structures to house the nanoparticles, similar to the approach for catalytic materials.[91] Nanoparticles can be grafted to the inside of such monoliths, securing the nanoparticle but retaining the ability to efficiently and selectively entrap the targeted radionuclides. Once the radionuclides are absorbed, the pores can be sealed to create a robust containment matrix in a hierarchical waste form.

The multiscale nature of these materials necessary to achieve the overall functionality can be described as follows (Figure 7).

- Centimeter-scale support: The support acts both as a solid support containing the extractant for the extraction step and as a precursor of the containment matrix. To improve long-term behavior and to minimize the surface to volume ratio of the final waste, a centimeter scale is preferred for sequestering the final waste form.
- Macroporosity within the support: Pores of the scale of 200 to 500 μm are needed for the extraction process in order to minimize the pressure drop in the case of liquid effluent. Indeed, in the case of high level waste, low pressure processes are preferred.
- Mesoporosity within the support: Communication to the grafted nanoparticles requires 2 to 50 nm pores to improve the rate of diffusion of radionuclides from the effluent, in the case of actinides, to the organic ligands anchored to the mesoporous support.
- Nanoporosity of the adsorbent: For irreversibly incorporating radionuclides, pores of <2 nm are needed to efficiently include them into the structure of the adsorbent.

Silica-based materials were chosen for the monolithic support structure because synthesis of multiscale porous silica is well understood,[91] in particular porous glass-based materials.[92] PBA nanoparticles developed as Cs "adsorbents" have been the first adsorbents grafted to the inside of the pores of silica based monolithic supports, thus already demonstrating aspects of the concept.

The classical way to synthesize PBA is via a salt precipitation route that involves mixing a precursor solution of $Fe(CN)_6$ with a solution containing the transition metal cation. Subsequently, the insertion of Cs is achieved by simply immersing the solid PBA into a cesium salt solution. An adaptation of this route has been used to create the first centimeter-scale samples exhibiting multiscale porosity, where nanoparticles of PBA are incorporated into the mesoporosity of the monolith and Cs cations are incorporated into the PBA molecular cages. Initial studies have demonstrated that the nature of the transition metal contained in the PBA



after extraction step

after confinement step

Figure 7. Multiscale materials designed for extraction and confinement of radionuclides.

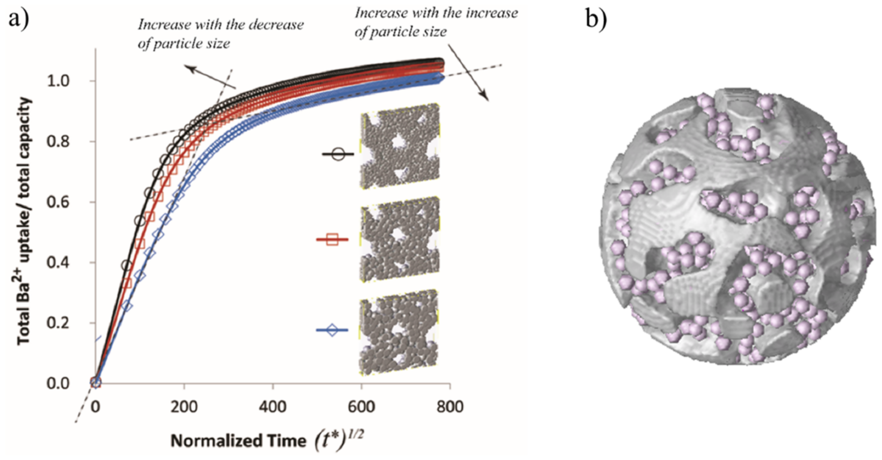


Figure 8. (a) Phase-field modeling results of ion exchange in a simulation cell $256l_0 \times 256l_0 \times 32l_0$. The average particle radius is $6.3l_0$, $10.0l_0$, and $12.9l_0$, respectively. (b) Generated microsized PBA particles to be used in model validation.

nanoparticles directly impacts the insertion of Cs into the structure.[93,94] It as well affects the sintering behavior of the monolith for confining the radionuclides and its long-term stability under radiation exposure. A current objective is to understand Cs insertion into the crystalline structure during the synthesis steps so as to allow eventual optimization of its retention through final thermal processing and the environment.

The results in Figure 8 show that the radionuclide capacity and the efficiency of the extraction process strongly depend on the hierarchical waste form multiscale structure.[87,90−92,95] Therefore, thermomechanical and kinetic properties such as chemical driving force and mobility of radionuclides in different phases affect the efficiency of the extraction and insertion processes. To optimize the waste form structure to high capacity and efficient extraction, it is crucial to understand the mechanisms of ion diffusion and predict the effect of hierarchical structures and inhomogeneous thermodynamic and kinetic properties on ion diffusion, capacity, and ion extraction kinetics.

Multiscale modeling and simulation[96−99] are being applied to framework and porous materials DFT is used to analyze structure and bonding of cations and water within zeolite frameworks.[100,101] MD simulations are used to study the free energy and cation thermodynamic and kinetic properties.[102−104] Monte Carlo (MC) techniques allow calculation of cation selectivity and equilibrium ion exchange properties,[105−107] and thermodynamic calculations can assess the effect of micropores on the free energy and phase stability.[45,108,109] With knowledge from the atomic-level simulations and thermodynamic calculation of phase stability, mesoscale phase-field methods offer a promising modeling tool to predict the effect of 3D microstructure and processing parameters on microstructure evolution and material performance.[98,110] These and other modeling approaches are being pursued to obtain a useful understanding of the multiscale materials and various interacting processes. As an example of the utility of such multiscale modeling, a phase-field model has been developed to investigate the radionuclide extraction kinetics in three-dimensional, multiscale porous structures. On the basis of the microstructure features in the monolithic waste form, such as the volume fraction and average pore size in the support structure, and the size distribution of the nanosized particles that could be zeolite, SIMs, or MOFs, the model can generate a 3D structure for ion extraction simulations. Figure 8a shows the effect of zeolite particle sizes on Ba^{2+} extraction kinetics in an aggregation of zeolite microcrystals. The simulations were carried out based on the spatial and concentration dependent mobility of Na^{+} and Ba^{2+} for a constant Ba^{2+} solution concentration which mimics a flowing waste stream. The results show that the Ba^{2+} extraction kinetics increase with decreasing particle size and are limited by two diffusion processes, i.e., surface layer and bulk diffusion in the particles, which is in agreement with the experiment. The model needs to further integrate additional physics such as fluid flow, interface reactions, electrochemical interactions, and accurate thermodynamic and kinetic properties. There is a need, therefore, to obtain atomistic simulations and thermodynamic representations supported by experimental data to obtain the level of understanding that will eventually be required to optimize hierarchical waste form structures and performance.

■ CONCLUSION

The development of new hierarchical materials as a foundational basis for the development of alternative, new waste forms is expected to culminate in a suite of materials that can support existing technologies, providing systems for more effectively and efficiently immobilizing nuclear waste elements. Key to that will be an understanding of the underlying crystal chemistry, which will lay the groundwork for the design, local structure control, and synthesis of new forms of matter with tailored properties. Expanding the synthetic boundaries to create novel structure types, including surface functionalized multimetallic nanoparticles, SIMs, MOFs, and porous silica, that can simultaneously sequester multiple radionuclides is the first step in the creation of safe, long lasting waste forms for problematic fission product and transuranic elements.

In expanding the understanding and palate of metallic elements forming nanoparticles, it will be possible to provide for low temperature processing of volatile radionuclides such as Cs and Tc. The result could be alloyed materials with multiple radionuclide components having significantly lower chemical activities. It would offer the ability to create materials without concern for evolving vapor species, as well as provide a stable phase for their sequestration. This constituent can thus become an attractive component of any waste form. In the broader scientific and technical realm, the understanding being developed through this integration of synthesis and characterization with first-principles and atomistic modeling for these nanoscale alloys can open a window into another level of materials complexity and design for unique properties.

The successful synthesis and structural characterization of a multitude of SIMs with inorganic silicate, germanate, phosphate, and aluminophosphates frameworks has provided a substantial database to support the development of the ability to tailor the elaborate molecular structures. New efforts, such as the in situ monitoring of the formation of novel hierarchical structures in high temperature, extreme molten salt environments are expected to reveal how to better control the structure and composition of products under conditions far from equilibrium. It has already been demonstrated using DFT and thermodynamic calculations, such as VBT, that the salt inclusions can be exchanged, and they can help us begin to predict the formation of stable product phases. Targeting new framework compositions to allow us to incorporate actinides and select problem radionuclides, such as Tc, into the inorganic framework will provide one level of sequestration. Sizing the channels in these structures to optimize the fit of volatile species such as Cs and I will together allow future development of practical multiradionuclide waste forms having assured long-term stability.

Development of novel actinide-based MOFs has been a necessary first step in gaining the crucial topological and mechanistic insights needed to engineer MOF-based waste-form platforms. Fundamental understanding of the actinide integration mechanisms inside the MOF matrix (e.g., transmetalation, metal node extension, or chelation to organic linkers) and observations of the differences in chemical behavior in comparison to molecular species have yet to be elucidated and are important to guiding synthesis. However, the already existing An frameworks can be utilized as precursors for investigating sequential construction of hierarchical complexity in An-based structures and, therefore, enhancement of MOF actinide loading. That together with the ongoing efforts in the field of An-MOFs to expand the composition and functionalization of frameworks will open new pathways for An integration in extended structures as well as development of new sequestration approaches, creating principles for more efficient nuclear waste management.

The initial success in creating hierarchical monoliths from the nanoscale PBAs to the ultimate macroscale support, for the extraction and storage of select hazardous and volatile radionuclides, provides another viable option for the long-term sequestration of components of nuclear waste streams. The current investigations are resulting in a better understanding of the chemistry of the various steps involved in the monolithic sequestration process, an essential prerequisite for the continued improvement of handling these radionuclides and that of others in the future. The development of a sufficient basic understanding to eventually allow optimization of this type of hierarchical waste form and the extension of this work to encompass other radionuclides to generalize the approach is the focus of the ongoing efforts.

The development of a spectrum of new, complex materials, that can perform multiple containment functions, ranging from the incorporation of the waste radionuclides into a robust framework to the absorption or ion-exchange and encapsulation of these elements, depends on an interdisciplinary research effort. It requires expertise in materials synthesis, characterization, and modeling among universities and national laboratories, utilizing high-end instrumentation including national facilities, such as synchrotrons and neutron sources, and latest generation supercomputers and software, with efforts integrated to comprehensively understand the materials and related processes. Resolving the problems associated with complex wastes has now become a recognized need, with a response seen in the formation of integrated academic and national laboratory teams to to develop a variety of new waste form materials, including hierarchical ones, that can be used to augment the current waste processing effort and to safely and efficiently contain radionuclides for millennia to come.

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Chem. Mater. 2018, 30, 4475−4488

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Scott T. Misture holds an Inamori Professorship at Alfred University, in the Kazuo Inamori School of Engineering. Misture uses advanced in situ structural characterization tools to understand the effects of structure on the atomic and nanoscales, primarily X-ray and neutron scattering. His research has focused on oxides for energy conversion, including materials for high temperature fuel cells, photocatalysts, and most recently electrochemical charge storage. His current research includes the study of nano- and mesostructured oxides, where he aims to understand the roles of defects in nanoscale materials, in particular 2-D oxides.

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